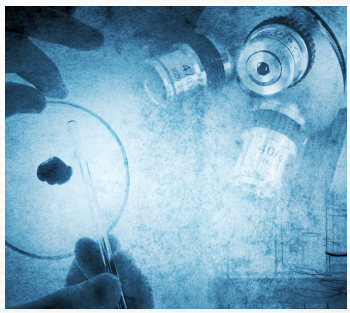
SciX is the 39th Annual Meeting of FACSS

FACSS PRESENTS

SCIX2012

The Great SCIentific eXchange

FINAL PROGRAM BOOK OF ABSTRACTS



KANSAS CITY, MO

SEPTEMBER 30 – OCTOBER 5

SHERATON KANSAS CITY HOTEL AT CROWN CENTER

SciX welcomes attendees from around the world to the 39th Annual Meeting of FACSS covering the whole of Analytical Chemistry and Allied Sciences.

National Meeting of the Society for Applied Spectroscopy (SAS)

facss.org

SciXConference.org

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Attention Presenters: Check this final program to verify the schedule of your talk or poster. Changes may have occurred since the preliminary program.

SciX Conference and FACSS International Office
2019 Galisteo Street, Building I-1, Santa Fe, NM 87505
(505) 820-1653 ❍ (505) 820-1483 ❍ facss@facss.org ❍ www.scixconference.org ❍ www.facss.org

WELCOME TO FACSS 2012

The Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) is an organization designed to further the interests of analytical chemistry and spectroscopy on behalf of its member organizations. On behalf of the Governing Board and the Executive Committee of FACSS and this year's organizing committee and the ten member organizations of FACSS, it is my pleasure to welcome you to Kansas City for our 39th annual meeting, **SciX 2012**, and the National meeting of the Society for Applied Spectroscopy.

SciX-the great SCIentific eXchange, is presented by FACSS and has been organized by a highly dedicated team headed by General Chair Brandye Smith-Goettler, Program Chair Steven Ray, Local Chair Luisa Profeta, Workshops Chair Heather Brooke, Exhibits Chair Mike Carrabba, Employment Chair Matt Schumerick, Marketing Chair Mark Hayes, Awards Chair Mike George, and Social Media Chair Michelle Meighan. Each of these individuals has poured countless hours of their time, as unpaid volunteers, into this meeting to provide a truly unique scientific conference that represents the latest in analytical sciences. Please join with me in thanking them for all their efforts and I ask you to please take a few minutes during the week to share your thoughts on this year's meeting with them. To this team we are indebted to the dedicated professional staff of the FACSS / SciX International Office – Cindi Lilly and Marin Walker and the support of Chris Wheeler's Ignite Design & Advertizing team.

The foundation of SciX is the technical program which this year, boasts an impressive list of invited speakers as well as hundreds of contributed talks and posters (from academic, industrial, and government laboratories). The conference will open with a plenary lecture from **Chris McKay,** of NASA, who will present some of the latest scientific information from the analytical instrumentation on-board NASA's Curiosity mission to MARS. FACSS is proud that the SciX conference is the site of a large number of awards symposia for its member societies, and equally proud that a large proportion of the program comes in the form of contributed papers and posters.

The 2012 SciX conference will again feature the ***FACSS Innovation Award. This unique award is*** presented to the authors of the most innovative and outstanding new research advancement that is debuted at SciX. Many submissions were received this year and the quality of the research highlighted was extremely high. The finalists will present their work in a plenary session in front of a panel of judges on Thursday afternoon. This plenary session will be preceded by the presentation of the FACSS Distinguished Service and several other FACSS awards. Please join us there to thank and congratulate these award recipients.

2012 is a year of significant change at FACSS which saw the debut of the name for the annual conference, SciX, and the addition of three new member organizations - the largest expansion of FACSS since its formation in 1972. With the addition of the AES Electrophoresis Society, the Spectroscopical Society of Japan (SpSJ), and the North American Society for Laser Induced Breakdown Spectroscopy (NASLIBS), to the federation's existing member organizations including the Division of Analytical Chemistry of the American Chemical Society, American Society for Mass Spectrometry (ASMS), ANACHEM, the Coblentz Society, the International Society for Automation (ISA) – Analysis Division, the Royal Society of Chemistry (RSC) Analytical Division, and the Society for Applied Spectroscopy (SAS), FACSS is now 10-members strong. This expansion reflects a unique element of FACSS and the SciX conference in that all areas and aspects of analytical chemistry are welcomed, bringing together leading scientists from among many disciplines for **scientific exchange**.

Here at SciX I look forward to welcoming old friends, familiar faces, and new attendees to this unique and vibrant community of scientific societies and to the excellent conference organized by the 2012 team. Please take a few moments during your week to talk to members of the current SciX, FACSS, or member organization's leadership to express your ideas and interest on how to make this conference better serve you. FACSS and SciX always needs new volunteers to lead the organization and the meeting forward – please consider volunteering and help shape the future.

Ian R. Lewis
FACSS Governing Board Chair 2012-2013

GENERAL INFORMATION

LOCATION. The plenary and award lectures, exhibits, and several evening events are located in the Exhibit Halls in the Crown Center. All other symposia, workshops, and SAS wine and cheese event are located in the Sheraton Hotel.

PROGRAM. This printed program contains titles and abstracts as submitted by the authors. It is not possible to edit these submissions.

SPEAKERS. There will be an LCD projector for each symposium. Speakers must supply their own computer with their presentation. Please arrive 30 minutes before your session begins. Each speaker should adhere to the time allotted for the talk.

POSTER SESSIONS.

Sunday SAS Sponsored Student Poster Session
Exhibit Hall B

- 7:00 – 9:00 pm SAS Poster Session & SciX Welcome Mixer

Monday Poster Session – *Exhibit Hall B*
Set up posters between 7:00 – 7:30 am and remove by 5:00 pm

- 9:10 – 10:20 am - Poster Session
- 3:00 – 3:50 pm – Poster viewing and break

Tuesday and Wednesday Poster Session – *Exhibit Hall A*
Posters remain up all day on their designated day. Set up posters between 7:30 – 8:00 am and remove Tuesday posters by 4:30 pm and Wednesday posters by 4:00 pm

- 9:00 – 10:20 am – Poster Session
- 3:00 – 3:50 pm – Poster viewing and dessert break

Thursday Poster Session – *Exhibit Hall B*
Posters remain up all day. Set up posters between 7:00 – 7:30 am and remove at 3:50 pm.

- 9:00 – 10:20 am – Poster Session
- 3:00 – 3:50 pm – Poster viewing and break

WORKSHOPS. A list of workshops, descriptions, and the locations begin on page 40. You must register for a SciX workshop at the conference registration desk.

EMPLOYMENT BUREAU. The bureau is located in the Exhibit Hall A during exhibit hours. See page 4 for additional information.

EXHIBITS. The exhibition is located in Exhibit Hall A and will be open as follows: See page 29 for details.

Monday (Opening Reception)	5:30 pm – 7:30 pm
Tuesday	9:00 am – 4:30 pm
Wednesday	9:00 am – 4:00 pm

BREAKS.
Monday

- 9:00 – 10:20 am & 3:00 – 3:50 pm – *Exhibit Hall B*

Tuesday and Wednesday

- 9:00 – 10:20 am & 3:00 – 3:50 pm – *Exhibit Hall A*

Thursday

- 9:00 – 10:20 am & 3:00 – 3:50 pm – *Exhibit Hall B*

INTERNET ACCESS. Complimentary wireless internet access will be available in Exhibit Hall A

REGULATIONS. The following regulations are in the best interest of the conference.

1. There is no smoking in any conference area.
2. An official name badge is required at all times.
3. No advertising may be placed in the conference area.
4. Only official exhibitors may display in the Exhibit Hall.
5. No distribution of product/meeting literature in sessions.

SPECIAL EVENTS.

SUNDAY

3:30 – 7:00 pm **"What's Hot" Exhibitor Presentations**, Exhibit Hall B

7:00 – 9:00 pm **Welcome Mixer and SAS Sponsored Student Poster Session**, SAS, Coblentz Student, and FACSS Student Award Presentations, *Exhibit Hall B*

MONDAY

7:50 am **Opening Address.** *Exhibit Hall B*

8:00 am **Keynote Lecture.** The Search for Life on Other Worlds**; Chris McKay,** *NASA Ames Laboratory***,** *Exhibit Hall B*

5:30 – 7:30 pm **Reception for Exhibit Opening** (wine, beer, light hors d'ouvres) *Exhibit Hall A*

TUESDAY

8:00 am **Coblentz Society's Craver Award.** SERS Used for Analysis of New Biological Interactions; **Duncan Graham,** *University of Strathclyde, Exhibit Hall A*

8:30 am **FACSS Charles Mann Award for Applied Raman Spectroscopy.** Successful Application of Raman Spectroscopy in Pharmaceutical Discovery Research**; Don Pivonka,** *Incyte Pharmaceuticals, Exhibit Hall*

12:00 pm **Free Lunch and Employment Discussion for Students, sponsored by SABIC.** *Benton A*

6:00 pm **Raman Reception,** *Exhibit Hall B*

7:30 pm **Society for Applied Spectroscopy Wine and Cheese Award Reception,** *Atlanta Room*

WEDNESDAY

8:00 am **ACS Division of Analytical Chemistry Award for Distinguished Service in the Advancement of Analytical Chemistry.** Service and Research: Symbiosis or Conflict?; **Gary Hieftje,** *Indiana University, Exhibit Hall B*

8:30 am **ANACHEM Award.** The Impact of Chemometrics on Open-Path FT-IR Atmospheric Monitoring; **Peter R. Griffiths,** *University of Idaho., Exhibit Hall B*

6:00 pm **Wednesday Evening All Inclusive Event,** complimentary for all conferees**.** *Exhibit Hall B*

THURSDAY

8:00 am **SAS Applied Spectroscopy William F. Meggers Award.** Spatial Heterodyne Raman Spectrometer for Wide-Area Standoff Detection**; Mike Angel,** *University of South Carolina, Exhibit Hall B*

8:30 am **SAS Lester W. Strock Award.** Vapor Generation – Make It Your Second Thought for Sample Introduction**; Ralph Sturgeon,** *National Research Council Canada, Exhibit Hall B*

3:50 pm **Plenary Session**
FACSS Distinguished Services Awards
FACSS Innovation Awards, *Exhibit Hall B*

FRIDAY

8:00 am **Special Plenary Session: Welcoming Three New Member Organizations into FACSS**

COMPANION REGISTRATION. Does not include access to symposia. Cost is $55 and includes the following: **Sun.** Evening Welcome Mixer, **Mon.** coffee/pastries 9:00 AM *and* Exhibit Hall Opening Reception, **Wed.** Evening Event.

EVENTS OF SPECIAL INTEREST TO STUDENTS

Sunday Evening, *Exhibit Hall B*

- Welcome Mixer; 7:00 – 9:00 PM
- SAS Sponsored Student Poster Session; 7:00 – 9:00 PM
    - SAS and Coblentz Student Award presentations.
    - FACSS Student Award and Tomas Hirschfeld Scholar Award presentations

Monday through Thursday

- FACSS Student Poster Awards will be presented daily.

Monday through Thursday

- Employment Bureau (Monday evening through Wednesday), *Exhibit Hall A;* Thursday, *Exhibit Hall Foyer*

SPECIAL INVITATION TO STUDENT ATTENDEES

- Tuesday 8:00 am – noon. **Resume Writing and Interviewing Skills for Students.**
  SABIC is hosting this free workshop. Your career search is one of the most influential investments in your future. This interactive half-day workshop will prepare attendees to make a positive and lasting impression both in-print and in-person. Receive tips and best practices, avoid common mistakes, learn how to tailor your resume for different prospective employers, and prepare yourself for important interview styles. Instructors: Drew Manica and Patrick Reuss from SABIC. Directly following the workshop, students are invited to join the Free Lunch and Employment Discussion hosted by SABIC.

- Tuesday 12:30 pm - **Free Lunch and Employment Discussion for Students. Hosted by SABIC**
  Eat lunch and chat with professionals from a wide range of professional fields (academic, government, chemical industry, pharmaceuticals, goods and services, etc.) It's a unique opportunity to ask questions, get helpful tips, and discuss topics that relate to your specific career-seeking situation within the current job market. *Benton A*. ***Sign up at conference registration desk***.

- Wednesday 9:00 am – 5:00 pm. **Professional Analytical Chemists in Industry: What Does an Analytical Chemist Do?**
  This seminar begins with a discussion of the education requirements and salaries that an analytical chemist may expect in industry. The different roles (including scientific consultant, methods developer, and problem solver) of the industrial analytical chemist are explained. A majority of time is spent on problem solving, both the process and solving real-world problems. Students will learn a "framework" for approaching problems. Time will be available to ask questions on these topics and other related subjects. The course text includes supplementary material on finding a job, summer employment, etc. The entire course, especially the problem solving, is structured for extensive participation and interaction. Additional information is available at http://www.pg.com/science/prof_chemists.jhtml. The course is intended primarily for undergraduate students to educate them about careers as analytical chemists in industry. However, graduate students, high school teachers, and college faculty have indicated it was worth their time to attend. Instructors: Judson Haynes and Diane Parry, Procter and Gamble.

EMPLOYMENT BUREAU

The Employment Bureau is located in Exhibit Hall A in the internet café Monday evening and open through close of the hall on Wednesday afternoon.

EMPLOYERS: Bring either hard copy or electronic copy of job opportunities and display on poster board in the employment area. There will be copies of resumes for you to review or to take with you.

JOB SEEKERS: Bring an electronic copy of your resume and copies will be made available for prospective employers to review.

A message board will be available for employers and job seekers to communicate. There will also be space available to meet and conduct interviews. Contact Mat at matthew.schulmerich@gmail.com with any questions.

FACSS and SciX CONFERENCE ORGANIZATION

Member Organizations of FACSS

AES Electrophoresis Society
American Chemical Society, Analytical Division
American Society for Mass Spectrometry
ANACHEM
Coblentz Society
International Society of Automation – Analysis Division
North American Society for Laser-Induced Breakdown Spectroscopy
Royal Society of Chemistry
Society for Applied Spectroscopy
Spectroscopical Society of Japan

SciX 2012 is the 39th annual North American Meeting of FACSS, the 51st National Meeting for the Society for Applied Spectroscopy, and the Main National Meeting for the Coblentz Society

2012 SciX Conference Chair Persons

General Chair	**Brandye Smith-Goettler,** *Merck & Co.* E-mail : brandyemichelle_smithgoettler@merck.com
Program Chair	**Steven Ray,** *Indiana University* E-mail: sjray@indiana.edu
Local Chair	**Luisa Profeta**, *MRIGlobal*
Exhibit Chair	**Mike Carrabba,** *The Hach Company* E-mail: mcarrabba@hach.com
Workshop Chair	**Heather Brooke***, Merck & Co*
Employment Chair	**Matthew Schulmerich,** *University of Illinois*
Marketing Chair	**Mark Hayes,** *Arizona State University*
Social Media Chair	**Michelle Meighan**

2012 Program Section Chair Persons

Atomic Spectroscopy	Carsten Engelhard, *University of Muenster*
Awards	Mike George, *University of Nottingham*
Chemometrics	Rene JiJi, *University of Missouri-Columbia*
Electrophoresis	Mark Hayes, *Arizona State University*
LIBS	Jose Almiral, *Florida International University and* Matthieu Baudelet, *Townes Laser Institute, CREOL, University of Central Florida*
Mass Spectrometry	Rachel Loo, *University of California, Los Angeles*
Molecular Spectroscopy	Linda Kidder, *Malvern Instruments*
Process Analytical	James Rydzak**,** *GlaxoSmithKline*
Raman Spectroscopy	Ian R. Lewis, *Kaiser Optical Systems, Inc.*
Security and Forensics	Greg Klunder, *Lawrence Livermore National Lab*
Surface Plasmon Resonance	Jean-Francois Masson, *University of Montreal*

2012 FACSS Executive Committee

Governing Board Chair	**Ian R. Lewis**, *Kaiser Optical Systems, Inc.* E-mail: irlewis@kosi.com
Governing Board Chair Elect	**Greg Klunder,** *LLNL – Forensic Science Center*
Past Governing Board Chair	**S. Douglass Gilman,** *Louisiana State University*
Second Past Governing Board Chair	**Becky Dittmar,** *3M*
Secretary	**Christopher Palmer,** *University of Montana*
Treasurer	**Scott McGeorge,** *Transition Technologies, Inc.*

FACSS / SCIX CHAIRS

GOVERNING BOARD CHAIR, FACSS

Ian R. Lewis

Kaiser Optical Systems

Ian R. Lewis was born in 1968, Somerset, UK. He obtained his undergraduate degree in Chemistry and Chemical Technology at the University of Bradford in 1989 and his Ph.D. in 1992 in the field of infrared and Raman spectroscopic characterization of polydienes in the IRC in Polymer Science and Technology under the joint direction of IRC associate director Professor Anthony Johnson and Professor Howell Edwards. Following his appointment as an Honorary Visiting Researcher to the IRC, he went to the University of Idaho in 1993 to work as a postdoc in Professor Peter Griffiths's lab. During this time he also acted as a consultant on the application of Raman spectroscopy to several industrial companies. In 1996 he joined Kaiser Optical Systems as a Laser Spectroscopy Specialist and is currently global Marketing Manager. In this later role, Ian has been able to collaborate with a number of laboratories and process scientists around the world on a variety of different projects. These collaborations have been extremely valuable and rewarding.

He has been an active participant in past-FACSS conferences as the Raman section chair in 2000, and from 2002 to the present, program chair for the Memphis meeting in 2007, and is current serving as the FACSS Governing Board Chair for 2012 and 2013. He has organized scientific sessions at several additional conferences including EAS and Pittcon, and participated as a program committee member for a number of meetings including, ICORS (2010), and ICAVS (2011). He serves as the Chair of ASTM subcommittee E13.08 on Raman Spectroscopy (2002 to present), served as the secretary of E13.10 on Molecular Optic Imaging (2001-2003), and was the co-liaison from E13 to E55. From 2004 through 2008 he served on the Board of Managers of the Coblentz Society and from March 2009 to March 2011, he served as the president of the Coblentz Society. He has been a member of SAS since 1992 when he joined as an international student, he was the president of the Detroit SAS section in 2011, was elected as a Fellow of SAS in 2011, and ran for SAS president in 2012. He has published approximately 46 scientific papers in refereed journals, has co-authored 7 book chapters, and is co-editor of Handbook of Raman Spectroscopy: From Research Laboratory to the Process Line (published in 2001). He currently serves on the editorial advisory board of Spectroscopy Magazine, and American Pharmaceutical Review. He is an active reviewer for a number of international journals including Applied Spectroscopy and a member of several scientific societies including ANACHEM, the Analytical Division of ACS, Coblentz Society, IRDG, MacroGroup UK, RSC, and SAS. In 2008, he was presented with the Charles Mann Award for Analytical Raman Spectroscopy awarded by FACSS.

Ian has been married to Dr. Mary Lewis, also a vibrational spectroscopist, since 1994. Mary and Ian met at University of Idaho where they both worked in the Griffiths lab. They currently have nine children, 5 girls and 4 boys. The children's ability to contribute in a creative way to deadlines (and to create new deadlines) is always a source of interest to their parents. Ian would like to take this opportunity to thank his family, especially his wife, for their support and his mum Valerie for encouraging him to come to the US and seek new opportunities.

GENERAL CHAIR, SciX

Brandye Smith-Goettler

Merck

Brandye Smith-Goettler is an associate principal analytical chemist within the manufacturing division at Merck in West Point, PA. She received undergraduate degrees in Chemistry and Biochemistry at East Carolina University in 1995, her M.S. in Chemometrics at ECU in 1997 and her Ph.D. in Analytical Chemistry at North Carolina State University in 2003. Brandye's graduate studies focused on chemometrics and process analytical chemistry under the direction of Professor Paul Gemperline and infrared spectroscopy to characterize biologicals under the direction of Professor Stefan Franzen, respectively. During and after graduate school, she has worked in the scientific software development, biotechnology and pharmaceutical industries. Her current work involves integrating analytical technologies into drug product manufacturing processes. This role provides an exciting assortment of spectroscopy, process engineering, chemometrics and automation.

Brandye serves as a member of the Coblentz Society governing board (2009-2012). Additionally, she has served as the Coblentz delegate to the Eastern Analytical Symposium governing board and a delegate to the Federation of Analytical Chemistry and Spectroscopic Sciences governing board since 2007. She is a current member of the Society of Applied Spectroscopy and served as Parliamentarian on the Executive Committee in 2006 and 2007. Brandye has been an active participant in FACSS, organizing process sessions and serving as workshop chair 2007-2011. Brandye's first FACSS conference was in 1996 in Kansas City. Now 16 years later, she is pleased to be back in Kansas City for her first SciX conference.

Brandye and her husband Steve, also a chemist, are contently busy with two sons (Darius and Matteo, both 11) and two girls (Zipper - lab/beagle mix and Stella – terrier mix). Together they enjoy a variety of sports and outdoor activities.

SciX CHAIRS

PROGRAM CHAIR, SciX

Steven Ray

Indiana University

Steven Ray is currently an Associate Scientist in the Indiana University Department of Chemistry, where he works in the Laboratory for Spectrochemistry. Steven received his B.S. in Chemistry from Hope College (Holland, MI), and his Ph.D. in Analytical Chemistry from Indiana University working with Professor Gary Hieftje. He also served as the Director of the Mass Spectrometry Core Facility at Indiana University while working towards his degree, before rejoining the Laboratory for Spectrochemistry to pursue research full-time. Steven currently serves on the editorial advisory boards of *Spectrochimica Acta, Part B* and the *Journal of Analytical Atomic Spectrometry,* and recently served as the JAAS News Editor for the later journal (2010-2012). Steven is currently a member of the American Chemical Society Analytical Division, the Royal Society of Chemistry, the American Society for Mass Spectrometry, and the Society for Applied Spectroscopy. He has served within the FACSS organization as a session organizer (2008), Atomic Spectroscopy Section Chair (2009-2010), Awards Chair (2011), and now as the first SciX Program Chair.

Dr. Ray's research interests involve novel aspects of analytical instrumentation, focusing predominantly on atomic spectroscopy, plasma spectrochemistry, and mass spectrometry. Steven has authored more than 50 manuscripts, 4 book chapters, and holds 5 patents. Recently, he and his colleagues received the 2011 R&D100 award for their role in developing an array detector for mass spectrometry. Steven and his wife Jill, who is a biochemist also working at Indiana University, have two sons, Nico (4) and Timmy (1), who keep them more than busy.

EXHIBITS CHAIR, SciX

Mike Carrabba

The Hach Company

Dr. Mike Carrabba joined the Hach Company in 2004 as the Director of Hach Homeland Security Air Systems and he is currently the Global Director of Open Innovation where he has the responsibility of finding and developing relationships for new and emerging technologies.

He received his B.S. in Chemistry (*magna cum laude*) from Salem State College in 1981 and his Ph.D. in Physical Chemistry from Tufts University in 1985. Dr. Carrabba's graduate work was conducted under the tutelage of Dr. Jonathan Kenny and focused on the utilization of laser-induced fluorescence to examine ultra-cooled gas phase molecules in a supersonic jet molecular beam. After graduate school, Dr. Carrabba joined EIC Laboratories where he eventually became Vice-President for the Spectroscopy Division. He conducted a variety of research programs, including photoelectrochemical etching of semiconductors, fiber optic chemical sensors and state-of-the-art Raman spectroscopy. During this time, he introduced the use of holographic filters for Raman spectroscopy and developed numerous types of field Raman instrumentation and techniques, several of which resulted in U.S. patents. After leaving EIC, he joined Chromex, Inc, a manufacturer of Raman spectroscopy systems, as Marketing Manager and was previously the OEM Division Manager at Jobin Yvon, Inc.

Dr. Carrabba has been very active in the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) over the years. He has served as Governing Board Chair (2002), Program Chair (2000), Program Section Chair for Raman (1992-1999, 2001), Chairperson of the Long Range Planning Committee (1999-2008) and as a member of the Governing Board. Since 2006 he has been serving as the SciX Exhibits Chair.

In 2003 Dr. Carrabba received the ASTM Award of Merit for his 12 years of service as the Chairman of the ASTM Subcommittee on Raman Spectroscopy. In 2004 he received the FACSS Charles Mann Award for Applied Raman Spectroscopy and in 2007 he received the Williams-Wright Award for Industrial Vibrational Spectroscopy. He has also been honored with the 2009 FACSS Distinguished Service Award and the 2011 Society of Applied Spectroscopy (SAS) Distinguished Service Award. Dr. Carrabba is a member SAS, ASTM, and the Coblentz Society. On the home front, Professor Mary Widmark Carrabba of Southern Oregon University, a highly skilled Infrared microscopist and the former treasurer for SAS, complements Mike's Raman background

PROGRAM and CONFERENCE SPONSORS

SciX 2012 and FACSS greatly appreciates the support it receives from its sponsors

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ATOMIC SPECTROSCOPY

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JAAS/Royal Society of Chemistry Analytical Division
Meinhard, division of Elemental Scientific
Glassblowing
Metallomics/Royal Society of Chemistry
Photon Machines
Royal Society of Chemistry
Society for Applied Spectroscopy

AWARDS

ANACHEM
Coblentz Society
Royal Society of Chemistry
Society for Applied Spectroscopy

BIOMEDICAL AND BIOANALYTICAL

ACS Analytical Division
Analyst/Royal Society of Chemistry
Analytical Methods/Royal Society of Chemistry
LEAP Technologies
Renishaw
Royal Society of Chemistry Analytical Division
Sierra Analytics

FLUORESCENCE

HORIBA Scientific
Society for Applied Spectroscopy

INFRARED/NEAR INFRARED SPECTROSCOPY

Anasys Instruments
Council for Near Infrared Spectroscopy
Infrared Associates
Society for Applied Spectroscopy
ThermoFisher Scientific

MASS SPECTROMETRY

American Society for Mass Spectrometry
LECO
ThermoFisher Scientific

PROCESS

Bruker Optics
CPACT
International Society of Automation – Analysis Division
Mettler Toledo
Society for Applied Spectroscopy

RAMAN

Advanstar / Spectroscopy Magazine
HORIBA Scientific
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STUDENT SPONSORS

Mike and Mary Carrabba
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STUDENT EMPLOYMENT LUNCH AND PANEL DISCUSSION

SABIC

FACSS AWARDS

DISTINGUISHED SERVICE AWARDS

Awarded to an individual(s) for recognition of exceptional, long-term service to the FACSS organization. The 2012 recipients have served with excellence in many different capacities and contributed to the continuing success of FACSS through consistent dedication and sacrifice.

Awards will be presented Thursday, 3:50 pm, *Exhibit Hall B*

Bruce Chase

University of Delaware

Bruce Chase received his B. A. from Williams College in 1970 and his Ph.D. in physical chemistry from Princeton University in 1975, where he worked with Professor Donald S. McClure on studies of charge transfer excitation of transition metal ions in alkali fluorides. He then joined E. I. DuPont de Nemours as a research chemist in the Spectroscopy Division of the Central Research Department. He retired from DuPont in 2009 as a DuPont Fellow and Chair of the DuPont Fellows Forum. He is now a Research Professor in the Department of Materials Science and Engineering at the University of Delaware and the Chief Technical Officer of Pair Technologies, LLC. Dr. Chase's primary area of research is in vibrational spectroscopy, FT-IR and Raman techniques, and applications to industrial analytical problems. In collaboration with Dr. Tomas Hirschfeld (deceased) he developed an FT-Raman spectrometer which demonstrated the utility of near infrared excitation. Recent efforts include the development and utilization of polarized Raman scattering for the determination of orientation in fibers. Parallel work has involved developing multichannel detection instrumentation for the near infrared. In collaboration with Professor John Rabolt at the University of Delaware he has developed an approach to infrared spectroscopy based on focal plane area detectors. He was the 1989 winner of the Williams-Wright award and the 1990 EAS New York Section Gold Medal awardee. He also received the 1991 Delaware Valley ACS Section Award. He received the 1994 SSP Award from the Spectroscopy Society of Pittsburgh and is co-winner of the 1994 Bunsen-Kirchhoff Prize from the German Chemical Society. He received the 1998 Bomem-Michelson Award in March of 1998, and received the ACS Analytical Division Award in Spectrochemical Analysis in November 1999. In 2002 he received the ANACHEM Award, in 2005 the FACSS Charles Mann award for Applied Raman spectroscopy, and also in 2005 the EAS Award for Analytical Chemistry. In 2007 he was recognized with the Hasler Award. In 2011 he was made an Honorary Member of the Coblentz Society for his contributions to the field of vibrational spectroscopy including forwarding the aims and purpose of the Coblentz Society.

O. Karmie Galle

University of Kansas

O. Karmie Gale is a retired member of the Kansas Geological Survey, and a former professor at the University of Kansas's Geology department. Karmie was born in Valley Center, Kansas, and is a graduate of Bethel College, North Newton, Kansas. For 40 years, until his retirement, Karmie utilized analytical science as part of the Kansas Geological Survey. Throughout Karmie's life he has volunteered and served others. He served FACSS in several officer capacities over almost two decades including Governing Board Chair in 1992 in Philadelphia, the General Chair of the FACSS meeting held in 1996 in Kansas City, treasurer, and long-term governing Board member. He also wrote the FACSS Operational Manual. Karmie was a charter member of the Kansas City Section of SAS. Karmie served as President-Elect, President, and Past-President of SAS during 1983-1985 and as SAS Parliamentarian 1986-1988. He authored the original SAS 72-page Officers and Committee Members Handbook which outlined the responsibilities of Offices, Executive Committee members, and committee chairs and members. He served on the Meggers award committee and was co-managing editor of Applied Spectroscopy publications. In 1990, SAS presented Karmie with the Distinguished Service award for his years of dedicated and outstanding service to SAS. At his church he has served as Elder, Clerk of Session (many years), and member of both the church chancel choir and the hand bell choir. On the home front Karmie and Edna have recently celebrated 55 years of marriage and have one daughter, Suzanne. His hobbies over those years have included model railroading, gardening, bridge, and traveling - domestic and abroad.

PREVIOUS AWARDEES:

1993	Edward Brame and Syd Fleming	2003	Jeanette Grasselli Brown
1994	L. Felix Schneider	2009	Paul Bourassa and Mike Carrabba
2001	David Coleman	2010	Scott McGeorge and Alexander Scheeline
		2011	Jon W Carnahan and Patricia B Coleman

FACSS AWARDS

The FACSS Student and the Tomas Hirschfeld Scholar(s) Award recognize outstanding contributions by individuals who are Ph.D. and M.Sc. candidates.

FACSS STUDENT AWARD

Ali Khumaeni

University of Fukui, Japan

Presentation: Mon.., 4:30 pm, Atlanta A

Ali Khumaeni is currently a senior Ph.D student at the Quantum Electronics Laboratory and Kagawa laboratory, University of Fukui, Japan. Ali earned his B.Sc degree from the Department of Physics, Diponegoro University, Indonesia, in 2006, with a judicium of cum-laude. During undergraduate study, Ali conducted a research on laser plasma spectroscopy at the Radiation Physics Laboratory (Diponegoro University) and the Maju Makmur Mandiri Research Center (MMM, Indonesia) under the supervisions of Professor Wahyu Setiabudi, Sofjan Firdausi, and Dr. Hendrik Kurniawan (MMM). In 2007, he entered the Department of Physics, University of Fukui, Japan and joined the group of Kagawa laboratory as a research student. Under the direction of Professor Kiichiro Kagawa, he directs his research into laser plasma spectroscopy by utilizing a pulsed transversely excited atmospheric (TEA) CO_2 laser. In 2009, he entered the Program of Nuclear Power and Energy Safety Engineering, University of Fukui (M.Eng and D.Eng), with the same research topic of laser plasma spectroscopy using a pulsed TEA CO_2 laser under the supervisions of Professor Hideaki Niki and Professor Kiichiro Kagawa. During the research, Ali and his team have developed a novel method of LIBS by utilizing the specific characteristics of a TEA CO_2 laser (wavelength of 10.64 μm, pulse duration of 200 ns, energy of several hundreds of mJ). In this method, a high temperature and very large gas plasma was induced when a TEA CO_2 laser was focused on a metal surface without ablating the metal surface; this phenomenon never appears in the case of standard LIBS using Nd:YAG laser because the metal itself was ablated. This gas plasma is very suitable for the highly sensitive and in-situ elemental analysis in various samples. We called this method "TEA CO_2 laser-induced gas plasma spectroscopy (LIGPS)". By devising many unique sampling techniques, Ali and his team have proved that the LIGPS method can be applied for highly sensitive and direct elemental analyses in various samples including powder, organic solid, aerosols, liquid, soils, and so on. Ali published 17 peer-reviewed articles (9 as primary author) and 1 peer-reviewed conference proceeding. His work was presented in more than twenty national and international scientific meetings. He currently holds scholarship from the Japanese Government (Monbukagakusho scholarship). He received various awards for his academic record and for the excellence of his scientific communications. In 2008, he was awarded as the young scientist award for his outstanding research on herb medicine and food powder analysis using TEA CO_2 laser-induced gas plasma spectroscopy from the 4th International Conference on Laser Probing LAP 2008 held in Nagoya, Japan. He was further awarded as the 2nd place poster award from the 6th International Conference on Laser-Induced Breakdown Spectroscopy held in Memphis Tennessee USA on September 2010. He earned award as the outstanding poster presentation for a category of security analysis from the International Chemical Congress of Pacific Basin Societies held in Hawaii USA on December 2010. in addition, he earned student travel awards from the 10th International Conference on Laser Ablation held in Singapore on November 2009 and the 3rd North American Symposium on Laser-Induced Breakdown Spectroscopy held in Florida USA on July 2011.

TOMAS HIRSCHFELD SCHOLARS

Nathaniel Gomer

University of South Carolina

Presentation: Mon., 4:10 pm, Atlanta A

Nathaniel Gomer graduated from the University of Florida in May 2008 with a B.S. in Biochemistry. During his time at UF, he conducted undergraduate research with Dr. Richard Yost, analyzing polypeptides using Mass Spectrometry. Following his time at UF, he attended the University of South Carolina, where he currently studies spectroscopy under his research advisor, Dr. S. Michael Angel. His research has focused on the development of a spatial heterodyne spectrometer (SHS) for Raman spectroscopy. He first presented his results at FACSS 2010 and received 1st place in the FACSS Student Poster Competition. In 2011, he received a student award from the Coblentz Society, a Joseph W. Bouknight Teaching Award from USC, as well as an Innovation Award at FACSS 2011. In 2012, he was given the USC Department of Chemistry's Guy F. Lipscomb Award for Excellence in Chemistry and Biochemistry and took 2nd place in USC's Graduate Student Day oral presentation competition. His first paper, discussing the use of a spatial heterodyne spectrometer for Raman spectroscopy, earned the 2012 William F. Meggers Award. He is also the recipient of the 2012 Tomas Hirschfeld Student Award.

Rohith Reddy

University of Illinois

Presentation: Mon., 3:50 pm, Atlanta A

Rohith Reddy is a Bioengineering graduate student in the Chemical Imaging and Structures Laboratory, headed by Professor Rohit Bhargava at the University of Illinois at Urbana Champaign. His research interests include design of instrumentation, creation of new imaging techniques and formulation of robust data analysis tools for infrared spectroscopy. His current research is focused on creating and enhancing mid-Infrared Spectroscopic Imaging techniques for biomedical applications. His work also presents important advances in using FT-IR imaging for tissue type identification and cancer detection in prostate and breast tissue. Previously, he obtained his B.Tech and M.Tech. in Electrical Engineering from Indian Institute of Technology (IIT) Madras. In his doctoral work he has so far published 11 peer reviewed papers, 2 book chapters and filed 1 patent. As a graduate student he has won the FACSS student poster award in 2007, 2009 and 2011, the Bioengineering Student Award (2010) and Graduate Student Achievement Award (2009) at the University of Illinois and co-authored the bronze medal winning paper at Genetic and Evolutionary Computation Conference (GECCO) 2007 held at London. He has also been awarded the Society of Applied Spectroscopy Graduate Student award, the Coblentz Student Award and the William G. Fateley Student Award for 2011.

FACSS AWARDS

FACSS STUDENT AND TOMAS HIRSCHFELD SCHOLAR AWARDS - Call for Applications for 2013

The Tomas Hirschfeld Scholar(s) and the FACSS Student Awards recognize the most outstanding papers submitted to FACSS by a graduate student. Recipients will receive financial support to help them attend the SciX 2013 conference in Milwaukee, WI (September 29 – October 4). In 2012 one FACSS Student Award and two Tomas Hirschfeld Scholars are being presented. In order to have your presentation considered for a Tomas Hirschfeld Scholar Award or FACSS Student Award, students should submit their abstract using the SciX web site submission form and indicate on the dropdown menu on the form their interest in these awards.

The submission process involves submitting an abstract, completing the web site submission form, and submitting the following electronically to facss@facss.org:

a) the form, available on the SciX web site

b) a 250 word abstract of the work to be reported

c) two letters of nomination, one by the student's mentor. An explanation of the inventive contributions by the student to the work should be given. Creativity was a primary characteristic of Tomas's work, and thus should be a characteristic of the awardee

d) a copy of the candidates resumé

e) a copy of the candidate's graduate transcript

f) copies of reprints and/or preprints of research accomplished.

The recipients will be included in a session highlighting young scientists and their work.
The SciX Web site will begin accepting abstracts and applications for FACSS student awards in January 2013**.** Go to www.scixconference.org to submit an application.

FACSS INNOVATION AWARD

FACSS Innovations Awards will be given for the most innovative and outstanding new research advancements debuted orally at the SciX Conference. All program areas are included. Only research findings presented for the first time in the public domain qualify for entry (work based on submitted papers not yet published electronically or in print at the time of abstract submission qualifies). Papers submitted for SciX will be considered for these awards – authors can check the appropriate box for their papers to be entered. Finalists will be selected for presentations at the SciX conference in special award sessions. Award winners will be selected after the award sessions are concluded. Each award includes: A cash prize of $1500; a plaque; and publicity

The 2011 FACSS Innovation Award Winners As Selected In Reno

Ultrasound Enhanced ATR Mid-IR Fibre Optic Probe for Spectroscopy of Particles in Suspensions; Cosima Koch, Markus Brandstetter, Stefan Radel, Bernhard Lendl; *Vienna University of Technology, Austria*

Large-Area Standoff Planetary Raman Measurements Using a Novel Spatial Heterodyne Fourier Transform Raman Spectrometer; S. Michael Angel, *University of South Carolina*; Nathaniel R. Gomer, *University of South Carolina*; Shiv K. Sharma, *University of Hawaii*; J. Chance Carter, *Lawrence Livermore National Laboratory*

Single Molecule Fluorescence Imaging Studies of Dynamic Processes in Reversed Phase Chromatographic Materials; Justin Cooper, Eric Peterson, Joel Harris, *University of Utah*

Laser Ablation Molecular Isotopic Spectrometry - New Dimension of LIBS ; Alexander Bol'shakov, *Applied Spectra, Inc*.; Richard Russo, *Applied Spectra Inc. and LBNL*; Xianglei Mao, *LBNL*; Dale Perry, *LBNL*; Osman Sorkhabi, *LBNL*; Chris McKay, *NASA-Ames Research Center*

2012 FACSS INNOVATION AWARD FINALISTS
Thursday Afternoon 3:50 – 5:10 pm, *Exhibit Hall B*
Organizer and Presider: Michael George
The winner of the 2012 Innovation Award will be announced at the Friday morning session.

Paper #

(721) **Punctuated Microgradients for Electric Field Separations**; Mark Hayes[1], Stacy Kenyon[1], Paul Jones[1]; [1]Arizona State University

(722) **Far-Field, Sub-Diffraction Fluorescence Lifetime Imaging**; Emily Smith[1, 2], Michael Lesoine[1, 2], Sayantan Bose[1, 2], Jacob Petrich[1, 2]; [1]Iowa State University, [2]The Ames Laboratory

(723) **Desorption Ionization with the Liquid Sampling-Atmospheric Pressure Glow Discharge Microplasma**; R. Kenneth Marcus[1], Carolyn Q. Burdette[1], Benjamin T. Manard[1], Lynn X. Zhang; [1]Clemson University

(724) **Advancing Infrared Microscopy Instrumentation by Theory and Computation**; Rohit Bhargava[1], P. Scott Carney[1], Rohith Reddy[1], Kevin Yeh[1], Thomas van Dijk[1], Matthew Gelber[1], Matthew V. Schulmerich[1]; [1]University of Illinois, Beckman Institute for Advanced Science and Technology

FACSS CHARLES MANN AWARD

For Achievements in the Field of Applied Raman Spectroscopy

Don E. Pivonka

Incyte Pharmaceuticals

Presentation: Tuesday, 8:30 am
Exhibit Hall B

Don Pivonka received his Ph.D. in analytical chemistry from Kansas State University, under the direction of Dr. Robert C. Fry. While at Kansas State, Don received several research awards including the Phillips Petroleum Fellowship Award as the outstanding researcher in the graduate chemistry program. Don was the inaugural recipient of the Tomas Hirschfeld award presented at the 1987 Pittsburgh Conference. In his professional career, Don spent 5 years at Hercules, Inc. (1987-1992) where he used vibrational spectroscopy to further the understanding of polymer processes and performance. In 1992, Don joined Imperial Chemical Industries (ICI) and through a series of mergers, Don's role transitioned from ICI to Zeneca (1993) and finally to AstraZeneca (2000). Don's research focus accordingly shifted from specialty chemicals to pharmaceutical research. Within pharmaceutical discovery, he has been a leader in application of infrared and Raman spectroscopy as it applies to the understanding of solid phase reaction mechanisms and kinetics of solid phase combinatorial synthesis. He has also championed novel applications of Raman spectroscopy for understanding relationships between the electronic properties of drug candidates and their ligand/receptor interaction in biological systems. This work has resulted in the discovery of various novel drug candidate molecules across a diverse range of central nervous system receptor targets. In 2011, Don joined Incyte Pharmaceuticals as a senior principal chemist working in the Chemistry, Manufacturing and Control (CMC) division. Don holds numerous publications and book chapters pertaining to applications of Raman spectroscopy in pharmaceutical research. He has presented numerous invited/plenary lectures worldwide, and was co-editor of the J. Wiley & Sons book titled "Applications of Vibrational Spectroscopy in Pharmaceutical Research and Development."

SOCIETY FOR APPLIED SPECTROSCOPY AWARDS

DISTINGUISHED SERVICE AWARD

Recognizing members for their long-time service to the society

David J. Butcher

Western Carolina University

David J. Butcher is currently Professor of Chemistry and Associate Dean of the College of Arts and Sciences at Western Carolina University (WCU) in Cullowhee, NC. He is married to Dr. Karen Butcher and has two children, Emily 21 and Neil 18, with whom he enjoys leisure time. He received his bachelor's degree in 1982 from the University of Vermont. After three years of employment at Pfizer and Bowdoin College, he received his Ph.D. from the University of Connecticut in 1990. His graduate work, conducted under the direction of Robert G. Michel, involved the development of instrumentation for laser excited atomic fluorescence and ionization spectroscopies. He joined the faculty at WCU in 1990 as an Assistant Professor of Chemistry, was promoted to Associate Professor in 1997, was promoted to Professor in 2001, and became Department Head in 2002. Prof. Butcher became Associate Dean in April, 2004. Prof. Butcher has more than 50 publications in a variety of areas of analytical chemistry, including graphite furnace atomic absorption spectrometry, diode laser atomic absorption spectroscopy, and ion trap mass spectrometry. Along with Prof. Joseph Sneddon, he is co-author of the volume "A Practical Guide to Graphite Furnace Atomic Absorption Analysis. His current research interests include environmental analytical chemistry; currently he is involved in a phytoremediation project to remove lead and arsenic from the soil at a housing development in Western North Carolina. He has also been involved in a number of novel teaching innovations in general and analytical chemistry. He serves as Associate Editor for Book Reviews of the *Microchemical Journal*, and Associate Editor for Education for *Spectroscopy Letters*. He received the 1998 WCU University Scholar Award as the outstanding researcher. He serves on the Editorial Boards of *Microchemical Journal*, *Spectroscopy Letters* and *Applied Spectroscopy Reviews*. He served as Chair of the American Microchemical Society Undergraduate Award Committee and is currently Chair of the A.A. Benedetti-Pichler Award Committee. In 2001, he served as Program Chair for 28th FACSS meeting held in Detroit, MI. In 2009, he became Editor-in-Chief of *Analytical Letters*. In 2010, he became Editor-in-Chief of *Instrumentation Science and Technology*. He served as the General Chair for the 37th FACCS meeting held in Raleigh, NC in 2010, and as Chair of the Western Carolinas ACS Section in 2011.

HONORARY MEMBERSHIP AWARD

Recognizing those individuals who have made exceptional contributions to spectroscopy.

Joel M. Harris

University of Utah

Joel M. Harris is currently Distinguished Professor of Chemistry at the University of Utah, where he also holds an adjunct appointment in the Department of Bioengineering. Harris received a B.S. degree from Duke University and his Ph.D. from Purdue University. He joined the faculty of the University of Utah in 1976. Harris's research has focused on the development of new techniques in applied spectroscopy; he and his students have advanced new concepts in photothermal detection, methods to analyze multi-dimensional spectroscopic data, Raman spectroscopy and microscopy techniques, and quantitative fluorescence detection at the single-molecule level. They have applied these techniques to investigate the kinetics and energetics of excited-state and reactive-intermediates, the chemistry of liquid/solid interfaces and dispersed particles, the kinetics of molecular transport, adsorption, and binding governing separations and analysis at interfaces. Harris is Fellow of the Society for Applied Spectroscopy and of the American Association for the Advancement of Science. For 12 years, he served as Editor-in-Chief of *Applied Spectroscopy*. He is the recipient of an Alfred P. Sloan Fellowship, the Coblentz Award in Molecular Spectroscopy, the University of Utah Distinguished Research Award, the ACS Division of Analytical Chemistry Award in Chemical Instrumentation, the SAS New York Section Gold Medal Award in Spectroscopy, the Pittsburgh Analytical Chemistry Award, the University of Utah Robert W. Parry Teaching Award, the Society for Applied Spectroscopy Distinguished Service Award, the Benedetti-Pichler Award in Microchemistry, the Bomem-Michelson Award of the Coblentz Society, and the American Chemical Society Award in Analytical Chemistry.

SOCIETY FOR APPLIED SPECTROSCOPY AWARDS

EMERITUS MEMBERSHIP AWARD

Recognizing those individuals who have who have contributed to spectroscopy and have been members of the Society for Applied Spectroscopy for 15 years, and now have retired from active scientific endeavor.

Howard J. Mark

Mark Electronics

Howard was awarded the BS degree in chemistry from the City College of New York in 1963, the MA degree in chemistry from the City University of New York in 1966, where he became interested in the application of electronics and instrumentation to chemical analysis, applied to the measurement of air pollution. He was awarded the Ph.D. degree in physical chemistry from New York University in 1972 and remained at NYU as a research fellow, performing research in applications of the then-new field of FTIR spectroscopy, adapting and modifying the FTIR hardware and software to specialized measurement situations. Howard joined Technicon Instrument Corporation in 1976, for development and applications of the then-new field of near-infrared analysis. While at Technicon, Howard learned about the power and usage of the science of Statistics, and later, Chemometrics. He created, designed and developed new algorithms for NIR quantitative and qualitative analysis and applied statistical and chemometric methods to optimize in-house test procedures. He was the first spectroscopist to apply the concept of Mahalanobis Distance to spectroscopic analysis. Howard began writing (with Jerry Workman) a series of columns "Statistics in Spectroscopy" (later "Chemometrics in Spectroscopy"), a series that is still ongoing. He wrote several books to explain the concepts involved in statistical thinking, in terms meaningful for chemists. When Technicon closed, Howard became an independent consultant and is currently president of Mark Electronics, a consulting company providing services in the fields of near-infrared analysis, hemometric and statistical data analysis, and custom instrument design and development. He is also founder and president of The Near Infrared Research Corporation, designing, developing and marketing both custom and standard accessories for near-infrared instrumentation, and also novel and unique software applications in addition to the hardware products. Howard was awarded the 2003 Eastern Analytical Symposium Award for Outstanding Achievement in Near Infrared Spectroscopy, and the Williams-Wright award from the Coblentz Society at the 2011 Pittcon. He is past-chair and past-secretary of the Council for Near-Infrared Spectroscopy (CNIRS), past-chair and past-treasurer of the New York Section of the Society for Applied Spectroscopy (NYSAS) and is exhibit committee chair for the International Diffuse Reflectance Conference (IDRC). He is an active member of the American Society for Testing and Materials (ASTM), and is chair of the Terminology subcommittee of the Molecular Spectroscopy committee of the ASTM. He has authored or co-authored seven patents; over 190 publications, 85 oral presentations and 13 books and book chapters on NIR analysis and on the application of statistics and chemometrics to spectroscopic analysis.

LESTER W. STROCK AWARD

Established by the SAS New England section to recognize an author(s) of an outstanding paper or series of papers.

Ralph E. Sturgeon

National Research Council Canada

Presentation: Thursday, 8:30 am, Exhibit Hall B

Ralph E. Sturgeon received his BSc (1973) and PhD (1977) in analytical chemistry from Carleton University, Ottawa Canada. Following graduation he immediately accepted a position as Research Associate in the Analytical Chemistry Group, Division of Chemistry at the National Research Council, Ottawa. Although primarily tasked with the development of Certified Reference Materials, he was given the latitude to pursue interest in fundamental studies in analytical spectroscopy. In 1998 he became a Principal Research Officer and in 2000 was appointed Group Leader for Chemical Metrology in the Institute for National Measurement Standards, NRC, a position he held until 2010. His interests lie in inorganic analytical chemistry, comprising trace element analysis, vapor generation, instrument development, organometallic speciation and production of Certified Reference Materials with a focus on atomic and mass spectrometric detection. He currently serves on the advisory boards of a number of international analytical chemistry journals and holds an Adjunct Research professor position with the Department of Chemistry, Carleton University. Since 2000, he has represented Canada on the Comité consultatif pour la quantité de matière (CCQM) under the auspices of the International Committee of Weights and Measures, participating in the working groups for both Inorganic Analysis as well as the Joint Committee on Traceability in Laboratory Medicine. Ralph Sturgeon's ongoing research activities are in the areas of vapor generation for sample introduction, mass bias fractionation in inorganic mass spectrometry and traceability of chemical measurements. His contributions to analytical atomic spectroscopy have been recognized through a number of awards, including Fellowship in the Chemical Institute of Canada (1990), the Barringer (1986) and Herzberg (2002) awards of the Spectroscopy Society of Canada, the McBryde Medal (1990) and Maxxam Award (2007) from the Chemical Institute of Canada, the Ioannes Marcus Marci award (1998) of the Czech Spectroscopic Society and an NRC Outstanding Achievement Award for 2009.

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SOCIETY FOR APPLIED SPECTROSCOPY

WILLIAM F. MEGGERS AWARD

Recognizing the author(s) of an outstanding paper appearing in Applied Spectroscopy

Presented for *Raman Spectroscopy Using a Spatial Heterodyne Spectrometer: Proof of Concept*

Volume 65, Issue 8, (August 2011), pp. 849-857.

S. Michael Angel

Presentation: Thursday, 8:00 am, Exhibit Hall B

S. Michael Angel is currently Professor and Fred M. Weissman Palmetto Chair in Chemical Ecology in the Chemistry and Biochemistry Department at The University of South Carolina. Dr. Angel received his PhD in analytical chemistry from North Carolina State University. His postdoc work was done under Tomas Hirschfeld at Lawrence Livermore National Laboratory where he also worked as an Environmental Scientist and Group Leader of the Advanced Measurement Sciences Group before leaving to become an Associate Professor of Chemistry at The University of South Carolina where he holds his current Professorship and Chairmanship. His research interests include optical instrumentation for remote and in-situ measurements in extreme environments. Dr. Angel has been honored with numerous awards including 2011 AAAS Fellow (American Association for the Advancement of Science), 2011 FACSS/SciX Innovation Award, 2009 USC Educational Foundation Research Award for Science, Mathematics and Engineering, and 2006 Physics and Advanced Technologies Directorate Award, Lawrence Livermore National Laboratory. In 2011 Mike was voted South Carolina Chemist of the Year by the South Carolina Section of the American Chemical Society.

Nathaniel Gomer graduated from the University of Florida in May 2008 with a B.S. in Biochemistry. During his time at UF, he conducted undergraduate research with Dr. Richard Yost, analyzing polypeptides using Mass Spectrometry. Following his time at UF, he attended the University of South Carolina, where he currently studies spectroscopy under his research advisor, Dr. S. Michael Angel. His research has focused on the development of a spatial heterodyne spectrometer (SHS) for Raman spectroscopy. He first presented his results at FACSS 2010 and received 1st place in the FACSS Student Poster Competition. In 2011, he received a student award from the Coblentz Society, a Joseph W. Bouknight Teaching Award from USC, as well as an Innovation Award at FACSS 2011. In 2012, he received the USC Department of Chemistry's Guy F. Lipscomb Award for Excellence in Chemistry and Biochemistry and took 2nd place in USC's Graduate Student Day oral presentation competition. His first paper, discussing the use of a spatial heterodyne spectrometer for Raman spectroscopy, earned the 2012 William F. Meggers Award. He is also the recipient of the 2012 Tomas Hirschfeld Student Award and the SAS Graduate Student Award.

Christopher Gordon grew up in the Pocono Mountains of Pennsylvania. He did his undergraduate work at Muhlenberg College in Allentown Pennsylvania. After graduation, he decided he had enough of the cold weather in the north and moved to South Carolina where he got his M.S. in analytical chemistry/spectroscopy from the University of South Carolina. After graduating, Gordon was hired to teach chemistry as a contract faculty at Harford Community College in Bel Air, Maryland. After his first year, HCC hired him on as an Assistant Professor where he still teaches. This fall, Gordon will start pursuing his Ed.D. in science education at Morgan State University.

Paul G. Lucey is a member of the faculty of the Hawaii Institute of Geophysics and Planetology at the University of Hawaii. He pursues research in planetary science and in remote sensing instrument development and teaches courses through the Department of Geology and Geophysics

Shiv Sharma's interdisciplinary research interests include: (a) development of instrumentation for remote and stand-off Raman spectroscopy for detecting chemicals and minerals on planetary surfaces, (b) Micro-Raman and IR spectroscopy of minerals, biominerals, meteorites and synthetic and natural glasses, and the role of volatile in silicate glasses and melts at ambient and high pressure and temperature. He studied Physics at the Indian Institute of Technology, Delhi, India, and was awarded a Ph. D. degree in 1973 for his dissertation, "Raman spectroscopic study of the structure of electrolytes in aqueous solutions and hydrated melts". He worked as a Research Associate (1974-1977) with Professor David M. Adams in the Chemistry Department at the University of Leicester (England), and as a Post-Doctoral Fellow (1977-1980) at the Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C. (USA). He joined the faculty of the Hawaii Institute of Geophysics, University of Hawaii, in 1980 as Assistant Professor and established the Raman spectroscopy laboratory with focus on the applications of Raman spectroscopy in the Earth and planetary science. Currently he serves as Research Professor and Associate Director at the Hawaii Institute of Geophysics and Planetolgy, School of Ocean and Earth Science and Technology, University of Hawaii at Manoa, Honololulu, Hawaii. Shiv Sharma has authored or coauthored over 250 research papers.

J. Chance Carter is currently the High Explosives Analytics and Spectroscopy group leader for the Chemical Sciences Division in the Physical and Life Sciences Directorate at Lawrence Livermore National Laboratory. Dr. Carter holds a Ph.D. from the University of South Carolina in Analytical Chemistry. His research interests are mainly focused on the development of spectroscopy-based analytical methods and systems.

SOCIETY FOR APPLIED SPECTROSCOPY

GRADUATE STUDENT AWARDS

Barbara Stull Graduate Student Award
Recognizing a graduate student for outstanding research in spectroscopy and presented in honor of our longtime colleague Barbara L. Stull

Ruchira Chatterjee
Rensselaer Polytechnic

Presentation: Monday, 5:10 pm, Atlanta A

Ruchira Chatterjee is a doctoral student in the Department of Chemistry and Chemical Biology at Rensselaer Polytechnic Institute. She has been developing structural methods to directly probe the light-driven water oxidation reaction in the photosynthetic protein complex, photosystem II. Her research on understanding the fundamental principles of solar water oxidation in nature might enable the design of a new generation of cost-effective and highly efficient devices for solar energy conversion. Ruchira joined Rensselaer Polytechnic Institute as a doctoral student in 2007, after earning her Bachelor's degree in Chemistry at St. Xavier's College (Calcutta, India) and a Master's degree in Physical Chemistry at the University of Delhi (Delhi, India). In early 2008, she joined the research group of Professor K. V. Lakshmi in the Department of Chemistry and Chemical Biology. Chatterjee's graduate research is focused on developing advanced multi-dimensional multi-frequency pulsed EPR spectroscopic methods to disentangle the individual steps that lead to solar energy conversion by photosystem II. The solar water-splitting protein complex, photosystem II (PSII), catalyzes one of the most energetically demanding reactions in Nature by using light energy to drive a catalyst capable of oxidizing water. Elucidating the water oxidation chemistry of photosystem II is of major importance in developing catalytic systems for solar fuels production. In addition to addressing important chemical problems related to energy conversion, her research also addresses the methodological void that exists in this field. She is exploiting the diverse potentials of EPR spectroscopy to interrogate the structure and dynamics of photochemical reaction intermediates. This approach brings new and otherwise unobtainable structural and functional insights to the problem.

Recognizing a graduate student for outstanding research in spectroscopy

Nathaniel Gomer
University of South Carolina

Presentation: Monday , 4:10 pm, Atlanta A

Nathaniel Gomer graduated from the University of Florida in May 2008 with a B.S. in Biochemistry. During his time at UF, he conducted undergraduate research with Dr. Richard Yost, analyzing polypeptides using Mass Spectrometry. Following his time at UF, he attended the University of South Carolina, where he currently studies spectroscopy under his research advisor, Dr. S. Michael Angel. His research has focused on the development of a spatial heterodyne spectrometer (SHS) for Raman spectroscopy. He first presented his results at FACSS 2010 and received 1st place in the FACSS Student Poster Competition. In 2011, he received a student award from the Coblentz Society, a Joseph W. Bouknight Teaching Award from USC, as well as an Innovation Award at FACSS 2011. In 2012, he was given the USC Department of Chemistry's Guy F. Lipscomb Award for Excellence in Chemistry and Biochemistry and took 2nd place in USC's Graduate Student Day oral presentation competition. His first paper, discussing the use of a spatial heterodyne spectrometer for Raman spectroscopy, earned the 2012 William F. Meggers Award. He is also the recipient of the 2012 Tomas Hirschfeld Scholar Award and the SAS Graduate Student Award.

SAS Undergraduate Student Grant Recipients

Priyanka Basnet, *Hampshire College*
Kevin Higgins, *Idaho State University*
Catherine McKenas, *Austin College*
Jonathan Palmer, *Idaho State University*

SOCIETY FOR APPLIED SPECTROSCOPY

FELLOWS AWARD

Recognizes individual members for their outstanding service to the field of spectroscopy

Paul W. Bohn received his B.S. in Chemistry from the University of Notre Dame in 1977 and his Ph.D. in Chemistry from the University of Wisconsin-Madison in 1981. After a two-year stint at Bell Laboratories, Murray Hill, NJ, he joined the faculty at the University of Illinois at Urbana-Champaign (UIUC). While at UIUC, he served as Centennial Professor in Chemical Sciences, Interim Director of the School of Chemical Sciences (1993-94), and Head of the Chemistry Department (1994-99). In 2001-02, he was Interim Vice Chancellor for Research, the senior research officer of the UIUC campus. In August 2006, he left UIUC to join the faculty at the University of Notre Dame as the Arthur J. Schmitt Professor of Chemical and Biomolecular Engineering and Professor of Chemistry and Biochemistry. He served as Editor for the Americas for the Royal Society of Chemistry journal *Analyst* (2007-09), is currently Chair of the Editorial Board for *Analyst*, and sits on numerous editorial and scientific boards. Prof. Bohn also serves as Project Director for the Advanced Diagnostics and Therapeutics Initiative, one of five inaugural Strategic Research Initiatives established in 2008 at Notre Dame. Dr. Bohn has received a number of awards and recognitions including the Coblentz Award (1990) for his outstanding contributions to the field of molecular spectroscopy by investigators under the age of 36, the ACS Award in Spectrochemical Analysis (1997), the Pittsburgh Spectroscopy Society Award (2004) for his pioneering contributions to the optical spectroscopy of condensed matter interfaces, the Bomem-Michelson Award from the Coblentz Society (2005), and the Theophilus Redwood Award of the Royal Society of Chemistry (2010). He was elected Fellow of the American Association for the Advancement of Science in 1998 and a Fellow of the Royal Society of Chemistry (UK) in 2008. Dr. Bohn's research interests include integrated microfluidic and nanofluidic chemical measurement strategies for personal monitoring, chemical and biochemical sensing in mass-limited samples, and molecular approaches to nanotechnology. He has authored/coauthored over 215 publications in the field and has 6 patents issued and 1 pending in technologies related to these efforts. In addition, he has delivered over 250 invited lectures at universities, national laboratories, and industrial laboratories throughout the world and has served as a consultant for companies both in the United States and in Europe.

Michael Carrabba

Dr. Mike Carrabba joined the Hach Company in 2004 as the Director of Hach Homeland Security Air Systems and he is currently the Global Director of Open Innovation where he has the responsibility of finding and developing relationships for new and emerging technologies. He received his B.S. in Chemistry (*magna cum laude*) from Salem State College in 1981 and his Ph.D. in Physical Chemistry from Tufts University in 1985. Dr. Carrabba's graduate work was conducted under the tutelage of Dr. Jonathan Kenny and focused on the utilization of laser-induced fluorescence to examine ultra-cooled gas phase molecules in a supersonic jet molecular beam. After graduate school, Dr. Carrabba joined EIC Laboratories where he eventually became Vice-President for the Spectroscopy Division. He conducted a variety of research programs, including photoelectrochemical etching of semiconductors, fiber optic chemical sensors and state-of-the-art Raman spectroscopy. During this time, he introduced the use of holographic filters for Raman spectroscopy and developed numerous types of field Raman instrumentation and techniques, several of which resulted in U.S. patents. After leaving EIC, he joined Chromex, Inc, a manufacturer of Raman spectroscopy systems, as Marketing Manager and was previously the OEM Division Manager at Jobin Yvon, Inc. Dr. Carrabba has been very active in the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) over the years. He has served as Governing Board Chair (2002), Program Chair (2000), Program Section Chair for Raman (1992-1999, 2001), Chairperson of the Long Range Planning Committee (1999-2008) and as a member of the Governing Board. Since 2006 he has been serving as the FACSS Exhibits Chair. In 2003 Dr. Carrabba received the ASTM Award of Merit for his 12 years of service as the Chairman of the ASTM Subcommittee on Raman Spectroscopy. In 2004 he received the FACSS Charles Mann Award for Applied Raman Spectroscopy and in 2007 he received the Williams-Wright Award for Industrial Vibrational Spectroscopy. He has also been honored with the 2009 FACSS Distinguished Service Award and the 2011 Society of Applied Spectroscopy (SAS) Distinguished Service Award. Dr. Carrabba is a member SAS, ASTM, and the Coblentz Society. On the home front, Professor Mary Widmark Carrabba of Southern Oregon University, a highly skilled Infrared microscopist and the former treasurer for SAS, complements Mike's Raman background

Robert M. Corn is a Professor in the Departments of Chemistry and Biomedical Engineering at the University of California, Irvine. He received a B. A. in Chemistry summa cum laude in 1978 from the University of California, San Diego, and subsequently earned a Ph. D. in 1983 from the University of California, Berkeley, under the direction of Professor Herbert L. Strauss in the application of Fourier transform infrared spectroscopy to the study of motion in molecular solids. From 1983-1984, he was a Visiting Scientist at the IBM Research Laboratory in San Jose, California, where he applied the techniques of surface plasmon-enhanced Raman scattering and optical second harmonic generation to electrochemical surfaces. Following IBM, he spent a year as a Visiting Assistant Professor in the area of Physical Chemistry at Swarthmore College in Swarthmore, Pennsylvania. In 1985, he moved to Wisconsin where he was a Professor of Chemistry and a member of the Analytical Sciences Division of the Department of Chemistry and the Water Chemistry Program until 2004. In July of 2004, he joined the faculty at the University of California, Irvine. Prof. Corn is a leader in the development and application of surface-sensitive spectroscopic methods including polarization-modulation Fourier transform infrared spectroscopy (PM-FTIR), optical second harmonic generation (SHG) and surface plasmon resonance imaging (SPRI). He has previously applied these spectroscopic methods to the study of single crystal electrode surfaces, ion transfer processes at liquid/liquid interfaces, and the implementation of DNA computing algorithms at surfaces. Currently, his primary research interests include the study of biopolymer adsorption onto surfaces, the chemical modification of surfaces for the creation of ultrathin films and adsorption-based biosensors and the development of novel surface enzyme chemistries for ultrasensitive biosensing. He also has ongoing research projects in the creation of nanowire diffraction grating structures and nanofluidic channel networks for biosensing applications, and the fabrication of ordered superparamagnetic nanoparticle arrays for high frequency inductor applications. Prof. Corn has over 140 publications and patents, and is a Fellow of the American Association for the Advancement of Science. He received the 2007 Pittsburgh Spectroscopy Award from the Spectroscopy Society of Pittsburgh and the 2007 Award in Spectrochemical Analysis from the ACS Division of Analytical Chemistry.

SOCIETY FOR APPLIED SPECTROSCOPY

FELLOWS AWARD

Recognizes individual members for their outstanding service to the field of spectroscopy

Volker Deckert received his PhD from the University of Wurzburg under the direction of Professor Wolfgange Kiefer. He is currently the Head of the Nanoscopy Department at the Friedrich Schiller University in Jena and the Institute for Photonic Technolgies (Jena) where he established a research direction aiming towards label free detection of bio-molecules with ultimate sensitivity and lateral resolution. Dr. Deckert is the recipient of the 2002 Sofia Kovalskaya of the Alexander von Humboldt Foundation, the 2006 Bunsen-Kirchhoff-Award of the DASp/GDCh, and the 2012 Research Award of the State of Thuringia.

Prof. Max Diem received his undergraduate education at the Universität Karlsruhe, Germany, and his PhD at the University of Toledo, OH. After postdoctoral fellowship with L. Nafie at Syracuse University, he rose through the academic ranks at the City University of New York (1979 – 2005) and has been Professor of Chemistry at Northeastern University since 2006. He held a Guest Professorship in Lehrstuhl Biophysik at the Ruhr Universität Bochum, Germany, in 2011. The research in Prof. Diem's laboratory centers on the development of spectral methods to diagnose and screen for disease. To this end, two complimentary spectroscopic methods are utilized, confocal Raman micro-spectroscopy, and infrared spectral imaging microscopy, in conjunction with multivariate statistical methods. Both spectral methods detect subtle, yet reproducible variations in the biochemical composition of human cells and tissue sections when progressing from normal to diseased states. These spectral changes are subsequently correlated to pathological and cytological results using supervised methods of multivariate analysis. Prof. Diem has published 2 books, 9 refereed book chapters, approximately. 170 refereed papers and 7 patents.

Paul Farnsworth is a professor in the Department of Chemistry and Biochemistry at Brigham Young University. He earned his B.S. degree in 1977 from BYU, then went on for doctoral work at the University of Wisconsin in Madison under the direction of John Walters. He did postdoctoral work with Gary Hieftje at Indiana University, and then returned to BYU as an assistant professor in 1983. He has had two appointments as a visiting scientist at the Joint Research Center of the European Commission in Ispra, Italy, the first in 1989 and the second in 1998, working in the laboratories of Nicolò Omenetto. In 2003 he spent a semester as a visiting professor at the University of Utah working with Joel Harris. Paul's research interests include laser and atomic spectroscopy and mass spectrometry. He began his research career studying energy transport and excitation mechanisms in inductively coupled plasmas used as emission sources. In recent years he has been using laser-excited fluorescence as a tool to study ion transport through the vacuum interface of an inductively coupled plasma mass spectrometer. His work on ion transport was recognized with the *Spectrochmica Acta* atomic spectroscopy award in 1998 and 2006. His work in atomic spectroscopy was recognized with the Lester W. Strock Award from the Society for Applied Spectroscopy in 2006. In addition to the atomic spectroscopy, Paul's research group has studies ion formation and transport in atmospheric-pressure ionization sources for mass spectrometry. Paul has been a member of the Society for Applied Spectroscopy for over thirty years. He served as editor for *Applied Spectroscopy* for twelve years, and was recognized with the society's distinguished service award in 2009.

Professor. Mike George received his B.Sc. and Ph.D. from the University of Nottingham in 1987 and 1990, respectively. He remained at Nottingham for a further 18 months as a Postdoctoral Fellow. He was awarded a Royal Society/STA of Japan Postdoctoral Fellowship to work on organic photochemistry with Professor Hiro-o Hamaguchi at the Kanagawa Academy of Science and Technology (KAST). He returned to the University of Nottingham as an Experimental Officer (1993) and was appointed to a Lectureship in Inorganic Chemistry in 1998. He was promoted to a chair in 2002. He was awarded the Royal Society of Chemistry Edward Frankland Fellowship (2002-03); Corday-Morgan Medal (2004) and Photochemistry Award (2005). He was also awarded the 2005 Masao Horiba Special Award by Horiba Ltd. Japan.

Duncan Graham obtained his BSc Honours in Chemistry from the University of Edinburgh in 1992 and his PhD in Bioorganic Chemistry in 1996 under the direction of Prof. Tom Brown investigating the use of modified oligonucleotides to inhibit HIV. He then moved to the University of Strathclyde where he joined the group of Prof. Ewen Smith as a postdoctoral fellow to examine the use of surface enhanced resonance Raman scattering (SERRS) for DNA analysis with Zeneca Diagnostics. Breakthroughs during that period of research lead to the award of a five-year David Phillips fellowship from the BBSRC to examine the area of DNA analysis by SERRS. In 2002 he won the RSC's Analytical Grand Prix Fellowship which provided funding for another period of five years to further develop his chosen area of using synthetic chemistry to create and develop new methods of bioanalysis using optical spectroscopy. In 2004 he was awarded the SAC Silver medal for the '*Innovative synthesis of new analytical reagents for sensitive and selective analysis*' and in 2005 he was presented with the Nexxus Young Life Scientist of Year award. In 2007 he was elected to the fellowship of the Royal Society of Edinburgh and is a cofounder and director of Renishaw Diagnostics Ltd (formerly D3 Technologies Ltd) which formed in 2007 and has 30 full time employees. He is currently Director of WestCHEM (the joint chemical sciences research school of Strathclyde and Glasgow Universities), Co-director of the Centre for Molecular Nanometrology, and Head of Research for Chemistry at the University of Strathclyde,. He has published over 150 papers and 13 patents, was appointed as a lecturer in 2002 and promoted to professor in 2004. He was awarded the Corday Morgan prize of the Royal Society of Chemistry in 2009 for '*outstanding and pioneering contributions to nanometrology in support of molecular manipulation and chemical and biological systems*' and a Royal Society Wolfson Merit Award in 2010. His interests are in using synthetic chemistry to produce nanosensors that respond to a specific biological species or event as measured by surface enhanced Raman scattering and collaborating with scientist from different disciplines to exploit these approaches.

SOCIETY FOR APPLIED SPECTROSCOPY

FELLOWS AWARD

Recognizes individual members for their outstanding service to the field of spectroscopy

Pavel Matousek obtained his MSc and PhD degrees in physics from the Czech Technical University (Prague, Czech Republic). For over 20 years, he has worked at the Rutherford Appleton Laboratory (Oxford, UK) in the areas of nonlinear optics and steady state and ultrafast time-resolved vibrational spectroscopy. He pioneered the concepts of Kerr-gated Raman spectroscopy, Spatially Offset Raman Spectroscopy (SORS) and introduced transmission Raman spectroscopy into pharmaceutical analysis. Currently, he is developing these for a range of novel applications including non-invasive disease diagnosis (cancer and bone), aviation security, and pharmaceutical quality control. Pavel has published over 170 peer-reviewed articles, filed over 10 patents, and co-edited a book on Raman spectroscopy (with Prof. Michael Morris, University of Michigan). His honours include 2009 Charles Mann Award for Applied Raman Spectroscopy (FACSS) and 2002 and 2006 Meggers Awards from the Society for Applied Spectroscopy (SAS). He acted as the Program Chair of FACSS 2011 (Reno, NV) and is currently the Chair of UK's Regional Section of SAS. Recently, he served as the Chair of the Meggers Award Selection Committee and is currently the Chair of the Coblentz Award Selection Committee and the Chair-Elect of SAS Publications Committee. Pavel sits on the editorial boards of *Applied Spectroscopy* and *Analyst* and the editorial advisory board of *Journal of Raman Spectroscopy*. He is a Fellow of the Royal Society of Chemistry, a Fellow of the Science and Technology Facilities Council, a visiting professor of the University College London and a founding director of Cobalt Light Systems Ltd, a spin out company commercializing SORS and transmission Raman spectroscopy.

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Dr. John Rabolt received his PhD in Molecular Physics (Chemical Physics) from Southern Illinois University. He is currently Karl W. and Renate Böer Professor of Materials Science and Engineering. He has spent the last 25 years investigating the relationship between the chemical architecture and shape of long chain organic molecules/polymers and their mechanical, electrical, optical and electronic properties. Along the way he has brought an understanding to how polymers can be made into conductive wires and how thin saran-wrap type films can be used to confine laser light in a narrow beam for telecommunications. Recently, his research group demonstrated how flat panel computer screen technology can be used to detect and identify DNA sequences visually through changes in color. Another area of Dr. Rabolt's research centers on the possibility of bringing polymers into the world of diagnostic medicine. He predicts the day when a computer chip the size of a piece of dust, or a tiny piece of plastic, can be swallowed and used to take diagnostic readings of what's going on inside the body. Before coming to the University of Delaware in 1996, Dr. Rabolt was a research staff member at the IBM Almaden Research Center, where he served as co-director of the NSF Center on Polymer Interfaces and Macromolecular Assemblies (a Stanford/IBM/University of California at Davis Materials Research Science and Engineering Center). During his career, Dr. Rabolt developed several laser-based analytical instruments and has been awarded three patents for optical-based microelectronic devices. He has authored or co-authored 175 research articles in peer-reviewed journals and is the recipient of several international awards in spectroscopy. Currently, Dr. Rabolt is an associate editor for *Macromolecules*, an American Chemical Society journal.

ACS Division of Analytical Chemistry Award for Distinguished Service in the Advancement of Analytical Chemistry

Gary M. Hieftje

Indiana University

Presentation: Wednesday, 8:00 am, Exhibit Hall B

The Analytical Division of the American Chemical Society is proud to announce that Gary M. Hieftje will receive the 2012 ACS Division of Analytical Chemistry Award for Distinguished Service in the Advancement of Analytical Chemistry.

Gary M. Hieftje is Distinguished Professor and Mann Chair of Chemistry at Indiana University in Bloomington, Indiana. His research interests include the investigation of basic mechanisms in atomic emission, absorption, fluorescence and mass spectrometric analysis, and the development of instrumentation and techniques for atomic and molecular methods of analysis. He is also interested in the on-line computer control of chemical instrumentation and experiments, the use of time-resolved luminescence processes for analysis, the application of information theory to analytical chemistry, analytical mass spectrometry, near-infrared reflectance analysis, metallomics, and the use of stochastic processes to extract basic and kinetic chemical information. He has won numerous awards in the fields of analytical chemistry, chemical instrumentation, and spectroscopy, has held major offices in several scientific societies, has delivered many named lectures, and has served on the editorial boards of many major journals. He is the author of over 560 publications, 10 books, and 18 patents. More than 65 students have received doctorates under his direction; many others have received M.S. degrees, and scores of undergraduates and visiting scientists have performed research in his laboratories. In the realm of service, Hieftje has chaired the Division of Analytical Chemistry of the ACS, has served as President of the SAS, has chaired review committees for several national laboratories, governmental institutions, and universities, has been chair of editorial boards of journals, and has served on such editorial boards for 13 journals. He has also been chair or a member of many national and international award committees and has delivered short courses on a range of subjects at national and international venues.

COBLENTZ SOCIETY'S CLARA CRAVER AWARD

The Craver Award is presented annually to an outstanding young molecular spectroscopist whose efforts are in the area of applied analytical vibrational spectroscopy.

Recognizing a young individual under the age of 45, who has made significant contributions in applied analytical vibrational spectroscopy.

Duncan Graham

University of Strathclyde

Presentation, Tuesday, 8:00 am, Exhibit Hall B

The Coblentz Society is pleased to announce that **Professor Duncan Graham**, University of Strathclyde, Glasgow has been selected as the recipient of the 2012 Craver Award. In 2006, the Coblentz Society created an award to recognize the efforts of young professional spectroscopists that have made significant contributions in applied analytical vibrational spectroscopy. The society has named this award for Clara D. Craver in recognition of her pioneering efforts in promoting the practice of infrared vibrational spectroscopy and her many years of service to the Coblentz Society. Further, the Craver Award is the society's complement of its prestigious 'Coblentz Award' that recognizes young spectroscopists for efforts in fundamental aspects of vibrational spectroscopy. This award is presented to Professor Graham in recognition of his pioneering work in surface enhanced Raman scattering (SERS) to generate ultra-sensitive and highly selective methods of detection for a range of analytes, especially bio-analytical targets. Duncan Graham obtained his BSc Honours in Chemistry from the University of Edinburgh in 1992 and his PhD in Bioorganic Chemistry in 1996 under the direction of Prof. Tom Brown investigating the use of modified oligonucleotides to inhibit HIV. He then moved to the University of Strathclyde where he joined the group of Prof. Ewen Smith as a postdoctoral fellow to examine the use of surface enhanced resonance Raman scattering (SERRS) for DNA analysis with Zeneca Diagnostics. Breakthroughs during that period of research led to the award of a five-year David Phillips fellowship from the Biotechnology and Biological Sciences Research Council (BBSRC) to examine the area of DNA analysis by SERRS. In 2002 he won the Royal Society of Chemistry's Analytical Grand Prix Fellowship which provided funding for another period of five years to further develop his chosen area of using synthetic chemistry to create and develop new methods of bioanalysis using optical spectroscopy. In 2004 he was awarded the SAC Silver medal for the '*Innovative synthesis of new analytical reagents for sensitive and selective analysis*' and in 2005 he was presented with the Nexxus Young Life Scientist of Year award. In 2007 he was elected to the fellowship of the Royal Society of Edinburgh and is a cofounder and director of Renishaw Diagnostics Ltd (formerly D3 Technologies Ltd) which formed in 2007 and has 30 FTE. He is currently Director of WestCHEM (the joint chemical sciences research school of Strathclyde and Glasgow Universities), Co-director of the Centre for Molecular Nanometrology, and Head of Research for Chemistry at the University of Strathclyde. He has published over 150 papers and 13 patents, was appointed as a lecturer in 2002 and promoted to professor in 2004. He was awarded the Corday Morgan prize of the Royal Society of Chemistry in 2009 for '*outstanding and pioneering contributions to nanometrology in support of molecular manipulation and chemical and biological systems*' and a Royal Society Wolfson Merit Award in 2010. His interests are in using synthetic chemistry to produce nanosensors that respond to a specific biological species or event as measured by surface enhanced Raman scattering and collaborating with scientist from different disciplines to exploit these approaches.

The Coblentz Society – fostering understanding and application of vibrational spectroscopy

Call for Award Nominations - See http://www.coblentz.org/ for more informa

ABB Bomem-Michelson Award: ABB sponsors the Bomem-Michelson Award to honor scientists whom have advanced the technique(s) of vibrational, molecular, Raman, or electronic spectroscopy. Contributions may be theoretical, experimental, or both. The recipient must be actively working and at least 37 years of age. The nomination should include a resume of the candidate's career as well as a synopsis of the special research achievements that make the candidate an eligible nominee for the ABB sponsored Bomem-Michelson Award. Nominations for the award are open February 1st to **May 1st** each year. Further information: www.coblentz.org/awards/the-bomem-michelson-award.

Coblentz Award: The Coblentz Award is presented annually to an outstanding young molecular spectroscopist under the age of 40. The candidate must be under the age of 40 on January 1st of the year of the award. Nominations should include a detailed description of the nominee's accomplishments, a curriculum vitae and as many supporting letters as possible. Annual updates of files of nominated candidates are encouraged. Nominations for the Coblentz Award are open between January 3rd and **July 15th** each year. Further information regarding the Coblentz Award is available at www.coblentz.org/awards/the-coblentz-award.

Craver Award: The Craver Award is presented annually to an outstanding young molecular spectroscopist whose efforts are in the area of applied analytical vibrational spectroscopy. The candidate must be under the age of 45 on January 1st of the year of the award. The work may include any aspect of (near-, mid-, or far-infrared) IR, THz, or Raman spectroscopy in applied analytical vibrational spectroscopy. Nominees are welcome from academic, government, or industrial research. Nominations must include a detailed description of the nominee's accomplishments, curriculum vitae or resume, and a minimum of three supporting letters. Nominations for the Craver Award are open between March 30th and **August 30th** each year. Further information: www.coblentz.org/awards/the-craver-award.

Ellis R. Lippincott Award: The Ellis R. Lippincott Award is presented annually in recognition of significant contributions and notable achievements in the field of vibrational spectroscopy. The medal is jointly sponsored by the Coblentz Society, the Optical Society of America and the Society for Applied Spectroscopy. Recipients must have made significant contributions to vibrational spectroscopy as judged by their influence on other scientists. Because innovation was a hallmark of the work of Ellis R. Lippincott, this quality in the contributions of candidates will be carefully appraised. Nominations for the award are open January 1st to **October 1st** each year. Nominations should be submitted to: Lippincott Award Chairperson, awards@osa.org. Further information: www.coblentz.org/awards/the-lippincott-award.

Honorary Membership: The Coblentz Society awards honorary memberships in the Society to people who have made outstanding contributions to the field of vibrational spectroscopy or any other field related to the purposes of the Society. Nominations close on **February 1st** each year, with awards announced at the Annual Members Meeting at Pittcon and presented at FACSS. Send your nomination to Prof. Michael Myrick, Coblentz Society President at michael.myrick@coblentz.org.

COBLENTZ SOCIETY'S WILLIAM G. FATELEY STUDENT AWARD

The William G. Fateley Student Award is given by the Coblentz Society annually to recognize outstanding contributions to vibrational spectroscopy during a current Ph.D. program. William G. (Bill) Fateley was among the first winners (1965) of the Coblentz award, and worked tirelessly to promote the Pittsburgh Conference and FACSS. Author of more than 350 publications and recipient of numerous other awards, he returned to his alma mater, Kansas State University, as chairman of his department in 1972 and served there until his retirement 1997 and beyond. He served as the Editor of *Applied Spectroscopy* for 20 years, and served as mentor to a generation of spectroscopists

Xiaohua (Sarah)Zhou
Presentation: Monday, 4:50 pm, Atlanta

Xiaohua (Sarah) Zhou is completing her Ph.D. degree in Chemistry at the University of Missouri-Kansas City with Dr. James R. Durig. Her research is focused on understanding the structural properties and dynamics of quasi-linear molecules with a special emphasis on molecules containing the isocyanate moiety. The research is conducted by utilizing infrared, Raman, and microwave spectroscopy along with theoretical investigation. She has published 14 peer-reviewed papers and is expected to have 5 more prior to her graduation in May 2013. During her graduate studies, she worked as a research assistant in the University of Kansas Medical Center carrying out research on the molecular and thermodynamic mechanism of allosteric regulations by utilizing Hydrogen/Deuterium Exchange Mass Spectrometry. Some awards that Xiaohua has received include the Gates Millennium Scholars-Asian & Pacific Islander American Scholarship, the Outstanding Merit Award from the UMKC Women's Council, and a 1st place award for her poster presentation at FACSS 2011.

The Coblentz Society – fostering understanding and application of vibrational spectroscopy

Call for Student Award Nominations
See http://www.coblentz.org/ for more information

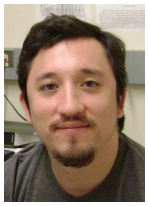
In addition to Awards for professionals in industry, academia and government laboratories, the Coblentz Society encourages young scientists to pursue studies in all forms of vibrational spectroscopy through the presentation of Student Awards. The Coblentz Student Award recognizes excellence in research involving vibrational spectroscopy and/or coursework including vibrational spectroscopy. The William G. Fateley Student Award is presented to one of the nominees each year in honor of Bill Fateley, former editor of Applied Spectroscopy and an early recipient of the Coblentz Award. Nominators must be members of the Coblentz Society. To become a member, contact Mark Druy at druy@psicorp.com, visit the Coblentz Society website at www.coblentz.org, or register when renewing your Society for Applied Spectroscopy membership at www.s-a-s.org.

Coblentz and William G. Fateley Student Awards: The Coblentz Society seeks nominations of outstanding students for the Coblentz Student Awards. Awardees receive a copy of the Society's Desk Book, a certificate, and a year's membership in the Society. Their names and the names of their faculty advisors appear in the Society's Newsletter. All awardees who attend FACSS will receive their award in person from the Coblentz Society's president at a presentation during Sunday Evening's SAS Student Poster session. All nominees for the Coblentz Student Award will automatically be considered for the William G. Fateley Student Award. The William G. Fateley award recipient will be given the opportunity to speak in the Student Awards session at SciX or in another appropriate venue, and will receive a $1000 prize supported by an endowment established in Professor Fateley's name by his former students, friends and colleagues.

Nominations for the Coblentz and William G. Fateley Student Awards must be submitted by February 1st. Additional information regarding eligibility for the Coblentz Society student awards and nomination requirements can be found at www.coblentz.org/awards/coblentz-student-awards.

COBLENTZ SOCIETY'S STUDENT AWARDS

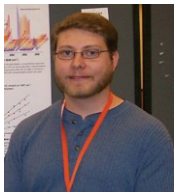
For many years, the Coblentz Society has encouraged young scientists to pursue studies in spectroscopy by seeking nominations of outstanding students for the Coblentz Student Awards. The awardees receive a copy of the Society's Deskbook, a certificate, and a year's membership in the Society. Their names, the names of their faculty advisors, their institution, and their anticipated graduation date appear in the Society's Newsletter in the August issue of Applied Spectroscopy.



Eduardo Berrios was born in Santiago, Chile. He did his undergraduate studies at the University of Chile from 2002-2007, where he obtained his bachelor degree in chemistry and also his professional degree as chemist. His graduation thesis was titled *Effect of the presence of sucrose monoesters on the membrane of DPPC liposomes*. In 2007 he was awarded with a Fulbright-CONICYT scholarship to pursue a doctoral degree in The United States of America. Since January 2009, he has been researching in Martin Gruebele's group in The University of Illinois at Urbana-Champaign. There his research involves the study of molecular vibrations and its application in quantum computing theoretically and experimentally.

Marleen Kerssens is currently pursuing her PhD in the Biophotonics Research Unit, Gloucestershire Hospitals, NHS Foundation Trust, under the supervision of Professor Nick Stone and Professor Pavel Matousek. Her research explores the relationship between breast calcification and cancer diagnosis. By utilizing deep-Raman techniques and FTIR molecular and structural information on calcifications and surrounding tissue interfaces is provided which can advance both diagnostics and clinical scientific understanding of the processes involved. Previously, she obtained a BSc in chemistry and an MSc in analytical chemistry from VU University, Amsterdam, The Netherlands.

In 2008, **Rajesh Morampudi** completed his Bachelor of Science in Pharmaceutical Science degree from the College of Pharmacy at Andhra University, Andhra Pradesh, India. As an undergraduate student, Rajesh performed research to evaluate the nootropic effects of Quercetin in normal and diabetic rats and later investigated the solubility and dissolution rate of Nimesulide by complexation with β-cyclodextrin. In August 2008, Rajesh was accepted into the PhD program in bioanalytical and clinical chemistry at Cleveland State University in Cleveland, Ohio. As part of his dissertation research, Rajesh has developed a new high resolution optical disperser based on a virtually imaged phased array for Raman and Brillouin line scan imaging of polymer bone implant materials. The new imaging device will be used to non-invasively characterize electromechanical implant properties during periods of bone cell culture and will help establish cell response to electromechanical stress.



Jonathan Schaefer is a chemistry doctoral student in the analytical division at the University of Utah in Joel M. Harris's research group. His work focuses on structural and chemical changes in single vesicle lipid bilayers. In order to study individual vesicles, he uses a single-objective optical trap to immobilize the vesicle at the focus of an excitation laser beam. Raman scattered light from the optically trapped vesicle is collected back through the objective and focused through a confocal aperture, isolating a ~1.5 fL detection volume around the vesicle. Jon has used Raman spectroscopy to study the polymerization kinetics and thermochromic phase transitions of individual diacetylenic phospholipid vesicles, research that was published in the *Journal of Raman Spectroscopy*. His more recent research efforts have focused on measuring temperature-controlled release from individual phospholipid vesicles found in formulations used in chemotherapy treatments. Results from the temperature-controlled release study were presented at FACCS in October, 2011 and are currently being written up for publication.

Andreas Wilk was born in Augsburg, Bavaria, Germany in 1980. He performed his undergraduate studies at the University of Ulm, Baden-Württemberg, Germany, and has received his Diploma degree in Chemistry in 2008. Having joined Prof. Dr. Boris Mizaikoff's research group in the same year, he is currently pursuing his PhD in Analytical Chemistry with focus on next-generation gas sensors operating in the mid-infrared (3-12 μm) spectral regime. His research involves the development of spectrally resolved simulation schemes of entire mid-infrared sensor platforms including modeling the spectral response to virtual analytes with particular interest in applications for enclosed space monitoring and breath diagnostics. The experimental studies are focused on the development, fabrication, and characterization of innovative substrate-integrated hollow waveguides, which have been established during an ongoing collaborative work with the Lawrence Livermore National Laboratory (LLNL, Livermore, CA, USA). To date, he is author of two peer-reviewed research publications and one book chapter with four manuscripts currently in preparation, and is co-author on one filed patent. He has contributed to international scientific conferences with three posters (EUROANALYSIS 2009, EUROPTRODE 2010) and one oral presentation (FACSS 2011).

Xiaohua (Sarah) Zhou is completing her Ph.D. degree in Chemistry at the University of Missouri-Kansas City with Dr. James R. Durig. Her research is focused on understanding the structural properties and dynamics of quasi-linear molecules with a special emphasis on molecules containing the isocyanate moiety. The research is conducted by utilizing infrared, Raman, and microwave spectroscopy along with theoretical investigation. She has published 14 peer-reviewed papers and is expected to have five more prior to her graduation in May 2013. During her graduate studies, she worked as a research assistant in the University of Kansas Medical Center carrying out research on the molecular and thermodynamic mechanism of allosteric regulations by utilizing Hydrogen/Deuterium Exchange Mass Spectrometry. Xiaohua has received several awards which include the Gates Millennium Scholars-Asian & Pacific Islander American Scholarship, the Outstanding Merit Award from the UMKC Women's Council, and a 1st place for her poster presentation at FACSS 2011.

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COBLENTZ SOCIETY'S HONORARY MEMBERSHIP AWARD

Recognizing those individual who are deemed by the Board of Managers of the Society to have made outstanding contributions to the field of vibrational spectroscopy or to any other field related to the purposes of the Society.

Recognition for pioneering work in the application of chemometrics to spectroscopic and spectral imaging analyses

David M. Haaland received his PhD in Physical Chemistry from the University of Rochester and was employed by Sandia National Laboratories from 1972 until 2008. He is currently a contract employee with Sandia, the sole proprietor of Spectral Resolutions Consulting, and North American Editor of the Journal of Chemometrics. David's research interests have been the application of chemometric methods to the quantitative and qualitative analysis of spectral data. The work of David and his collaborators has included development of classical least squares (CLS) methods for quantitative spectral analysis, automation of factor selection for PLS and PCR, and invention of new augmented classical least squares (ACLS) methods that are ideally suited to updating quantitative multivariate calibration models. Dr. Haaland led a team in the development of a new 3D hyperspectral confocal fluorescence microscope with associated multivariate curve resolution (MCR) software to investigate cell signaling in eukaryotic cells and the photosynthetic processes in bacteria and plants. His current research interests involve the application MCR to hyperspectral imaging from fluorescence spectrometers and the analysis of magnetic resonance spectral images of human brains. Dr. Haaland has published over 135 journal articles and conference proceedings, presented 160 invited talks, and has 13 issued U.S. patents licensed to U.S. industry. He has received the Chemistry in Statistics Award (1991), SCR Technical Excellence Award with Niemczyk (1993), New Mexico Inventor of the Year Award (1994), the Bomem–Michelson Award (2004), the EAS Award for Achievements in Chemometrics (2005), an R&D 100 Award (2009), and the Meggers Award with Gemperline, Cutler, and Andries (2010). He is a Fellow of AAAS and SAS. He has supported the Coblentz Society as a board member from 1991-1994 and served as its president elect and president from 1998 to 2001.

Recognition for research and broad development of vibrational circular dichroism and Raman optical activity for the analysis of chiral molecules

Laurence A. Nafie received his Ph.D. from the University of Oregon in 1973, studying resonance Raman scattering, and from 1973 to 1975 he was a postdoctoral associate at the University of Southern California, working on the discovery and confirmation of infrared vibrational circular dichroism (VCD). In 1975 he joined the Chemistry faculty at Syracuse University to establish a research program in VCD and Raman optical activity (ROA). In 1978, he was named an Alfred P. Sloan Foundation Fellow and was promoted to Professor in 1982. In 1978 he proposed and carried out the first measurements of Fourier transform VCD, now the basis of all commercial VCD instrumentation. He was appointed Chairman of the Chemistry Department in 1984 and served until 2000. In 1988 he measured the scattered circular polarization (SCP) form of ROA for the first time that is now used in the only commercially available ROA spectrometer. In 1989 he predicted theoretically a new form of ROA called dual circular polarization (DCP) ROA that was confirmed experimentally in his laboratory in 1991. In 1995 he became founding Editor of the journal *Biospectroscopy*, published by John Wiley & Sons and continued as Associate Editor of *Biopolymers* until 2010. In 1996, he co-founded with Dr. Rina Dukor the company BioTools, Inc. to market advanced vibrational spectroscopy instrumentation, including the Chiral*IR* VCD and Chiral*RAMAN* ROA spectrometers. In 1996 he published the theory of resonance ROA and its predictions were confirmed by its first observation in 1998. In 2000, he was named Distinguished Professor of Chemistry at Syracuse University. He was awarded the Coblentz Award (1981), the Bomem Michelson Award (2001), the William F. Meggers Award (2001) and the Distinguished Service Award of the Society of Applied Spectroscopy (2007). He served on the Governing Board of the Coblentz Society from 1984 to 1988 and was President from 1993 to 1995. In 2003, he served as President of the Society of Applied Spectroscopy, and in 2008 he became a Fellow of the Society of Applied Spectroscopy. In January 2010 he retired from full-time service at Syracuse University to become Distinguished Professor Emeritus and at the same time Editor-in-Chief of the *Journal of Raman Spectroscopy* published by John Wiley & Sons. In 2011 he published a comprehensive book on the fundamental theory, instrumentation, measurement, calculation and application of vibrational optical entitled *Vibrational Optical Activity: Principles and Applications* Wiley, Chichester (2011). He has over 290 publications and several patents.

ANACHEM AWARD

The ANACHEM Award is presented annually to an outstanding analytical chemist based on activities in teaching, research, administration or other activity, which has advanced the art and science of the field.

Peter R. Griffiths

University of Idaho

Presentation: Wednesday, 8:30 am, Exhibit Hall B

Peter Griffiths received his doctorate in physical chemistry at Oxford University and did postdoctoral research at the University of Maryland. He then worked as Product Specialist at Digilab, where the first FT-IR spectrometer of the modern era was developed. He was subsequently appointed as Manager of Analytical Services at Sadtler Research Laboratories in Philadelphia (now the Bio-Rad Informatics Division.) He started his academic career at Ohio University where he ultimately named achieved the rank of distinguished professor. He then moved to the University of California, Riverside before being appointed chair of the Chemistry Department of the University of Idaho where he is now professor emeritus. Dr. Griffiths has worked in many different aspects of vibrational spectroscopy since 1964. The research in his laboratory has been largely centered on the application of infrared and Raman spectrometry to the solution of problems of analytical, environmental and structural chemistry. Topics on which he has published extensively include various types of infrared reflection spectroscopy, Raman spectroscopy, chemometrics and data processing, developments of instrumentation for infrared spectroscopy (especially FT-IR), hyphenated techniques, open-path atmospheric monitoring and surface-enhanced infrared and Raman spectroscopy. He is the author of over 300 refereed papers and 45 book chapters, and his written or edited 12 books on various aspects of vibrational spectroscopy, including *Fourier Transform Infrared Spectrometry* (two editions) and the five-volume *Handbook of Vibrational Spectroscopy*. He has been very active in activities of the Society for Applied Spectroscopy. He was President of SAS in 1994 and was awarded honorary membership in the Society, as well as the Distinguished Service Award. He served as Associate Editor of the journal *Applied Spectroscopy* for almost twenty years and took over as Editor-in-Chief in July 2009. He has won a number of awards including the Coblentz award, the Spectroscopy Society of Pittsburgh Award, the Birth Award for near-infrared spectroscopy, the Bomem-Michelson Award, the Prëgl medal of the Austrian Society of Analytical Chemistry and the Gold Medal of the New York Section of the SAS. He was awarded an Alexander von Humboldt Research Fellowship that enabled him to spend a year at the Technical University of Dresden and, most recently, an Erskine Fellowship to the University of Canterbury, New Zealand. He directs the week-long summer courses on the interpretation and applications of infrared and Raman spectra that held annually at Bowdoin College in Brunswick, ME and occasionally in Sweden.

2011 JOSEPH BLACK AWARD
Presented by the Royal Society of Chemistry

Christy L. Hayes

University of Minnesota

Presentation: Monday, 10:20 am, New York B

Christy L. Haynes is currently an Associate Professor of Chemistry at the University of Minnesota, mentoring a group of 11 doctoral students and 9 undergraduate researchers in the area of bioanalytical chemistry.

Haynes did her undergraduate training at Macalester College in St. Paul, MN, graduating in 1998 before beginning graduate training at Northwestern University. At Northwestern, Haynes earned her Ph.D. in 2003 working with Richard P. Van Duyne in the areas of nanoparticle optics and surface-enhanced Raman scattering sensors. She performed postdoctoral research as a NIH NRSA fellow with R. Mark Wightman at the University of North Carolina – Chapel Hill, using carbon-fiber microelectrochemistry to characterize single cell secretion. Prof. Haynes then joined the University of Minnesota as a faculty member in 2005, where her research focus has been on employing carbon–fiber microelectrode amperometry as an assay of nanoparticle toxicity. In addition, her group has performed the first ever real-time measurements of chemical messenger secretion from individual blood platelets, characterizing serotonin concentration and release kinetics critical in hemostasis, and developed an active materials science program in the area of nanoparticle therapeutics.

Since beginning her independent career, Prof. Haynes has co-authored more than 30 peer-reviewed manuscripts and been the recipient a Kinship Foundation Searle Scholar Award (2006), a NIH New Innovator Award (2008), a Camille and Henry Dreyfus Teacher-Scholar Award (2009), and an Alfred P. Sloan Fellowship (2010).

PREVIOUS FACSS BOARD AND MEETING CHAIRS

1973	
Jeannette Grasselli	Governing Board Chair
1974 – Atlantic City	
James White	Governing Board Chair
George Heinz	General
James White	Program
Edward Ruffing	Exhibit
1975 - Indianapolis	
James Holcombe	Governing Board Chair
Gerald Wallace	General
James Holcomb	Program
Edward Ruffing	Exhibit
1976 - Philadelphia	
Edward Brame	Governing Board Chair
Edward Brame	General
Edward Dunlap	Program
Douglas Robinson	Arrangements
Edward Ruffing	Exhibit
1977 - Detroit	
Edgar Peck	Governing Board Chair
Mitch Kapron and James Burns	General
Jeannette Grasselli	Program
L. Felix Schneider	Arrangements
Edward Ruffing	Exhibit
1978 - Boston	
James Williamson	Governing Board Chair
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James Cornwell	Arrangements
Edward Ruffing	Exhibit
1979 - Philadelphia	
Peter Keliher	Governing Board Chair
Douglas Robinson	General
Philip LeFleur	Program
Sydney Fleming	Arrangements
Edward Ruffing	Exhibit
1980 - Philadelphia	
L. Felix Schneider	Governing Board Chair
Sydney Fleming	General
Theodore Rains	Program
Robert Barford	Arrangements
Edward Ruffing	Exhibit
1981 - Philadelphia	
Jack Katon	Governing Board Chair
Robert Barford	General
Mary Kaiser	Program
James Cavanaugh	Arrangements
Peter Keliher	Exhibit
1982 – Philadelphia	
Sydney Fleming	Governing Board Chair
James Cavanaugh	General
Andrew Zander	Program
Matthew O'Brien	Arrangements
Peter Keliher	Exhibit
1983 - Philadelphia	
Mary Kaiser	Governing Board Chair
Matthew O'Brien	General
John Lephardt	Program
D. Bruce Chase	Arrangements
Peter Keliher	Exhibit
1984 - Philadelphia	
Theodore Rains	Governing Board Chair
D. Bruce Chase	General
Patricia Rouse Coleman	Program
Fred Corcoran	Arrangements
Peter Keliher	Exhibit
1985 - Philadelphia	
Robert Barford	Governing Board Chair
Fred Corcoran	General
Matthew Klee	Program
Marshall Fishman	Arrangements
Peter Keliher	Exhibit
1986 - St. Louis	
Ronald Schroeder	Governing Board Chair
Marshall Fishman	General
Alexander Scheeline	Program
Terry Hunter	Arrangements
Edward Brame	Exhibit
1987 - Detroit	
Patricia Rouse Coleman	Governing Board Chair
David Coleman and L. Felix Schneider	General
John S. Beaty	Program
Edward Brame	Exhibit
1988 - Boston	
James Cavanaugh	Governing Board Chair
Frank Plankey and John S. Beaty	General
Roger Gilpin	Program
Edward Brame	Exhibit
1989 - Chicago	
Alexander Scheeline	Governing Board Chair
Paul Bourassa	General
Robert Michel	Program
Edward Brame	Exhibit
1990 - Cleveland	
Nancy Miller-Ihli	Governing Board Chair
Charles Belle	General
Steven Hughes	Program
Edward Brame	Exhibit
1991 - Anaheim	
David Coleman	Governing Board Chair
Richard Deming and Constance Sobel	General
James Holcombe	Program
Edward Brame	Exhibit
1992 - Philadelphia	
Karmie Galle	Governing Board Chair
Matthew Klee	General
Barry Lavine	Program
Edward Brame	Exhibit

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1993 - Detroit

Robert Watters	Governing Board Chair
L. Felix Schneider and David Coleman	General
Julian Tyson	Program
Mildred Barber	Exhibit

1994 - St. Louis

Paul Bourassa	Governing Board Chair
Terry Hunter	General
John Koropchak	Program
Mildred Barber	Exhibit

1995 – Cincinnati

Jon W. Carnahan	Governing Board Chair
Joseph A. Caruso	General
Richard F. Browner and R. Kenneth Marcus	Program
Mildred Barber	Exhibit

1996 – Kansas City

Rachael Barbour	Governing Board Chair
O. Karmie Galle	General
William Fateley and John A. Graham	Program
Scott McGeorge	Exhibit

1997 - Providence

Mildred Barber	Governing Board Chair
Chris Brown	General
John Olesik	Program
Scott McGeorge	Exhibit

1998 - Austin

John Graham	Governing Board Chair
David Laude	General
Isiah Warner and Linda McGown	Program
Scott McGeorge	Exhibit

1999 - Vancouver

Robert G. Michel	Governing Board Chair
Michael Blades	General
Ronald Williams	Program
Scott McGeorge	Exhibit

2000 - Nashville

John Koropchak	Governing Board Chair
Arlene Garrison	General
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2001 – Detroit

David A. Laude	Governing Board Chair
David Coleman and L. Felix Schneider	General Co-Chairs
David J. Butcher	Program
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2002 – Providence

Michael Carrabba	Governing Board Chair
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2003 – Fort Lauderdale

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2004 – Portland

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George Agnes	Program
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2005- Quebec City, Canada

Mark Hayes	Governing Board Chair
Denis Boudreau	General
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Scott McGeorge	Exhibit

2006 – Orlando

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Christine Wehlburg	General
S. Douglass Gilman	Program
Mike Carrabba	Exhibit

2007 – Memphis

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Paul Bourassa	General
Ian R Lewis	Program
Mike Carrabba	Exhibit

2008 – Reno

Gary Brewer	Governing Board Chair
John Hellgeth	General
Greg Klunder	Program
Mike Carrabba	Exhibit

2009 – Louisville

Becky Dittmar	Governing Board Chair
Jessica Jarman	General
Curtis Marcott	Program
Mike Carrabba	Exhibit

2010 – Raleigh

S. Douglass Gilman	Governing Board Chair
David J. Butcher	General
André J. Sommer	Program
Mike Carrabba	Exhibit

2011 – Reno

S. Douglass Gilman	Governing Board Chair
Greg Klunder	General
Pavel Matousek	Program
Mike Carrabba	Exhibit

SOCIETY AND COMMITTEE MEETINGS AND EVENTS

FACSS/SciX ORGANIZATION

Sunday, September 30
9:00-10:00 am FACSS (Federation) LRP, *Van Horn A/B*
6:00 pm Program Committee, *Van Horn A/B*
Monday, October 1
3:00–3:50 pm SciX (Conference) LRP, *Van Horn A/B*
Tuesday, October 2
3:00-3:50 pm Site Selection, *Van Horn C*
Wednesday, October 3
1:00 pm Budget and Finance Committee, *Chouteau B*
3:00-3:50 pm 2013 Planning/Budget Committee, *Chouteau B*
Thursday, October 4
Noon Executive Committee, (lunch will be provided), *Van Horn A/B*
3:00-3:50 pm 2014 Planning/Budget Committee, *Van Horn A/B*
6:00 pm Governing Board Meeting, (light dinner will be provided), *Van Horn A/B*

COBLENTZ SOCIETY

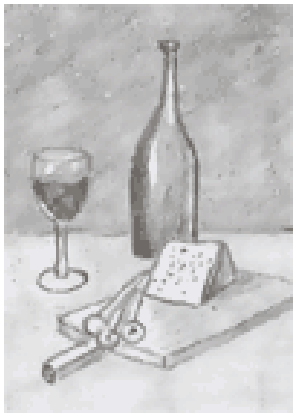
Monday, October 1
12:30 pm Board Meeting, *Van Horn C*
Wednesday, October 3
12:00-2:00 pm William G. Fateley and Ellis R. Lippincott Awards Benefit Luncheon sponsored by SAS and Coblentz, *Van Horn A/B*

SOCIETY FOR APPLIED SPECTROSCOPY

Saturday, September 29
3:00–8:00 pm SAS Executive Committee, *Fremont Room*
Monday, October 1
8:00–10:00 am Editorial Board Meeting, *Van Horn A/B*
8:00–11:00 pm Student Event
Tuesday, October 2
8:00–10:00 am Membership Committee, *Van Horn A/B*
12:00–2:00 pm Publication Committee, *Van Horn A/B*
4:30–6:30 pm SAS Governing Board Meeting, *Van Horn A/B*
7:30-10:00 PM SAS Wine and Cheese Reception, *Atlanta*
Wednesday, October 3
12:00-2:00 pm William G. Fateley and Ellis R. Lippincott Awards Benefit Luncheon sponsored by SAS and Coblentz, *Van Horn A/B*

6:00 PM
WEDNESDAY EVENING EVENT ALL INCLUSIVE EVENT
Exhibit Hall B

SciX continues the tradition of a Wednesday Evening Networking Event with festivities for all at the SciX conference attendees. The Theme of the event is "**Back to the Eighties**." There will be a contest/prizes for the best 80's costumes. Whether you just want to network with colleagues or dance the night away, you can bet this will be a fun evening. There will be a live band, Retroactive, a DJ, quiet areas, and plenty of food and beverage. Look forward to seeing you there!



The Society for Applied Spectroscopy
Cordially Invites
You to Join Us at Our Annual
Wine and Cheese Awards Reception
Tuesday, October 2, 2012 7:30 p.m.
In the Atlanta Room of the
Sheraton Kansas City Hotel

SciX EXHIBITORS

The exhibit is one of the focal points of the SciX Conference. Exhibits are the realization of the research presented during the scientific symposia and include innovation instrumentation, software, and supplies. New technologies and products will be shown and you will find an interesting mix of sales, scientific, and engineering expertise among their representatives.

Sunday, 3:30 pm, What's Hot Exhibitor Presentations in Hall B
Tuesday and Wednesday posters sessions are held in the exhibit hall as well as the coffee and dessert breaks.
Tuesday and Wednesday, 9:00 – 10:20 am – Poster Session and Coffee Break
Tuesday and Wednesday, 3:00 – 3:50 pm – Poster Viewing and Dessert Break

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EXHIBITOR DESCRIPTIONS

ABB Analytical Measurement **Booth 12**
585 boul. Charest E., Ste 300
Quebec, PQ, G1K 9H4 CANADA
www.abb.com/analytical
Founded in 1973, ABB Analytical Measurements (formerly Bomem Inc) designs, manufactures and markets high-performance, FT-IR / FT-NIR spectrometers as well as turnkey analytical solutions for Petroleum, Chemical, Life Sciences, Semiconductor, Academic, Metallurgy, OEM industries and spectroradiometers for Remote Sensing/Aerospace market. ABB capabilities encompass one of the largest portfolios in the world for laboratory, at-line and process FT-IR/FT-NIR analyzers. They perform real-time analysis of the chemical composition and/or physical properties of a process sample stream. ABB's advanced solutions combine analyzers, advanced process control, data management, process and application knowledge to improve the operational performance, productivity, capacity and safety of industrial processes for customers while lowering environmental impact.

AES Electrophoresis Society **Booth 7**
1202 Anne Street
Madison, WI 53713
www.aesociety.org
AES Electrophoresis Society is a unique non-profit, international organization founded to improve and promote the wide variety of techniques and technologies relying upon electric field mediated separations and manipulations. The field of electrophoresis is broad including isoelectric focusing, 2-D gel electrophoresis, SDS polyacrylamide gel electrophoresis (PAGE), capillary, free-flow, dielectrophoresis as well as wide forms of electrokinetics. Electrokinetic fields now intersect microfluidics and microdevices, biotechnology, and material synthesis. Electrophoretic technologies play a central role in scientific investigations in clinical, basic, and applied disciplines from cancer research to molecular biology. Thus, promoting excellence in electrophoretic technologies and their use will improve the overall quality and sophistication of vast endeavors. Membership is open to everyone with an interest in electrophoretic applications.

Agilent Technologies, Inc. **Booths 81, 82**
2850 Centerville Rd.
Wilmington, DE 19808
www.agilent.com/chem
Agilent manufactures and distributes a complete line of instrumentation serving the clinical, analytical, biotech, environmental, pharmaceutical, forensic science, food and flavor, academia, and all other laboratory markets that have needs for the best in quality, performance, and serviceability in the instruments they purchase.

AIST-NT Inc. **Booth 40**
359 Bel Marin Keys Blvd
Ste 20
Novato, CA 94949
www.aist-nt.com
Key Products/ Description: Atomic Force/ Scanning Probe Microscopes; Combined AFM & Raman Spectroscopy systems; TERS-enabled Solutions AIST-NT manufactures the only Scanning Probe Microscope system that has been designed from the ground up for spectroscopy applications and specifically for Nano-Raman and TERS. With individual members having 15 or more years of AFM, STM and Nano-Raman development experience, AIST-NT brings to bear on your projects the capabilities of the most innovative team in the industry. Advanced Integrated Scanning Tools for Nano Technologies is exactly what AIST-NT stands for. Please visit our booth and see our technology in real time – you will feel most welcome!

American Pharmaceutical Review **Table Top**
9225 Priority Way West Drive
Indianapolis, IN 46240
www.americanpharmaceuticalreview.com
American Pharmaceutical Review is the leading review journal for business and technology in the pharmaceutical industry throughout North America. Each issue offers American Pharmaceutical Review's 30,000 readers unbiased editorial coverage of the latest developments in: drug delivery, information technology, research & development, analytical development and control, equipment and facility manufacturing and regulatory affairs. With its in-depth coverage, American Pharmaceutical Review is able to keep its readership of senior executives, technical personnel, scientists, and others fully abreast of the latest trends and developments in the process of pharmaceutical manufacturing.

Anasys Instruments Corp. **Booth 80**
121 Gray Avenue, Ste 100
Santa Barbara, CA 93101
www.anasysinstruments.com
Anasys Instruments is dedicated to delivering innovative products and solutions that measure nanoscale material properties. Understanding structure-property correlation, especially for samples with spatially varying physical and chemical properties, is critical in a diverse range of fields, including polymers, materials science, life science, semiconductors, and data storage, to name but a few. Anasys Instruments introduced nanothermal analysis (nano-TA™) based on self-heating ThermaLever™ AFM cantilever probes in 2006, allowing nanoscale measurements of thermal properties. In 2010, Anasys Instruments proudly introduced the breakthrough multiple award-winning nanoIR™ technology. This AFM-based solution enables chemical characterization utilizing infrared spectroscopy techniques at the nanoscale. By combining AFM and infrared spectroscopy, Anasys Instruments offers researchers an unprecedented suite of chemical, mechanical, and thermal property measurement capabilities. Anasys Instruments unveiled the afm+ in Fall 2011. The afm+ is the first fully integrated AFM platform which offers three important analytical capabilities. The afm+ includes Anasys' proprietary thermal probe technology (nano-TA™), Scanning Thermal Microscopy (SThM) and Transition temperature microscopy (TTM™) capabilities. The afm+ is fully upgradable to the Anasys nanoIR system.

Andor Technology **Booth 74**
425 Sullivan Ave. #3
S. Windsor, CT 06074-1942
www.andor.com
Andor is a world leader in spectroscopy and low light imaging, with a portfolio spanning high-performance scientific CCD, EMCCD, ICCD, sCMOS, spectrographs, and microscopy confocal and white light systems. Andor now counts over 300 employees in 16 offices worldwide, offering over 70 products to 10,000 scientific research and OEM customers worldwide.

Applied Spectra, Inc. **Booth 32**
46661 Fremont Blvd
Fremont, CA 94538
www.appliedspectra.com
We are a leading supplier of analytical instruments based on laser ablation technology. We offer a comprehensive suite of innovative LIBS (Laser Induced Breakdown Spectroscopy), LA (Laser Ablation) and tandem LIBS/LA instruments for rapid elemental and isotopic analysis without sample prep. Our analytical products are helping our customers perform effective and efficient forensic analysis, QC work during solar and battery manufacturing, and hazardous substance detection in the environment. We are world

class LIBS/LA experts ready to support our customers with measurement method and application development.

Avantes **Booth 67**
9769 W. 119th Dr., ste 4
Broomfield, CO 80021-2560
www.avantes.com
Avantes is a leader in field of fiber optic spectroscopy offering a range of spectrometers, light sources, and fiber optics to support measurements in the range from 190-2500 nm. With an installed base of over 10,000 systems throughout the world and 17 years of experience in fiber optic spectroscopy, Avantes is equipped to meet the challenges presented by applications facing our customers. Avantes instruments and system configurations support fluorescence, UV/VIS absorbance, reflectometry/thin film metrology, LIBS, Raman, UV/VIS and NIR radiometry, optical emission spectroscopy and many other spectroscopic techniques.

B&W Tek, Inc. **Booth 31**
19 Shea Way, ste 301
Newark, DE 19713
www.bwtek.com
B&W Tek is an advanced instrumentation company producing optical spectroscopy, laser instrumentation and laboratory, portable and handheld Raman systems. B&W Tek provides solutions for the pharmaceutical, biomedical, physical, chemical, LED lighting and research communities. Our commitment to innovating solutions has made B&W Tek a leader in Raman spectroscopy solutions worldwide. With a strong vertical integration capability, B&W Tek also provides custom product development, design and manufacturing.

BaySpec, Inc. **Booth 45**
1101 McKay Drive
San Jose, CA 95120
www.bayspec.com
BaySpec, Inc., founded in 1999 with 100% manufacturing in the USA (San Jose, California), is a vertically integrated spectroscopy company. The company designs, manufactures and markets advanced spectral instruments, from UV-VIS-NIR and Raman spectrometers to handheld and portable NIR and Raman analyzers, to bench-top in-line process and Raman microscopes for the biomedical, pharmaceuticals, chemical, food, semiconductor, and homeland security industries. BaySpec's core technologies include: ultra-high throughput Volume Phase Gratings (VPG^{TM}), optimized deep-cooled detector/cameras, and high power narrowband lasers, which allow for cost effective customized solutions without the custom expenses. Designs are optimized for performance and long-term reliability featuring no moving parts. The company has experience shipping over 35,000 spectral engines of all types. For more information visit us at www.bayspec.com.

BioTools, Inc. **Booth 59**
17546 Bee Line Highway
Jupiter, FL 33458
www.btools.com

Block Engineering **Booth 58**
377 Simarano Dr. #130
Marlborough, MA 01752
www.blockeng.com
Founded in 1956, Block Engineering, LLC is a leading manufacturer and marketer of high performance Quantum Cascade Laser (QCL) and FTIR spectrometers for military, government, commercial, and industrial customers. Block's Mobile Chemical Agent Detector (MCAD) system is a fixed site, passive FTIR spectrometer offered in partnership with Northrop Grumman Corp. Block's PORTHOS™ is a portable, passive FTIR spectrometer system that remotely detects chemical threats as far as three miles and protects against chemical warfare agents and weapons of mass destruction. Block Engineering is also manufacturing and selling a line of revolutionary QCL-based spectrometers, including LaserScan™, LaserBench™ and LaserScope™ for non contact, non destructive, real time surface chemical analysis for applications ranging from detection of explosives and liquid/solid chemical warfare agents to control of manufacturing operations and verification of surface conditions in a variety of industrial processes.

BrightSpec, Inc. **Booth 16**
675 Peter Jefferson Pkwy, Suite 480
Charlottesville, VA 22911
www.brightspec.com
CP/FT Spectroscopy Devices and solutions for manufacturing, diagnostic and environmental monitoring markets.

Bruker Corporation **Booth 76,77**
19 Fortune Drive
Manning Park
Billerica, MA 01821
www.bruker.com
Bruker is a leading provider of high-performance scientific instruments and solutions for molecular and materials research, as well as for industrial and applied analysis. www.bruker.com

CAMO Software **Booth 54**
One Woodbridge Center, Ste 319
Woodbridge, NJ 07095
www.camo.com
CAMO Software's analytical modeling, prediction and optimization solutions are the preferred choice for over 25,000 data analysts worldwide across a wide range of industries. CAMO Software's flagship simulation and prediction software product is The Unscrambler® X, which is recognized for its ease of use, exceptional data visualization and advanced multivariate methods. CAMO also offer a range of software products which can be integrated directly into scientific instruments, process monitoring solutions, as well as optimization software. Headquartered in Oslo, CAMO's passion is the comprehension and simplification of complex data, resulting in efficient identification, cost, research and design as well as faster analytical results. This allows our clients to benefit from an accelerated return on investment in product development and manufacturing and improved business analytics capabilities.

Catalina Scientific Instruments, LLC **Booth 6**
1870 West Prince Road, Ste 21
Tucson, AZ 85713
www.catalinasci.com
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Coblentz Society **Booth 64**
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Columbia, SC 29208
www.coblentz.org
Professional organization that fosters the understanding and application of vibrational spectroscopy. Through the voluntary efforts of its members, the society sponsors scientific conferences, creates symposia for research presentations, provides social activities to stimulate informal discussion, and recognizes excellence in vibrational spectroscopy through four sponsored awards (the Coblentz, Craver, Williams-Wright, and Lippincott Awards). The society also administers the ABB Bomem-Michelson Award. The Coblentz website can be found at http://www.coblentz.org.

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Wenatchee, WA 98801
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Cambridge, UK CB4 0WF
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The Royal Society of Chemistry (RSC) is the largest organisation in Europe for advancing the chemical sciences, supported by 45,000 members worldwide and an internationally acclaimed publishing business. The Analytical Division of the RSC advances analytical chemistry and science by providing a forum for analytical chemists and scientists to exchange information and ideas. It organises meetings and via, the Analytical Chemistry Trust Fund, finances studentships, Schools Analyst competitions, awards, lectureships and VSO students. Our analytical portfolio of journals features wide coverage across all areas of analytical science, from chemistry and physics to biology and engineering. From Analyst which highlights premier fundamental discoveries, inventions and applications in the analytical and bioanalytical sciences, Analytical Methods which publishes early applied demonstrations of new analytical methods with clear societal impact, to Journal of Analytical Atomic Spectrometry (JAAS) which is considered to be the number-one journal for innovative research in the theory, practice and application of spectrometric techniques to elemental research. Analytical Methods also now features AMC Technical Briefs published on behalf of the Analytical Methods Committee. These articles are free to access and provide up-to-date technical information, concentrating on items that are important for analytical scientists, currently topical, and which are not readily available from other sources. Analytical chemistry underpins chemical discovery and innovation across the key global challenges which have been identified by the RSC roadmap, "Chemistry for Tomorrow's World." At SCIX 2012, the Analytical Division of the RSC, along with the ACS-DAC, is presenting two symposia on the "Current status of analytical science" focusing on the area of Human Health. Whether it's to become an RSC member, engage with the RSC Analytical Division in advancing analytical chemical science, meet a member of RSC Publishing staff or find out the latest news from our analytical journals, please come and visit our booth at SCIX 2012!

RPMC/Oxxius **Booth 30**
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www.rpmclasers.com
RPMC Lasers, Inc. offers innovative Diode Pumped Solid-State Lasers and Laser diode Modules for industrial and scientific applications. Its compact laser modules, featuring wavelengths in the visible and near-UV spectrum, have outstanding performance with market-leading power levels. The SLIM line features a monolithic resonator technology that ensures true single-frequency emission along with excellent power, wavelength and pointing stability.

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Shimadzu offers a full line of analytical instrumentation, including UV Visible and Fluorescence Spectrophotometers; FTIR Spectrometers; Automated FTIR Microscope; HPLC systems and components; LC/MS; Gas Chromatography; GC/MS; MALDI-TOF Mass Spectrometers; Data Stations for Spectroscopy and Chromatography; Thermal Analyzers, TOC, Atomic Absorption Spectrometers, ICP, EDX, Particle Size Analyzers, Balances, Capillary Rheometers, Mooney Viscometers, Universal Testing Equipment and more

Snowy Range Instruments **Booth 38**
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www.wysri.com
Snowy Range Instruments (SnRI) uses a wide range of optical, electrical, mechanical, and software methods to solve difficult spectroscopic problems. Creative, cost-effective solutions are made possible by SnRI's experience with diverse optical technologies and our experience with complex applications. Our team takes pride in our on-time delivery of cost-effective designs and instrumentation. SnRI introduces its Sierra Series of spectroscopic readers. Built on a decade of experience in Raman instrument design the Sierra readers address many of the issues of optical analysis. Our spectrometers are constructed from the best components in a solid aluminum body for rugged long-life time usage.

Society for Applied Spectroscopy **Booths 61-63**
201B Broadway Street
Frederick, MD 21701-6501
www.s-a-s.org
The Society for Applied Spectroscopy is a non-profit, membership organization dedicated to serving and educating scientists in the field of spectroscopy. Membership includes a subscription to the

internationally recognized, peer-reviewed journal, Applied Spectroscopy

Spectroscopy Magazine / Advanstar **Booth 4**
485F US Highway 1 South, Ste 100
Iselin, NJ 08830
www.spectroscopyonline.com
Spectroscopy's mission is to enhance productivity, efficiency, and the overall value of spectroscopic instruments and methods as a practical analytical technology across a variety of fields. Scientists technicians, and laboratory managers gain proficiency and competitive advantage for the real- world issues they face through unbiased, peer-reviewed technical articles, trusted troubleshooting advice, and best-practice application solutions.We serve subscribers by using print and digital media to disseminate highly focused editorial content that combines peer-reviewed scientific articles with practical, solutions-based information, helping readers to become better spectroscopists whether they work in the laboratory, on the process line, or in the field.

Technology Networks.com **Table Top**
Woodview
Bull Lane
Sudbury
Suffolk, CO10 0FD, UK
www.technologynetworks.com/spectroscopy
From our UK headquarters Technology Networks run, update and provide an outstanding web-based information solution for those working within the Life Science and Drug Discovery communities. Since our humble beginnings running just one website based on Combinatorial Chemistry, Technology Networks has expanded its portfolio to comprise 27 communities, which include sites dedicated to spectroscopy, mass spectrometry and chromatography. Providing a base for our members to discuss their thoughts and ideas on the latest scientific technologies and research, our communities are designed with the user in mind, meaning they are easy to navigate, interactive, with clearly displayed up-to-date content and a rich offering of the latest product and technical information.

Text and Academic Authors Association **Booth 70**
S2874 Spruce Street
Fountain City, WI 54629
www.TAAonline.net
The Text and Academic Authors Association (TAA) is a national membership association for textbook and academic authors providing resources such as publication grants, audio conferences and webinars, an online library of how-to articles, annual conferences, and a variety of mentoring and networking opportunities. TAA sponsors a selection of textbook and academic authoring and publishing workshops available to institutions across the country. Individual dues start at $30 for first-time members and $15 for graduate students. TAA also offers a discounted institutional chapter membership structure.
Please visit TAAonline.net for more information.

Thermo Fisher Scientific **Booths 36, 37**
5225 Vernona Road
Madison, WI 53711
www.thermo.com
Thermo Fisher Scientific offers end to end solutions for many of the challenges and daily analyses of today's spectroscopists. Highlighted at SCIX, Thermo Scientific Raman microscopes and spectrometers for researchers and investigators combine top performance and best-in-class usability. Every day, people are turning to Raman spectroscopy because of its analytical power, but usability and reliability determine its potential for a user. Our design emphasizes successful use without compromise of performance, helping the spectroscopist, the materials researcher and the forensic investigator all to leverage Raman within the unique challenges they face each day.

Tornado Medical Systems **Booths 78,79**
555 Richmond Street West, Ste 705
Box 218
Toronto, ON M5V 3B1 Canada
www.tornado-medical.com
Tornado Medical Systems develops optical spectroscopy solutions for sample identification, detection, diagnosis, and imaging. Our "powered by Tornado" partnership model enables OEMs to turbo-charge their end-user applications and products with our high-performance free-space spectroscopy and nanophotonics (aka spectroscopy-on-chip) technologies. Tornado's HyperFlux line of high-sensitivity, high-resolution spectrometers overcomes the trade-off between light throughput and spectral resolution, typically offering a 10-15x increase in throughput over conventional spectrometer designs. HyperFlux is available in several off the shelf models and can be easily customized with the band pass, resolution, footprint, and branding required to meet OEM needs. Tornado's nanophotonic spectrometer is an on-chip solution which never requires alignment and can be customized for high resolution or broad bandwidth preferences. Extreme miniaturization allows for multiple independent spectrometers in one integrated system.

TSI, Inc. **Booth 17A**
500 Cardigan Road
Shoreview, MN 55126
www.tsi.com
The TSI 3000 Series Desktop LIBS Elemental Analyzer offers rapid elemental analysis for minute quantities of solid materials. Based on advanced laser-induced breakdown spectroscopy (LIBS), the TSI 3000 Series instruments are designed to analyze organic elements (C, H, O, N) and heavy metals simultaneously to determine impurities in powders like Carbon Nanotubes and empirical formulas. TSI's LiquiScan ES for liquid nano material characterization will also be displayed.

Wasatch Photonics **Booth 52**
4020 Stirrup Creek Dr., Ste 115
Durham, NC 27703
www.wasatchphotonics.com
Wasatch Photonics, Inc. is the leader in high performance Volume Phase Holographic Gratings (VPHGs) and Volume Phase Holographic Optical Elements (VHOEs). Products developed by our world class design team include; Raman sensors and instrumentation, advanced holographic components for spectroscopy, hyperspectral imaging, astronomy and OCT. Company headquarters and the holographic component manufacturing facility are located in Logan, Utah. Instrumentation is manufactured at our Systems Division facility located in Research Triangle Park, NC. High efficiency VPH Gratings combined with low F number optics allow unprecedented throughput for our Raman spectrometers. Our Raman systems provide ultimate sensitivity for process control, rapid SERS tag identification and unknown substance identification for homeland security.

Wiley-Blackwell **Booth 65**
The Atrium Southern Gate
Chichester
West Sussex, UK PO19 8SQ
http://www.wiley.com
Wiley publishes a large range of top quality consumer, professional, educational and research material, from the well-known 'For Dummies' guides, to college textbooks, highly ranked peer-reviewed primary research and evidence based medicine. Wiley,

Blackwell, the scientific, technical, medical and scholarly publishing business of John Wiley & Sons, publishes on behalf of societies and membership associations and offers libraries and individuals 1250 online journals, thousands of books in print and online, reviews, reference works, databases, and many other innovative resources for teaching and learning. At the SciX conference we will be providing free copies of our leading spectroscopy-related journals as well as promotional details for our print and electronic books spectroscopy books programme.

WITec Instruments **Booth 24A**
122 McCammon
Maryville, TN 37804
www.WITec-Instruments.com
WITec is a manufacturer of high resolution optical and scanning probe microscopy solutions for scientific and industrial applications. A modular product line allows the combination of different microscopy techniques such as Raman, NSOM or AFM in one single instrument for flexible analyses of optical, chemical and structural properties of a sample.

Tuesday and Wednesday Posters Sessions
Exhibit Hall A
9:00 – 10:20 am
Coffee Break

Tuesday and Wednesday Poster Viewings
Exhibit Hall A
3:00 – 3:50 pm
Dessert Break

WORKSHOPS

Workshops are a valuable component of the SciX conference and are conducted by leading experts. There is an additional charge for most workshops. See on-site registration form for costs.

ANALYTICAL RAMAN SPECTROSCOPY

Brian Marquardt, *University of Washington;* **Jeremy Shaver,** *Eigenvector Research, Inc.;* **Ian R. Lewis,** *Kaiser Optical*

Sunday, 8:00 am – Noon

The course will provide an overview of modern Raman spectroscopy beginning with an introduction to Raman scattering and the differences between IR and Raman spectra. It will include discussion of sampling, calibration, data analysis methods (pre-treatments and modeling approaches), and successful application developments. Modern instrument configurations and configuration choices will be covered. The course will include a thorough introduction to the major approaches to sample illumination and spectrum collection, emphasizing fiber optic probes and Raman microprobes. Raman imaging will be briefly discussed. The applicability of and successes with Raman will be surveyed with numerous applications examples. This ½ day course will be split 50 / 50 between a) Raman practical considerations and theory and b) applications. Course materials will be supplied at the conference on a USB flash drive only (no hard copies).

CHEMOMETRICS WITHOUT EQUATIONS

Eigenvector University

Sunday and Monday, 9:00 am – 4:30 pm

Chemometrics without Equations concentrates on two areas of chemometrics: 1) exploratory data analysis and pattern recognition, and 2) regression. Participants will learn to safely apply techniques such as Principal Components Analysis (PCA), Principal Components Regression (PCR), and Partial Least Squares (PLS) Regression. Examples will include problems drawn from process monitoring and quality control, predicting product properties, and others. The target audience includes those who collect and/or manage large amounts of data that is multivariate in nature. This includes bench chemists, process engineers, and managers who would like to extract the most information from their measurements. The course will finish with a short section on how to apply these models for online predictions, Multivariate Statistical Process Control and inferential sensing. This is a 2 day course and computers will be provided. Course materials will be supplied at the conference on a USB flash drive only (no hard copies).

INDUCTIVELY COUPLED PLASMA- MASS SPECTROMETRY (ICP-MS): INTRODUCTION

R. S. Houk, *Ames Laboratory USDOE, Iowa State University*

Sunday, 1:00 – 5:00 pm

This course describes fundamental principles behind the instrumentation for ICP-MS. Specific topics are:

1. General analytical capabilities
2. Applications survey
3. Sample preparation and sample introduction
4. ICP as ion source
5. Ion extraction, transmission and focusing
6. Mass analysis – quadrupole, magnetic sector
7. Ion detection
8. Matrix effects
9. Removing polyatomic ions – cool plasma, solvent removal, collision cells

Course materials will be supplied at the conference on a USB flash drive only (no hard copies).

AMBIENT DESORPTION/IONIZATION-MASS SPECTROMETRY: FROM FUNDAMENTALS TO APPLICATIONS

Jacob T. Shelley, Purdue University; Carsten Engelhard, *University of Muenster*

Sunday, 1:00 – 5:00 pm

Recently a number of atmospheric-pressure ionization sources for mass spectrometry have emerged in the literature to yield a field that is collectively referred to as Ambient Desorption/Ionization-Mass Spectrometry (ADI-MS). These sources include: Desorption ElectroSpray Ionization (DESI), Direct Analysis in Real Time (DART), and Flowing Atmospheric-Pressure Afterglow (FAPA). Collectively, these ADI-MS sources have numerous advantages over conventional ionization sources, including high ionization efficiency, soft ionization, and direct analysis of solid, liquid, and gaseous samples. This workshop will cover fundamental principles of the desorption and ionization processes, as well as real-world applications of ADI-MS sources. A particular emphasis will be placed on plasma-based systems.

Key words: Direct Analysis, Soft Ionization, Mass Spectrometry, DART, DESI, Glow Discharge, Ambient Ionization Sources, Pharmaceutical Analysis, Homeland Security

FT-IR SPECTROMETRY OPTIMIZATION

James A. de Haseth, *Light Light Solutions, LLC* and **Ellen V. Miseo**, *Analytical Answers, Inc*.

Monday, 9:00 am – 1:00 pm

FT-IR spectrometers are very sensitive and precise instruments but operated improperly can provide poor or inaccurate data. Learn how to tune for optimum performance. This course covers how to optimize your instrument by setting up the appropriate parameters for each experiment. We will also cover appropriate sampling methods for different sample types and how to prepare your sample effectively. Learn how to recognize the limits of the spectrometer and how to turn precision into accuracy.

HANDS-ON CHEMOMETRIC ANALYSIS WITH THE UNSCRAMBLER®

Katherine Bakeev, *CAMO Software*

Tuesday, 9:00 am – 4:30 pm

This workshop is aimed at giving an overview of the principles and use of multivariate methods with exercises and examples specific to spectroscopic data analysis. It provides a combination of theory and practice, with an emphasis on PCA and PLS model development and interpretation. (Computers will be provided). Course materials will be supplied at the conference on a USB flash drive

RESUME WRITING AND INTERVIEWING SKILLS FOR STUDENTS

Drew Manica and Patrick Reuss, *SABIC*

Tuesday, 8:00 am – noon

SABIC is hosting this free workshop. Your career search is one of the most influential investments in your future. This interactive half-day workshop will prepare attendees to make a positive and lasting impression both in-print and in-person. Receive tips and best practices, avoid common mistakes, learn how to tailor your resume for different prospective employers, and prepare yourself for important interview styles. Directly following the workshop, students are invited to join the Free Lunch and Employment Discussion hosted by SABIC.

ENTREPRENEURIAL CHEMISTS - SETTING UP CONSULTANT BUSINESS

John Coates, *Coates Consulting*

Wednesday, 9:00 am – 1:00 pm

This course will benefit from audience participation, be prepared to become involved.

Introduction: A personal view of being an entrepreneur, personal motivation, why go there? Are you OK working alone? A quick review of situations from course participants.

Key Components of a Business: Defining the business - what do you want to do - what is your skill set; Setting up the business, Sole Proprietorship, LLC or Corporation, the pros and cons; the office - location and services; the accounts and the annual dread (filing taxes).

Setting up a Network: Your personal and business networks are your company's lifeline; what to do and how to maintain.

Funding the Business: All businesses require funds; How to fund and what to fund, the importance of a personal investment...having skin in the game; do you go for external investment, the pros and cons (mainly cons); and what about government funding.

Marketing: Getting known in the business (beyond the network), setting up a web site, attending conferences, listings and directories (which ones work, which ones to select), advertising - does it work? Collateral - what to invest in.

You Have a Potential Client, What Next?: Once a client and project are identified what do you do next? Is it a one time project? How many days? How many months? Defining expectations and documenting - writing the winning proposal.

Doing the Job and Delivering: Under commit and over deliver - how to provide realistic goals and a timetable; Communications - the name of the game

Getting Paid: Rule #1, consultants do not work as charities! Your time is your money...use it sparingly and wisely; what to give away and what to get paid for; Invoicing - when and how often.

A Hands-On Tutorial with Audience Participation: Becoming a conultant is not a trivial job and it is easy to under estimate what is required. This section will be a wrap-up of the session and will involve the participants indicating what their feelings are about having a go at business...are you in or are you out? Course materials will be supplied at the conference on a USB flash drive only (no hard copies). A downloadable version will also be made available should you want to print out hard copies before your workshop.

RAMAN CHEMICAL IMAGING AND TECHNOLOGIES AND METHODS

Ryan J. Priore and Matt Nelson, *ChemImage*

Wednesday 1:00 pm – 5:00 pm

Chemical Imaging is a rapidly maturing discipline that involves the integration of digital imaging with molecular spectroscopy, relying on Raman, fluorescence, visible, NIR and IR absorption/reflectance techniques. It has evolved as a powerful approach for non-invasive characterization of chemical heterogeneity. Among these techniques, Raman Chemical Imaging is particularly suited for microspectroscopy and imaging due to the inherent selectivity and sensitivity of Raman spectroscopy. Two different imaging approaches, spatial and wavelength scanning, are used to acquire a hyperspectral data cube containing wavelength, intensity, x, y and z- spatial information. This course emphasizes wavelength scanning approaches to Raman Chemical Imaging which enable rapid image acquisition with diffraction-limited spatial resolution. In widefield Raman Chemical Imaging, thousands of Raman spectra are simultaneously collected from a field of view. The spectral data is used to generate chemically-specific images. Intricate image and spectral processing techniques may be applied to the chemical imaging data to produce various qualitative and/or quantitative parameters associated with the often complex sample matrix. This short course is designed as a comprehensive overview of theoretical and practical aspects of Raman Chemical Imaging and associated instrumentation. The special emphasis is placed on Raman Chemical Imaging applications in pharmaceutical and biothreat detection fields. This course will be useful to analytical, forensic, biomedical and materials chemists. Course materails will be supplied at the conference on a USB flash drive only (no hard copies). A downloadable version will also be made available should you want to print out hard copies before your workshop.

ADVANCED CHEMOMETRICS WITHOUT EQUATIONS

Eigenvector University

Wednesday, 9:00 am – 4:30 pm

Target Audience: Advanced Chemometrics Without Equations (or Hardly Any) is designed for those who wish to explore the problem solving power of chemometric tools, but are discouraged by the high level of mathematics found in many software manuals and texts. Course emphasis is on proper application and interpretation of chemometric methods as applied to real-life problems. The objective is to teach in the simplest way possible so that participants will be better chemometrics practitioners and managers.

Course Description: Advanced Chemometrics without Equations (ACWE) takes up where our popular Chemometrics without Equations course leaves off. It is assumed that participants will have a working knowledge of Principal Components Analysis(PCA) and regression with Partial Least Squares (PLS). ACWE concentrates on improving chemometric models via 1) advanced preprocessing methods and 2) variable selection. The critical difference between inadequate and successful chemometric models is often data preprocessing, i.e. what is done to the data before using PCA, PLS etc. The goal of preprocessing is to remove variation not related to the problem of interest so that the variation of interest is more evident and can be more easily modeled. The variables selected, e.g. spectral regions, can also greatly affect the success of the application. ACWE focuses on advanced preprocessing methods, including Extended Multiplicative Scatter Correction (EMSC) and Generalized Least Squares (GLS), for improving models. Variable selection techniques, such as interval PLS (iPLS) are also considered. The effect of preprocessing and variable selection on robustness of the final models is also considered.

Computers will be provided. Course materials will be supplied at the conference on a USB flash drive only (no hard copies)

WORKSHOPS

PROFESSIONAL ANALYTICAL CHEMISTS IN INDUSTRY: WHAT DOES AN ANALYTICAL CHEMIST DO?

Judson Haynes and Diane Parry, *Procter and Gamble*

Wednesday, 9:00 am – 4:30 pm

This seminar begins with a discussion of the education requirements and salaries that an analytical chemist may expect in industry. The different roles (including scientific consultant, methods developer, and problem solver) of the industrial analytical chemist are explained. A majority of time is spent on problem solving, both the process and solving real-world problems. Students will learn a "framework" for approaching problems. Time will be available to ask questions on these topics and other related subjects. The Course text includes supplementary material on finding a job, summer employment, etc. The entire course, especially the problem solving, is structured for extensive participation and interaction. Additional information is available at http://www.pg.com/science/prof_chemists.jhtml. The Course is intended primarily for undergraduate students to educate them about careers as analytical chemists in industry. However, graduate students, high school teachers, and college faculty have indicated it was worth their time to attend.

Typical Course Schedule

1. Course Introduction and Personal Perspectives
2. Perspectives: The Industrial Analytical Chemist
3. Problem Solving I: The Bulging Drum Problem
4. Break
5. Questions and Answers
6. An Approach to Problem Solving
8. Problem Solving II: Potential Issues Concerning Use of Recycled Plastics
9. Questions & Answers II
10. Problem Solving III: Problem Solving by Student Teams
11. Summary and Evaluation

ANALYSIS WITHOUT SAMPLE PREP: NEAR IR, THE VERSATILE SPECTROSCOPY

Don Burns

Thursday, 9:00 am – 4:30 pm

Course Description

MORNING

Basic NIR Concepts

Overview & history; principles & theory; advantages & disadvantages; basis of absorptions (overtones & combination bands).

Calibration & Wavelength Selection

Search strategies; teaching/learning & confirmation sets; MLR, PCR; hidden information (via derivatives & zero-crossing techniques).

Software & Chemometrics

Mahalanobis distances; discriminant analysis; spectral reconstruction; indicator variables; 3rd Party offerings; qualitative & quantitative analysis; error propagation.

Method Development

General rules; how many samples (and why?); feasibility studies; some basic statistics.

AFTERNOON

On-Line Analysis

Liquids, solids, gases; use of fiber optics; case study with plastics.

Applications

Tobacco & cigars; agricultural products; polymers; pharmaceuticals; medical uses; artwork; food & beverages; petrochemicals; textiles; lignin; actinides; detection of counterfeit items (drugs, ivory, animal feeds, turquoise, currency).

Instrumentation – who makes what?

Classification; principle of operation (filters, gratings, diode arrays, scanning, FT, AOTF); attachments (fiber optics, samplers); dedicated units.

The Future – How to Learn More

Meetings, courses, books & journals, audio seminars, groups to join, the Internet, a basic bibliography on disk.

VIDEOS

Several short video clips are included featuring the inner workings of a typical scanning monochromator, using a fiber optic attachment, a medical use for Near-IR, a novel sample holder, and detection of counterfeiting (currency & turquoise).

Course materials will be supplied at the conference on a USB flash drive only (no hard copies).

CONCEPTS IN SUSTAINABILITY AND GREEN CHEMISTRY

Doug Raynie, *South Dakota State University*

Thursday, 9:00 am – 4:30 pm

This short course is designed to provide participants with an understanding of the principles of sustainability and green chemistry. Upon successful completion of the course, the participant will have an understanding of the principles of green chemistry, the principles of green engineering, and resources to further their understanding of green chemistry. The course will begin by discussing principles of sustainable development. Case studies will be presented to exemplify key concepts in toxicology, life cycle analysis, and supply chain issues. Then the principles of green chemistry will be discussed relative to sustainability goals. Finally, green chemistry education and resources will be presented. Throughout the course both principles and practical aspects of the outlined topics will be presented. Course materials will be supplied at the conference on a USB flash drive only (no hard copies).

PROCESS ANALYTICAL CHEMISTRY: OUT OF THE LAB AND INTO THE PIPE

James Rydzak, *GlaxoSmithKline*

Wednesday, 9:00 am – 4:30 pm

Process Analytical Technology, PAT, has become accepted in the Pharmaceutical Industry as it had previously in the Chemical industry. Out of the Lab and into the pipe will give the participant a background review of spectroscopic instrument and interfaces such as Mid-IR, Raman, NIR, MS, and UV, as well as other sensors used to monitor a variety of processes. The course gives a good comparison of which techniques are beneficial to particular process and chemistry. We will discuss how these techniques have been applied to processes such as in-situ reaction monitoring, distillation, crystallization, drying, powder blending, and others. We will focus on the application of these techniques interfaced at-line, on-line, and in-line to applications in the refining, chemical, petrochemical, food, personal care pharmaceutical, and life science industries. The course is suited for graduate students to broaden your background for industry, analytical lab chemists looking to understand the application of these techniques to in-situ process monitoring, quality control, industrial process engineers, and plant management looking to improve quality and efficiency, and reduce your carbon footprint to produce a greener manufacturing plant.Course materials will be supplied at the conference on a USB flash drive only (no hard copies).

PROGRAM OVERVIEW

SUNDAY

3:30 – 7:00 pm **What's Hot Vendor Presentations,** *Exhibit Hall B*

7:00 – 9:00 pm **Welcome Mixer, SAS Sponsored Student Poster Session, Coblentz Student Awards, FACSS Student and Tomas Hirschfeld Scholar Awards,** *Exhibit Hall B*

MONDAY MORNING

7:50 am Opening Address

8:00 am **KEYNOTE LECTURE,** The Search for Life on Other Worlds; **Chris McKay**, *Exhibit Hall B,* page 54

9:00 am **POSTER SESSION**, *Exhibit Hall B***,** page 54
Mass Spectrometry
Biological Applications of Spectroscopy
Microfluidics, Electrophoresis, Chromatography, and Bio-Analysis
New Approaches to BioAssay

10:20 am **SYMPOSIA,** page 56
New Plasmas, New Instrumentation, and New Approaches at the Frontier of Atomic Spectrometry, *Chicago A*
Current Status of the Analytical Sciences: Focus on Human Health*, New York B*
Advanced Techniques in Fluorescence Microscopy and Spectroscopy, *Empire A*
New Applications of Quantum Cascade Lasers in Chemical Analysis, *Chicago C*
Chemistry in Art and Archaeology I*, Empire B*
Microbes in Mass Spectrometry, *New York A*
SAS PAT Technical Section I: PAT in the Biopharma and Pharma Industries*, Chicago B*
Raman Spectroscopy in Astrobiology and Planetary Sciences, *Atlanta*
Nontraditional Approaches for Chemical and Biological Sensing, *Empire C*

MONDAY AFTERNOON

1:20 pm **SYMPOSIA,** page 58
Chemistry in Art and Archaeology II, *Empire B*
BioAnalytical Applications of Micro- and Nanofluidics, *New York B*
Calibration Maintenance and Transfer for NIR Instrument Networks, *Chicago C*
Ionic Liquids for and by Analytical Chemistry, *Chicago B*
Fundamental Aspects of LIBS, *Chicago A*
in vitro and *in vivo* Modifications of Biomolecules Assessed by Mass Spectrometry, *New York A*
SAS PAT Technical Section: PAT in the Biopharmaceutical and Pharmaceutical Industries, *Empire A*
Emerging Raman Techniques and Applications, *Atlanta*
Nuclear Forensics*, Empire C*

3:00 pm **POSTER VIEWING**

3:50 pm **SYMPOSIA,** page 60
Isoscapes: Redefining the Landscape in the Archaeological and Geological Sciences with High Fidelity Isotope Ratio Analysis, *Empire B*
FACSS Student Awards, *Atlanta*
Higher-order Structure in Proteins by MS-based Approaches, *New York A*
Microfluidics and Nanofluidics, *New York B*
Advances in NIR Spectroscopy in the Pharmaceutical Industry*, Chicago C*
Data Analysis in LIBS, *Chicago A*
Industrial Process Analytical Spectroscopy, *Empire A*
Standoff Raman: Applications and Key Issues, *Chicago A*
Infrared and Raman Spectroscopy of Organic Semiconductors and Conductors*, Empire C*

TUESDAY MORNING

PLENARY LECTURES, *Exhibit Hall B,* page 62

8:00 am **Coblentz Society's Craver Award,** Duncan Graham

8:30 am **FACSS Charles Mann Award for Applied Raman Spectroscopy**, Don Pivonka

9:00 am **POSTER SESSION,** *Exhibit Hall A***,** page 62
Pharmaceutical Analysis
Microscopy and Spectroscopy
Laser Ablation and Atomic Analysis
Glow Discharge Spectroscopy
New IR and Raman Instrumentation

10:20 am **SYMPOSIA,** page 64
Current Status of the Analytical Sciences: Focus on Human Health, *Chicago B*
Charles Mann Award Session Honoring Don Pivonka, *Atlanta*
Novel Optical Reporters, Dyes, and Tags in Molecular and Raman Spectroscopy, *Empire A*
Forensic and Environmental Applications of Chemometrics, *Empire B*
Recent Advancements in Electrophoretic Separation, *Chicago C*
Pushing the Limits of LIBS in Analytical Science, *Chouteau A*
Instrument and Method Development in MS, *New York A*
Tip-enhanced Raman Spectroscopy – New Trends, *New York B*
Very Remote Spectroscopy: Exploring Extreme Environments, *Empire C*
Surface Plasmon Resonance Applications and Instrumentation*, Chicago A*

TUESDAY AFTERNOON

1:20 pm **SYMPOSIA,** page 66
Speciation Analysis: Progress in Trace Metal Speciation, *Chicago B*
The Ever Expanding Capacities of the Analytical Glow Discharge, *Chicago A*
Coblentz Society's Craver Award Session, *Atlanta*
Next Generation Electric-Field Driven Separation, *Chicago C*
Two-Dimensional Correlation Spectroscopy I, *Empire B*
Advanced Vibrational Probes for Biomedical Sensing, *Empire C*
Laser-Induced Breakdown Spectroscopy, *Chouteau A*
Topics in Tandem Mass Spectrometry, *New York A*
Pharmaceutical Applications of Raman Imaging, *New York B*
On the Scent: Vapor and Aroma Analysis for Forensic and Security Applications, *Empire A*

3:00 pm **POSTER VIEWING**

TUESDAY AFTERNOON, continued

3:50 pm **SYMPOSIA,** page 68
Atomic Spectrometry and the Analysis of Nanomaterials, *Chicago A*
Biological Applications of Chemometrics, *Empire A*
Microscale Phenomena, *Chicago C*
Two-Dimensional Correlation Spectroscopy II, *Empire B*
Pharmaceutical Applications of Raman Spectroscopy, *Chicago B*
UV Raman /UV SERS, *New York B*
Elemental Signatures for Forensics, *Chouteu A*
Recent Progress in SERS, *New York A*
Portable Instrumentation and Standoff Detection Techniques, *Empire C*

WEDNESDAY MORNING

PLENARY LECTURES, *Exhibit Hall B,* page 71
8:00 am **ACS Division of Analytical Chemistry Award for Distinguished Service in the Advancement of Analytical Chemistry,** Gary Hieftje
8:30 am **ANACHEM Award**, Peter R. Griffiths
9:00 am **POSTER SESSION,** page 71
Chemometrics and Spectroscopic Investigation
Ambient Mass Spectrometry
Forensic Applications of Spectroscopy
SERS: New Substrates and Analyses
10:20 am **SYMPOSIA,** page 73
ACS Division of Analytical Chemistry Honoring Gary Hieftje, *Atlanta*
Spectroscopy in the Biomedical and Clinical Sciences, *Chicago B*
Chemometrics and Molecular Spectroscopy, *Empire A*
Light and Separations: A Powerful Combination, *Chicago A*
Forensic Investigations with Molecular Spectroscopy, *Empire B*
Raman Spectroscopy for Pharmaceutical Surveillance and Process Control, *Chicago C*
Making the Most of Spectral and Other Process Data, *Empire C*
Raman Optical Activity, *New York B*
Nanomaterials for Plasmonics I, *New York A*

WEDNESDAY AFTERNOON

1:20 pm **SYMPOSIA,** page 74
Fundamental Aspects of Plasma Spectrochemistry: Using What We Learn to Improve Analytical Atomic Spectroscopy, *Chicago A*
Novel Applications using the Inductively-Coupled Plasma, *Empire A*
ANACHEM Award Session Honoring Peter R. Griffiths, *Atlanta*
Information-Rich Approaches in BioMedical Spectroscopy, *Chicago B*
Molecular Spectroscopy as a Physician's Friend, *Empire B*
Young Scientists in SERS, *New York B*
Ambient Ionization Techniques for Forensics, Security and Biological Analysis, *Chicago C*
Innovations in Optical Instrumentation, *Empire C*
Nanomaterials for Plasmonics II, *New York A*
3:00 pm **POSTER VIEWING**
3:50 pm **SYMPOSIA,** page 76
Sampling the World with Laser Ablation and Atomic Spectrometry, *Chicago A*
Student Poster Awards, *Empire A*
Novel Microscopic and Spectroscopic Techniques at the Nanoscale, *Empire C*
Droplets, Digital Microfluidics, and Single Cell Chemical Analysis, *Chicago B*
Industrial Applications of Vibrational Spectroscopy, *Empire B*
Celebrating 120 Years of the IRDG and the Coblentz Society, *Atlanta A*
Disease Diagnostics using SERS, *New York B*
Ambient Mass Spectrometry: Fundamental Findings and the Future, *Chicago C*
Nanomaterials for Plasmonics III, *New York A*

THURSDAY MORNING

PLENARY LECTURES, *Exhibit Hall B,* page 79
8:00 am **Applied Spectroscopy William F. Meggers Award,** Mike Angel
8:30 am **SAS Lester W. Strock Award,** Ralph Sturgeon
9:00 am **POSTER SESSION,** page 79
Atomic Spectrometry: Sample Introduction and New Technology
Atomic Spectrometry, Speciation Analysis and Environmental Applications
Environmental Analysis
Fuel, Biomass and Exhaust Analysis
Polymer Spectroscopy and Materials Analysis
Food, Bio-Extracts, and Materials Characterization
10:30 am **SYMPOSIA,** page 81
SAS Lester Strock Award Session Honoring Ralph Sturgeion, *Atlanta*
Raman Spectroscopy: A Noninvasive Method for Discrimination of Cells and Cell Population I, *Chicago C*
Optical and Photoacoustic tomography and Microscopy, *New York A*
From Ag to Ag(riculture): Analytical Chemistry in the Midwest, *Empire C*
Hand-Held Devices for PAT and Industrial Uses, *Empire B*
Nanoparticles and SERS for Analysis, *New York B*
Advances in Analytical Forensics, *Chicago B*
Polymers, Polymerization, & Spectroscopy, *Chicago A*
Novel Spectroscopic Approaches in Analytical Chemistry, *Empire A*

THURSDAY AFTERNOON

1:20 pm **SYMPOSIA,** page 83
Novel Sample Introduction Techniques and Tools for Atomic Spectroscopy, *Empire B*
New Plasmas, New Instrumentation and New Approaches at the Frontier of Atomic Spectrometry – the Coda, *Empire A*
SAS Applied Spectroscopy Meggers Award Session Honoring Mike Angel, *Atlanta*
Raman Spectroscopy: A Noninvasive Method for Discrimination of Cells and Cell Populations II, *Chicago C*
Applications of Chemometrics in Vibrational Spectroscopy, *NewYork B*
New Techniques in the Separation Sciences, *Chicago A*

THURSDAY AFTERNOON, continued

Instrumentation and Applications: Probing the Limits in Molecular Spectroscopy, *New York A*
Applications and Advances in Handheld and Portable Spectroscopy, *Empire C*
Applications of Raman Spectroscopy and Microscopy, *Chicago B*

3:50 pm **SYMPOSIA,** page 85
FACSS Distinguished Service Awards
FACSS Innovation Awards Symposium
SciX 2013 Preview

FRIDAY MORNING SPECIAL PLENARY SESSIONS
Empire A

8:00 am **Special Plenary Session,** page 85
Welcoming Three New Organizations into FACSS.
Announcement of 2012 FACSS Innovation Award Winner.

TECHNICAL PROGRAM OVERVIEW BY TOPIC

ASTROBIOLOGY and PLANETARY SCIENCES

Monday AM
Raman Spectroscopy in Astrobiology and Planetary Sciences, *Atlanta*
Tuesday Poster Session
Laser Induced Breakdown Spectroscopy
Tuesday AM
Very Remote Spectroscopy: Exploring Extreme Environments, *Empire C*

ATOMIC SPECTROSCOPY

Monday AM
New Plasmas, New Instrumentation, and New Approaches at the Frontier of Atomic Spectrometry, *Chicago A*
Monday PM (1:20 pm session)
Chemistry in Art, *Empire B*
Nuclear Forensics, *Empire C*
Monday PM (3:50 pm session)
Isotopes: Redefining the Landscape in the Archaeological and Geological Sciences with High Fidelity Isotope Ratio Analysis, *Empire B*
Tuesday Poster Session
Laser Induced Breakdown Spectroscopy
Laser Ablation and Atomic Analysis
Glow Discharge
Tuesday AM
Current Status of the Analytical Sciences: Focus on Human Health, *Chicago B*
Very Remote Spectroscopy: Exploring Extreme Environments, *Empire C*
Tuesday PM (1:20 pm session)
Speciation Analysis: Progress in Trace Metal Speciation, *Chicago B*
The Ever Expanding Capacities of the Analytical Glow Discharge, *Chicago A*
Tuesday PM (3:50 pm session)
Atomic Spectrometry and the Analysis of Nanomaterials, *Chicago A*
Elemental Signatures for Forensics, *New York A*
Portable Instrumentation and Standoff Detection Techniques, *Empire C*
Wednesday AM
ACS Division of Analytical Chemistry Distinguished Service Award Honoring Gary Hieftje, *Atlanta*
Wednesday PM (1:20 pm session)
Fundamental Aspects of Plasma Spectrochemistry: Using What We Learn to Improve Analytical Atomic Spectroscopy, *Chicago A*
Novel Applications using the Inductively-Coupled Plasma, *Empire A*
Wednesday PM (3:30 pm session)
Sampling the World with Laser Ablation and Atomic Spectrometry, *Chicago A*
Thursday Poster Session
Atomic Spectroscopy: Sample Introduction and New Technology
Atomic Spectrometry, Speciation Analysis and Environmental Applications
Thursday AM
SAS Lester Strock Award Honoring Ralph Sturgeon, *Atlanta*
From Ag to Ag(riculture): Analytical Chemistry in the Midwest, *Empire C*
Thursday PM (1:20 pm session)
Novel Sample Introduction Techniques and Tools for Atomic Spectroscopy, *Empire B*
New Plasmas, New Instrumentation and New Approaches at the Frontier of Atomic Spectrometry – the Coda, *Empire A*
SAS Applied Spectroscopy Meggers Award Honoring Mike Angel, *Atlanta*
New Techniques in the Separation Sciences, *Chicago A*
Thursday PM (3:50 pm session)
FACSS Innovation Awards

AWARDS

Tuesday AM
Plenary Lecture: Coblentz Society's Craver Award, Duncan Graham, *Exhibit Hall B*
Plenary Lecture: FACSS Charles Mann Award for Applied Raman Spectroscopy, Don Pivonka, *Exhibit Hall B*
FACSS Charles Mann Award Session Honoring Don Pivonka, *Atlanta*
Tuesday PM (1:20 pm session)
Coblentz Society's Craver Award Session Honoring Duncan Graham, *Atlanta*
Wednesday AM
Plenary Lecture: ACS Division of Analytical Chemistry: Gary Hieftje, *Exhibit Hall B*
ANACHEM Award, Peter R. Griffiths, *Exhibit Hall* B
ACS Division of Analytical Chemistry Distinguished Service Award Honoring Gary Hieftje, *Atlanta*
Wednesday PM (1:20 pm session)
ANACHEM Award Session Honoring Peter Griffiths, *Atlanta*
Thursday AM
SAS Applied Spectroscopy William F. Meggers Award: Mike Angel, *Exhibit Hall B*
SAS Lester W. Strock Award: Ralph Sturgeon, *Exhibit Hall B*
SAS Lester Strock Award Session Honoring Ralph Sturgeon, *Atlanta*
Thursday PM (1:20 pm session)
SAS Applied Spectroscopy Meggers Award Session Honoring Mike Angel, *Atlanta*
Thursday PM (3:50 pm session)
FACSS Innovation Awards, *Exhibit Hall B*

BIOMEDICAL AND BIOANALYTICAL SCIENCES

Monday Poster Sessions
Mass Spectrometry
Microfluidics, Electrophoresis, Chromatography and Bio-Analysis
New Approaches to BioAssay
Monday AM
Current Status of the Analytical Sciences: Focus on Human Health, *New York B*
Advanced Techniques in Fluorescence Microscopy and Spectroscopy, *Empire A*
Microbes in Mass Spectrometry, *New York A*
Monday PM (1:20 pm session)
BioAnalytical Applications of Micro- and Nanofluidics, *New York B*
in vitro and *in vivo* Modifications of Biomolecules Assessed by Mass Spectrometry, *New York A*
Monday PM (3:50 pm session)
Higher-order Structure in Proteins by MS-based Approaches, *New York A*
Microfluidics and Nanofluidics, *New York B*
Tuesday AM
Current Status of the Analytical Sciences: Focus on Human Health, *Chicago B*
Novel Optical Reporters, Dyes, and Tags in Molecular and Raman Spectroscopy, *Empire A*
Recent Advancements in Electrophoretic Separation, *Chicago C*

BIOMEDICAL AND BIOANALYTICAL SCIENCES, cont.

Tuesday AM, continued
Surface Plasmon Resonance Applications and Instrumentation, *Chicago A*
Tuesday PM (1:20 pm session)
Speciation Analysis: Progress in Trace Metal Speciation, *Chicago B*
Coblentz Society's Craver Award Session Honoring Duncan Graham, *Atlanta*
Advanced Vibrational Probes for Biomedical Sensing, *Empire C*
Topics in Tandem Mass Spectrometry, *New York A*
Tuesday PM (3:50 pm session)
Biological Applications of Chemometrics, *Empire A*
Microscal Phenomena, *Chicago C*
Recent Progress in SERS, *New York A*
Wednesday Poster Session
SERS: New Substrates and Analyses
Wednesday AM
Spectroscopy in the Biomedical & Clinical Sciences, *Chicago B*
Chemometrics and Molecular Spectroscopy, *Empire A*
Wednesday PM (1:20 pm session)
Information-Rich Approaches in BioMedical Spectroscopy, *Chicago B*
Wednesday PM (3:50 pm session)
Novel Microscopic and Spectroscopic Techniques at the Nanoscale, *Empire C*
Disease Diagnostics using SERS, *New York B*
Droplets, Digital Microfluidics, and Single Cell Chemical Analysis, *Chicago B*
Thursday AM
Raman Spectroscopy: A Noninvasive Method for Discrimination of Cells and Cell Population I, *Chicago C*
Optical and Photoacoustic Tomography and Microscopy, *New York A*
From Ag to Ag(riculture): Analytical Chemistry in the Midwest, *Empire C*
Thursday PM (1:20 pm session)
Raman Spectroscopy: A Noninvasive Method for Discrimination of Cells and Cell Populations I, *Chicago C*
Applications of Raman Spectroscopy & Microscopy, *Chicago B*
Thursday PM (3:50 pm session)
FACSS Innovation Awards, *Exhibit Hall B*

CHEMOMETRICS

Monday PM (1:20 pm session)
Calibration Maintenance and Transfer for NIR Instrument Networks, *Chicago C*
Monday PM (3:50 pm session)
Advances in NIR Spectroscopy in the Pharmaceutical Industry, *Chicago C*
Data Analysis in LIBS, *Chicago A*
Tuesday Poster Session
Pharmaceutical Analysis
Tuesday AM
Forensic and Environmental Applications of Chemometrics, *Empire B*
Tuesday PM (3:50 pm session)
Biological Applications of Chemometrics, *Empire A*
Wednesday Poster Session
Chemometrics and Spectroscopic Investigation
Wednesday AM
Chemometrics and Molecular Spectroscopy, *Empire A*
Making the most of Spectral and Other Process Data, *Empire C*
Information-rich Approaches in BioMedical Spectroscopy, *Chicago B*
Thursday Poster Session
Polymer Spectroscopy and Materials Analysis
Thursday PM (1:20 pm session)
Applications of Chemometrics in Vibrational Spectroscopy, *New York B*
Instrumentation and Applications: Probing the Limits in Molecular Spectroscopy, *New York A*
Applications of Raman Spectroscopy & Microscopy, *Chicago B*
Thursday PM (3:50 pm session)
FACSS Innovation Awards, *Exhibit Hall B*

CHROMATOGRAPHY

Monday Poster Session
Microfluidics, Electrophoresis, Chromatography, and Bio-Analysis
Monday PM (1:20 pm session)
BioAnalytical Applications of Micro- and Nanofluidics, *New York B*
Tuesday Poster Session
Pharmaceutical Analysis
Tuesday AM
Recent Advancements in Electrophoretic Separation, *Chicago C*
Wednesday Poster Session
Forensic Applications of Spectroscopy
Wednesday AM
Light and Separations: A Powerful Combination, *Chicago A*
Thursday Poster Session
Atomic Spectrometry: Sample Introduction and New Technology
Atomic Spectrometry, Speciation Analysis and Environmental Applications
Environmental Analysis
Fuel, Biomass, and Exhaust Analysis
Polymer, Spectroscopy and Materials Analysis
Food, Bio-Extract, and Materials Characterization
Thursday PM (1:20 pm session)
New Techniques in the Separation Sciences, *Chicago A*

ELECTROPHOREIS and MICROFLUIDICS

Monday Poster Session
Microfluidics, Electrophoresis, Chromatography, and Bio-Analysis
New Approaches to BioAssay
Monday AM
Current Status of the Analytical Sciences: Focus on Human Health, *New York B*
Monday PM (1:20 pm session)
BioAnalytical Applications of Micro- and Nanofluidics, *New York B*
Monday PM (3:50 pm session)
Microfluidics and Nanofluidics, *New York B*
Tuesday AM
Recent Advancements in Electrphoretic Separation, *Chicago C*
Tuesday PM (1:20 pm session)
Next Generation Electric-Field Driven Separation, *Chicago C*
Tuesday PM (3:50 pm session)
Microscale Phenomena – Joint AES an FACSS Symposium, *Chicago C*
Wednesday AM
Light and Separations: A Powerful Combination, *Chicago A*
Wednesday PM (1:20 pm session)
Innovations in Optical Instrumentation, *Empire C*
Wednesday PM (3:50 pm session)
Droplets, Digital Microfluids, and Single Cell Chemical Analysis, *Chicago B*
Thursday PM (1:20 pm session)
New Techniques in the Separation Sciences, *Chicago A*

ELECTROPHOREIS and MICROFLUIDICS, *continued*

Thursday PM (3:50 pm session)
FACSS Innovation Awards, *Exhibit Hall B*

FLUORESCENCE

Monday Poster Sessions
New Approaches to BioAssay
Microfluidics, Electrophoresis, Chromatography, and Bio-Analysis
Monday AM
Advanced Techniques in Fluorescence Microscopy and Spectroscopy, *Empire A*
Tuesday Poster Session
Microscopy and Spectroscopy
Tuesday AM
Novel Optical Reporters, Dyes, and Tags in Molecular and Raman Spectroscopy, *Empire A*
Wednesday PM
Novel Microscopic and Spectroscopic Techniques at the Nanoscale, *Empire C*
Thursday PM (3:50 pm session)
FACSS Innovation Awards, *Exhibit Hall B*

FORENSICS AND SECURITY

Monday AM
Nontraditional Approaches for Chemical and Biological Sensing, *Empire C*
Monday PM (1:20 pm session)
Nuclear Forensics, *Empire C*
Monday PM (3:50 pm session)
Standoff Raman: Applications and Key Issues, *Chicago B*
Tuesday AM
Forensic and Environmental Applications of Chemometrics, *Empire B*
Pushing the Limits of LIBS in Analytical Science, *Chouteau A*
Tuesday PM (1:20 pm session)
On the Scent: Vapor and Aroma Analysis for Forensic and Security Applications, *Empire A*
Tuesday PM (3:50 pm session)
Elemental Signature for Forensics, *Chouteau A*
Portable Instrumentation and Standoff Detection Techniques, *Empire C*
Wednesday Poster Session
Forensic Applications of Spectroscopy
Ambient Mass Spectrometry
Wednesday AM
Forensic Investigations with Molecular Spectroscopy, *Empire B*
Wednesday PM (1:20 pm session)
Ambient Ionization Techniques for Forensics, Security and Biological Analysis, *Chicago C*
Wednesday PM (3:50 pm session)
Ambient Mass Spectrometry: Fundamentals Findings and the Future, *Chicago, C*
Thursday AM
Advances in Analytical Forensics, *Chicago B*
Thursday PM (3:50 pm session)
FACSS Innovation Awards, *Exhibit Hall B*

LIBS

Monday AM
New Plasmas, New Instrumentation, and New Approaches at the Frontier of Atomic Spectrometry, *Chicago A*
Monday PM (1:20 pm session)
Fundamental Aspects of LIBS, *Chicago A*
Monday PM (3:50 pm session)
Data Analysis in LIBS, *Chicago A*
Tuesday Poster Session
Laser Induced Breakdown Spectroscopy
Tuesday AM
Pushing the Limits of LIBS in Analytical Science, *Chouteau A*
Very Remote Spectroscopy: Exploring Extreme Environments, *Empire C*
Tuesday PM (1:20 pm session)
Laser-Induced Breakdown Spectroscopy, *Chouteau A*
Tuesday PM (3:50 session)
Elemental Signatures for Forensics, *Chouteau A*
Wednesday AM
ACS Division of Analytical Chemistry Distinguished Service Award Honoring Gary Hieftje, *Atlanta*
Wednesday PM (1:20 pm session)
Fundamental Aspects of Plasma Spectrochemisty: Using What We Learn to Improve Analytical Atomic Spectroscopy, *Chicago A*
Wednesday PM (3:50 pm session)
Sampling the World with Laser Ablation and Atomic Spectrometry, *Chicago A*
Thursday PM 91:20 pm session
SAS Applied Spectroscopy Meggers Award Honoring Mike Angel, *Atlanta*
Thursday PM (3:50 pm session)
FACSS Innovation Awards, *Exhibit Hall B*
Friday AM
Friday Morning Plenary Session, *Empire A*

MASS SPECTROMETRY

Monday Poster Sessions
Mass Spectrometry
Monday AM
Microbes in Mass Spectrometry, *New York A*
Monday PM (1:20 pm session)
in vitro and *in vivo* Modifications of Biomolecules Assessed by Mass Spectrometry, *New York A*
Monday PM (3:50 pm session)
Isoscapes: Redefining the Landscape in the Archaeological and Geological Sciences with High Fidelity Isotope Ratio Analysis, *Empire B*
Higher-order Structure in Proteins by MS-based Approaches, *New York A*
Tuesday Poster Session
Pharmaceutical Analysis
Tuesday AM
Current Status of the Analytical Sciences: Focus on Human Health, *Chicago B*
Instrument and Method Development in Mass Spectrometry, *New York A*
Tuesday PM (1:20 pm session)
Topics in Tandem Mass Spectrometry, *New York A*
Tuesday PM (3:50 pm session)
Portable Instrumentation and Standoff Detection Techniques, *Empire C*
Wednesday Poster Session
Forensic Applications of Spectroscopy
Ambient Mass Spectromentry
Wednesday AM
ACS Division of Analytical Chemistry Distinguished Service Award Honoring Gary Hieftje, *Atlanta*
Wednesday PM (1:20 pm session)
Ambient Ionization Techniques for Forensics, Security and Biological Analysis, *Chicago C*
Wednesday PM (3:50 pm session)
Ambient Mass Spectrometry: Fundamental Findings and the Future, *Chicago C*

MASS SPECTROMETRY, continued

Thursday Poster Session
Environmental Analysis
Atomic Spectroscopy: Speciation Analysis and Environmental Applications
Thursday PM (1:20 pm session)
New Plasmas, New Instrumentation and New Approaches at the Frontier of Atomic Spectroscopy – the Coda, *Empire A*
Thursday PM (3:50 pm session)
FACSS Innovation Awards

MICROSCOPY and SPECTROSCOPY

Monday AM
Advanced Techniques in Fluorescence Microscopy and Spectroscopy, *Empire A*
Chemistry in Art and Archaeology I, *Empire B*
Monday PM (1:20 pm session)
BioAnalytical Applications of Micro- and Nanofluidics, *New York B*
Tuesday Poster Session
Microscopy and Spectroscopy
Tuesday AM
Novel Optical Reporters, Dyes, and Tags in Molecular and Raman Spectroscopy, *Empire A*
Tip-enhanced Raman Spectroscopy – New Trends, *New York B*
Tuesday PM (1:20 pm session)
Pharmaceutical Applications of Raman Imaging, *New York B*
Wednesday AM
Spectroscopy in the Biomedical and Clinical Sciences, *Chicago B*
Chemometrics and Molecular Spectroscopy, *Empire A*
Light and Separations: A Powerful Combination, *Chicago A*
Wednesday PM (1:20 pm session)
Information-Rich Approaches in BioMedical Spectroscopy, *Chicago B*
Innovations in Optical Instrumentation, *Empire C*
Wednesday PM (3:50 pm session)
Novel Microscopic and Spectroscopic Techniques at the Nanoscale, *Empire C*
Thursday AM
Raman Spectroscopy: A Noninvasive Method for Discrimination of Cells and Cell Populations I, *Chicago C*
Optical and Photoacoustic Tomography and Microscopy, *New York A*
Thursday PM (1:20 pm session)
Raman Spectroscopy: A Noninvasive Method for Discrimination of Cells and Cell Populations II, *Chicago C*
Applications of Raman Spectroscopy & Microscopy, *Chicago B*

MOLECULAR SPECTROSCOPY (IR and NIR)

Monday AM
New Applications of Quantum Cascade Lasers in Chemical Analysis, *Chicago* C
Chemistry in Art and Archaeology I, *Empire B*
Monday PM (1:20 pm session)
Calibration Maintenance and Transfer for NIR Instrument Networks, *Chicago C*
Ionic Liquids for and by Analytical Chemistry, *Chicago B*
Chemistry in Art and Archaeology II, *Empire B*
Monday PM (3:50 pm session)
Advances in NIR Spectroscopy in the Pharmaceutical Industry, *Chicago C*
Industrial Process Analytical Spectroscopy, *Empire A*
Infrared and Raman Spectroscopy of Organic Semiconductors and Conductors, *Empire C*
Tuesday Poster Session
Pharmaceutical Analysis
Microscopy and Spectroscopy
New IR and Raman Instrumentation
Tuesday AM
Charles Mann Award Honoring Don Pivonka, *Atlanta*
Novel Optical Reporters, Dyes, and Tags in Molecular and Raman Spectroscopy, *Empire A*
Tuesday PM (1:20 pm session)
Two-Dimensional Correlation Spectroscopy I, *Empire B*
Advanced Vibrational Probes for Biomedical Sensing, *Empire C*
On the Scent: Vapor and Aroma Analysis for Forensic and Security Application, *Empire A*
Tuesday PM (3:50 pm session)
Two-Dimensional Correlation Spectroscopy II, *Empire B*
Wednesday Poster Session
Chemometrics and Spectroscopic Investigation
Forensic Applications of Spectroscopy
Wednesday AM
Spectroscopy in the Biomedical & Clinical Sciences, *Chicago B*
Chemometrics and Molecular Spectroscopy, *Empire A*
Forensic Investigations with Molecular Spectroscopy, *Empire B*
Wednesday PM (1:20 pm session)
ANACHEM Award Honoring Peter Griffiths, *Atlanta*
Information-Rich Approaches in BioMedical Spectroscopy, *Chicago B*
Molecular Spectroscopy as a Physician's Friend, *Empire B*
Innovations in Optical Instrumentation, *Empire C*
Wednesday PM (3:50 pm session)
Novel Microscopic and Spectroscopic Techniques at the Nanoscale, *Empire C*
Industrial Applications of Vibrational Spectroscopy, *Empire B*
Celebrating 120 Years of the Infrared and Raman Discussion Group (IRDG) and the Coblentz Society, *Atlanta*
Thursday Poster Session
Environmental Analysis
Fuels, Biomass, and Exhaust Analysis
Polymer Spectroscopy and Materials Analysis
Food, Bio-Extract, and Materials Characterization
Thursday AM
Optical and Photoacoustic Tomography and Microscopy, *New York A*
From Ag to Ag(riculture): Analytical Chemistry in the Midwest, *Empire C*
Hand-Held Devices for PAT and Industrial Uses, *Empire B*
Advances in Analytical Forensics, *Chicago B*
Polymers, Polymerization, and Spectroscopy, *Chicago A*
Novel Spectroscopic Approaches in Analytical Chemistry, *Empire A*
Thursday PM (1:20 pm session)
Applications of Chemometrics in Vibrational Spectroscopy, *New York B*
Instrumentation and Applications: Probing the Limits in Molecular Spectroscopy, *New York A*
Applications and Advances in Handheld and Portable Spectroscopy, *Empire C*
Thursday PM (3:50 pm session)
FACSS Innovation Awards
Friday Morning
Friday Morning Plenary Session

PHARMACEUTICAL AND INDUSTRIAL SPECTROSCOPY

Monday AM
SAS PAT Technical Section: PAT in the Biopharmaceutical and Pharmaceutical Industries, *Chicago B*

PHARMACEUTICAL AND INDUSTRIAL SPECTROSCOPY, continued

Monday PM (1:20 pm session)
SAS PAT Technical Section: PAT in the Biopharmaceutical and Pharmaceutical Industries, *Empire A*
Monday PM (3:50 pm session)
Advances in NIR Spectroscopy in the Pharmaceutical Industry, *Chicago C*
Industrial Process Analytical Spectroscopy, *Empire A*
Infrared and Raman Spectroscopy of Organic Semiconductors and Conductors, *Empire C*
Tuesday Poster Session
Pharmaceutical Analysis
Tuesday AM
Charles Mann Award Honoring Don Pivonka, *Atlanta*
Tuesday PM (1:20 pm session
Pharmaceutical Applications of Raman Imaging, *New York B*
Tuesday PM (3:50 pm session)
Atomic Spectrometry and the Analysis of Nanomaterials, *Chicago A*
Pharmaceutical Applications of Raman Spectroscopy, *Chicago B*
Wednesday Poster Session
Chemometrics and Spectroscopic Investigation
Wednesday AM
Raman Spectroscopy for Pharmaceutical Surveillance and Process Control, *Chicago C*
Making the most of Spectral and Other Process Data, *Empire C*
Wednesday PM (1:20 pm session)
Nanomaterials for Plasmonics, *New York A*
Wednesday PM (3:50 pm session)
Industrial Applications of Vibrational Spectroscopy, *Empire B*
Thursday Poster Sessions
Atomic Spectroscopy: Speciation Analysis and Environmental Application
Environmental Analysis
Fuel, Biomass, and Exhaust Analysis
Polymer Spectroscopy and Materials Analysis
Food, Bio-Extract, and Materials Characterization
Thursday AM
From Ag to Ag(riculture): Analytical Chemistry in the Midwest, *Empire C*
Hand-Held Devices for PAT and Industrial Uses, *Empire B*
Polymers, Polymerization, and Spectroscopy, *Chicago A*
Thursday (1:20 pm session)
Applications and Advances in Handheld and Portable Spectroscopy, *Empire C*
Applications of Raman Spectroscopy and Microscopy, *Chicago B*
Thursday PM (3:50 pm session)
FACSS Innovation Awards

PROCESS ANALYTICAL TECHNOLOGY

Monday AM
SAS PAT Technical Section: PAT in the Biopharmaceutical and Pharmaceutical Industries, *Chicago B*
Monday PM (1:20 pm session)
Calibration Maintenance and Transfer for NIR Instrument Networks, *Chicago C*
SAS PAT Technical Section: PAT in the Biopharmaceutical and Pharmaceutical Industries, *Empire A*
Monday PM (3:50 pm session)
FACSS Student Awards, *Atlanta A*
Industrial Process Analytical Spectroscopy, *Empire A*
Tuesday Poster Session
Pharmaceutical Analysis
Tuesday AM
FACSS Charles Mann Award Session Honoring Don Pivonka, *Atlanta*
Tuesday PM (3:50 pm session)
Pharmaceutical Applications of Raman Spectroscopy, *Chicago B*
Portable Instrumentation & Standoff Detection Techniques, *Empire C*
Wednesday Poster Session
Chemometrics and Spectroscopic Investigation
Wednesday AM
Raman Spectroscopy for Pharmaceutical Surveillance and Process Control, *Chicago C*
Making the Most of Spectral and Other Process Data, *Empire C*
Thursday AM
Hand-Held Devices for PAT and Industrial Uses, *Empire B*
Thursday PM (1:20 pm session)
Applications and Advances I Handheld and Portable Spectroscopy, *Empire C*

RAMAN

Monday Poster Session
Microfluidics, Electrophoresis, Chromatography, and Bio-Analysis
New Approaches to BioAssay
Monday AM
Chemistry in Art and Archaeology I, *Empire B*
Raman Spectroscopy I Astrobiology and Planetary Sciences, *Atlanta*
Monday PM (1:20 pm session)
Chemistry in Art and Archaeology II, *Empire B*
Emerging Raman Techniques and Applications, *Atlanta*
Monday PM (3:50 pm session)
Standoff Raman: Applications and Key Issues, *Chicago B*
Infrared and Raman Spectroscopy of Organic Semiconductors and Conductors, *Empire C*
Tuesday Poster Session
Pharmaceutical Analysis
Microscopy and Spectroscopy
New IR and Raman Instrumentation
Tuesday AM
FACSS Charles Mann Award Session Honoring Don Pivonka, *Atlanta*
Tip-enhanced Raman Spectroscopy – New Trends, *New York B*
Tuesday PM (1:20 pm session)
Coblentz Society's Craver Award Session Honoring Duncan Graham, *Atlanta*
Pharmaceutical Applications of Raman Imaging, *New York B*
Tuesday PM (3:50 pm session)
Pharmaceutical Applications of Raman Spectroscopy, *Chicago B*
UV Raman / UV SERS, *New York B*
Recent Progress in SERS, *New York A*
Wednesday Poster Session
Chemometrics and Spectroscopic Investigation
Forensic Applications of Spectroscopy
SERS: New Substrates and Analyses
Wednesday AM
Chemometrics and Molecular Spectroscopy, *Empire A*
Raman Spectroscopy for Pharmaceutical Surveillance and Process Control, *Chicago C*
Raman Optical Activity, *New York B*

RAMAN, continued

Wednesday PM (1:20 pm session)
ANACHEM Award Session Honoring Peter Griffiths, *Atlanta*
Information-Rich Approaches in BioMedical Spectroscopy, *Chicago B*
Molecular Spectroscopy as a Physician's Friend, *Empire B*
Young Scientists in SERS, *New York B*
Innovations in Optical Instrumentation, *Empire C*

Wednesday PM (3:50 pm session)
Novel Microscopic and Spectroscopic Techniques at the Nanoscale, *Empire C*
Disease Diagnostics using SERS, *New York B*

Thursday Poster Session
Environmental Analysis
Fuel, Biomass, and Exhaust Analysis
Polymer Spectroscopy and Materials Analysis
Food, Bio-Extract, and Materials Characterization

Thursday AM
Raman Spectroscopy: A Noninvasive Method for Discrimination of Cells and Cell Population I, *Chicago C*
Hand-Held Devices for PAT and Industrial Uses, *Empire B*
Polymers, Polymerization, and Spectroscopy, *Chicago A*

Thursday PM (1:20 pm session)
Raman Spectroscopy: A Noninvasive Method for Discrimination of Cells and Cell Populations II, *Chicago C*
Applications and Advances in Handheld and Portable Spectroscopy, *Empire C*
Applications of Raman Spectroscopy and Microscopy, *Chicago B*

Thursday PM (3:50 pm session)
FACSS Innovation Awards

Friday Morning
Friday Morning Plenary Session

REMOTE INSTRUMENTATION and CHEMICAL SENSORS

Monday Poster Session
New Approaches to BioAssay

Monday AM
Nontraditional Approaches for Chemical and Biological Sensing, *Empire C*

Tuesday PM (1:20 pm session)
On the Scent: Vapor and Aroma Analysis for Forensic and Security Applications, *Empire A*

Tuesday PM (3:50 pm session)
Portable Instrumentation and Standoff Detection Techniques, *Empire C*

Wednesday PM (1:20 pm session)
Innovations in Optical Instrumentation, *Empire C*

Thursday AM
Hand-Held Devices for PAT and Industrial Uses, *Empire B*
Applications and Advances in Handheld and Portable Spectroscopy, *Empire C*

SURFACE PLASMON RESONANCE

Tuesday AM
Novel Optical Reporters, Dyes, and Tags in Molecular and Raman Spectroscopy, *Empire A*
Surface Plasmon Resonance Applications and Instrumentation, Chicago A

Wednesday AM
Nanomaterials for Plasmonics I, *New York A*

Wednesday PM (1:20 pm session)
Nanomaterials for Plasmonics II, *New York A*

Wednesday PM (3:50 pm session)
Nanomaterials for Plasmonics III, New York A

PROGRAM HIGHLIGHTS

SUNDAY	MONDAY	TUESDAY	WEDNESDAY	THURSDAY
	Exhibit Hall B Foyer 7:30 Wake up coffee	*Exhibit Hall B Foyer* 7:30 Wake up coffee	*Exhibit Hall B Foyer* 7:30 Wake up coffee	*Exhibit Hall B Foyer* 7:30 Wake up coffee
8:00 am – 5:00 pm Workshops	*Exhibit Hall B* 7:50 am Opening Remarks **Steve Ray** 8:00 am Keynote Lecture **Chris McKay** *NASA Ames Laboratory*	*Exhibit Hall B* 8:00 am Coblentz Society's Craver Award **Duncan Graham** *University of Strathclyde* 8:20 am FACSS Charles Mann Award **Don Pivonka** *Incyte Pharmaceuticals*	*Exhibit Hall B* 8:00 am ACS Division of Analytical Chemistry Award for Distinguished Service in the Advancement of Analytical Chemistry **Gary Hieftje** *Indiana University* 8:30 AM ANACHEM Award **Peter R. Griffiths** *University of Idaho*	*Exhibit Hall B* 8:00 am SAS Applied Spectroscopy William F. Meggers Award **Mike Angel** *University of South Carolina* 8:30 am SAS Lester W. Strock Award **Ralph Sturgeon** *National Research Council Canada*
	9:00 am – 5:00 pm Workshops	9:00 am – 5:00 pm Workshops	9:00 – 5:00 pm Workshops	9:00 – 5:00 pm Workshops
		Exhibit Hall A 9:00 am – 4:30 pm Exhibits Open	*Exhibit Hall A* 9:00 AM – 4:00 pm Exhibits Open	
	Exhibit Hall B 9:00 – 10:20 pm Poster Session and Break	*Exhibit Hall A* 9:00 – 10:20 am Poster Session and Break	*Exhibit Hall A* 9:00 – 10:20 am Poster Session and Break	*Exhibit Hall B* 9:00 – 10:20 pm Poster Session and Break
	10:20 am – 12:00 am Oral Symposia	10:20 am – 12:00 am Oral Symposia	10:20 am – 12:00 am Oral Symposia	10:20 am – 12:00 am Oral Symposia
	Noon Lunch on own	Noon Lunch on own	Noon Lunch on own	Noon Lunch on own
		Van Horn C 12:30 PM Lunch and Roundtable discussion for students. Sponsored by SABIC		
Exhibit Hall B 3:30 – 7:00 pm What's Hot Vendor Presentations	1:20 – 3:00 pm Oral Symposia	1:20 – 3:00 pm Oral Symposia	1:20 – 3:00 pm Oral Symposia	1:20 – 3:00 pm Oral Symposia
	Exhibit Hall B 3:00 – 3:50 pm Poster Viewing and Break	*Exhibit Hall A* 3:00 – 3:50 pm Poster Viewing and Break	*Exhibit Hall B* 3:00 – 3:50 pm Poster Viewing and Break	*Exhibit Hall A* 3:00 – 3:50 pm Poster Viewing and Break
	3:50 – 5:30 pm Oral Symposia	3:50 – 5:30 pm Oral Symposia	3:50 – 5:30 pm Oral Symposia	3:50 – 5:30 pm Oral Symposia
		Exhibit Hall B 6:00 pm Raman Reception Sponsored by Kaiser Optical Systems, Inc.		**FRIDAY** *Empire A* 8:00 – 10:00 am – Special Plenary Session Welcoming Three New Member Organizations into FACSS Announcement of the FACSS Innovation Award Winner
Exhibit Hall B 7:00 – 9:00 pm Welcome Mixer and SAS Sponsored Student Poster Session Coblentz Student Awards FACSS Student and Tomas Hirschfeld Scholar Awards	*Exhibit Hall A* 5:30 – 7:30 PM Exhibit Opening Reception	*Atlanta Room* 7:30 pm SAS Reception *(SAS members only)*	*Exhibit Hall B* 6:00 pm All Inclusive Wednesday Evening Event "Back to the Eighties"	

"What's Hot" Symposium, Presider: Brian Dable**,** *Exhibit Hall B*

3:30 **HORIBA,** PP-TOF MS Plasma Profiling TOF MS. Another Addition to Our "Solids" Family

3:40 **TBD**

3:50 **Opotek,** Optical Parametric Oscillator (OPO) Devices for Instrument Integration, Portability and In Vivo Pre-clinical Imaging Applications

4:00 **PerkinElmer,** What's Hot from PerkinElmer - Award Winning Solutions

4:10 **Daylight Solutions,** Progress Towards Ultra Broadband Tuning in External Cavity Quantum Cascade Lasers

4:20 **Pyreos,** New Opportunities in Mid IR Analysis

4:30 **Mettler Toledo,** Understanding the Challenges: Implementing Inline FTIR Analysis with ReactIR™ 45P

4:40 **B&W Tek**, The Next Generation of Protable Raman Spectrometers

4:50 **Princeton Instruments,** Aberration-Free Spectroscopy: The IsoPlane from Princeton Instruments

5:00 **Bruker Optics**

5:10 **Renishaw,** New Raman Imaging Techniques

5:20 **BaySpec,** 1064nm Dispersive Raman for Fluorescence-Free Spectral Sensing

5:30 **Thermo Fisher,** Introducing the Nicolet iS50 FT-IR Spectrometer. Full research-grade multi-technique capabilities seamless integrated into a compact system with push button simplicity

5:40 **Centice,** Low-cost Deep-UV Raman spectrometer

5:50 **Iridian Spectral Technologies,** What's Hot in Optical Filters

6:00 **Arjae Spectral / Tornado, Sensei:** Innovative optical dispersive spectrometer design platform which increases throughput >10 times without sacrificing spectral resolution

6:10 **Kaiser Optical Systems,** The State of the Art in Raman Sampling: An Overview

6:20 **Agilent,** New advances in ICP-MS for greater capability and sensitivity

6:30 **WITec,** Diffraction Limited in Three Dimensions: High Resolution, Ultrafast 3D Confocal Raman Imaging

6:40 **Innovative Photonic Solutions,** Ultra-stable Raman and Metrology laser sources and advantages of integrated Raman Probes

6:50 **Horiba**, Evolution. Intelligent Design. Not Mutually Exclusive. Raman that is both powerful and easy

SUNDAY 7:00 PM
WELCOME MIXER
SAS Sponsored Student Poster Session, Coblentz Student Awards, and FACSS Student and Tomas Hirschfeld Scholar Awards
Exhibit Hall B

SAS
Student Poster Showcase and Awards

Please join us in celebrating the
future of spectroscopy as SAS students showcase their research and
compete for the annual SAS Student Poster Awards.

Sunday, September 30, 2012, 7-9 p.m. *(during the SciX mixer)*

Sponsored by
The Society for Applied Spectroscopy and SciX

TECHNICAL PROGRAM – MONDAY
Welcome- 7:50 am and Keynote Lecture – 8:00 am
Presider: Steven J. Ray

8:00 am Keynote Lecture, *Exhibit Hall* B

(1) **Remote Spectroscopy in the Search for Life on Other Worlds**; Chris McKay; NASA Ames

Chris McKay, *NASA Ames Laboratory*; PhD in AstroGeophysics from the University of Colorado

Dr. McKay's research focuses on the evolution of the solar system and the origin of life, as well as being actively involved in planning for future Mars missions including human exploration. He has been involved with polar and desert research, traveling to the Antarctic Dry Valleys, the Atacana Desert, the Arctic, and the Namib Desert to conduct research in these Mars-like environments.

Monday Poster Session
9:00 – 10:20 am
Exhibit Hall B

All Monday posters should be put up between 7:30 – 8:00 am and removed by 4:30 pm

Mass Spectrometry

Board #

1 (2) **Evaluation of a Quadrupole Mass Spectrometer for High Resolution of Light Gases**; William Spencer[1], Kevin Kuchta[2]; [1]SRNS/ SRNL, [2]Extrel LLC

2 (3) **Alternative MALDI Matrix Found in Silver Nanoparticles Produced via Soft-Landing Ion Mobility**; Barbara Walton[1], Guido Verbeck[1]; [1]University of North Texas

3 (4) **Travelling Wave Ion Mobility-Mass Spectrometry Study of the Influence of Group I Metal-Cation Adduction on Conformation of Isomeric Carbohydrates**; Yuting Huang[1], Eric Dodds[1]; [1]University of Nebraska-Lincoln

4 (5) **Hydrogen/Deuterium Exchange Mass Spectrometry Determination of the Allosteric Mechanisms Relating to the Phosphorylation Regulation of Human Liver Pyruvate Kinase**; Xiaohua (Sarah) Zhou[1], Charulata B. Prasannan[1], Maria T. Villar[1], Antonio Artigues[1], Aron W. Fenton[1]; [1]University of Kansas Medical Center

5 (6) **Probing Amino Acid Content of Foodstuffs Using Microwave Hydrolysis Coupled with Desorption Electrospray Ionization Mass Spectrometry**; Jonathan Person[1], Christopher Mulligan[1]; [1]Illinois State University

6 (7) **Dual Online Extraction Method for H/D Exchange Mass Spectrometry in the Presence of Crowding Agents**; Farai Rusinga[1], David Weis[1]; [1]University of Kansas

7 (8) **Multi-analysis Platform Incorporating Raman Microscopy and Multiple Internal Reflection-Infrared Spectroscopy for the *in situ* Analysis of Soft-Landed Clusters**; James Fox[1], William Hoffmann[1], Guido Verbeck[1]; [1]University of North Texas

8 (9) **Hydrogen/deuterium Exchange Mass Spectrometry Analysis of Structural Changes in Calcineurin Induced by Calmodulin**; Mohammed Al-Naqshabandi[1], Tori Dunlap[2], Trevor Creamer[2], David Weis[1]; [1]Department of Chemistry, University of Kansas., [2]Center for Structural Biology, Department of Molecular and Cellular Biochemistry, University of Kentucky

Biological Applications of Spectroscopy

9 (10) **Single Cell Identification via Raman Microscopy and Multivariate Analysis**; Yelena Ilin[1], Mary Kraft[1]; [1]University of Illinois at Urbana-Champaign

10 (11) **Micro-Raman Spectroscopy to Evaluate the Effect of Oral Cancer Radiotherapy on Tooth Chemical Structure**; Changqi Xu[1, 2], Rachel Reed[1, 2], Ying Liu[1, 2], Jeff Gorksi[1, 2], Yong Wang[1,2], Mary Walker[1, 2]; [1]University of Missouri-Kansas City School of Dentistry, [2]Deparment of Oral Biology

Board #

11 (12) **Characterization of Poly-L-lactic Acid Biodegradable Implant Materials by Differential Scanning Calorimetry**; Sudha Muttavarapu[1], John F. Turner II[1]; [1]Cleveland State University

12 (13) **Wide-field Raman Chemical Imaging of Cold-Drawn Poly-L-Lactide Bioimplants**; Venkata N K Rao Bobba[1], John F. Turner II[1]; [1]Cleveland State University

13 (14) **Untangling Fibrillogenesis: A Combined Spectroscopic study of Fibril Formation**; Benjamin Gardner[1], Tanja Deckert-Gaudig[2], Vitali Sikirzhytski[3], Dmitry Kurouski[3], Igor Lednev[3], Volker Deckert[2], Ewan Blanch[1]; [1]University of Manchester, [2]Institute of Photonic Technology, [3]University at Albany

14 (15) **Using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy to Monitor Pyridoxal Phosphate in the Active Site of Aspartate Aminotransferase**; Jessica Moore[1], Elyse Towns[1], Joesph Price[1], Mateo Hernandez[1], Michael Toney[1], Don Land[1]; [1]UC Davis

15 (16) **A Novel Approach for Non-Invasive Quality Measurements of Intact Salmon using Spatially Offset Raman Spectroscopy**; Nils Kristian Afseth[1], Matthew Bloomfield[2], Jens Petter Wold[1], Darren Andrews[2], Pavel Matousek[2, 3]; [1]Nofima – Norwegian Institute of Food, Fisheries and Aquaculture research, Ås, Norway, [2]Cobalt Light Systems, Harwell Oxford, UK, [3]Central Laser Facility, STFC Rutherford Appleton Laboratory, UK.

16 (17) **Degree of Conversion of Self-Etch Adhesives on Enamel: A Micro-Raman Spectroscopic Study**; Ying Zhang[1], Yong Wang[1]; [1]University of Missouri-Kansas City

17 (18) **Diffuse Reflectance Adds a New Spectroscopic Dimension for Real-Time Detection of Microcalcification in Breast Needle Biopsies**; Jaqueline S. Soares[1], Ishan Barman[1], Narahara Chari Dingari[1], Zoya Volynskaya[1, 4], Wendy Liu[2, 3], Nina Klein[2, 3], Donna Plecha[2, 3], Ramachandra R. Dasari[1], Maryann Fitzmaurice[2, 3]; [1]George R. Harrison Spectroscopy Laboratory, Massachusetts Institute of Technology, [2]Case Western Reserve University, [3]University Hospitals Case Medical Center, [4]Current Address, Aperio Technologies, Inc.

18 (19) **Spectrochemical Imaging at the Infrared Diffraction Limit Reveals Similarities in Brain Tissue from Transgenic Mouse Models of Alzheimer Disease**; Catherine Liao[1], Jillian Lund[1], Margaret Rak[1], Miriam Unger[2], Carol Hirschmugl[2], Benedict Albensi[1], Kathleen Gough[1]; [1]University of Manitoba, [2]University of Wisconsin-Milwaukee

Board #

19 (20) **Early Detection of Chytrid Infections in Algal Biomass using Hyperspectral Imaging and Fluorescence Spectroscopy**; Howland Jones[1], Aaron Collins[1], Robert McBride[3], Craig Behnke[3], Thomas Reichardt[2], Michael Sinclair[1], Jerilyn Timlin[1]; [1]Sandia National Laboratories, [2]Sandia National Laboratories, [3]Sapphire Energy

20 (21) **Measuring Phytoplankton Community Structure via Fluorescence Imaging Multivariate Optical Computing**; Joseph Swanstrom[1], Shawna Tazik[1], Tammi Richardson[1], Timothy Shaw[1], Michael Myrick[1]; [1]Univ. of South Carolina

21 (22) **Comparison of Various Techniques for Searching for Bio/organic Chemicals Indicative of Life in Na-Sulfate Minerals**; Jill R. Scott[1], Gary S. Groenewold[1], C. Doc Richardson[1, 2], Nancy W. Hinman[1, 2]; [1]Idaho National Laboratory, [2]University of Montana

22 (25) **GC-MSMS Method for Quantifying 11 Aromatic Amines in Urine of Smokers and Nonsmokers**; Elizaebth A. Cowan[1], Tiffany H. Seyler[1], Jenny G. Kim[1]; [1]Centers for Disease Control and Prevention

23 (26) **Identification of Volatile Biomarker Profiles of Lung Diseases in Canine using Active SPME GCMS**; Shamitha Dissanayake[1], Patty Lathan[2], Todd Mlsna[1]; [1]Department of Chemistry, Mississippi State University, [2]Department of Clinical Sciences, Mississippi State University

24 (27) **A High-Throughput Flow Injection ICP-MS Method for Quantitation of siRNA Molecules**; Qiang Tu[1], Fanyu Meng[1], Tiebang Wang[1], Bing Mao[1], Vincent Antonucci[1]; [1]Project Analytical Chemistry, Merck Research Laboratories

25 (28) **Sequestration of Zinc in Activated Macrophages is Essential to Restrict Survival of an Intracellular Pathogen**; Julio Alberto Landero Figueroa[1], Kavitha Subramanian[2], Aleksey Porollo[3], Jospeh A. Caruso[1], George S Deepe, Jr[2, 4]; [1]University of Cincinnati / Agilent Technologies Metallomics Center of the Americas, [2]Department of Molecular Genetics, Biochemistry, Microbiology and Immunology, University of Cincinnati, [3]Department of Environmental Health, University of Cincinnati, [4]Veterans Affairs Hospital, Cincinnati

26 (29) **Investigating the Commutability of Digested and Dilute-and-Shoot Approach for the Determination of Electrolytes in Human Serum by using Isotope Dilution ICP-MS**; Lee L. Yu[1], W. Clay Davis[1], Yoana Nuevo Ordonez[1], Stephen E. Long[1]; [1]National Institute of Standards and Technology

27 (30) **Metalloproteome of Histoplasma capsulatum: Mn, Fe, Cu, and Zn**; Anna Daigle[1], Julio Landero[1], Kavitha Subramanian[2], George Deepe[2], Joseph Caruso[1]; [1]University of Cincinnati Department of Chemistry, [2]University of Cincinnati College of Medicine

Microfluidcs, Electrophoresis, Chromatography, and Bio-Analysis

28 (31) **Isolating a Single DNA Molecule via a Corral Trap**; Xavier Udad[1], Alaknanda Amin-Patel[1], Christine Carlson[1], Jorg Woehl[1]; [1]University of Wisconsin-Milwaukee

29 (32) **Microcolumn Chromatographic-Based Competitive Binding Immunoassays for TBI Biomarkers**; Jeanethe Anguizola[1], Erika Pfaunmiller[1], Michelle Koke[2], Marie Paula Paulemond[3]; [1]University of Nebraska, [2]Nebraska Wesleyan University, [3]Bennett College

30 (33) **Optimization of Protein Entrapment for Preparing High Performance Affinity Supports**; John Vargas[1], Abby Jackson[1], Jeanethe Anguizola[1], Giana Rada[1], David Hage[1]; [1]University of Nebraska-Lincoln

Board #

31 (34) **Fabrication of an Integrated Microfluidic Device for Single Molecule Trapping**; Christine Carlson[1], Xavier Udad[1], Jörg Woehl[1]; [1]University of Wisconsin Milwaukee

32 (35) **Spectroscopic Studies of the Influence of Membrane Fluidity on Protein Structure**; Michael K. Eagleburger[1], Neeta R. Thawani[1], Elizabeth Reardon[1], Jason W. Cooley[1], Renee D. JiJi[1]; [1]University of Missouri

33 (36) **Study Of Influence Microwaves Radiation Coupled with HPLC. Effect of Ion Concentration in Mobile Phase**; Jose-Luis Todoli[1], Silvia Carballo[1], Amanda Terol[1], Juan-Pedro Diaz[1], Soledad Prats[1], Salvador Maestre[1]; [1]university of Alicante

34 (37) **Redox-Magnetohydrodynamic Pumping, Spatially Separated from Redox Processes at Active Electrodes**; Preston Scrape[1], Ingrid Fritsch[1]; [1]University of Arkansas

35 (38) **Microfluidics with Magnetohydrodynamic Pumping and Stirring using PEDOT-modified Electrodes**; Christena Nash[1], Ingrid Fritsch[1]; [1]University of Arkansas, [2]University of Arkansas

36 (39) **Selective Trapping of Single Human Breast Cancer Cells by Insulator Based Dielectrophoresis in a Microfluidic Device**; Sanchari Bhattacharya[1], Tzu-Chiao Chao[1], Alexandra Ros[1]; [1]Arizona State University

37 (40) **Microfluidics Involving Flat Flow Profile and Fluid Stirring Guided by Redox-Magnetohydrodynamics (MHD): toward Lab on a Chip (LOC) Immunoassays**; Vishal Sahore[1], Ingrid Fritsch[1]; [1]University of Arkansas, Fayetteville

38 (41) **CO2-Laser Atmospheric Pressure Ionization of Acoustically Levitated Droplets**; Merwe Albrecht[1], Arne Stindt[1], Ulrich Panne[1], Jens Riedel[1]; [1]BAM Federal Institute for Materials Research and Testing

39 (42) **Fluorescence Correlation Spectroscopy (FCS) to Quantify Flow Patterns in Electrochemically-Driven Microfluidic Devices**; Feng Gao, Adam Kreidermacher, Ingrid Fritsch, Colin Heyes; [1]Department of Chemistry and Biochemistry, University of Arkansas

40 (43) **Using Bead Video Microscopy to Observe Electrochemically Generated Density Gradient Based Fluid Flow in a Microfluidic Setting.**; Adam Kreidermacher[1], Vishal Sahore[1], Ingrid Fritsch[1]; [1]University of Arkansas

41 (44) **Direct Quantification of Tenofovir in Simulated Biological Fluids from pH-Sensitive Microparticles using 1H-NMR**; Chi Zhang[1], Tao Zhang[2], Bi Botti Youan[2], Nathan Oyler[1]; [1]Department of Chemistry, University of Missouri-Kansas City, [2]School of Pharmacy, University of Missouri-Kansas City

New Approaches to BioAssay

42 (45) **Optimizing Bioassay Performance using Dye Functionalized Whispering Gallery Mode Microresonators**; Daniel Kim[1], Kevin Armendiaz[1], Sarah Wildgen[1], Robert Dunn[1]; [1]University of Kansas[4]

43 (46) **Whispering Gallery Mode Imaging for the Early Detection of Ovarian Cancer**; Sarah Wildgen, Heath Huckabay; [1]University of Kansas

44 (47) **N-linked Glycoengineering for Therapeutics: Rapid Confirmation of Glycan Incorporation**; Melinda L Toumi[1], Heather Desaire[1]; [1]University of Kansas, Department of Chemistry

Board #

45 (48) **Extraction and Determination of Oxytetracycline in Muscle and Skin Salmon by Fluorimetry Based on Ionic Pair Formation**; M. Inés Toral[1], Grace Paillavil[1], Nicolas Silva[1], Pablo Richter[1]; [1]University of Chile

46 (49) **Extraction of Oxolinic Acid and Flumequine from Salmon Muscle and Simultaneous Determination by Fluorimetry**; M. Inés Toral, Karina Seguín, Muriel Andrade, Pablo Richter; [1]University of Chile

47 (50) **Modification of Protein Fluorescence by AuNPs: Inner-Filter Effect, Surface Enhancement, and Fluorescence Quenching**; Charles Nettles[1], Dr. Dongmao Zhang[1]; [1]Mississippi State University

48 (51) **Determination of Protein Glycation Levels by Surface Plasmon Resonance - A Preliminary Study**; Phillip Page[1], Thomas Ryan[1], Mary Murphy[1], Peter McDonnell[2], Tony New[2], Ian Davison[2]; [1]Reichert Technologies, Analytical Instruments Division, [2]Genzyme Corporation, Haverhill Operations, UK

49 (52) **Single Molecule Fluorescence Correlation Spectroscopy of Apoptotic Cells using a Red-Fluorescent Caspase Probe**; Michelle Martinez[1], Meicong Dong[1], Michael Mayer[1], Dimitri Pappas[1]; [1]Texas Tech University *(*2011 Applied Spectroscopy Focal Point Author)*

50 (53) **Combining Luminescence and Mid-Infrared Sensors for Advanced Breath Diagnostics**; Paula Fortes[1, 2], Andreas Wilk[2], Ivo Raimundo Jr[1], Boris Mizaikoff[2]; [1]University of Campinas, [2]University of Ulm

51 (54) **Redox Cycling Behavior of Catecholamines on Gold Microelectrode Arrays**; Mengjia Hu[1], Ingrid Fritsch[1]; [1]Department of Chemistry and Biochemistry, University of Arkansas

52 (55) **Detection and Identification of Reactive Nitrogen Species using Microchip Electrophoresis with Electrochemical Detection**; Dulan Gunasekara[1, 2], Diogenes do Santos[2, 3], Pann Pichetsurnthorn[2, 4], Ryan Grigsby[2], Susan Lunte[1, 2, 4]; [1]Department of Chemistry, University of Kansas, Lawrence, KS, [2]Ralph N. Adams Institute for Bioanalytical Chemistry, University of Kansas, Lawrence, KS, [3]Federal University of Alagoas, Maceio, Brazil, [4]Department of Chemical Engineering, University of Kansas, Lawrence, KS

53 (56) **Electrochemical Enzyme Linked Bioassay Development on Nanoporous Gold Surface**; Binod Pandey[1, 2], Yih Horng Tan[1, 2], Jay Kishan Bhattarai[1, 2], Kohki Fujikawa[1], Papapida Pornsuriyasak[1], Alexei V. Demchenko[1], Keith J. Stine[1, 2]; [1]University of Missouri-St.Louis, Department of Chemistry and Biochemistry, [2]University of Missouri-St.Louis, Center for Nanoscience

54 (57) **Electrochemical Detection using an all PMMA Microfluidic Flow-cell with an Integrated Carbon Microelectrode**; Anne Regel[1, 2], Susan Lunte[1, 2, 3]; [1]University of Kansas Department of Chemistry, [2]Ralph N. Adams Institute for Bioanalytical Chemistry, [3]University of Kansas Department of Pharmaceutical Chemistry

Monday Morning, *Chicago A*
NEW PLASMAS, NEW INSTRUMENTATION AND NEW APPROCHES AT THE FRONTIER OF ATOMIC SPECTROMETRY
Organizer and Presider: Carsten Engelhard

10:20 (58) **Single Cell Analysis by Use of ICP-MS**; Norbert Jakubowski[1], Ulrich Panne[1], Janina Kneipp[1], Heike Traub[1], Kaori Shigeta[1], Daniela Drescher[1], Gunda Koellensperger[2], Evelyn Rampler, Charlotte Giesen[1], , [1]BAM Federal Institute for Materials Research, [2]BOKU

10:40 (59) **Elucidation of Selenium Metabolism by Tracer Experiment of Mice Injected with Selenium Stable Isotopes**; Naoki Furuta[1], Yoshinari Suzuki[1], Yoshiteru Hashiura[1], Tatsuya Sakai[1], Takao Yamamoto[1], Takahisa Matsikawa[2], Atsuko Shinohara[2]; [1]Chuo University, [2]Juntendo University School of Medicine

11:00 (60) **New Interface and Collision Cell Design for ICP-MS**; Lothar Rottmann[1], Alexander Makarov[1], Gerhard Jung[1]; [1]Thermo Fisher Scientific; Bremen

11:20 (61) **A Comparative Study of the Magnetic Data Layers on Terabyte Hard Drives by Glow Discharge Compositional Depth Profile Analysis**; Kim Marshall[1], Gregory Schilling[1], Diane Goodman[1]; [1]LECO Corporation

11:40 (62) **One- and Two-Dimensional Microplasma Arrays**; Jeffrey Hopwood[1], Alan Hoskinson[1], Chen Wu[1], Naoto Miura[1]; [1]Tufts University

Monday Morning, *New York B*
CURRENT STATUS OF THE ANALYTICAL SCIENCES: FOCUS ON HEALTH I
Organizers: Royal Society of Chemistry and ACS Analytical Division; Presiders: John Chalmers and May Copsey

10:20 (63) **Exploring the Platelet Secretome**; Christy Haynes[1], Secil Koseoglu[1], Audrey Meyer[1], Sarah Gruba[1]; [1]University of Minnesota

10:40 (64) **Functionalised Nanoparticles and SERRS for Biomedical Applications**; Duncan Graham[1], Karen Faulds[1], Hainan Xie[1], Sarah McAughtrie[1], Alan Hutton[1], Tara Donnelly[1]; [1]University of Strathclyde *(*2011 Applied Spectroscopy Focal Point Author)*

11:00 (65) **Prospects for *in vivo* Raman Diagnostics**; Nick Stone[1]; [1]University of Exeter / Gloucestershire Hospitals

11:20 (66) **Progress toward On-Animal Separation Based Sensors using Microdialysis Coupled to Microchip Electrophoresis.**; Susan Lunte[1], David Scott[1], Simon Pfieffer[1]; [1]University of Kansas

11:40 (67) **Simplifying Human Health Problems and their Solutions by Giving more Attention to Chemistry**; Dana Spence[1]; [1]Michigan State University

Monday Morning, *Empire A*
***SAS APPLIED SPECTROSCOPY FOCAL POINT SESSION*: ADVANCED TECHNIQUES IN FLUORESCENCE MICROSCOPH AND SPECTROSCOPY**
Organizers: Steve Ray and Yan Yu; Presider: Yan Yu

10:20 (68) **Bioanalytical Fluorescence Correlation Spectroscopy**; Dimitri Pappas[1]; [1]Texas Tech University *(*2011 Applied Spectroscopy Focal Point Author)*

10:40 (69) **High-Precision Tracking with Non-Blinking Quantum Dots Resolves Nanoscale Vertical Displacement**; Ning Fang[1], Kyle Marchuk[1]; [1]Iowa State University and Ames Laboratory, U.S. Department of Energy

11:00 (70) **Imaging and Tracking Cell Signaling in Membranes**; Yan Yu[1]; [1]Chemistry Department, Indiana University

11:20 (71) **Multivariate Curve Resolution Applied to Hyperspectral Images: Progress toward Automated Analyses**; David Haaland[1], Howland Jones[1], Jerilyn Timlin[1], David Melgaard[1], Aaron Collins[1], Michael Sinclair[1]; [1]Sandia National Laboratories

11:40 (72) **Single Molecule Tracking and Imaging Fluorescence Correlation Spectroscopy Studies of Molecular Transport in Reversed Phase Chromatographic Materials**; Justin Cooper[1], Eric Peterson[1], Joel Harris[1]; [1]University of Utah

TECHNICAL PROGRAM – MONDAY
Orals 10:20 am – 12:00 pm

Monday Morning, *Chicago C*
NEW APPLICATIONS OF QUANTUM CASCADE LASERS IN CHEMICAL ANALYSIS
Organizer and Presider: Bernhard Lendl

10:20 (73) **Advanced Mid-Infrared Breath Diagnostics**; Boris Mizaikoff[1]; [1]University of Ulm, Institute of Analytical and Bioanalytical Chemistry

10:40 (74) **Sub-Parts-Per-Billion Level Detection of SF6 with a Fiber-Coupled QCL-QEPAS Sensor**; Vincenzo Spagnolo[1], Pietro Patimisco[1], Simone Borri[1], Gaetano Scamarcio[1], Bruce E. Bernacki[2], Jason Kriesel[3]; [1]Dipartimento Interateneo di Fisica, University and Politecnico of Bari, CNR-IFN UOS BARI, [2]Pacific Northwest National Laboratory, [3]Opto-Knowledge Systems Inc.

11:00 (75) **Atmospheric Trace Gas Monitoring Using Latest Advances in mid-IR Quantum Cascade Lasers**; Mark Zahniser[1], David Nelson[1], J. Barry McManus[1], Joanne Shorter[1], Scott Herndon[1]; [1]Aerodyne Research Inc

11:20 (76) **External Cavity Quantum Cascade Lasers for Measurements in Liquids**; Bernhard Lendl[1], Markus Brandstetter[1], Andreas Genner[1]; [1]Vienna University of Technology

11:40 (77) **Tip-enhanced Mid-infrared and Terahertz Photoexpansion Nanospectroscopy**; Mikhail Belkin[1], Feng Lu[1]; [1]The University of Texas at Austin

Monday Morning, *Empire B*
CHEMISTRY IN ART AND ARCHAEOLOGY I
Organizers and Presiders: Mary Kate Donais and Peter Vandenabeele

10:20 (78) **Portable and Laboratory Multi-Analytical Techniques to Diagnose Environmental Impacts on Walls and Wall Paintings of Insula IX, 3 (Pompeii, Italy)**; Juan M. Madariaga[1], Maite Maguregui[1], Kepa Castro[1], Ulla Knuutinen[2], Irantzu Martinez-Arkarazo[1], Anastasia Giakoumaki[1], Silvia Fdez-Ortiz de Vallejuelo[1]; [1]University of the Basque Country, Department of Analytical Chemistry, [2]Helsinki Metropolia University of Applied Sciences

10:40 (79) **Multianalytical Approaches in Art and Archaeology - Conceptions and Misconceptions**; Antonio Candeias[1, 2], Cristina Dias[1,2], Teresa Caldeira[1, 2], Jose Mirao[1, 3], Luisa Carvalho[4]; [1]HERCULES Laboratory, Évora University, Évora, Portugal, [2]Evora Chemistry Centre and Chemistry Department, Evora University, [3]Evora Geophysics Centre and Geosciences Department, Évora University, [4]Lisbon University Atomic Physics Centre, Lisbon University

11:00 (80) **Micro-elemental Analysis and Characterisation of Australian Aboriginal Ochre Pigments and Objects by Synchrotron X-Ray Fluorescence Microscopy (XFM).**; Rachel Popelka-Filcoff[1], Claire Lenehan[1], Erica Donner[2], Enzo Lombi[2], Daryl Howard[3], Keryn Walshe[4], Martin De Jonge[3], David Paterson[3], Allan Pring[4], Jamie Quinton[1]; [1]Flinders University, [2]University of South Australia, [3]Australian Synchrotron, [4]South Australian Museum

11:20 (81) **Chemical and Architectural Examination of a Tower in Monterubiaglio, Umbria (Italy) Utilizing Portable X-Ray Fluorescence Spectrometry**; Mary Kate Donais[1], Anthony Desmond[1], Bradley Duncan[2], David George[1]; [1]Saint Anselm College, [2]University of Massachusetts, Amherst

11:40 (82) **Microarchaeology of Ceramic and Salt Production Facilities in the Mangrove Forests of Southern Mesoamerica**; Hector Neff[1]; [1]IIRMES, CSULB

Monday Morning, *New York A*
MICROBES IN MASS SPECTROMETRY
Organizer and Presider: Robert Hettich

10:20 (83) **Modified Poteins in Environmental Microbes**; Rachel Ogorzalek Loo[1], Hong Nguyen[1], Deborah R. Leon[2], Bryan Crable[3], Michael McInerney[3], Robert Gunsalus[3], Joseph Loo[1]; [1]University of California-Los Angeles, [2]Boston University, [3]University of Oklahoma

10:40 (84) **Application of Targeted Metabolomics and Kinetic Flux Profiling to Understand the Physiology of Microbial Consortia**; Shawn Campagna; [1]University of Tennessee, Knoxville

11:00 (85) **Targeted Proteomics for the Optimization of Biofuel Pathways in E. coli**; Christopher Petzold[1], Pragya Singh[1], Alyssa Redding-Johanson[1], Tanveer Batth[1], Becky Rutherford[1], Taek Soon Lee[1], Jay Keasling[1], Paul Adams[1]; [1]Joint BioEnergy Institute, Lawrence Berkeley National Laboratory

11:20 (86) **Characterization of Natural Microbial Communities using Quantitative Proteomics**; Chongle Pan[1], Zhou Li[1], Nicholas Justice[2], Jill Banfield[2], Bob Hettich[1]; [1]Oak Ridge National Laboratory, [2]University of California, Berkeley

11:40 (87) **High-Resolution Imaging of Cholesterol and Sphingolipid Distribution in Cell Membranes using Secondary Ion Mass Spectrometry**; Mary L. Kraft[1], Jessica F. Frisz[1], Haley A. Klitzing[1], Kaiyan Lou[1], Joshua Zimmerberg[2], Peter K. Weber[3]; [1]University of Illinois, School of Chemical Sciences, [2]National Institutes of Health, Eunice Kennedy Shriver National Institute of Child Health and Human Develop, [3]Lawrence Livermore National Laboratory, Glenn T. Seaborg Institute

Monday Morning, *Chicago B*
SAS PAT TECHNICAL SECTION I: PAT IN THE BIOPHARMACEUTICAL AND PHARMACEUTICAL INDUSTRIES
Organizers and Presiders: Edita Botonjic and Brandye Smith-Goettler

10:20 (88) **Real-Time Process Monitoring and Control Solutions Using Mid Infra Red and UV-Vis Spectroscopy**; Kirby Amponsah-Manager[1], Charles Goss[1]; [1]GlaxoSmithKline

10:40 (89) **Near Infrared Monitoring of the State of Fluid Bed Processes**; Stephen W. Hoag[1], Ravi Kona[1], Bhavesh H. Kothari[1], Raafat Fahmy[2]; [1]University of Maryland, Baltimore, [2]FDA

11:00 (90) **Understanding Sampling and the Impact on PAT Method Performance for Solid Dosage Manufacturing**; Gary McGeorge[1], Dongsheng Bu[1], Dimuthu Jayawickrama[1]; [1]Bristol Myers Squibb

11:20 (91) **Pharmaceutical Process Scale-up Optimization and Control Using PAT**; Neil MacPhail[1], Brandye Smith-Goettler[1], Colleen Neu[1]; [1]Merck and Co., Inc

11:40 (92) **The Expanding Role of Raman Spectroscopy at Amgen: Key Advantages and Translation to Diverse Applications**; Dawn Cohen[1]; [1]Amgen

Monday Morning, *Atlanta*
RAMAN SPECTROSCOPY IN ASTROBIOLOGY AND PLANETARY SCIENCES
Organzier and Presider: Craig Marshall

10:20 (93) **Raman Spectroscopy of Terrestrial Extremophiles from Hot and Cold Deserts: Analytical Astrobiology and the Search for Life on Mars**; Howell Edwards[1, 2], Ian Hutchinson[2], Richard Ingley[2]; [1]University of Bradford, [2]University of Leicester

10:40 (94) **Raman Spectroscopy in Hypersaline Environments - Importance in Astrobiology**; Jan Jehlicka[1], Aharon Oren[2], Petr Vitek[1], Howell G.M. Edwards[3]; [1]Charles University in Prague, IGMMR, [2]The Hebrew University of Jerusalem, The Institute of Life Sciences, [3]Centre for Astrobiology and Extremophiles Research, University of Bradford

11:00 (95) **Requirements for Mobile Raman Instrumentation for *in situ* Analysis**; Peter Vandenabeele[1], Jan Jehlicka[2], Howell G.M. Edwards[3]; [1]Ghent University, [2]Charles University, [3]University of Bradford

11:20 (96) **A Comprehensive Picture of Planetary Materials by Stand-alone Raman Investigation**; Alian Wang[1]; [1]Washington University in St. Louis

11:40 (97) **Applications of Time-Resolved Stand-off Raman and Laser-Induced Native Fluorescence (LINF) Systems for Planetary Exploration**; Shiv Sharma[1], Anupam Misra[1], Paul Lucey[1]; [1]University of Hawaii, Hawaii Institute of Geophy. & Planetology

Monday Morning, *Empire C*
NON-TRADITIONAL APPROACHES FOR CHEMICAL AND BIOLOGICAL SENSING
Organizer and Presider: Radislav Potyrailo

10:20 (98) **Non-invasive Chemical Sensing with Temperature-Programmed Microsensors: Overcoming Complex Analytical Problems with Multidimensional Databases**; Baranidharan Raman[1, 2], Douglas Meier[2], Kurt Benkstein[2], Steve Semancik[2]; [1]Washington University, [2]National Institute of Standards and Technology

10:40 (99) **Sensitive Chemical and Biological Sensing Enabled by Self-Assembled Photonic Crystals and Plasmonic Crystals**; Peng Jiang[1]; [1]University of Florida

11:00 (100) **Bio-Chemical Sensors based on Photonic Crystals**; Marko Loncar[1]; [1]Harvard University, School of Engineering and Applied Sciences

11:20 (101) **Wireless Low Cost Sensors Based on RFID Technology**; Fabio Di Francesco[1], Sabrina Bianchi[1], Matteo Grossi[1], Nicola Calisi[1], Valter Castelvetro[1]; [1]University of Pisa

11:40 (102) **Chemical and Biological Sensors: Industrial R&D Perspective**; Radislav Potyrailo; [1]GE Global Research

Monday Afternoon, *Empire B*
CHEMISTRY IN ART AND ARCHAEOLOGY II
Organizers and Presiders: Mary Kate Donais and Peter Vandenabeele

1:20 (103) **Non-Invasive Spectral Imaging Advances Preservation of Cultural Heritage**; Fenella France; [1]Library of Congress *(*2011 Applied Spectroscopy Focal Point Author)*

2:00 (104) **Scales of Production: Provenancing Glass Making in the Hellenistic-Roman World**; Patrick Degryse[1, 3], Dieter Brems[1, 3], Monica Ganio[1, 3], Tom Fenn[1, 3], Kris Latruwe[2], Frank Vanhaecke[2]; [1]KU Leuven - Div. Geology, Centre for Archaeological Sciences, [2]UGent - Analytical Chemistry

2:20 (105) **Raman Spectroscopy in Art and Archaeology : The Illumination of Ancient Mysteries at the Interface between Science and Cultural Heritage**; Howell Edwards[1]; [1]University of Bradford

2:40 (106) **Raman Spectroscopy and X-ray Fluorescence Analysis: Two Complementary Approaches of Interest for Archaeometry Research**; Peter Vandenabeele[1]; [1]Ghent University

Monday Afternoon, *New York B*
BIOANALYTICAL APPLICATIONS OF MICRO- AND NANOFLUIDICS
Organizers and Presiders: Dana Spence and Sue Lunte

1:20 (107) **Microfluidic Devices for Automated Cell Synchronization and Analysis**; Stephen C. Jacobson[1], Michelle D. Hoffman[1], Seth M. Madren[1], Pamela J. B. Brown[2], David T. Kysela[2], Yves V. Brun[2]; [1]Department of Chemistry, Indiana University, [2]Department of Biology, Indiana University

1:40 (108) **Single Cell Analysis on Microfluidic Devices**; Christopher Culbertson[1], Metto Eve[1], Lunte Susan[2], Dulan Gunasekara[2]; [1]Kansas State University, [2]University of Kansas

2:00 (109) **Digital Microfluidic Approaches for Single Cell Genetic Analysis**; Yong Zeng[1]; [1]University of Kansas[4]

2:20 (110) **FTIR Spectroscopic Imaging of Live Cells and Microfluidics**; Sergei Kazarian[1], Ka Lung Andrew Chan[1]; [1]Imperial College London *(*2011 Applied Spectroscopy Focal Point Author)*

2:40 (111) **Frequency Modulated Magnetic Traps for Enhanced Biochemical Sensors**; Lane Baker[1], Joe Basore[1], Rashid Zakeri[1]; [1]Indiana University

Monday Afternoon, *Chicago C*
CALIBRATION MAINTENANCE AND TRANSFER FOR NIR INSTRUMENT NETWORKS
Organizer and Presider: Benoit Igne

1:20 (112) **Managing a Global NIR Network: What I Have Learned over 25 Years and Have Yet to Learn**; David Ryan; [1]Solae, LLC

1:40 (113) **The Trials and Tribulations of Applying Quantitative Methods in a Global Environment**; Dimuthu Jayawickrama[1], Gary McGeorge[1], Tim Stevens[1], Boyong Wan[1], John Spirig[1]; [1]Bristol Myers Squibb

2:00 (114) **NIR Calibration Monitoring and Transfer for Pharmaceutical Tablets**; Carl Anderson[1], James Drennen[1]; [1]Duquesne University Center for Pharmaceutical Technology

2:20 (115) **Data Sampling for Extending the Life of NIR-Based Models**; Jeremy Shaver, Randall Bishop, Neal Gallagher, Barry Wise; [1]Eigenvector Research, Inc

2:40 (116) **Calibration Optimization in Near-Infrared Spectroscopy**; Nanning Cao[1], Charles Hurburgh[1]; [1]Iowa State University

Monday Afternoon, *Chicago B*
IONIC LIQUIDS FOR AND BY ANALYTICAL CHEMISTRY
Organizer and Presider: Chieu D. Tran

1:20 (117) **Mechanistic and Analytical Characterizations of Methane oxidation in Ionic liquids by Electrochemistry and *in situ* Infrared Spectroelectrochemistry Techniques**; Xiangqun Zeng[1], Zhe Wang[1]; [1]Oakland University

1:40 (118) **Facts and Fallacies In Ionic Liquid Luminescence**; Gary Baker[1]; [1]University of Missouri-Columbia

2:00 (119) **Exploiting the Versatility of Ionic Liquids and Polymeric Ionic Liquids in Chromatographic Separations and Microextractions**; Jared Anderson[1]; [1]The University of Toledo

2:20 (120) **Microwave-assisted Extractions of Pyrethroids by Ionic Liquids**; Sheila N. Baker[1], Jing Wang[1], Jian Xiong[2], Renee JiJi[2]; [1]University of Missouri, Dept of Chemical Engineering, [2]University of Missouri, Dept of Chemistry

2:40 (121) **Polysaccharide Ecocomposite Materials: Synthesis, Characterization and Applications**; Chieu Tran, Simon Duri[1], April Harkins[1]; [1]Marquette University

TECHNICAL PROGRAM – MONDAY
Orals 1:20 – 3:00 pm

Monday Afternoon, *Chicago A*
FUNDAMENTAL ASPECTS OF LIBS
Organizers and Presiders: Jose Almirall and Matthieu Baudelet

1:20 (122) **Elemental Analysis and Isotope Ratio Determinations of Objects in the Field by Means of a Portable Laser Ablation Sampling Device**; Detlef Günther, Reto Glaus[1], Ladina Dorta[1], Norman Lüchinger[2], Samuel Halim[1, 2], Daniel Tabersky[1]; [1]ETH Zurich, D-CHAB, [2]Nanograde, Spinoff ETH Zurich *(*2011 Applied Spectroscopy Focal Point Author)*

1:40 (123) **Kinetic Model of Atomic and Molecular Emissions in Laser-Induced Breakdown Spectroscopy of Organic Compounds**; Paul Dagdigian[1], Qianli Ma[1]; [1]Johns Hopkins University

2:00 (124) **High Spatial and Depth Resolution Sampling in Ultrafast LIBS**; Vassilia Zorba[1], Yuan Lu[1], Xianglei Mao[1], Richard Russo[1]; [1]Lawerence Berkeley National Laboratory

2:20 (125) **Temporal Evolution of the LIBS Spectra of a Representative Nitro Compound**; Jonathan Merten[1], Nathan Bullock[1], Cheyenne Sheppard[1], Matthew Jones[1], Christian Parigger[1, 2], Susan Allen[1]; [1]Arkansas State University, [2]University of Tennessee Space Institute

2:40 (126) **High-Resolution Optical Diagnostics of Uranium Transitions in a Laser Induced Plasma: A Time-Resolved Line Profile Study**; Nicholas Taylor; [1]Pacific Northwest National Laboratory

Monday Afternoon, *New York A*
IN VITRO AND IN VIVO MODIFICATIONS OF BIOMOLECULES ASSESSED BY MASS SPECTROMETRY
Organizer and Presider: Heather Desaire

1:20 (127) **Laser Ablation Imaging Mass Spectrometry Incorporating Separations**; Kermit Murray[1], Sung-Gun Park[1]; [1]Louisiana State University

1:40 (128) **MALDI Imaging Mass Spectrometry of Three-Dimensional Cell Culture Systems**; Amanda Hummon[1], Haohang Li[1], Eric Weaver[1]; [1]University of Notre Dame

2:00 (129) **Multidimensional Approaches to Glycopeptide Analysis**; Eric Dodds; [1]University of Nebraska - Lincoln

2:20 (130) **A "Radical" Approach to the Characterization of Disulfide Bonds within Peptides and Proteins – Application of Gas-Phase Ion/Radical Reactions**; Yu Xia, Lei Tan, Kirt Durand, Craig A. Stinson; [1]Purdue University

2:40 (131) **Reporter Peptides for an Expedited Disulfide Shuffling Analysis: How to Guarantee Aberrant Assignments are not Artifacts of Sample Preparation**; Daniel F. Clark[1], Eden P. Go[1], Heather Desaire[1]; [1]University of Kansas

Monday Afternoon, *Empire A*
SAS PAT TECHNICAL SECTION II: PAT IN THE BIOPHARMACEUTICAL AND PHARMACEUTICAL INDUSTRIES
Organizers and Presiders: Edita Botonjic and Brandye Smith-Goettler

1:20 (132) **SAM-Spec® - Innovative and Flexible PAT Systems**; Richard Escott, Fabien Chauchard; [1]Indatech

1:40 (133) **PAT for a Continuous Process: Strategy, Challenges and Development**; Peter Hamilton[1, 3], Luke Bellamy[2], Ralph Caricofe[1], Rahn Mckeown[1], Darryl Ertl[1], David Littlejohn[3]; [1]GlaxoSmithKline R+D, [2]GlaxoSmithKIlne GMS, [3]CPACT/ WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde

2:00 (134) **Assessment of Continuous Reactor Technologies for the Cooling Crystallisation of L-Glutamic Acid**; David Littlejohn[1], Laura Palmer[1], Denise Logue[1], Naomi Briggs[1], Alison Nordon[1], Alastair Florence[1], Jan Sefcik[1], Lihua Zhao[1], Visal Raval[1]; [1]University of Strathclyde

2:20 (135) **Understanding Pharmaceutical Transformations Using Raman Spectroscopy: Influence of Polymeric Excipients**; Alan D. Gift[1], Jacob A. Hettenbaugh[1], Leslie A. Southard[1], Amanda L. Riesberg[1]; [1]University of Nebraska at Omaha

2:40 (136) **A Novel Approach to in- and at-line Transmission Raman Spectroscopy**; Frank Roche[1], Manu Toivainen[2], Jussi Tenhunen[2], Mikko Juuti[1, 2]; [1]GMS Technical, GlaxoSmithKline, UK, [2]VTT Technical Research Centre of Finland

Monday Afternoon, *Atlanta*
EMERGING RAMAN TECHNIQUES AND APPLICATIONS
Organizers and Presiders: Ian R. Lewis and Pavel Matousek

1:20 (137) **Low-frequency Raman and THz Studies on Higher-Order Structures of Polymers**; Yukihiro Ozaki[1], Shigeki Yamamoto[1], Yusuke Morisawa[1, 2], Hiromichi Hoshina[1, 3]; [1]Kwansei Gakuin University, [2]Kinki University, [3]RIKEN, [4]Miyagi University of Education

1:40 (138) **Towards Raman Spectroscopy on a Microchip**; Imran Akca[1], Nur Ismail[1], Lantian Chang[1], Kerstin Worhoff[1], René M. de Ridder[1], Markus Pollnau[1]; [1]University of Twente

2:00 (139) **Studies of Photopolymer Heterogeneties by Confocal Raman Microscopy**; Céline Dietlin[1], François Courtecuisse[1], Bandar El Fouhaili[1], Céline Croutxe-Barghorn[1], Xavier Allonas[1]; [1]Laboratory of Macromolecular Photochemistry and Engineering, ENSCMu, UHA

2:20 (140) **The Key Role of Surface Chemistry in Surface Enhanced Raman Spectroscopy: From Label-Free DNA Analysis to Drugs of Abuse**; Steven Bell[1], Maighread McCourt[1], Evanthia Papadopoulou[1], Alan Stewart[1], Shuai Zheng[1]; [1]Queen

2:40 (141) ***In vivo* and *in vitro* Glucose Sensing in Complex Biological Environments by Surface-Enhanced Raman Spectroscopy**; Richard Van Duyne[1]; [1]Northwestern University

Monday Afternoon, *Empire C*
NUCLEAR FORENSICS
Organizer and Presider: Greg Klunder

1:20 (142) **New and Improved Mass Spectrometric Reference Materials**; Richard M. Essex[1], Jeffrey J. Morrison[1, 2]; [1]New Brunswick Laboratory, [2]DHS National Technical Nuclear Forensics Center

1:40 (143) **Identification of Uranium Ore Concentrate Species by Near Infrared Spectroscopy**; Gregory Klunder[1], Jonathan Plaue[1], Paul Spackman[1], Patrick Grant[1], Martin Robel[1], Lars Borg[1], Rachel Lindvall[1], Ian Hutcheon[1]; [1]Lawrence Livermore National Laboratory

2:00 (144) **Geochemistry of the Trinity Nuclear Test: Investigation of Trinitite Glass at High Spatial Resolution**; Jeremy J. Bellucci[1], Antonio Simonetti[1], Christine Wallace[1], Elizabeth C. Koeman[1], Peter Burns[1]; [1]University of Notre Dame

2:20 (145) **Computational Age Dating of Special Nuclear Materials**; Ding Yuan[1], Paul Guss[1]; [1]National Security Technologies

2:40 (146) **Nuclear Forensics: Separation and Measurement of Lanthanoid Isotopic Ratios in Spent Research Reactor Nuclear Fuel**; Nicholas Sharp[1], William McDonough[1, 2], Alice Mignerey[1], Donna Beals[3]; [1]Department of Chemistry and Biochemistry, University of Maryland, [2]Dept of Geology, University of Maryland, [3]Savannah River National Lab

3:00 – 3:50 pm Exhibit Hall B
BREAK AND POSTER VIEWING

Monday Afternoon, *Empire B*
ISOSCAPES: REDEFINING THE LANDSCAPE IN THE ARCHAEOLOGICAL AND GEOLOGICAL SCIENCES WITH HIGH FIDELITY ISOTOPE RATIO ANALYSIS
Organizer and Presider: Frank Vanhaecke

3:50 (147) **The Application of Combined Radiogenic and Light Stable Isotope Studies to Forensics, Ecology and Archaeology**; Gareth Davies[1], Janne Koornneef[1], Laura Font[1], Jason Laffoon[1, 2]; [1]VU University Amsterdam, [2]Leiden University

4:30 (148) **MC-ICPMS: Enhanced Ion Yields for Measuring "Almost Nothing in Not Very Much" and for Those Hard to Measure Elements**; Charles Douthitt[1], Johannes Schwieters[1], Nicholas Lloyd[1], Claudia Bouman[1]; [1]Thermo Fisher Scientific

4:50 (149) **Bringing Speciation Tools (GC-MC-ICPMS) in Geochemistry for Fast and Precise Lead Isotope Ratio Determination in Complex Matrices. Application to Crude Oil Exploration.**; Christophe Pecheyran[1], Georgia Sanabria Ortega[1], Olivier F. X. Donard[1], Sylvain Bérail[1], Mike Lewan[3], Alain Prinzhoffer[2]; [1]University of Pau, LCABIE/IPREM, [2]Ipex co., [3]U. S. Geological Survey

5:10 (150) **Automated Sample Preparation for Radiogenic Isotopes: Removing an Analytical Barrier to Generating Sr, Nd and Pb Isoscapes**; Paul Field[1], Gwyneth W. Gordon[2], Stephen Romaniello[2], Daniel Wiederin[1], Ariel Anbar[2, 3]; [1]Elemental Scientific, Omaha, NE, [2]School of Earth & Space Exploration, Arizona State University, Tempe, AZ, [3]Dept of Chemistry, Arizona State University, Tempe, AZ

Monday Afternoon, *Atlanta*
FACSS STUDENT AWARDS
Organizers: Steve Ray and Mike George; Presider: Mike George

Tomas Hirschfeld Scholar Award

3:50 (151) **Classification of Prostate and Breast Tissue Data from High-Resolution Fourier Transform Infrared (FT-IR) Spectroscopic Imaging**; Rohith Reddy[1], David Mayerich[1], Michael Walsh[1], Matthew Schulmerich[1], Paul Scott Carney[1], Rohit Bhargava[1]; [1]University of Illinois at Urbana Champaign

Tomas Hirschfeld Scholar Award

4:10 (152) **Standoff Raman Spectroscopy of Large Areas Using Defocused Excitation with a Spatial Heterodyne Raman Spectrometer**; Nathaniel Gomer[1], S. Michael Angel[1]; [1]University of South Carolina

FACSS Student Award

4:30 (153) **TEA CO_2 Laser-Induced Gas Plasma Spectroscopy (LIGPS): A Breakthrough Method in LIBS**; Ali Khumaeni[1], Zener Sukra Lie[1], Hideaki Niki[1], Kazuyoshi Kurihara[1, 2], Kiichiro Kagawa[1, 3]; [1]Program of Nuclear Power and Energy Safety Engineering, Graduate School of Engineering, University of Fukui, [2]Department of Physics, Faculty Education and Regional Studies, University of Fukui, [3]Research Institute of Nuclear Engineering, University of Fukui

Coblentz Society's William G. Fateley Student Award

4:50 (154) **Variable Temperature Study of the Infrared Spectra by Utilizing Xenon Solution and Microwave Spectroscopy for the Conformational Analysis of Cyclohexylisocyanate**; Xiaohua (Sarah) Zhou[1], James R. Durig[1]; [1]Department of Chemistry, University of Missouri-Kansas City

SAS Graduate Student Award

5:10 (155) **Pulsed EPR Studies of Photosystem II Elucidating the Mechanism of Solar Water Oxidation**; Ruchira Chatterjee[1], Sergey Milikisiyants[1], Christopher Coate[1], K. V. Lakshmi[1]; [1]Rensselaer Polytechnic Institute

Monday Afternoon, *New York A*
HIGHER-ORDER STRUCTURE IN PROTEINS BY MS-BASED APPROACHES
Organzier and Presider: David Weis

3:50 (156) **Discovering Protein Linear Interaction Motifs with Proteome-Scale H/D Exchange Mass Spectrometry**; David Weis[1]; [1]University of Kansas

4:10 (157) **Protein Dynamics and Interaction Probed by Hydrogen Exchange Mass Spectrometry**; Igor Kaltashov[1]; [1]University of Massachusetts-Amherst

4:30 (158) **Biophysical Characterization of Virus Particles as Gene Delivery Vehicles**; Brian Bothner; [1]Montana State University

4:50 (159) **Covalent Labeling and Mass Spectrometry for Studying the Structures of Protein-Protein Complexes**; Richard Vachet[1], Yuping Zhou[1], Jia Dong[1], Vanessa Mendoza[1]; [1]University of Massachusetts Amherst

5:10 (160) **Top-Down Mass Spectrometry and Supercharging for Characterizing Protein Assemblies**; Joseph Loo[1], Jiang Zhang[1]; [1]University of California, Los Angeles

Monday Afternoon, *New York B*
MICROFLUIDICS AND NANOFLUIDICS
Organizers and Presiders; Dana Spence and Edgar D. Goluch

3:50 (161) **Controlling Oxygen via Microfluidic Devices for Cells and Tissues in vitro**; David Eddington[1]; [1]University of Illinois, Chicago

4:10 (162) **Polystyrene-based Microfluidic Devices for Integrating Cell Immobilization with Analysis**; R. Scott Martin[1]; [1]Saint Louis University

4:30 (163) **Microchip Electrophoresis Based Methods to Monitor Nitric Oxide Metabolism and Reactive Nitrogen Species**; Susan M. Lunte[1], Christopher T. Culberston[1, 2], Dulan Gunaserkera[1], Francassi daSilva[1], Tom H. Linz[1], Eva Metto[2]; [1]Ralph N. Adams Institute for Bioanalytical Chemistry, Kansas State University, [2]Dept of Chemistry, Kansas State University

4:50 (164) **Monitoring Bacterial Production of Pyocyanin using Microfabricated Electrochemical Sensors**; Edgar Goluch[1], Thaddaeus Webster[1], Nil Tandogan[1], Pegah Abadian[1]; [1]Northeastern University

5:10 (165) **Effects of Confinement on Macromolecular Transport in Nanochannels Studied by Fluorescence Correlation Spectroscopy**; Dane Grismer[1], Paul Bohn[1]; [1]University of Notre Dame

Monday Afternoon, *Chicago C*
ADVANCES IN NIR SPECTROSCOPY IN THE PHARMACEUTICAL INDUSTRY
Organizer and Presider: Robert W. Bondi

3:50 (166) **NIR in Enabling Real-Time Release**; Gary McGeorge[1]; [1]Bristol-Myers Squibb

4:10 (167) **A Novel Sample Selection Strategy by Near Infrared Spectroscopy (NIRS)-based High Throughput Tablet Tester for Content Uniformity in Early Phase Pharmaceutical Product Development**; Zhenqi Shi[1], James Hermiller[1], Thomas Gunter[1], Xiaoyu Zhang[1], David Reed[1]; [1]Eli Lilly and Company

4:30 (168) **Use of NIR Hyperspectral Integrated Computational Imaging for Quality Control of Pharmaceuticals**; Brittney Metts[1], Robert Lodder[1, 2]; [1]Department of Chemistry, University of Kentucky, [2]College of Pharmacy, University of Kentucky

4:50 (169) **Developing Content Uniformity Thresholds Independent of Scale of Scrutiny of a NIR Spectrometer**; Sameer Talwar[1], Zhenqi Shi[2], Steven Short[3], Carl Anderson[1], James Drennen[1]; [1]Duquesne University, [2]Eli Lilly, [3]Merck

5:10 (170) **Distribution Analysis of Dissolution Process for Pharmaceutical Tablets by using a Developed Portable NIR Imaging Device**; Daitaro Ishikawa[1], Koudai Murayama[2], Takuma Genkawa[5], Kimie Awa[4], Yoko Torigoe[1], Sergei Kazarian[3], Makoto Komiyama[2], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]Yokogawa Electric Co., [3]Imperial College London, [4]Dainippon Sumitomo Pharma Co., Ltd.; [5]University of Tsukuba

Monday Afternoon, *Chicago A*
DATA ANALYSIS IN LIBS
Organizers and Presiders: Jose Almirall and Matthieu Baudelet

3:50 (171) **Signal Processing of Spectral Information for Chemometrics: from the Big Picture to Key Details**; Leslie Collins[1], Kenneth Morton[1], Peter Torrione[1]; [1]Duke University

4:10 (172) **Determination of Isotope Ratios in Ambient Air at Atmospheric Pressure for Nuclear Forensics using LIBS**; François Doucet[1], Rick Kosierb[2], Paul Bouchard[1], Mohamad Sabsabi[1]; [1]NRC-CNRC, [2]CNSC-CCSN

4:30 (173) **When Chemometrics Becomes an Added Value for Quantitative LIBS : Example of Soils Analysis**; Bruno Bousquet[1], Josette El Haddad[1], Lionel Canioni[1]; [1]Univ. Bordeaux, LOMA, UMR 5798. CNRS, LOMA, UMR 5798

4:50 (174) **Quantitative LIBS Analysis of Standard Reference Materials of Various Categories under Low Pressure Conditions**; Soo-Jin Choi[1], Kang-jae Lee[1], Jong H. Yoo[2], Jack J. Yoh[1]; [1]Seoul National University, [2]Applied Spectra Inc

5:10 (175) **Laser ablation Methods for Analysis of Urinary Stones: Comparison Study Based on Calibration Pellets**; Karel Novotný[1], Kateřina Stepánkova[1], Michaela Vašinová Galiová[1], Viktor Kanický[1], Jozef Kaiser[2], David Hahn[3]; [1]Department of Chemistry, Faculty of Science, Masaryk University, [2]X-ray micro CT and nano CT research group, CEITEC - Central European Institute of Technology, Brno University of Technology, [3]Department of Mechanical & Aerospace Engineering, University of Florida

Monday Afternoon, *Empire A*
INDUSTRIAL PROCESS ANALYTICAL SPECTROSCOPY
Organizer and Presider: Serena Stephenson

3:50 (176) **Assuring Ehylene Purity: Reliable Sub-PPM Measurement of Ammonia and Water With Online TDL Analyzers**; Mohamad Dabboussi[1], Greg Lankford[1], Xiang (Sherry) Liu[1], HsuHung (Steven) Huang[1], Kuan-Ting (Gary) Yeh[1], Wnehai Ji[1], Alfred Feitisch[1], William Jenko[1]; [1]SpectraSensors, Inc.

4:10 (177) **Small Optical Sensors for Oxygen Monitoring in Challenging Environments**; Brian Marquardt[1], Lauren Hughs[1], Charles Branham[1], Wesley Thompson[1]; [1]Applied Physics Laboratory, University of Washington

4:30 (178) **Mid-Infrared Light Emitting Diode-Based In Situ Gas Phase Diagnostics for Microelectronics Thermal Deposition Processes**; James Maslar[1], William Kimes[1]; [1]National Institute of Standards and Technology

4:50 (179) **Spectroscopic Analysis of Solvent Exchanges: Distillate Line versus Distillate Vessel**; John Wasylyk[1], Robert Wethman[1], Ming Huang[1], Richard Schild[1], Thomas Raglione[1]; [1]Bristol-Myers Squibb Co

5:10 (180) **Monitoring Emulsion Polymerization by Raman Spectroscopy**; Serena Stephenson, Kishori Deshpande, Ravindra Dixit; [1]The Dow Chemical Company

Monday Afternoon, *Chicago B*
STANDOFF RAMAN: APPLICATIONS AND KEY ISSUES
Organziers and Presiders: J. Chance Carter and S. Michael Angel

3:50 (181) **Deep UV Raman Measurements of Energetic Materials and their Photochemical Products**; Sanford Asher[1], David Tuschel[1], Luling Wang[1]; [1]University of Pittsburgh

4:10 (182) **Ultraviolet Resonance Raman Cross Sections of Solid State Explosive Materials**; Erik Emmons[1], Ashish Tripathi[1], Jason Guicheteau[2], Augustus Fountain[2], Steven Christesen[2]; [1]SAIC, [2]U.S. Army Edgewood Chemical Biological Center

4:30 (183) **Wide-Area Standoff Raman Spectroscopy Using a Spatial Heterodyne Raman Spectrometer**; Mike Angel[1], Nathaniel Gomer[1], Nirmal Lamsal[1]; [1]Univ. of South Carolina, Dept. of Chem. & Biochem *(*2012 Applied Spectroscopy Focal Point Author)*

4:50 (184) **Detection of Hazardous Chemicals in Glass and Plastic Bottles with Standoff Time-Resolved Raman System**; Shiv Sharma, Anupam Misra, John Porter, David Bates; [1]University of Hawaii, Hawaii Institute of Geophy. & Planetology *(*2012 Applied Spectroscopy Focal Point Author)*

5:10 (185) **Standoff Raman using Tunable Laser Excitation in the UV and NIR**; J. Chance Carter[1], S. Michael Angel[1, 2], Paul Steele[1], Christine N. Paulson[1]; [1]Lawrence Livermore National Laboratory, [2]University of South Carolina

Monday Afternoon, *Empire C*
INFRARED AND RAMAN SPECTROSCOPY OF ORGANIC SEMICONDUCTORS AND CONDUCTORS
Organizer and Presider: Yukio Furukawa

3:50 (186) **Photoexcitation Infrared Spectroscopy of Bulk-Heterojunction Films**; Yukio Furukawa[1], Jun Eguchi[1], Hiroki Yoshida[1]; [1]Waseda University

4:10 (187) **Understanding the Electronic Structure of Thiophene Systems and Donor Acceptor Copolymers using Spectroscopic and Computational Chemistry**; Keith Gordon[1]; [1]University of Otago

4:30 (188) **Nanoscale IR Spectroscopy of Organic Semiconductors**; Curtis Marcott[1], Michael Lo[2], Kevin Kjoller[2]; [1]Light Light Solutions, [2]Anasys Instruments

4:50 (189) **Raman Spectroscopic Study of the Interaction between poly(3-hexylthiophene) and Metal Oxide**; Jun Yamamoto[1], Yukio Furukawa[1]; [1]Waseda University

5:10 (190) **Optical Spectroscopy of Active Organic Electronic Devices**; Richard McCreery[1, 2], Rajesh Kumar[2], Rajesh Pillai[2], Nikola Pekas[1], Lian Shoute[2]; [1]National Institute for Nanotechnology, [2]University of Alberta

TECHNICAL PROGRAM – TUESDAY
Plenary Lectures, Exhibit Hall B
Presider: Michael George

8:00 am - Coblentz Society's Craver Award.
(191) Biological Analysis using SERS - The Strathclyde Story; **Duncan Graham**; University of Strathclyde

8:30 am – FACSS Charles Mann Award for Applied Raman Spectroscopy
(192) Successful Application of Raman Spectroscopy in Pharmaceutical Discovery Research; **Don Pivonka**; Incyte Pharmaceuticals

TUESDAY POSTER SESSION
9:00 – 10:20 am
Exhibit Hall A

All Tuesday posters should be put up between 7:30 – 8:00 am and removed by 4:30 pm

Pharmaceutical Analysis

Board #

1 (194) **Development and Implementation of Spectroscopy Methods for Quantitative and Qualitative Analysis of Pharmaceutical Reagents**; Bernard Agyei[1], John Wasylyk[1], Ming Huang[1], Robert Wethman[1], [1]Bristol Myers Squibb

2 (195) **Probing Degradation Pathways of Noradrenaline Pharmaceutical Formulations via Thermal, Light and Oxidative Stress**; Janet de los Reyes[1], Channa A. Wijesinghe[1], Molesworth Samuel[1]; [1]Hospira, Inc

3 (196) **Applications of Raman Spectroscopy in Formulation Development**; Kei Moriyama[1], Yulian Lin[1], Junichi Jinno[1], Toru Nishibayashi[1]; [1]Formulation Research Institute, Otsuka Pharmaceutical Co., Ltd

5 (197) **Isolation of Single Isomers using Supercritical Fluid Chromatography and Determination of Absolute Configuration of Warfarin using Vibrational Circular Dichroism**; Hiroyuki Yamashita[1], Tatsuhiro Tokunaga[1], Toshikazu Adachi[1], Masamichi Yuda[1], Toshio Teramura[1]; [1]Astellas Pharma Inc

5 (198) **Photochemical and Oxidative Degradation of Formulated and Unformulated Phytonadione and Elucidation of Degradants**; Tristan Walters[1], Tristan Walters[1]; [1]Hospira, Inc. McPherson, KS

6 (199) **Building Robust Transmission Raman Models: What if my Material Suppliers Change?**; Andrew Owen[1], Hilary Jeffreys[2], Steven Brown[2], Matthew Bloomfield[1], Pavel Matousek[3], Darren Andrews[1]; [1]Cobalt Light Systems, [2]Actavis UK Ltd., [3]Science & Technology Facilities Council

7 (200) **Raw Materials ID through Containers Using Spatially Offset Raman Spectroscopy**; Matthew Bloomfield[1], Guy Maskall[1], David Crawford[1], Pavel Matousek[2], Darren Andrews[1]; [1]Cobalt Light Systems, [2]Science & Technology Facilities Council

8 (201) **Parallel Determination of 17alpha-Ethinylestradiol and Desogestrel Content in Pharmaceutical Formulations by UV-visible Derivative Spectrophotometry.**; M. Inés Toral, Fallon Nacaratte[1]; [1]University of Chile

9 (202) **Analysis of the Binding of Second-Generation Sulfonylurea Drugs to Human Serum Albumin by High Performance Affinity Chromatography**; Ryan Matsuda[1], Jeanethe Anguizola[1], K.S. Joseph[1], David Hage[1]; [1]University of Nebraska-Lincoln

10 (203) **Analysis of Free Fractions for Drug Enantiomers by Multi-Dimensional High Performance Affinity Chromatography using Ultrafast Extraction Combined with a Chiral Stationary Phase**; Xiwei Zheng[1], Michelle Yoo[1], David Hage[1]; [1]Chemistry Department, University of Nebraska, Lincoln

Board #

11 (204) **Quality Evaluation of Pharmaceutical Tablets by using the New NIR Camera (Compovision) Developed for High Speed Wide Area Measurement**; Kimie Awa[1, 2], Daitaro Ishikawa[1], Fumiaki Mizuno[1, 3], Takashi Nishii[1], Yoko Torigoe[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]Dainippon Sumitomo Pharma Co., Ltd., [3]Sumitomo Electric Industries, Ltd

12 (205) **A Study on Penetration Depth of Near-Infrared Diffuse-Reflectance Light from Bilayer Tablets by using a Compact NIR Photo-Diode Array Spectrometer**; Koudai Murayama[1], Daitaro Ishikawa[2], Takuma Genkawa[3], Yoko Torigoe[2], Makoto Komiyama[1], Yukihiro Ozaki[2]; [1]Yokogawa Electric Corporation, [2]Kwansei Gakuin University, [3]University of Tsukuba

13 (206) **A Survey of Metal Contamination in Pharmaceutical Excipients**; Gang Li[1], John Kauffman[1]; [1]Division of Pharmaceutical Analysis, FDA

Microscopy and Spectroscopy

14 (207) **Tip-Enhanced Raman Scattering (TERS) for Nano-Bioanalytical Applications**; Jennifer A. Dougan[1], K. L. Andrew Chan[1], Sergei G. Kazarian[1]; [1]Imperial College London

15 (208) **Tip and Tricks for Successful Tip-Enhanced Raman Imaging**; Emmanuel Leroy[1]; [1]HORIBA

16 (209) **Adding Tip-enhanced Raman Spectroscopy Functionality to the "NanoBits" Toolbox Concept for Atomic Force Microscopy**; Gerardo Gamez[1], Victor LeNader[1], Pierre Brodard[1, 2], Malte Bartenwerfer[1, 3], Johann Michler[1]; [1]EMPA, Swiss Federal Laboratories for Materials Science and Technology, [2]College of Engineering and Architecture of Fribourg, [3]OFFIS, Institute for Information Technology

17 (210) **Thermogravimetric Analysis and Atomic Force Microscopy Characterization of Concanavalin A Immobilization on Nanoporous Gold**; Yih Horng Tan[1, 2], Binod Pandey[1, 2], Kohki Fujikawa[1], Alexei V. Demchenko[1], Keith J. Stine[1, 2]; [1]Department of Chemistry and Biochemistry, University of Missouri – Saint Louis, [2]UM-St. Louis Center for Nanoscience, University of Missouri – Saint Louis

18 (211) **Influence of Tip-Sample Contact on Vibration Ring Down of AFM Cantilevers**; Ehsan Rezaei[1], Joseph Turner[1]; [1]University of Nebraska-Lincoln

19 (212) **Polarized Resonance Micro-Raman Spectroscopy of Pentacene**; David Tuschel[1]; [1]HORIBA Scientific

20 (213) **Micro-Raman and micro-XRF Mapping of Metal Oxide Grain Chemistry using Multivariate Statistical Analysis**; Robert Davis[1], Eric Telfeyan[1]; [1]GE Global Research Center

Board #

21 (214) **A Near-field Scanning Optical Module for Inverted Microscopes**; Taher Ababneh[1], Jorg Woehl[1]; [1]University of Wisconsin-Milwaukee

22 (215) **Design and Application of a Multiple-Source Fluorometer for Lanthanide-Sensitized Luminescence**; Guoying Chen[1, 3], Guyu Liu[2], Feng Qin[2]; [1]USDA, Agricultural Research Service, Eastern Regional Research Center, [2]Shanghai Institute for Food and Drug Control

23 (216) **Photon Trapping Spectroscopy: Design, Fabrication, and Testing of an Automated System of Real-Time Monitoring**; Ryan Schmeling[1], Peter Geissinger[1], Joseph Aldstadt[1]; [1]University of Wisconsin Milwaukee

24 (217) **Measurement of Heterogeneous Rate Constants Using Photomicroscopy**; Walter Bowyer[1], Tessa Sullivan[1], Gabriella Mylod[1], Alexa Hill[1], Katherine Delaney[1]; [1]Hobart and William Smith Colleges

25 (218) **Evaluating Optical Point Spread Function Fitting Methods**; Bradley M. Moran[1], Peter Geissinger[1], Jorg C. Woehl[1]; [1]University of Wisconsin Milwaukee

26 (219) **Construction of a Continuous Wave – Stimulated Emission Depletion Microscope: Applications in Analytical Chemistry**; Bhanu Neupane[1], Yaqing Zhao[1], Paul Tyrlik[1], Gufeng Wang[1]; [1]North Carolina State University

27 (220) **From RS to SORS to SERS to TERS: which Raman Spectroscopy for me?**; Renata Lewandowska[1]; [1]HORIBA Jobin Yvon

28 (221) **Extreme Surface Analysis of Polyethylenes by Attenuated Total Reflection Far-ultraviolet Spectroscopy — Comparison with Atomic Force Microscope Measurement**; Erika Tanimura[1], Yusuke Morisawa[1, 2], Harumi Sato[1], Naomi Kariyama[3], Noboru Higashi[3], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]Kinki University, [3]Kurabo Industries Ltd

Laser Induced Breakdown Spectroscopy

29 (222) **AlO Flame Emission Spectroscopy**; Christian Parigger[1], Alexander Woods[1], Jonathan Height[2], Burl Donaldson[2], Walter Gill[2]; [1]University of Tennessee Space Institute, [2]Sandia National Laboratories

30 (223) **LIBS: Measurement and Analysis of TiO Spectra**; Alexander C. Woods[1], Christian G. Parigger[1], James O. Hornkohl[2, 3]; [1]University of Tennessee/UT Space Institute, Center for Laser Applications, [2]Hornkohl Consulting

31 (224) **Simplification and Standardization of Method Development in Analytical LIBS**; Emily Schenk, B.Sc.[1], Jose Almirall, Ph.D[1]; [1]Department of Chemistry and Biochemistry, Florida International University

32 (225) **Ablation Chamber for Simultaneous DP-LIBS and Laser Ablation ICP-OES/MS**; Karel Novotný[1], Lucie Krajcarová[1], Aleš Hrdlička[1], Viktor Kanický[1], Jozef Kaiser[2], Radomír Malina[2], David Hahn[3]; [1]Department of Chemistry, Faculty of Science, Masaryk University, [2]X-ray micro CT and nano CT research group, CEITEC - Central European Institute of Technology, Brno University of Technology, [3]Department of Mechanical & Aerospace Engineering, University of Florida

33 (226) **Effects of Excitation Wavelength on LIBS Plume Morphology using Focused Shadowgraphy**; Amina Hussein[1 2], Prasoon Diwakar[1], Sivanandan Harilal[1], Ahmed Hassanein[1]; [1]Center for Materials under Extreme Environment, School of Nuclear Engineering, Purdue University, [2]Department of Physics, McGill University[4]

Board #

34 (227) **Effect of Spectral Interference on Uranium Lines in Laser-Induced Breakdown Spectroscopy**; Inhee Choi[1], Xianglei Mao[1], Dale L. Perry[1], Richard. E. Russo[1]; [1]Lawrence Berkeley National Laboratory

Laser Ablation and Atomic Analysis

35 (229) **Wavelength Effect on Detection Limits in nano- and femtosecond-LA-ICP-MS**; Nicole L. LaHaye[1], Prasoon K. Diwakar[1], Sivanandan S. Harilal[1], Ahmed Hassanein[1]; [1]Purdue University

36 (230) **Fluorescence Imaging of Analyte Profiles in an Inductively Coupled Plasma with Laser Ablation as a Sample Introduction Source**; Lance Moses[1], Paul Farnsworth[1]; [1]Brigham Young University

37 (231) **From Sample to Signal: A Comprehensive Study of the Influence of Laser Parameters on fs-LA-ICP-MS**; Prasoon Diwakar[1], Nicole LaHaye[1], Jhanis Gonzalez[2], Dayana Oropeza[2], Richard Russo[2], Ahmed Hassanein[1], Sivanandan Harilal[1]; [1]Purdue University, [2]Lawrence Berkeley National Laboratory

38 (232) **Use of Liquid Standard Addition into a Laser Ablation Stream for Elemental Analysis of Samples to Avoid the Need for Matrix-Matched Standards**; Melissa Zwilling[1], Jose Almirall[1]; [1]Florida International University

39 (233) **Bioimaging of Trace Metal Distribution in Rice Seeds (Oryza sativa) by LA-ICP-MS**; Priyanka Basnet[1], Dulasiri Amarasiriwardena[1]; [1]School of Natural Science, Hampshire College

40 (234) **Analysis of Laser-Induced Aerosols in LA-ICP-MS: Role of Wavelength in Elemental Fractionation**; Peter deVietien[1], Prasoon Diwakar[1], Sivanandan Harilal[1], Ahmed Hassanein[1]; [1]Center for Materials under Extreme Environment, School of Nuclear Engineering, Purdue University

41 (235) **Density and Temperature Evolution of nano- and femtosecond Laser Ablation Plumes in Vacuum and Ambient Air Environment**; Justin R. Freeman[1], Brandon Verhoff[1], Prasoon K. Diwakar[1], Sivanandan S. Harilal[1], Ahmed Hassanein[1]; [1]Purdue University

42 (236) **Time Resolved Powerchip Laser Diagnostics: Beyond the McWhirter Criterion**; Jonathan Merten[1], Ben Smith[1, 2], Nicolo Omenetto[2]; [1]Arkansas State University, [2]University of Florida

43 (237) **Effect of Electrode Characteristics and Ambient Gas on the Sensitivity of Aerosol Measurement using Spark Emission Spectroscopy**; Prasoon Diwakar[1], Pramod Kulkarni[2]; [1]Center for Materials under Extreme Environment, School of Nuclear Engineering, Purdue University, [2]Centers for Disease Control and Prevention (CDC), National Institute for Occupational Safety and Health (NIOSH)

44 (238) **Signal Enhancement Effects by Co-Existing Carbon in Inductively Coupled Plasma Mass Spectrometry and Inductively Coupled Plasma Optical Emission Spectrometry**; Daisuke Suzuki[1], Yoshinari Suzuki[1], Naoki Furuta[1]; [1]Chuo University

45 (239) **Comparing Theory and Experiment for Analyte Transport in the First Vacuum Stage of the ICP-MS**; Matthew Zachreson[1], Ross Spencer[1]; [1]Brigham Young University

TECHNICAL PROGRAM – TUESDAY

Posters 9:00 – 10:20 am ◆ Orals 10:20 am – 12:00 pm

Glow Discharge Spectroscopy

Board #

46 (240) **Glow Discharge Imaging Spectrometry with a Tilting Interference-Filter Spectrometer**; Andrew Storey[1], Steven Ray[1], Carsten Engelhard[2], Volker Hoffmann[3], Wolfgang Buscher[2], Maxim Voronov[3], Gary Hieftje[1]; [1]Indiana University, [2]University of Münster, [3]Leibniz Institute for Solid State and Materials Research Dresden

47 (241) **Depth Profiling Characterization by a Novel Plasma TOF MS Technique**; Philippe Hunault[1], Christophe Morin[1], Agnes Tempez[2], Patrick Chapon[2]; [1]HORIBA Scientic Elemental Analysis - Edison, NJ - USA, [2]HORIBA Jobin Yvon SAS - Longjumeau France

48 (242) **Glow Discharge Analytical Plasmas with OES or TOF MS Detection for Depth Profile Characterization of thin Film Solar Cells**; Philippe Hunault[1], Christophe Morin[1], Agnes Tempez[2], Celia Olivero[2], Sebastien Legendre[2], Patrick Chapon[2]; [1]HORIBA Scientific Elemental Analysis, [2]HORIBA Jobin Yvon SAS

49 (243) **Metastable Atom Formation in a Millisecond Pulsed Glow Discharge**; Kyler Robinson[1, 2]; [1]OSU-UML, [2]University of Tulsa

50 (244) **Mechanisms for Population Inversion in the Prepeak of Pulsed Glow Discharge Plasmas**; Tim Gustafson[1, 2]; [1]OSU-UML, [2]Oklahoma State University

New IR and Raman Instrumentation

51 (245) **Advances in Detectors for FTIR Imaging**; Christopher Lynch[1], Richard Spragg[2], Andrew Turner[2], Robert Hoult[2]; [1]PerkinElmer LAS Shelton CT, [2]PerkinElmer LAS Seer Green UK

52 (246) **Evaluation of Thermal Infrared Sources for AC Imaging Applications**; Nick Boltin[1], Scott Hoy[1], Stephanie DeJong[1], Stephen Morgan[1], Michael Myrick[1]; [1]University of South Carolina

53 (247) **A New Truly Easy-to-Use Dedicated Infrared Microscope**; Thomas Tague[1], Sergey Shilov[1], Fred Morris[1], Matthias Boese[1]; [1]Bruker Optics, Inc

54 (248) ***In-Situ* FT-IR Reaction Monitoring Using Standard Detector**; Matthias Rolland[1], Marc-André Laliberté[1], Mathieu Côté[1], Frederic Despagne[1]; [1]ABB Inc.

55 (249) **Adaptable Infrared Surface Plasmon Resonance Spectroscopy Accessory**; Nicola Menegazzo[1], Laurel Kegel[1], Yoon-Chang Kim[1], Derrick Allen[1], Karl Booksh[1]; [1]University of Delaware

56 (250) **Increasing the Resolution and Capabilities of the Czerny-Turner Imaging Spectrograph though a Novel Design Variant**; Jason McClure[1]; [1]Princeton Instruments

57 (251) **Sensei: Innovative Optical Dispersive Spectrometer Design Platform which Increases Throughput >10 Times without Sacrificing Spectral Resolution**; Jeffrey Meade[1], Bradford Behr[1]; [1]Arjae Spectral

58 (253) **An Integrated *in situ* Raman and Turbidity Sensor for High Level Waste Tanks**; Christina Gasbarro[1], Job Bello[1], Anton Smirnov[1], Samuel Bryan[2]; [1]EIC Laboratories, Inc., [2]Pacific Northwest National Laboratory

Tuesday Morning, *Chicago B*

CURRENT STATUS OF THE ANALYTICAL SCIENCES: FOCUS ON HUMAN HEALTH

Organizers Royal Society of Chemistry and ACS Analytical Division
Presiders: David Koppenaal and Niamh O'Connor

10:20 (254) **Persistent Nanoparticles - Where Do They Accumulate**; Detlef Günther, Tobias Walser[2, 3], Wendelin Stark[2], Stefanie Hellweg[3], Ludwig Limbach[2], Karin Birbaum[1], Robert Brogioli[1]; [1]Laboratory of Inorganic Chemistry, D-CHAB, ETH Zurich, [2]Institute for Chemical and Bioengineering, D-CHAB, ETH Zurich, [3]Institute of Environmental Engineering, D-BAUG, ETH Zurich

10:40 (255) **Elemental Mass Spectrometry from Laboratory to Clinic**; Barry Sharp[1]; [1]Loughborough University

11:00 (256) **Single-Cell Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for Deep Profiling of the Human Hematopoietic System**; Sean Bendall[1], Erin Simonds[1], Garry Nolan[1]; [1]Stanford University[4]

11:20 (257) **Mass Spectrometric Studies in (pre)clinical Research on Cancerostatic Metallodrugs**; Gunda Koellensperger[1], Gerrit Hermann[1], Stephan Hann[1]; [1]BOKU

11:40 (258) **Metallomics Approaches – Powerful Methods for State of the Art Clinical, Biomedical and Environmental Research**; Joseph Caruso[1], Karnakar Chitta[1], Edward Merino[1], Julio Landero[1], Phanichand Kodali[1], Kavitha Subramanian[1], Adeoye Opeolu[1], George Deepe[1]; [1]University of Cincinnati

Tuesday Morning, *Atlanta*

FACSS CHARLES MANN AWARD SESSION HONORING DON PIVONKA

Organizer and Presider: Howell G. M. Edwards

10:20 (259) **It's Raman, Just Stick a Probe in Your Batch, Right? Why Sampling is Critical.**; Ian Lewis[1], Kevin Davis[1], Sean Gilliam[1], Maryann Cuellar[1], David Strachan[1], Pat Wiegand[1], Joe Slater[1], Herve Lucas[2], Carsten Uerpmann[2]; [1]Kaiser Optical Systems, Inc., [2]Kaiser Optical Systems, SARL

10:40 (260) **Advances of VOA in Pharma and Don**; Rina K. Dukor[1]; [1]BioTools, Inc *(*2011 Applied Spectroscopy Focal Point Author)*

11:00 (261) **Otimising Image Fidelity in 3D Confocal Raman Imaging**; Neil Everall[1]; [1]Intertek-MSG

11:20 (262) **Electrospun Nanofibers: A Challenge and an Opportunity for Raman Spectroscopy**; Bruce Chase[1], John Rabolt[1], Wenqiong Tang[1], Wenwen Liu[1]; [1]University of Delaware, Department of Materials Science

11:40 (263) **Enhanced Transmission Raman Spectroscopy**; Michael Pelletier[1]; [1]Pfizer Worldwide Research & Development

Tuesday Morning, *Empire A*

NOVEL OPTICAL REPORTERS, DYES AND TAGS IN MOLECULAR AND RAMAN SPECROSCOPY

Organizer: Steve Ray; Presider Marcus Lay

10:20 (264) **A New *in vivo* Raman Probe for Enhanced Applicability to the Body**; Paul Pudney[1], Eleanor Bonnist[1], Peter Caspers[2, 3], Jean-Philippe Gorce[1], Chris Marriot[1], Gerwin Puppels[2, 3], Scott Singleton[1], Martin van der Wolf[2, 3]; [1]Unilever Discover, [2]River Diagnostics BV, [3]Erasmus MC

10:40 (265) **Bioanalytical Use of Symmetrical and Asymmetrical NIR Dyes**; Gabor Patonay[1], Maged Henary[1], Garfield Beckford[1], Eric Owens[1], Andy Levitz[1]; [1]Georgia State University

11:00 (266) **Enhancing the Electrical Properties of 2-D Single-Walled Carbon Nanotube Networks**; Marcus Lay[1], Pornnipa Vichchulada[1], Nidhi Bhatt[1], Darya Asheghali[1]; [1]University of Georgia

11:20 (267) **High Throughput Identification of Promiscuous Inhibitors Among Screening Libraries with the Use of an Intrinsically Fluorescent Probe**; Megan M. McCallum[1], Premchendar Nandhikonda[1], Leggy A. Arnold[1], Ajit Jadhav[2], Adam Yasgar[2], David Maloney[2], Leggy A. Arnold[1]; [1]University of Wisconsin - Milwaukee, [2]NIH Chemical Genomics Center

11:40 (268) **Probing DPPC/GM1 Model Membranes with Single Molecule Orientations of Acyl-Linked Fluorescent Lipid Analogs**; Kevin Armendariz[1], Robert Dunn[1]; [1]University of Kansas

Tuesday Morning, *Empire B*
FORENSIC AND ENVIRONMENTAL APPLICATIONS OF CHEMOMETRICS
Organizers: Barry Lavine and Renee JiJi; Presider: Karl Booksh

10:20 (269) **Improving PDQ Database Search Strategies to Enhance Investigative Lead Information for Automotive Paints**; Barry Lavine[1], Nikhil Mirjankar[1], Mark Sandercock[2]; [1]Oklahoma State University, [2]National Centre for Forensic Services

10:40 (270) **Nonparametric Permutation Hypothesis Testing: Application to Forensic Physical Evidence**; Michael Sigman[1], Liqiang Ni[2]; [1]University of Central Florida, Department of Chemistry, [2]University of Central Florida, Department of Statistics

11:00 (271) **Chemometrics and Databases for Comparisons of Spectral Data from Trace Evidence**; Stephen L. Morgan[1], Edward G. Bartick[2], John G. Goodpaster[3], Molly R. Burnip[1], Eric J. Reichard[3], Kevin Roberts[2]; [1]University of South Carolina, [2]Suffolk University, [3]Indiana University-Purdue University Indianapolis

11:20 (272) **Automated Analysis of Gamma-Ray Spectra for Detection of Radioisotopes**; Gary Small[1]; [1]University of Iowa

11:40 (273) **Bayesian Regression: Is it Worth the Trouble?**; Steven Brown; [1]University of Delaware

Tuesday Morning, *Chicago C*
RECENT ADVANCEMENTS IN ELECTROPHORETIC SEPARATION
Organizers and Presiders: Wenwan Zhong and Shramik Sengupta

10:20 (274) **Quantification of Drug Delivery by Capillary Electrophoresis**; Michael Heien[1], Nicholas Laude[1], Saliya Ratnayaka[1]; [1]University of Arizona

10:40 (275) **High Sensitive Approaches for the Fluorescence Imaging Detection of Human Serum Proteins after PAGE**; Jin Ouyang[1], Jing Zhang[1], Na Na[1]; [1]College of Chemistry, Beijing Normal University

11:00 (276) **Surface Electrophoresis of ds-DNA Molecues**; Arnab Ghosh[1], Venu Korampally[1], Keshab Gangopadhyay[1], Shantanu Bhattacharya[2], Shubhra Gangopadhyay[1]; [1]Department of Electrical and Computer Engineering, Univ of Missouri, Columbia, [2]Department of Mechanical Engineering, IIT Kanput, India

11:20 (277) **Dielectrophoretic Manipulation of Erythrocytes for Blood Typing**; Adrienne Minerick[1], Kaela Leonard[1]; [1]Michigan Technology University

11:40 (278) **Determination of Aptamer-Protein Binding Affinity using Open-Channel Separation Techniques**; Wenwan Zhong[1], Samantha Schachermeyer[1], Jonathan Ashby[1]; [1]University of California, Riverside

Tuesday Morning, *Chouteau A*
PUSHING THE LIMITS OF LIBS IN ANALYTICAL SCIENCE
Organizers and Presiders: Jose Almirall and Matthieu Baudelet

10:20 (279) **Fifty Years of LIBS and No Limits for Analysis**; Matthieu Baudelet[1], Yuan Liu[1], Matthew Weidman[1], Michael Sigma[2, 3], Martin Richardson[1]; [1]Townes Laser Institute, College of Optics and Photonics, UCF, [2]Chemisty Department, UCF, [3]National Center for Forensic Science, UCF

10:40 (280) **Microwave-Assisted Laser-Induced Breakdown Spectroscopy: Signal Enhancement and Beyond**; Yuan Liu[1], Matthieu Baudelet[1], Martin Richardson[1]; [1]the College of Optics and Photonics, University of Central Florida

11:00 (281) **Application of Laser-Based Spectrochemical Analysis (LA-ICP-MS and LIBS) for the Assessment of Authenticity of Questioned Documents**; Tatiana Trejos[1], Linet Kamandulis[1], Jose R. Almirall[1]; [1]Florida International University

11:20 (282) **Laser Ablation Molecular Isotopic Spectrometry for Rapid Analysis of Solid Materials**; Alexander Bol'shakov[1], Xianglei Mao[2], Inhee Choi[2], Dale Perry[2], Richard Russo[1, 2]; [1]Applied Spectra Inc., [2]Lawrence Berkeley National Laboratory

11:40 (283) **Application of Laser-Induced Breakdown Spectroscopy to Remote and *in situ* Analysis of Algal Biomass Utilisation for Industrial Biotechnology**; Jozef Kaiser[1], Ota Samek[2], Karel Novotný[3], Martin Trtílek, Pavel Pořízka[1, 4], David Prochazka[1], Radomír Malina[1], Klára Procházková[1]; [1]Institute of Physical Engineering, Faculty of Mechanical Engineering, Brno University of Technology, [2]Institute of Scientific Instruments of the ASCR v.v.i., Academy of Sciences of the Czech Republic, [3]Department of Chemistry, Faculty of Sciences, Masaryk University Kotlářská 2, [4]Photon Systems Instruments

Tuesday Morning, *New York A*
INSTRUMENT AND METHOD DEVELOPMENT IN MS
Organizer and Presider: Eric Dodds

10:20 (284) **Portable Linear Quadrupole Membrane Inlet Mass Spectrometer for Environmental Monitoring**; William Hoffmann[1], Jianing He[2], Dr. Guido Verbeck[1]; [1]University of North Texas, Department of Chemistry, [2]Texas Academy of Math and Science

10:40 (285) **Zoom-TOF: A New Mass Spectrometer that Combines Constant-Momentum Acceleration Time-of-Flight Mass Spectrometry (TOFMS) with Classical TOFMS for Improved Resolution**; Elise A. Dennis[1], Steven J. Ray[1], Alexander W. G. Graham[1], Christie G. Enke[, 2], David W. Koppenhaal[, 3], Charles J. Barinaga[, 3], Gary M. Hieftje[1]; [1]Department of Chemistry, Indiana University, [2]Department of Chemistry and Chemical Biology, University of New Mexico , [3]Pacific Northwest National Laboratory

11:00 (286) **Hyphenation of a Microfluidic Platform with MALDI-TOF Mass Spectrometry for Single Cell Analysis**; Mian Yang[1], Tzu-Chiao Chao[1], Randall Nelson[2], Alexandra Ros[1]; [1]Department of Chemistry and Biochemistry, [2]The Biodesign Institute

11:20 (287) **Assigning N-linked Glycopeptide Compositions in Automated Analysis of Their ETD Tandem Mass Spectra**; Zhikai Zhu[1], Daniel Clark[1], Eden Go[1], David Hua[1], Heather Desaire[1]; [1]Dept. of Chemistry, Univ. of Kansas

11:40 (288) **Prospects for Information-Rich Gas-Phase Analysis of Protein Subunits Directly from Their Non-Covalent Complexes**; Deepali Rathore, Eric Dodds; [1]University of Nebraska- Lincoln

Tuesday Morning, *New York B*
TIP-ENHANCED RAMAN SPECTROSCOPY – NEW TRENDS
Organizer and Presider: Volker Deckert

10:20 (289) **Nanoscale Chemical Imaging Using Tip-Enhanced Raman Spectroscopy**; Thomas Schmid[1], Lothar Opilik[1], Carolin Blum[1], Johannes Stadler[1], Renato Zenobi[1]; [1]ETH Zurich, Department of Chemistry and Applied Biosciences

10:40 (290) **Tip-enhanced Raman Spectroscopy for Nano-Scale Monitoring of Catalytic Processes**; Evelien van Schrojenstein Lantman[1], Tanja Deckert-Gaudig[2], Arjan Mank[1, 3], Volker Deckert[2], Bert Wekchuysen[1]; [1]Utrecht University, [2]Institute of Photonic Technology, [3]Philips Inovation Services

11:00 (291) **Structure and Composition of Insulin Fibril Surfaces Probed by TERS**; Igor Lednev[1], Dmitry Kurouski[1], Tanja Deckert-Gaudig[2], Volker Deckert[2, 3]; [1]University at Albany, State University of New York, [2]Institute of Photonic Technology, [3]Institute for Physical Chemistry, University of Jena

11:20 (292) **Analysis of Hemoglobin and Hemozoin using Tip Enhanced Raman Scattering (TERS)**; Bayden Wood[1], Elena Bailo[2], Mehdi Asghari-Khiavi[1], Leann Tilley[3], Don McNaughton, Tanja Decekrt-Guadig[4], Volker Deckert[2, 4]; [1]Monash University, School of Chemistry, [2]ISAS − Institute for Analytical Sciences, [3]Department of Biochemistry and Centre of Excellence for Coherent X-ray Science, La Trobe University, [4]Friedrich-Schiller-Universität Jena, eInstitute of Photonic Technology, IPHT

11:40 (293) **A Novel Approach to Near-field Stimulated Raman Microscopy**; Derek Nowak[1, 2], Kam Leang[1, 3], Kumar Wickramashinge[1,4]; [1]Molecular Vista Inc, [2]Department of Physics, Portland State University, [3]Department of Mechanical Engineering, University of Nevada, [4]Department of Electrical Engineering and Computer Science, University of California

Tuesday Morning, *Empire C*
VERY REMOTE SPECTROSCOPY: EXPLORING EXTREME ENVIRONMENTS
Organizer: Steve Ray, Presider: Shiv Sharma

10:20 (294) **MARS – Microbial Biomarker Analysis with Raman Spectroscopy**; Jan-Hein Hooijschuur[1, 2, 3, 4], Cees Gooijer[1, 2, 4], Gareth Davies[3, 4], Freek Ariese[1, 2, 4]; [1]Department of Biomolecular Spectroscopy, [2]LaserLaB Amsterdam, [3]Department of Petrology, [4]Vrije University

10:40 (295) **A Compact, Dual Excitation Raman Probe and Instrument for the Identification of Mineralogical Samples**; Job Bello[1], Christina Gasbarro[1], Anton Smirnov[1]; [1]EIC Laboratories, Inc

11:00 (296) **Advancements in Raman Spectroscopy for the Deep Ocean**; William Kirkwood[1], Peter Walz[1], Edward Peltzer[1], Peter Brewer[1]; [1]MBARI *(*2012 Applied Spectroscopy Focal Point Author)*

11:20 (297) **Geochemical Characterization of Layered Outcrops on Mars using LIBS (Laser-Induced Breakdown Spectroscopy)**; Pablo Sobron[1], Catherine Lefebvre[1], Richard Leveille[1], Alexander Koujelev[1], Timothy Haltigin[1], Hongwei Du[2], Alian Wang[2], Nathalie Cabrol[3], Kris Zacny[4], Jack Craft[4]; [1]Canadian Space Agency, [2]Washington University in St. Louis, [3]NASA Ames Research Center, [4]Honeybee Robotics

11:40 (298) **Laser-Induced Breakdown Spectroscopy in the Deep Ocean Environment**; Mike Angel[1]; [1]University of South Carolina

Tuesday Morning, *Chicago A*
SURFACE PLASMON RESONANCE APPLICATIONS AND INSTRUMENTATION
Organizer: Jean-Francois Masson; Presider: Amanda Haes

10:20 (299) **DC Magnetron Sputtered Polyaniline-HCl Thin Films for Chemical Sensing Applications**; Karl Booksh, Devon Boyn, Nicola Menegazzo, Holt Bui, Thomas Beebe; [1]University of Delaware

10:40 (300) **Mid-infrared Plasmons of Conducting Metal Oxides**; Stefan Franzen[1], Josh Guske[1], Misun Kang[1], Edward Sachet[1], Mark Losego[1], Jon-Paul Maria[1]; [1]North Carolina State University

11:00 (301) **Aptamer Functionalized SPR Surfaces for Selective Blood Protein Monitoring**; Nathan Reaver[1], Rui Zheng[1], Dong-Shik Kim[1], Brent Cameron[1]; [1]University of Toledo

11:20 (302) **Diazonium Derived Aryl Films on Gold for Surface Plasmon Resonance Imaging of Metabolytes**; Mark McDermott[1], John Toman[1], Shereen Elbayomy[1], Lars Laurentius[1]; [1]University of Alberta

11:40 (303) **On-chip Multiplexed Label Free Bio-Affinity Analysis and MALDI-MS Characterization of Bound Analyte**; Jeremy Pronchik[1], Sophie Bellon[1], Wilfrid Boireau[2], Patrick Ducoroy[3], Chiraz Frydman[1]; [1]Horiba Scientific, [2]Institut FEMTO, [3]CLIPP

Tuesday Afternoon, *Chicago B*
SPECIATION ANALYSIS: PROGRESS IN TRACE METAL SPECIATION
Organizer and Presider: Michael Sperling

1:20 (304) **Determination of Arsenic-Containing Phospholipids in Marine Samples**; Kevin Francesconi[1], Sara García-Salgado[2], Georg Raber[1]; [1]Institute of Chemistry-Analytical Chemistry, Karl-Franzens University Graz, [2]Civil Engineering: Hydraulic and Energy Technology Department, University College for the Technical Engineering of Public Works, Polytechnic University of Madrid

1:40 (305) **New Dimensions in Speciation Analysis : Implementing Isotopic Signatures at The Molecular Level**; Olivier F.X. Donard[1], Emmanuel Tessier[1], Vladimir Epov[1], Sylvain Berail[1], Christophe Pecheyran[1], David Amouroux[1]; [1]Lab. de Chimie Analytique Bioinorganique et Environnement, CNRS-UPPA, Hélioparc, Pau (France)

2:00 (306) **Advances in Higher Accuracy Elemental and Molecular Speciated Analyses using Updated EPA Method 6800**; H M Skip Kingston[1], Mizan Rahman[2], Matt Pamuku[2], Greg Zinn[1], Timothy Fahrenholz[2]; [1]Duquesne University, [2]Applied Isotope Technologies

2:20 (307) **The Speciation of Gold in Groundwaters with HPLC-ICP-MS**; Christine Ta[1], Frank Reith[2, 3], Joel Brugger[2, 4], Allan Pring[4], Claire E. Lenehan[1]; [1]School of Chemical and Physical Sciences, Flinders University., [2]Centre for Tectonics, Resources and Mineral Exploration (TRaX), School of Earth and Environmental Sciences, The University of Adelaide., [3]CSIRO Land and Water, Environmental Biogeochemistry, PMB2, Glen Osmond., [4]Department of Mineralogy, South Australian Museum

2:40 (308) **Speciation Analysis for Studying the Interaction of Metallodrugs with Blood Components**; Michael Sperling[1], Christine Brauckmann[1], Lena Telgmann[1], Christoph Wehe[1], Olga Reifschneider[1], Uwe Karst[1]; [1]University of Muenster, Institute of Inorganic and Analytical Chemistry

Tuesday Afternoon, *Chicago A*
THE EVER EXPANDING CAPACITIES OF THE ANALYTICAL GLOW DISCHARGE
Organizers: Steve Ray and Carsten Engelhard;
Presider: Carsten Engelhard

1:20 (309) **Liquid Sampling-Atmospheric Pressure Glow Discharge Ion Source: A Practical Microplasma**; R. Kenneth Marcus[1], Lynn X. Zhang[1], Benjamin T. Manard[1], Carolyn Q. Burdette[1]; [1]Clemson University

1:40 (310) **Further Work on the Use of Advanced Computational Statistics ("Expert Systems") for Automatic Evaluation of GD-OES Compositional Depth Profiles**; Arne Bengtson[1], Jonas Gurell[1]; [1]Swerea KIMAB

2:00 (311) **Development and Application of a Large Glow Discharge Source Suitable for Spatial Imaging**; Volker Hoffmann[1], Maxim Voronov[1], Wolfgang Buscher[2], Carsten Engelhard[2], Steven J. Ray[3], Andrew P. Storey[3], Gary M. Hieftje[3]; [1]Leibniz Institute for Solid State and Materials Research Dresden, IFW Dresden e.V., [2]University of Münster, Department of Inorganic and Analytical Chemistry, [3]Department of Chemistry, Indiana University

2:20 (312) **Atomic Spectrometry with Glow Discharges at Atmospheric Pressure for the Determination of Analytes in the Gaseous Phase**; José A.C. Broekaert[1]; [1]University of Hamburg, Institute for Inorganic and Applied Chemistry

2:40 (313) **Spatial Mapping with Glow Discharge Optical Emission Spectrometry: The Role of Reflectivity in Heterogeneous Matrices**; Gerardo Gamez[1], Juan Limon-Petersen[1], Johann Michler[1]; [1]Swiss Federal Laboratories for Materials Science and Technology (EMPA)

Tuesday Afternoon, *Atlanta*
COBLENTZ SOCIETY'S CRAVER AWARD SESSION HONORING DUNCAN GRAHAM: ADVANCES IN ANALYSIS
Organizer: Duncan Graham; Presider: Micky Myrick

1:20 (314) **2p or not 2p: Tuppence-based SERS for the Detection of Illicit Materials**; Roy Goodacre[1], Samuel Mabbott[1], David Cowcher[1], Clare Levene[1], Omar Alharbi[1], Elon Correa[1], Ewan Blanch[1]; [1]University of Manchester

1:40 (315) **Multiplexed and Sensitive Molecular Diagnostics using SERRS**; Karen Faulds[1], Jennifer Dougan[1], Kirsten Gracie[1], Mhairi Harper[1], Kristy McKeating[1], Duncan Graham[11]; [1]University of Strathclyde *(*2011 Applied Spectroscopy Focal Point Author)*

2:00 (316) **Single Molecule Studies of Transport and Reactivity under Conditions of Confinement and Crowding**; Paul W. Bohn[1], Jing Zhao[1], Dane A. Grismer[1], Sean P. Branagan[1]; [1]University of Notre Dame

2:20 (317) **Spatially Offset Raman Spectroscopy: From Aviation Security to Medical Diagnosis**; Pavel Matousek[1]; [1]Rutherford Appleton Laboratory

2:40 (318) **Practical Understanding of the SERS/SERRS Process Using Chemistry, Plasmon Resonance And Eels**; Ewen Smith[1, 2]; [1]University of Strathclyde, [2]Renishaw Diagnostics Ltd *(*2011 Applied Spectroscopy Focal Point Author)*

Tuesday Afternoon, *Chicago C*
NEXT GENERATION ELECTRIC-FIELD DRIVEN SEPARATION
Organizers and Presiders: Christa Hestekin and Lisa Holland

1:20 (319) **Fine-Tuning the Flow Profile, Direction, and Speed of Fluids on a Chip with Redox-Magnetohydrodynamics**; Ingrid Fritsch[1], Vishal Sahore[1], Christena Nash[1], Preston Scrape[1], Adam Kreidermacher[1]; [1]University of Arkansas

1:40 (320) **Low Cost Paper-PDMS Electrophoretic Separation Devices**; Christopher R. Harrison[1], Dylan C. Mitchell[1]; [1]San Diego State University

2:00 (321) **Electrodeionization for Selective Separations**; Alex Lopez[1]; [1]University of Arkansas

2:20 (322) **A On-animal Separation Based Sensor with Amperometric Detection**; David Scott[1, 2], Ryan Grigsby[1, 2], Susan Lunte[1, 2]; [1]University of Kansas, [2]Ralph N. Adams Institute for Bioanalytical Chemistry and Departments of Chemistry

2:40 (323) **Evaluation of Amyloid Protein Oligomer Formation Using Microchannel Electrophoresis**; Christa Hestekin[1], Elizabeth Pryor[1], Melissa Moss[2]; [1]University of Arkansas, [2]University of South Carolina

Tuesday Afternoon, *Empire B*
TWO-DIMENSIONAL CORRELATION SPECTROSCOPY I
Organizers: Young Mee Jung and Isao Noda; Presider: Young Mee Jung

1:20 (324) **Resolution Enhancement in 2D Correlation Spectroscopy**; Isao Noda[1]; [1]The Procter & Gamble Company

1:40 (325) **Analysis of the Molten Globule State of Bovine α-Lactalbumin by Using Vibrational Circular Dichroism**; Laurence A Nafie[1, 4], Soo Ryeon Ryu[2], Young Mee Jung[2], Bogusława Czarnik-Matusewiczb[3], Rina K Dukor[4]; [1]Syracuse University, [2]Kangwon National University, [3]University of Wrocław, [4]BioTools, Inc.*(*2011 Applied Spectroscopy Focal Point Author)*

2:00 (326) **2D-Correlation Spectroscopy in Polymer Chemistry**; Heinz Siesler[1], Miriam Unger[2]; [1]University of Duisburg-Essen, Department of Physical Chemistry, [2]Synchrotron Radiation Center

2:20 (327) **Concepts on Information Theory in Two-Dimensional Correlation Spectroscopy**; Nicolas Spegazzini[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University

2:40 (328) **2D Correlation Spectroscopy as a Tool for Spectral Interpretation**; James de Haseth[1], Franklin Barton, II[1]; [1]Light Light Solutions, LLC

Tuesday Afternoon, *Empire C*
ADVANCED VIBRATIONAL PROBES FOR BIOMEDICAL SENSING
Organizer and Presider: Ishan Barman

1:20 (329) **Frontiers of Biomedical Application of SERS : New Strategies for**; Yukihiro Ozaki[1]; [1]Kwansei Gakuin University

1:40 (330) **High Speed Single Cell Spectroscopy: Integrating Fluorescence and Raman Scattering in Cytometry**; John Nolan[1]; [1]La Jolla Bioengineering Institute

2:00 (331) **Deep-UV Resonance Raman Spectroscopy of Biomolecules**; Renee D. JiJi[1], Michael K. Eagleburger[1], Jian Xiong[1], Jason W. Cooley[1]; [1]University of Missouri-Columbia

2:20 (332) **Polarized Raman Spectroscopic Analysis of Polymeric Products**; Mark Henson[1]; [1]ExxonMobil Chemical Co

2:40 (333) **Monitoring the API Form in Drug Product Using Spectroscopy**; Shawn Mehrens[1], Heather Frericks[1], Slobodan Sasic[2]; [1]Pfizer Worldwide Research and Development, [2]Vertex Pharmaceuticals

Tuesday Afternoon, *Chouteau A*
LASER-INDUCED BREAKDOWN SPECTROSCOPY
Organizer: Steve Ray; Presider: Vassilia Zorba

1:20 (334) **High Resolution Laser-induced Breakdown Spectroscopy for Complex Spectra**; Jill Scott[1], Jeremy Hatch[1], Andrew J. Effenberger[2], Cynthia Hanson[1], Timothy McJunkin[1]; [1]Idaho National Laboratory, [2]University of California San Diego

1:40 (335) **Effects of Local Plasma Cooling in LIBS Analysis**; M. Asgill[1], D.W. Hahn[1], S. Groh[2], K. Niemax[3]; [1]University of Florida, [2]ISAS at Technische Universität Dortmund, [3]Federal Institute for Materials Research and Testing (BAM)

2:00 (336) **Detection of Organic Particles in the Organic Gas Background using LIBS and LIF**; Seok Hwan Lee[1], Jack Yoh[1]; [1]Seoul National University, School of Mechanical and Aerospace Engineering Department

2:20 (337) **LIBS Analysis of Coal Samples: Comparison of the Ablation Behavior between UV (266nm) and IR (1064nm) Laser Wavelengths**; Meirong Dong[1, 3], Jhanis Gonzalez[1, 2], Chunyi Liu[2], Jidong Lu[3], Richard Russo[1, 2]; [1]Lawrence Berkeley National Laboratory, [2]Applied Spectra, Inc, [3]South China University of Technology

2:40 (338) **Measurement of Silica in Coal Dust by Laser-Induced Breakdown Spectroscopy**; Art Miller[1], Chris Stipe[2], Jonathan Brown[3], Edward Guevara[3], Emanuele Cauda[1]; [1]CDC/NIOSH, [2]Photon Machines, Inc, [3]Seattle University

Tuesday Afternoon, *New York A*
TOPICS IN TANDEM MASS SPECTROMETRY
Organizer and Presider: Michael Van Stipdonk

1:20 (339) **Structural Identification of Fragment Ions Using Guided Ion Beam Tandem Mass Spectrometry**; Peter Armentrout[1]; [1]University of Utah

1:40 (340) **Inorganic and Organometallic Actinide Chemistry Studied by Tandem Mass Spectrometry**; John Gibson[1], Daniel Rios[1], Yu Gong[1], Ana Lucena[2], Joaquim Marçalo[2], Maria Michelini[3]; [1]Chemical Sciences Division, Lawrence Berkeley National Laboratory, [2]Instituto Tecnológico e Nuclear, Instituto Superior Técnico, Portugal, [3]Dipartimento di Chimica, Università della Calabria, Italy

2:00 (341) **Using Tandem-MS to Obtain Isomer-Specific Vibrational Spectra of D2-tagged ions Cooled in a Cryogenic Ion Trap**; Christopher Leavitt[1], Arron Wolk[1], Michael Kamrath[1], Etienne Garand[2], Joseph Fournier[1], Peter Jordan[1], Michael Van Stipdonk[3], Scott Miller[1], Mark Johnson[1]; [1]Yale University, [2]University of Wisconsin-Madison, [3]Lawrence University, [4]

2:20 (342) **Electron Capture Dissociation: An Introduction and Recent Developments**; Benjamin J. Bythell[1], Christopher L. Hendrickson[1, 2], Alan G. Marshall[1, 2]; [1]Ion Cyclotron Resonance Program, National High Magnetic Field Laboratory, Florida State University, [2]Department of Chemistry and Biochemistry

2:40 (343) **Structures and Activation Energies for Glycosidic Bond Cleavage of Protonated Nucleosides from Energy-Resolved Collision-Induced Dissociation and Theoretical Studies**; Mary T. Rodgers[1], Ranran Wu[1]; [1]Wayne State University

Tuesday Afternoon, *New York B*
PHARMACEUTICAL APPLICATIONS OF RAMAN IMAGING
Organizer and Presider: John Kauffman

1:20 (344) **Determining the Distribution of Magneisum Stearate in Tablets and Blends via Raman Chemical Mapping**; Slobodan Sasic[1], Martin Warman[1], Peter Ojakovo[1]; [1]Vertex Pharmaceuticals

1:40 (345) **Revisiting Analytical Approaches with Fast Confocal Raman Microscopy**; Don Clark[1], Jordan Cheyne[1]; [1]Pfizer Global Supply

2:00 (346) **Quantitative Descriptions of Pharmaceutical Architecture using Ripley's K-function with Raman Chemical Images**; Gary McGeorge[1]; [1]Bristol-Myers Squibb

2:20 (347) **Analysis of API distribution and Migration through the Intravaginal Ring using Raman Imaging**; Eunah Lee[1], Philo Morse[2], Robert Lee[2], Andrew Whitley[1]; [1]HORIBA Scientific, [2]Particle Sciences

2:40 (348) **3D Confocal Raman Imaging of Transparent and Opaque Samples**; Ute Schmidt[1, 2], Jianyong Yang[2], Thomas Dieing[1], Wei Liu[1, 2], Klaus Weishaupt[1]; [1]WITec GmbH, [2]WITec Instruments

Tuesday Afternoon, *Empire A*
ON THE SCENT: VAPOR AND AROMA ANALYSIS FOR FORENSIC AND SECURITY APPLICATIONS
Organizer and Presider: Charles Wilkins

1:20 (349) **Impurity Profiling in Chemical Forensics: Recent Developments and Path Forward**; Carlos Fraga[1]; [1]Pacific Northwest National Laboratory

2:00 (350) **Ultra Performance Liquid Chromatography and Mass Spectrometry for Forensic Characterization of Dyes Extracted from Millimeter-length Textile Fibers**; Stephen L. Morgan[1], Scott J. Hoy[1], Molly R. Burnip[1], Oscar G. Cabrices[1]; [1]University of South Carolina

2:20 (351) **Direct Injection Mass Spectrometry for Nondestructive Forensic Chemical Analysis and Tracking of Chemistry Networks from Source to User**; Guido Verbeck[1]; [1]University of North Texas

2:40 (352) **Direct Analysis of Forensic Samples by Laser Ablation Electrospray Tandem Mass Spectrometry (LAESI-MS/MS)**; Robert Deimler[1], Trust Razunguzwa[2], Brent Reschke[2], Matthew Powell[2], Glen Jackson[1]; [1]Ohio University, [2]Protea Biosciences, Inc.

3:00 – 3:50 pm Exhibit Hall A
DESSERT BREAK AND POSTER VIEWING

Tuesday Afternoon, *Chicago A*
ATOMIC SPECTROMETRY AND THE ANALYSIS OF NANOMATERIALS
Organizer and Presider: Petra Krystek

3:50 (353) **Detection and Preliminary Characterization of Inorganic Nanomaterials in Food by Asymmetric Flow Field Flow Fractionation Coupled to ICP-MS**; Julien Herault[1], Volker Nischwitz[1], Heidi Goenaga-Infante[1]; [1]LGC Limited

4:10 (354) **Analysis of Single Nanoparticles by ICP-MS: Where is the Limit?**; Carsten Engelhard[1], Bastian Franze[1], Ingo Strenge[1], Christoph Wehe[1], Michael Sperling[1], Uwe Karst[1]; [1]University of Muenster

4:30 (355) **Measurement and Calibration Strategy for ICP-MS Single-Particle Analysis**; Wing-Tat Chan[1], Thomas K.O. Lui[1], Jeff K.H. Lee[1]; [1]University of Hong Kong

4:50 (356) **Posttranslational Modifications as an Insight into Silver Nanoparticle Ecotoxicity**; Traci Hanley[1], Cheolho Yoon[1, 2], Ryan Saadaiw[1], Julio Landero[1], Joseph Caruso[1]; [1]University of Cincinnati, Department of Chemistry, [2]Korea Basic Science Institute, Seoul Center

5:10 (357) **Strategies about the Biodistribution of Nano Gold and Nano Silver by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)**; Petra Krystek[1]; [1]VU University Amsterdam, Institute for Environmental Studies (IVM)

Tuesday Afternoon, *Empire A*
BIOLOGICAL APPLICATIONS OF CHEMOMETRICS
Organizers: Barry Lavine and Renee JiJi; Presider: Frank Vogt

3:50 (358) **Multivariate Optical Computing Applied to Phytoplankton Fluorescence Excitation Spectroscopy**; Michael Myrick[1], Tammi Richardson[1], Timothy Shaw[1], Heidi Sosik[2], Robert Olsen[2], Joseph Swanstrom[1], Megan Baranowski[1], Larua Bruckman[1], Shawna Tazik[1], Elizabeth Abernathy[1]; [1]University of South Carolina, [2]Woods Hole Oceanographic Institution, [3]Sandia National Laboratory

4:10 (359) **Novel High Throughput EEM Detection for Flowing Samples—Obviation of Mie and Raman Scattering**; Timothy Corcoran, Charles Schreyer[1], Ivonne de la Torre[1], Jacob Balthazor[1], Phillip Allen[1], Alisha Lewis[1]; [1]California State Polytechnic University Pomona

4:30 (360) **Traps and Pitfalls when Applying Chemometrics to Biomedical Problems**; Jerome Workman[1, 2, 3]; [1]Unity Scientific, [2]National University, [3]Liberty University

4:50 (361) **Scrutinizing Attributes of Data of Very High Dimension**; Robert Lodder; [1]University of Kentucky

5:10 (362) **Raman, Infrared and NMR Spectroscopies on the Same Samples and the Etiology and Cure for Dry Eyes**; Douglas Borchman[1], Marta Yappert[1], Gary Foulks[1]; [1]University of Louisville

Tuesday Afternoon, *Chicago C*
MICROSCALE PHENOMENA – JOINT AES AND FACSS SYMPOSIUM
Organziers: Alexandra Ros and Adrienne Minerick

3:50 (363) **Dielectric and Dielectrophoretic Measurements and Manipulations of Cells for Human Health and Energy Applications**; Brian Kirby[1]; [1]Cornell University

4:10 (364) **Interfacial Microfluidics for Biochemical and Cellular Analysis**; Jachary Gagnon[1]; [1]Dept of Chemical and Biomoleuclar Engineering Johns Hopkins Univ

4:30 (365) **Dielectrophoresis of Polyelectrolytes in Nanofluidic Landscapes**; Robert Riehn[1], Chunda Zhou[1], Zubair Azad[1]; [1]North Carolina State University

4:50 (366) **Single-cell Electrofusion: Three DEP Elements in one Process Chain**; Magnus S. Jaeger[1]; [1]Fraunhofer Institute for Biomedical Engineering (IBMT)

5:10 (367) **A Dielectrophoretic Sorter for Nanoparticle and Nanocrystal Separation**; Bahige Abdallah[1], Tzu-Chiao Chao[1], Petra Fromme[1], Alexandra Ros[1]; [1]Arizona State University

Tuesday Afternoon, *Empire B*
TWO-DIMENSIONAL CORRELATION SPECTROSCOPY II
Organizers: Young Mee Jung and Isao Noda; Presider: Isao Noda

3:50 (368) **Sequential Identification of Model Parameters by Derivative Double Two-Dimensional Correlation Spectroscopy and Calibration-Free Approach in Chemical Reaction Systems**; Yukihiro Ozaki[1], Nicolas Spegazzini[1], Heinz W. Siesler[2]; [1]Kwansei Gakuin University, [2]University of Duisburg-Essen *(*2012 Applied Spectroscopy Focal Point Author)*

4:10 (369) **2D Correlation Raman Spectroscopy for Probing the Mechanism of Folding and Aggregation**; Igor Lednev[1], Vitali Sikirzhytski[1]; [1]University at Albany, State University of New York (*2011 Applied Spectroscopy Focal Point Author)*

4:30 (370) **Two-Dimensional Correlation Spectroscopy of Polymer in Terahertz Frequency Region**; Hiromichi Hoshina[1], Shinya Ishii[1, 2], Yusuke Morisawa[3], Harumi Sato[3], Shigeki Yamamoto[3], Isao Noda[4], Yukihiro Ozaki[3], Chiko Otani[1]; [1]RIKEN, [2]Miyagi University of Education, [3]Kwansei Gakuin University, [4]The Procter & Gamble Company

4:50 (371) **2D Correlation Analysis in Tracing the Absorbance Changes Caused by the Transitions of Polymer and Protein**; Young Mee Jung[1], Min Kyung Kim[1], Soo Ryeon Ryu[1], Bogusława Czarnik-Matusewicz[2], Isao Noda[3]; [1]Kangwon National University, [2]University of Wrocław, [3]The Procter & Gamble Company

Tuesday Afternoon, *Chicago B*
PHARMACEUTICAL APPLICATIONS OF RAMAN SPECTROSCOPY
Organizer and Presider: John Wasylyk

3:50 (372) **Raman Optical Activity Studies of Pharmaceutical Compounds**; Ewan Blanch[1], Clare Levene[1], Saeideh Ostovar pour[1], Belen Nieto-Ortega[2], Katarzyna Chruszcz-Lipska[3], Javier Ramirez[2], Babur Chodhry[4], Trevor Dines; [1]University of Manchester, [2]University of Malaga, [3]Jagiellonian University, [4]University of Greenwich

4:10 (373) **Detection of Polymorphism and Quantitative Determination of Active Ingredients in Pharmaceutical Formulations by Raman Spectroscopy**; Heinz Siesler[1]; [1]University of Duisburg-Essen

4:30 (374) **Use of Raman Spectroscopy to Investigate the Physical Stability of Compacted Solid Dispersions**; Ryanne N. Palermo[1], Benoit Igne[2], Carl A. Anderson[1, 2], James K. Drennen, III[1, 2]; [1]Duquesne University, Graduate School of Pharmacy, [2]Duquesne Center for Pharmaceutical Technology

4:50 (375) **Raman Spectroscopy for Monitoring the Production of Pharmaceutically Active Compounds in a Bioreactor**; Johannes Kiefer[1, 2], Kristina Noack[2], Christina Dilk[2], Matthias Schirmer[2], Rainer Buchholz[2], Alfred Leipertz[2]; [1]University of Aberdeen, [2]University of Erlangen-Nuremberg

5:10 (376) **Near-Infrared Spectroscopy for In-Line Monitoring of Protein Unfolding and its Interactions with Lyoprotectants during Freeze-Drying**; Thomas De Beer[1]; [1]Ghent University

Tuesday Afternoon, *New York B*
UV RAMAN / UV SERS
Organizer and Presider: Juergen Popp

3:50 (377) **UV-SERS for Electrochemical Interfaces**; Bin Ren[1], Li Cui, Zhi-Lin Yang[1], Zhong-Qun Tian; [1]State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, [2]Department of Physics, Xiamen University

4:10 (378) **Quantitative UV Resonance Raman Studies of Explosive Materials: Raman Cross Sections**; Sanford Asher[1], Luling Wang[1], Manash Ghogh[1]; [1]University of Pittsburgh, [2], [3], [4]

4:30 (379) **Structure and Formation Mechanism of Amyloid Fibrils: the Role of Disulfide Bonds**; Igor Lednev[1], Dmitry Kurouski[1], Jacqueline Washington[1], Mehmet Ozbil[2], Rajeev Prabhakar[2], Alexander Shekhtman[1]; [1]University at Albany, State University of New York, [2]University of Miami

4:50 (380) **Trace Detection of Organics and Microbes Using Fused Deep UV Raman & Native Fluorescence Spectroscopy**; Rohit Bhartia[1], William Hug[2], Everett Salas[2], Kripa Sijapati[2], Ray Reid[2]; [1]Jet Propulsion Laboratory, [2]Photon Systems, Inc

5:10 (381) **Deep UV Raman Spectroscopy of Biological and Mineralogical Samples**; Michael Schmitt[1], Petra Rösch[1], Ralph Heinke[1], Sandra Kloß[1], Ute Neugebauer[1, 2], Nicolae Tarcea[1], Thomas Dörfer[1], Hans Thiele[1, 3], Jürgen Popp[1, 2]; [1]Institut für Physikalische Chemie and Abbe Center of Photonics, Friedrich-Schiller-Universität Jena, [2]Institut für Photonische Technologien, [3]Kayser-Threde GmbH

Tuesday Afternoon, *Chouteau A*
ELEMENTAL SIGNATURES FOR FORENSICS
Organizer and Presider: Matthieu Baudelet

3:50 (382) **Discriminant Analysis in the Presence of Interferences: Combined Application of Target Factor Analysis and a Bayesian Soft-Class**; Michael Sigman[1], Caitlin Rinke[1]; [1]University of Central Florida, Department of Chemistry

4:10 (383) **A General Method for Predicting the Precision of Isotope Ratios Measured by Resonance Ionization Mass Spectrometry**; David Willingham[1], Michael R. Savina[1], Kim B. Knight[2], Michael J. Pellin[1], Ian D. Hutcheon[2]; [1]Argonne National Laboratory, [2]Lawrence Livermore National Laboratory

4:30 (384) **SF-ICPMS Determination of Plutonium Activities and Atom Ratios in Environmental and Biological Samples Collected from Amchitka Island, Alaska**; Kaixuan Bu[1], James Cizdziel[1]; [1]Department of Chemistry and Biochemistry, University of Mississippi

4:50 (385) **Total Metal Analysis in Hookah Tobacco Pre- and Post Consumption**; Ryan Saadawi[1], Traci Hanley[1], Julio Landero[1], Joseph Caruso[1]; [1]University of Cincinnati

5:10 (386) **Multivariate Analysis of Emission-Line Rich Spectra for Metal Alloy Identification**; Ryan Carn[1], Gary Rayson[1]; [1]New Mexico State University

Tuesday Afternoon, *New York A*
RECENT PROGRESS IN SERS
Organizer: Steve Ray; Presider: Keith Carron

3:50 (387) **Experimental and Computational Investigation of SERS Signal Variations**; Siyam Ansar[1], Dongmao Zhang[1, 2], Shengli Zou[2]; [1]Mississippi State University, [2]University of Central Florida

4:10 (388) **Parallel Raman and Surface-Enhanced Raman Microspectroscopy**; Wei-chuan Shih[1], Ji Qi[1]; [1]University of Houston

4:30 (389) **Label-Free Method to Detect Glycan-Lectin Interactions with Surface Enhanced Raman Spectroscopy**; Sharon Martin[1], Xiuru Li[1, 2], Richard Dluhy[1], Gert Jan Boons[1, 2]; [1]Department of Chemistry, University of Georgia, [2]Complex Carbohydrate Research Center, University of Georgia

4:50 (390) **Detection of SERS Active Labelled DNA Based on Surface Affinity to Silver Nanoparticles**; Mhairi Harper, Jennifer Dougan, Karen Faulds, Duncan Graham; [1]University of Starthclyde

5:10 (391) **Lab-on-a-Bubble: Direct and Indirect SERS Assays**; Keith Carron[1, 2], Aaron Strickland[1, 4], Richard Martoglio[1, 3], Virginia Schmit[1], Brandon Scott[1]; [1]University of Wyoming, [2]Snowy Range Instruments, [3]Depauw University, [4]iFyber

Tuesday Afternoon, *Empire C*
PORTABLE INSTRUMENTATION AND STANDOFF DETECTION TECHNIQUES
Organizer: Steve Ray; Presider: Radislav Potyrailo

3:50 (392) **Backpack Mass Spectrometer Combined with Ambient Ionization for Automated, In Situ Analyses**; Jacob Shelley[1], Paul Hendricks[1], Jon Dalgleish[1], Tsung-Chi Chen[1, 2], Jason Duncan[1, 3], Matt McNicholas[1, 4], Linfan Li[1, 2], John Denton[1, 4], Zheng Ouyang[2], Graham Cooks[1]; [1]Department of Chemistry, Purdue University, [2]Weldon School of Biomedical Engineering, Purdue University, [3]Center for Analytical Instrumentation Development, Purdue University, [4]Department of Electrical & Computer Engineering Technology, Purdue University

4:10 (393) **Toward Advanced Breath Diagnostics: Combining Mid-Infrared Sensors with Differential Ion Mobility Spectrometry**; Felicia Seichter[1], William Cheung[2], Michael Schivo[3], Frank Vogt[4], Cristina E. Davis[2], Boris Mizaikoff[1]; [1]Institute of Analytical and Bioanalytical Chemistry, University of Ulm, [2]Department of Mechanical and Aerospace Engineering, University of California, Davis, [3]Department of Internal Medicine, Division Pulmonary, Critical Care, & Sleep, School of Medicine, University of California, Davis, [4]Department of Chemistry, University of Tennessee, Knoxville

4:30 (394) **Standoff Detection of Chemical Warfare Agents with UV Raman Chemical Imaging**; Ryan Priore[1], Stephen Styk[1], Charles Gardner[1], Doug Green[2], David Schiering[2]; [1]ChemImage Corp., [2]Smiths Detection

4:50 (395) **Self-normalizing SERS-based Trace Detection of TNT**; Benoit Lauly[1], Marc Wadsworth[1], Paul Repasky[1], Jonathan Scaffidi[1]; [1]Miami University

5:10 (396) **MEMS Chemicapacitive Chemical Sensor Systems**; Todd Mlsna[1], Sanjay Patel[2]; [1]Mississippi State University, [2]Seacoast Science Inc

TECHNICAL PROGRAM – WEDNESDAY

Plenary Lectures, Exhibit Hall B

Presider: Michael George

8:00 am – ACS Division of Analytical Chemistry Award for Distinguished Service in the Advancemen of Analytical Chemistry
(397) Service and Research: Symbiosis or Conflict?; **Gary Hieftje**; Indiana University

8: 30 am- ANACHEM Award
(398) The Impact of Chemometrics on Open-Path FT-IR Atmospheric Monitoring; **Peter R. Griffiths**; University of Idaho

Wednesday Poster Session
9:00 – 10:20 am
Exhibit Hall A

All Wednesday posters should be put up between 7:30 – 8:00 am and removed by 4:00 pm

Chemometrics and Spectroscopic Investigation

Board #

1 (399) **Utilizing Spectral Information to Adaptively Mitigate Spectral Interferents**; Bryon Herbert[1], Karl Booksh[1]; [1]University of Delaware

2 (400) **Assessment of Sample Selection Methods for Local Modeling**; Kevin Higgins[1], John Kalivas[1]; [1]Idaho State University

3 (401) **Localized Model Selection for Multivariate Calibration Using Tikhonov Regularization with Net Analyte Signal**; Jonathan Palmer[1], John Kalivas[1]; [1]Idaho State University

4 (402) **Forensic Applications of Pattern Recognition Assisted Infrared Library Searching Techniques**; Ayuba Fasasi[1], Nikhil Mirjankar[1], Barry Lavine[1], Mark Sandercock[2]; [1]Oklahoma State University, [2]National Centre for Forensic Services (RCMP)

5 (403) **FTIR Spectral Searching - How to Assess a the Quality of a Match**; Michael Boruta[1]; [1]ACD/Labs, Inc.

6 (404) **Multivariate Calibration and Maintenance Using Principle Component Selection**; Trevor O[1], John Kalivas[2], Parviz Shahbazikhah[2]; [1]Texas Tech Univeristy, [2]Idaho State University

7 (405) **Calibration Maintenance without Laboratory Prepared or Determined Reference Analyte Values**; John Kalivas[1], Jeremy Farrell[1], Josh Ottaway[1]; [1]Idaho State University

8 (406) **A Bayesian Approach to Bridge Partial Least Squares**; Kenneth Morton[1], Leslie Collins[1], Peter Torrione[1]; [1]Duke University

9 (407) **Classification and Quantification of Edible Oils and Adulterants via Adaptive Regression by Subspace Elimination**; Joshua Ottaway[1], Bryon Herbert[1], Karl Booksh[1]; [1]University of Delaware

10 (408) **Taxonomic Classification of Natural Phytoplankton Populations**; Shawna Tazik[1], Joseph Swanstrom[1], Elizabeth Abernathy[1], Tammi Richardson[1], Timothy Shaw[1], Michael Myrick[1]; [1]University of South Carolina

11 (409) **Conformational Stability Determination of Cyclohexylisocyanate by Infrared, Raman and Microwave Spectroscopy**; Xiaohua (Sarah) Zhou[1], Michael J. Tubergen[2], Ranil M. Gurusinghe[2], James R. Durig[1]; [1]University of Missouri-Kansas City, [2]Kent State University

12 (410) **Crystal Structure and Thermal Behavior of Polyglycolide Studied by Vibrational Spectroscopy, Wide Angle X-ray Diffraction, and Quantum Chemical Calculation**; Mai Miyada[1], Harumi Sato[1], Shigeki Yamamoto[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University

Board #

13 (411) **Optical Constants and Vibrational Intensities of Tribromomethane and Trichloromethane**; Dale Keefe[1], Erica Campbell[1], Karanbir Pahil[1]; [1]Cape Breton University

14 (412) **Conformational and Structural Studies of Four and Five Membered Rings from Temperature Dependent Infrared and/or Raman Spectra of Xenon Solutions and ab initio Calculations**; Joshua Klaassen[1], James Durig[1]; [1]Dept of Chemistry, University of Missouri-Kansas City

15 (413) **Wavelength Dependence of the Production of No From Photdissociated C6H5NO2**; Christopher Lue[1, 2], Chakree Tanjaroon[1, 2], Scott Reeve[1, 2], Bruce Johnson[1, 2], Susan Allen[1, 2]; [1]Arkansas Center for Laser Applications and Science, [2]Department of Chemistry and Physics, Arkansas State University-Jonesboro

16 (414) **Application of a Multistage Algorithm to a Floppy Molecule: Normal Mode Assignments for 2-ethyl-1-hexanol**; Trocia Clasp[1], Tiffani Johnson[1], Michael Sullivan[1], Hideya Koizumi[2], Scott Reeve[1, 2]; [1]Arkansas Center for Laser Applications and Science (ArCLAS), Arkansas State University, [2]Arkansas State University

17 (415) **Raman and Infrared Spectra, r0 Structural Parameters, and Vibrational Assignments of (CH3)2PX where X= H, CN, and Cl**; Bhushan Deodhar[1], Savitha Panikar[1], Dattatray Sawant[1], Joshua Klaassen[1], June Deng[1], James Durig[1]; [1]University of Missouri - Kansas City

18 (416) **Are Molecular Interactions in Ionic Liquid-Cosolvent Mixtures Predictable?**; Kristina Noack[1, 2], Florian M. Zehentbauer[3], Marta Martinez Molina[3, 4], Johannes Kiefer[3]; [1]Institute of Engineering Thermodynamics, Friedrich-Alexander-University Erlangen-Nuremberg,, [2]Erlangen Graduate School in Advanced Optical Technologies (SAOT), Friedrich-Alexander-University Erlangen-Nuremberg, [3]School of Engineering, University of Aberdeen, [4]Department of Chemical Engineering, University of Bayreuth

19 (417) **Comparison of Solvent Models for Quantum-Chemical Predictions of Peptide Conformation and Spectral Properties**; Václav Parchaňský[1, 2], Jakub Kaminský[1], Josef Kapitán[3], Petr Bouř[1]; [1]Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic,, [2]Dept of Analytical Chemistry, Institute of Chemical Technology, Prague, [3]Department of Optics, Palacký University

20 (418) **Target Detection Applied to Detection of Adulterants in Powdered Raw Material using Near Infrared Hyperspectral Imaging**; Robert Roginski[1], Neal Gallagher[1], Gregory Israelson[2]; [1]Eigenvector Research, Inc., [2]Nestle Purina

Ambient and Mass Spectrometry

Board #

21 (419) **Parallel Factor Analysis of Multi- Excitation UV Resonance Raman Spectra for Protein Secondary Structure Determination.**; Olayinka Oshokoya[1], Renee JiJi[1]; [1]University of Missouri- Columbia

22 (420) **Direct Analysis in Real Time (DART) Analysis with a Modified GC/MS System**; Joseph LaPointe[1], Elizabeth Crawford[1], Michael Festa[1], Brian Musselman[1]; [1]IonSense, Inc

23 (421) **The Effects of Hydrogen on a Helium Based Dielectric-Barrier Discharge Ambient Desorption/Ionization Source**; Jonathan Wright[1], Matthew Heywood[1], Glen Thurston[1], Paul Farnsworth[1]; [1]Brigham Young University

24 (422) **Development and Characterization of a New Concentric-Geometry Flowing Atmospheric Pressure Afterglow**; Kevin P. Pfeuffer[1], J. Niklas Schaper[2], Jacob T. Shelley[3], Steven J. Ray[1], George C.Y. Chan[1], Nicolas H. Bings[2], Gary M. Hieftje[1]; [1]Department of Chemistry, Indiana University, [2]Institute for Inorganic and Analytical Chemistry, Johannes Gutenberg University Mainz, [3]Department of Chemistry, Purdue University

25 (423) **Analysis of Cosmetic–Related Chemicals Using Desorption Electrospray Ionization Mass Spectrometry**; Jamie Nizzia[1], Adam O[1], Christopher Mulligan[1]; [1]Illinois State University

26 (424) **Forensic Applications of a Portable Mass Spectrometer Capable of Ambient Ionization**; Kyle Vircks[1], Adam O[1], Christopher Mulligan[1]; [1]Illinois State University

27 (425) **Characterization of Thermally-Assisted Desorption Electrospray Ionization Mass Spectrometry for Water Contaminant Analysis**; Alain Ton[1], Christopher Mulligan[1]; [1]Illinois State University

28 (426) **Direct Analyte-Probed Nanoextraction coupled to Nanospray Ionization-Mass Spectrometry for Analysis of Illicit Drugs**; Kristina Clemons[1], Guido Verbeck[1]; [1]University of North Texas

29 (427) **A Study of the Ionization Behavior of Several Compound Families in Low Temperature Plasma Ambient Desorption/Ionization High Resolution Mass Spectrometry**; Carsten Engelhard, Anastasia Albert; [1]University of Muenster

Forensic Applications of Spectroscopy

30 (428) **Fingerprinting Network Architectures in Model Siloxane Networks through Multivariate Statistical Analysis of Pyrolytic Degradation Profiles**; James Lewicki[1], Rebecca Albo[1], Jasmine Finnie[1], Cynthia Alviso[1], Robert Maxwell[1]; [1]Lawrence Livermore National Laboratory

31 (429) **Forensic Profiling of Dye Extracts from Millimeter-Length Cotton Fibers using Ultra Performance Liquid Chromatography and Mass Spectrometry**; Scott Hoy[1], Molly Burnip[1], Stephen Morgan[1]; [1]University of South Carolina

32 (430) **Copper Material Source Discrimination using Trace Element Concentrations**; Joshua Dettman[1], Alyssa Cassabaum[1], JoAnn Buscaglia[2]; [1]Oak Ridge Institute for Science and Education, Federal Bureau of Investigation Laboratory, [2]Federal Bureau of Investigation Laboratory

33 (431) **Detection Limits for Blood on Fabrics using Diffuse Reflection Infrared Spectroscopy**; Stephanie DeJong[1], Wayne O[1], Brianna Cassidy[1], Zhenyu Lu[1], Stephen Morgan[1], Michael Myrick[1]; [1]University of South Carolina

Board #

34 (432) **Analysis of Blue Gel Inks by Micro FT-IR Spectroscopy**; Liling Cho[1], Hung-Yi Huang[2], Chia-Ching Kuo[3], Yi-Jyun Chang[4]; [1]Central Police University, [2]Taoyuan County Police Department, [3]Central Police University

35 (433) **Analysis of Stamped Seal Ink by ATR Microspectroscopy**; Kai-Bin Huang[1], Liling Cho[1], Chia-Ching Kuo[1]; [1]Central Police University

36 (434) **Forensic Classification of Blue Gel Inks using Raman Microspectroscopy**; Liling Cho[1], Shie-Ru Wang[2], Chia-Ching Kuo[1], Kai-Bin Huang[1]; [1]Central Police University, [2]Taipei City Police Dept Forensic Science Center

37 (435) **Differentiation of Bacterial Spores Grown under Different Culture Conditions using Raman Microspectroscopy**; Joshua Dettman[1], Kristina Scott[1], Leslie McCurdy[2], Jason Bannan[3], James M Robertson[4]; [1]Oak Ridge Institute for Science and Education, FBI Laboratory, [2]Chemical, Biological, Radiological, and Nuclear Sciences Unit, FBI Laboratory, [3]Biological Sciences Program Advisor, FBI Laboratory, [4]Counterterrorism and Forensic Science Research Unit, FBI Laboratory

38 (436) **Analysis of Color Printer Inks by Raman Microspectroscopy**; Liling Cho[1], Hung-Chieh Lin[2], Yun-Seng Giang[1], Kai-Bin Huang[1]; [1]Central Police University, [2]New Taipei City Police Department Forensic Science Center

SERS: New Substrates and Analyses

39 (437) **Determination of Colloidal Gold Nanoparticle Surface Areas, Concentrations, and Sizes through Quantitative Ligand Adsorption**; Manuel Gadogbe[1], Siyam Ansar[1], Dongmao Zhang[1]; [1]Mississippi State

40 (438) **Optimization of Self-Normalizing SERS-Based Trace Detection of TNT**; Marc Wadsworth[1], Benoit Lauly[1], Paul Repasky[1], Jonathan Scaffidi[1]; [1]Miami University

41 (439) **SERS Imaging of Fungi via *in vivo* Synthesis of Gold Nanoparticles**; Fatemeh Farazkhorasani[1], Martin Prusinkiewicz[2], Susan Kaminskyj[2], Kathleen Gough[1]; [1]Department of Chemistry, University of Manitoba, [2]Department of Biology, University of Saskatchewan

42 (440) **Surface-enhanced Raman Spectroscopy (SERS) of Ricin B Chain in Whole Human Blood**; Antonio Campos[1], Marty Blaber[2], Christy Haynes[1], Richard van Duyne[2]; [1]University of Minnesota, [2]Northwestern University

43 (441) **Determination of the SERS Enhancement Factors using Solvent as an Internal Reference**; Fathima Ameer[1], Dongmao Zhang[1]; [1]Mississippi State University

44 (443) **Facile Route to the Purification and Separation of High Aspect Ratio Single-Walled Carbon Nanotubes**; Nidh Bhatt[1], Pornnipa Vichchulada[1], Marcus Lay[1]; [1]University of Georgia

45 (444) **Reduction of Electrical Resistance in Carbon Nanotube Networks through Electrochemical Nanowelding**; Darya Asheghali[1], Pornnipa Vichchulada[1], Marcus Lay[1]; [1]University of Georgia

46 (445) **Trace Detection of Hazardous Materials with Commercial Surface Enhanced Raman Scattering (SERS) Substrates**; Mikella Farrell[1]; [1]US Army Research Labs

47 (446) **Optimization and Comparison of DC Magnetron and Thermally Evaporated Polyaniline Thin Films for Chemical Sensing Platforms**; Devon Boyne, Nicola Menegazzo[1], Karl Booksh[1]; [1]University of Delaware

48 (447) **Evaluating Plasmonic Substrates by Improved Surface Plasmon Penetration Depth Calculations and Extended vis-NIR Wavelength Range**; Laurel Kegel[1], Nicola Menegazzo[1], Karl Booksh[1]; [1]University of Delaware

TECHNICAL PROGRAM – WEDNESDAY
Orals 10:20 am – 12:00 pm

Wednesday Morning, *Atlanta*
ACS DIVISION OF ANALYTICAL CHEMISTRY DISTINGUISHED SERVICE AWARD HONORING GARY HIEFTJE
Organizer and Presider: David Koppenaal

10:20 (448) **Hookah Smoking - from an Analytical Point of View!**; Joseph Caruso[1], Ryan Saadawi[1], Julio Landero[1], Traci Hanley[1], Matthew Winfough; [1]University of Cincinnati

10:40 (449) **The Long and Winding Road of Laser Ablation Inductively Coupled Plasma Mass Spectrometry**; Detlef Günther[1], Joachim Koch[1], Bodo Hattendorf[1]; [1]ETH Zurich, D-CHAB, Laboratory of Inorganic Chemistry

11:00 (450) **Time and Distance: Exploring New Instrumentation Strategies in Mass Spectrometry**; Steven Ray[1], Elise Dennis[1], Alex Graham[1], Christie Enke[3], Charles Barinaga[2], Anthony Carado[2], David Koppenaal[2], Gary Hieftje[1]; [1]Indiana University, [2]Pacific Northwest National Laboratory, [3]University of New Mexico

11:20 (451) **Pioneering Contributions and Advances in Atomic Mass Spectrometry**; David Koppenaal[1, 2], Charles Barinaga[2], Anthony Carado[1, 2], M Lizabeth Aelxander[1, 2], R Kenneth Marcus[3]; [1]Environmental Molecular Sciences Laboratory (EMSL), [2]Pacific Northwest National Laboratory, [3]Clemson University

11:40 (452) **Basic and Applied Research: The two Sides of Spectrochemical Analysis**; Nicolo Omenetto[1]; [1]University of Florida *(*2011 Applied Spectroscopy Focal Point Author)*

Wednesday Morning, *Chicago B*
APPLIED SPECTROSCOPY FOCAL POINT SESSION: SPECTROSCOPY IN THE BIOMEDICAL AND CLINICAL SCIENCES
Organizer: Steve Ray; Presider: Pavel Matousek

10:20 (453) **Using Multimodal Imaging Techniques to Monitor Limb Ischemia: A Rapid, Non-Invasive Method for Assessing Extremity Wounds**; Rajiv Luthra[1], Nicole J. Crane[1, 2], Jonathan Forsberg[1, 2, 3], Eric A. Elster[1, 2, 4]; [1]Department of Regenerative Medicine, Naval Medical Research Center, Silver Spring, MD, [2]Department of Surgery, Uniformed Services University of Health Sciences, Bethesda, MD, [3]Department of Orthopedics and Rehabilitation, Walter Reed National Military Medical Center, Bethesda, MD, [4]Department of General Surgery, Walter Reed National Military Medical Center, Bethesda, MD

10:40 (454) **Raman Molecular Imaging in the Digital Pathology Laboratory: Distinguishing Chromophobe Renal Cell Carcinoma from Renal Oncocytoma**; Shona Stewart[1], Ryan Priore[1], Heather Kirschner[1], Maria Tretiakova[2], Pat Treado[1]; [1]ChemImage Corporation, [2]University of Chicago Medical Center

11:00 (455) **Surface Enhanced Raman Spectroscopy Analysis of the Mycolic Acid Profiles of Clinical Isolates of Mycobacterial Species**; Omar Rivera[1], Russ Karls[1], Frederick Quinn[1], Richard Dluhy[1]; [1]University of Georgia

11:20 (456) **Unexpected Complications: the Effect of Trace Contaminants on Bone Raman Spectra**; Karen Esmonde-White[1], Francis Esmonde-White[2], Michael Morris[2], Blake Roessler[1]; [1]University of Michigan Medical School, [2]University of Michigan

11:40 (457) **Cell-type Discrimination in Breast Tissue with Raman Imaging**; Matthew Schulmerich[1], Michael Walsh[1], Matthew Kole[1], Krishna Tangella[2], Andre Kajdacsy-Balla[3], Rohit Bhargava[3]; [1]University of Illinois at Urbana-Champaign, [2]Provena Covinent Medical Center, [3]University of Illinois at Chicago

Wednesday Morning, *Empire A*
CHEMOMETRICS AND MOLECULAR SPECTROSCOPY
Organizers: Barry Lavine and Renee JiJi; Presider: Rene JiJi

10:20 (458) **Selecting Multivariate Calibration Basis Set Vectors to Optimize Spectroscopic Performance**; John Kalivas[1], Parviz Shahbazikhah[1], Erik Andries[2, 3]; [1]Idaho State University, [2]Central New Mexico Community College, [3]Univeristy of New Mexico

10:40 (459) **Search Prefilters for Spectral Library Matching**; Barry Lavine[1], Ayuba Fasasi[1], Jerome Workman[2]; [1]Oklahoma State University, [2]Unity Scientific LLC

11:20 (460) **Fast Chemical Classification, Quantitation, and Imaging using Digital Compressive Detection**; Dor Ben-Amotz[1], David S Wilcox[1], Brad Lucier[1], Greg Buzzard[1], Nathan Gardner[1]; [1]Purdue University

11:00 (461) **Adaptive Regression by Subspace Elimination: Refined Algorithm, Various Applications**; Karl Booksh[1], Bryon Herbeert[1]; [1]University of Delaware

11:40 (462) **Pitfalls and Practical Issues in Chemometric Applications**; Susan Rose-Pehrsson[1], Kevin Johnson[1], Robert Morris[1], Jeffrey Cramer[1], Christian Minor[2]; [1]Naval Research Laboratory, [2]NOVA Research Inc.

Wednesday Morning, *Chicago A*
LIGHT AND SEPARATIONS: A POWERFUL COMBINATION
Organizer and Presider: James E. Patterson

10:20 (463) **Single Molecule Tracking Studies of Flow-Aligned Mesoporous Silica Monoliths: Aging-Time Dependence of Pore Order**; Seok Chan Park[1], Takashi Ito[1], Daniel Higgins[1]; [1]Department of Chemistry, Kansas State University

10:40 (464) **Investigation of the Mobile Phase-Stationary Phase Interface with Vibrationally Resonant Sum-Frequency Generation: Challenges and Successes**; James Patterson[1]; [1]Brigham Young University

11:00 (465) **Characterization of Microparticles Utilizing Optical Chromatographic Methods**; Soo Kim[1], Joseph Taylor[2], Alex Terray[2], Sean Hart[2]; [1]National Research Council postdoctoral fellow, [2]Naval Research Laboratory

11:20 (466) **Molecular Diffusion in Nanopores Studied with Super Resolution Optical Microscopy**; Gufeng Wang[1], Bhanu Neupane[1], Fang Chen[1]; [1]North Carolina State University

11:40 (467) **Probing Chemical Interactions and Transport Kinetics within Single Chromatographic Silica Particles**; Joel Harris[1], Justin Cooper[1], Jay Kitt[1], Jennifer Ramirez[1]; [1]University of Utah

Wednesday Morning, *Empire B*
FORENSIC INVESTIGATIONS WITH MOLECULAR SPECTROSCOPY
Organizer and Presider: Mary Miller

10:20 (468) **The Impact of Microspectroscopy on Forensic Investigations**; John Reffner[1]; [1]John Jay College, CUNY

10:40 (469) **Investigating Product Complaints and Contaminations by Spectroscopy**; Ming Zhou[1]; [1]MVA Scientific Consultants

11:00 (470) **Advances in Microanalytical Characterization of Forensic Paint Samples: Addressing New Developments in Paint Technology**; Jennifer Herb[1], Christopher Palenik; [1]Microtrace LLC

11:20 (471) **Advances in Handheld Spectrometers and their Applications**; Michael Hargreaves, Lin Zhang, Wayne Jalenak, Robert Green, Craig Gardner[1]; [1]Thermo Scientific Portable Analytical Instruments

11:40 (472) **COTS Technology and the Future of Chemical Analysis**; Alexander Scheeline[1]; [1]University of Illinois at Urbana-Champaign

Wednesday Morning, *Chicago C*
RAMAN SPECTROSCOPY FOR PHARMACEUTICAL SURVEILLANCE AND PROCESS CONTROL
Organizer and Presider: John Kauffman

10:20 (473) **Screening "The Good, The Bad and The Ugly" Pharmaceutical Counterfeits Using Raman and NIR Spectroscopy**; Ravi Kalyanaraman[1]; [1]Bristol-Myers Squibb

10:40 (474) **Deep UV Resonance Raman Spectroscopy of Formulated Proteins**; Sergey Arzhantsev[1]; [1]US Food and Drug Administration

11:00 (475) **Raman Identification through the Pharmaceutical Supply Chain**; Jeffry Denault[1]; [1]Jeffry W Denault

11:20 (476) **Particle Identification and Material Analysis in the Biopharmaceutical Industry with Raman Microspectroscopic Technique**; Xiaolin Cao[1]; [1]Amgen Inc

11:40 (477) **A Comparative Study of In-Line Measurements for the Real-Time Determination of Particle Size during Organic Bead Milling**; Peter Hamilton[1, 2], Ha Pham-Vu[1], Thomas Bentley[1], Darryl Ertl[1], David Littlejohn[2]; [1]GlaxoSmithKline, Research Triangle Park, Durham, NC, USA, [2]CPACT/ WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK

Wednesday Morning, *Empire C*
MAKING THE MOST OF SPECTRAL AND OTHER PROCESS DATA
Organizer and Presider: David Littlejohn

10:20 (478) **Extracting Data from a Dirty Bioprocess!**; David Lovett[1]; [1]Perceptive Engineering

10:40 (479) **Hierarchical Models: Adding Logic to Data-Driven Results**; Katherine Bakeev[1], Frank Westad[2]; [1]CAMO Software Inc, [2]CAMO Software AS

11:00 (480) **Characterisation of Pigment/Polymer Processing Using *in-situ* Molecular Spectroscopy**; Alison Nordon[1], David Wilsdon[1], Suresh Thennadil[1], Jill Johnston[2], Rupert McIntyre[2], Ewan Polwart[2]; [1]University of Strathclyde, [2]FujiFILM Imaging Colorants Ltd

11:20 (481) **Some Recent Applications of Calibration Transfer for Handheld Near-infrared (NIR) Spectrometer**; Lin Zhang[1], Suzanne Schreyer[1], Dan Klevisha[1]; [1]Thermo Fisher Scientific

11:40 (482) **Challenges to Fulfill on the Deployment of Handheld Raman For a More Comprehensive Raw Materials Identification.**; Travis Thompson[1], Enrique Lozano Diz[1]; [1]B&W Tek

Wednesday Afternoon, *New York B*
RAMAN OPTICAL ACTIVITY
Organizer and Presider: Ewan Blanch

10:20 (483) **Computer Modeling of the Raman Optical Activity**; Petr Bour[1]; [1]Academy of Sciences

10:40 (484) **Raman Optical Activity in Deep UV Spectral Region**; Josef Kapitan[1, 2], Laurence D. Barron[2], Lutz Hecht[2]; [1]Department of Optics, Palacky University in Olomouc, [2]School of Chemistry, University of Glasgow

11:00 (485) **Expanding ROA Beyond Structural Biology: Studying Non-Local Chirality and Resonance Effects**; Christian Johannessen; [1]University of Manchester

11:20 (486) **Structures of Native Insulin and its Amyloid Fibril Explored by Raman Optical Activity**; Shigeki Yamamoto[1]; [1]School of Science and Technology, Kwansei Gakuin University

11:40 (487) **Vibrational Optical Activity of Cysteine in Aqueous Solution: A Comparison of Theoretical and Experimental Spectra**; Maciej Kaminski[1], Magdalena Pecul[1], Andrzej Kudelski[1]; [1]University of Warsaw, Chemistry Department

Wednesday Morning, *New York A*
NANOMATERIALS FOR PLASMONICS I
Organizer and Presider: Jean-Francois Masson

10:20 (488) **Detecting Cancer Markers using Metallic Nanostructures**; Alexandre Brolo[1], Ting Yu[1], Chiara Valsecchi[1], Koh Yiin Hong[1]; [1]University of Victoria, Department of Chemistry

10:40 (489) **Plasmonic Response at Electrified Metal-Liquid Interfaces during Faradaic and non-Faradaic Reactions by Enhanced Optical Transmission**; Paul W. Bohn[1], Sean P. Branagan[1], Yang Yang[1]; [1]University of Notre Dame

11:00 (490) **Plasmonic Imaging Sensors using 1, 2 and 3 Dimension Structured Substrates**; Michael Canva, Maha Chamtouri, Alexandra Sereda, Mondher Besbes, Anne-Lise Coutrot, Julien Moreau; [1]CNRS Institut d

11:20 (491) **Comparative Study of SPR on Nanohole Arrays in Transmission and Kretchmann Configuration**; Jean-Francois Masson[1], Maxime Couture[1], Ludovic Live[1], Anuj Dhawan[2]; [1]Universite de Montreal, [2]IIT-Delhi

11:40 (492) **On-Chip Synthesis of RNA Aptamer and Protein Microarrays for Multiplexed Protein Biosensing with SPR and SPR Phase Imaging Measurements**; Ting Seefeld[1], Yulin Chen[1], Aaron Halpern[1], Wenjuan Zhou[1], Robert Corn[1]; [1]University of California, Irvine

Wednesday Afternoon, *Chicago A*
FUNDAMENTAL ASPECTS OF PLASMA SPECTROSCOPY: USING WHAT WE LEARN TO IMPROVE ANALYTICAL ATOMIC SPECTROSCOPY
Organizer and Presider: Nicolò Omenetto

1:20 (493) **Computer Modeling for Gaining a Better Insight in Plasma Spectrochemistry**; Annemie Bogaerts[1], Maryam Aghaei[1], Peter Simon[1], Helmut Lindner[1], David Autrique[1], Zhaoyang Chen[1]; [1]University of Antwerp

1:40 (494) **High Rep-Rate Saturation Time Resolved LIF applied to Surfatron Induced Plasmas in Argon and Argon Mixtures**; Joost van der Mullen[1], Emile Carbone[1], Simon Hubner[1], Jose-M Palomares[1], Wouter Graef[1]; [1]Eindhoven University of Technology

2:00 (495) **Effect of Electron-Ion Recombination on Laser-Induced Plasmas Spectra and Consequent Implications to LIBS Elemental Analysis**; Alessandro De Giacomo[1, 2], Marcella Dell[2], Rosalba Gaudiuso[1], Olga De Pascale[2]; [1]Department of Chemistry, University of Bari, [2]IMIP-CNR

2:20 (496) **New Developments in ICP-MS**; Sam Houk[1], Chris Ebert[1], Stan Bajic[1], Dan Zamzow[1], David Baldwin[1]; [1]Ames Laboratory USDOE

2:40 (497) **Aspects of Buffer-Gas-Assisted High Irradiance Laser Ionization Source**; Wei Hang[1]; [1]Xiamen University

Wednesday Afternoon, *Empire A*
NOVEL APPLICATIONS USING THE INDUCTIVELY-COUPLED PLASMA
Organizers: Carsten Englehard and Steve Ray;
Presider: Martin Resano

1:20 (498) **Flagging Matrix Effects and System Drift in Organic-solvent Based Analysis in Axial-Viewing ICP-AES**; Yan Cheung[1], George Chan[1], Gary Hieftje[1]; [1]Indiana University

1:40 (499) **fs-LA-ICP-MS Metal Analysis of Asphaltenes Samples After Separation using Thin Layer Chromatography**; Jose Chirinos[1, 2], Jhanis Gonzalez[1], Dayana Oropeza[1], Rick Russo[1], Maria Ranaudo[2], Francia Marcano[2]; [1]Lawrence Berkeley National Laboratory, [2]Universidad Central de Venezuela

2:00 (500) **TBD**

2:20 (501) **Identifying and Overcoming Spectral Overlaps in ICP-MS Measurements of Complex Samples**; Fang Liu[1], John Olesik[1]; [1]Ohio State University, [2, 3, 4]

2:40 (502) **Elemental Analysis of Single Droplets of Means of a Sector-field Mass Spectrograph Equipped with an Integrating Array Detector**; Jeremy A. Felton[1], Yuki Kaburaki[2], Steven J. Ray[1], Roger P. Sperline[3], M. Bonner Denton[3], Charles J. Barinaga[4], David W. Koppenaal[4], Akitoshi Okino[2], Gary M. Hieftje[1]; [1]Indiana University, [2]Tokyo Institute, [3]University of Arizona, [4]Pacific Northwest National Laboratory

Wednesday Afternoon, *Atlanta*
ANACHEM AWARD SESSION HONORING PETER R. GRIFFITHS
Organizer: Peter R. Griffiths; Presiders: Peter R. Griffiths and Keith Olsen
Please note: this sessions ends at 3:20

1:20 (503) **Will Tunable Lasers Have an Impact On Mid-Infrared Spectrometry in the Next Ten Years?**; Curtis Marcott; [1]Light Light Solutions

1:40 (504) **What May be the Next Advances in mid-IR Microspectrometry?**; Carol Hirschmugl; [1]University of Wisconsin-Milwaukee *(*2012 Applied Spectroscopy Focal Point Author)*

2:00 (505) **Medical Diagnostics and via Infrared Spectral Cytopathology and Spectral Histopathology**; Max Diem[1], Benjamin Bird[1], Miloš Miljković[1], Jennifer Schubert[1], Antonella Mazur[1]; [1]Northeastern University, Lab for Spectral Diagnosis

2:20 (506) **Next Advances in Mid-Infrared Spectroscopy: IR-on-a-Chip**; Boris Mizaikoff[1]; [1]University of Ulm, Institute of Analytical and Bioanalytical Chemistry

2:40 (507) **What may be the next advances in Raman spectrometry?**; Ian Lewis[1]; [1]FACSS

3:00 (508) **Recent Progress and Advances in Biomedical Raman Spectroscopy**; Michael Blades; [1]The University of British Columbia

Wednesday Afternoon, *Chicago B*
INFORMATION-RICH APPROACHES IN BIOMEDICAL SPECTROSCOPY
Organizer: Steve Ray; Presider: Rohit Bhargava

1:20 (509) **Predicting Wound Outcome from Raman Spectroscopic Data: Univariate versus Multivariate Techniques**; Nicole Crane[1, 2], Rajiv Luthra[1], Jonathan Forsberg[1, 2, 3], Eric Elster[1, 2, 4]; [1]Department of Regenerative Medicine, Naval Medical Research Center, [2]Department of Surgery, Uniformed Services University of Health Sciences, [3]Department of Orthopaedics and Rehabilitation, Walter Reed National Military Medical Center, [4]Department of General Surgery, Walter Reed National Military Medical Center

1:40 (510) **Microfluidic Tools Coupled to Numerical Simulations to Study Membrane Protein Crystallization**; Bahige Abdallah[1], Christopher Kupitz[1], Petra Fromme[1], Alexandra Ros[1]; [1]Arizona State University

2:00 (511) **Identifying the Differentiation Stages of Individual Hematopoietic Cells from Mice by Multivariate Analysis of Secondary Ion Mass Spectra**; Mary L. Kraft[1, 2], Jessica F. Frisz[2], Ji Sun Choi[1], Robert L. Wilson[2], Brendan A. C. Harley[1]; [1]University of Illinois, Department of Chemical and Biomolecular Engineering, [2]University of Illinois, Department of Chemistry

2:20 (512) **Transmission Raman Tomography on a Cylindrical Tissue Phantom**; Matthew R Kole[1], Matthew V Schulmerich[1], Matthew K Gelber[1], Rohit Bhargava[1, 2]; [1]University of Illinois at Urbana-Champaign, Department of Bioengineering, [2]Department of Electrical and Computer Engineering, Department of Mechanical Science and Engineering, University of Illinois Cancer Center

2:40 (513) **Determination of Spectroscopic Uncertainty for Non-Linear Regression Models and Its Implications for Biomedical Diagnostics**; Ishan Barman[1], Narahara Chari Dingari[1], Jaqueline S. Soares[1], Gajendra Pratap Singh[1], Ramachandra Rao Dasari[1], Janusz Smulko[2]; [1]G.R. Harrison Spectroscopy Laboratory, MIT, [2]Gdansk University of Technology

Wednesday Afternoon, *Empire B*
MOLECULAR SPECTROSCOPY AS A PHYSICIAN'S FRIEND
Organizer and Presider: Linda Kidder

1:20 (514) **Discrimination of Live Cell Differentiation Using Confocal Raman Spectroscopy**; Sota Takanezawa[1, 2], Shin-ichi Morita[1], Michio Hiroshima[1], Toshiyuki Mitsui[3], Yukihiro Ozaki[2], Yasushi Sako[1]; [1]RIKEN, [2]Kwansei Gakuin University, [3]Aoyama Gakuin University

1:40 (515) **High Resolution Imaging of Breast Calcification**; Marleen Kerssens[1, 4], Alina Zoladek[2], Pavel Matousek[3], Sergei Kazarian[2], Keith Rogers[4], Nick Stone[1, 4]; [1]Biophotonics Research Unit GRH NHS FT, [2]Imperial College, [3]Central Laser Facility, Rutherford Appleton Laboratory, [4]Cranfield University

2:00 (516) **An Assessment of Stored Red Blood Cells Using Raman Spectroscopy**; Chad Atkins[1], H. Georg Schulze[2], Michael Blades[1], Robin Turner[1, 2]; [1]University of British Columbia, [2]Michael Smith Laboratories

2:20 (517) **Sensitive and Specific Detection of Long-Term Glycemic Markers using Raman Spectroscopy**; Narahara Chari Dingari[1], Ishan Barman[1], Jaqueline Soares[1], Gary Horowitz[2], Ramachandra Dasari[1]; [1]Laser Biomedical Research Center, G. R. Harrison Spectroscopy Laboratory, Massachusetts Institute of Technology, [2]Division of Clinical Pathology, Beth Israel Deaconess Medical Center, Harvard Medical School

2:40 (518) **Flexible Correction in Spectroscopic Calibration for Noninvasive Glucose Tracking using a Physiological Glucose Dynamics Model**; Nicolas Spegazzini[1], Ishan Barman[2], Narahara Chari Dingari[2], Gajendra Pratap Singh[2], Ramachandra Rao Dasari[2], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]Massachusetts Institute of Technology

TECHNICAL PROGRAM – WEDNESDAY
Orals 1:20 – 3:00 pm and 3:50 – 5:30 pm

Wednesday Afternoon, *New York B*
YOUNG SCIENTISTS IN SERS
Organizer and Presider: Duncan Graham

1:20 (519) **Developing Improved Systems for the Reliable Detection of Analytes using Surface-Enhanced Raman Scattering (SERS) Techniques**; Brandon Scott[1], Keith Carron[1]; [1]University of Wyoming

1:40 (520) **SERS Nanoparticles for Biological Sensing**; Brent DeVetter[1], Sean Sivapalan[1], Timothy Yang[1], Thomas van Dijk[1], Matthew Schulmerich[1], P. Scott Carney[1], Catherine Murphy[1], Rohit Bhargava[1]; [1]University of Illinois at Urbana-Champaign

2:00 (521) **Looking Inside Catalyst Extrudates with Time-Resolved Surface-Enhanced Raman Spectroscopy**; Clare Harvey, Ingeborg Iping Petterson[, 2], Bert Weckhuysen[1], Cees Gooijer[2], Freek Ariese[2], Arjan Mank[3]; [1]Utrecht University, [2]VU University Amsterdam, [3]Philips Innovation Services

2:20 (522) **Shell Isolated Nanoparticle Enhance Raman Spectroscopy (SHINERS) Using a Picosecond Excitation Source**; Wenbin Jiang[1], Gary Rayson[1]; [1]Department of Chemistry and Biochemistry. New Mexico State University[4]

2:40 (523) **Detection and Identification of Influenza Virulence Factors**; Pierre Negri[1], Cheryl A. Jones[2], Stephen M. Tompkins[2], Richard A. Dluhy[1]; [1]Department of Chemistry, University of Georgia, [2]Department of Infectious Diseases, University of Georgia

Wednesday Afternoon, *Chicago C*
AMBIENT IONIZATION TECHNIQUES FOR FORENSICS, SECURITY AND BIOLOGICAL ANALYSIS
Organizer and Presider: Demian Ifa

1:20 (524) **Improved Spatial Resolution in the Imaging of Biological Tissue using Desorption Electrospray Ionization**; Dahlia I. Campbell[1], Christina R. Ferreira[1], Livia S. Eberlin[1], R. Graham Cooks[1]; [1]Purdue University

1:40 (525) **Forensic Analysis of Illicit Drugs and Trace Explosives using Ambient Pressure Ionization Mass Spectrometry**; Tim Brewer[1], Jennifer Verkouteren[1], Greg Gillen[1]; [1]National Institue of Standards and Technology

2:00 (526) **DART-MS in Forensic Science: Synthetic Cannabinoids and Other Applications**; Jason Shepard[1], Rabi Musah[1], Marek Domin[2]; [1]University at Albany, SUNY, [2]Boston College

2:20 (527) **Schlieren Diagnostics of a Flowing Atmospheric Pressure Afterglow (FAPA) Ambient Desorption/Ionization Source**; Kevin P. Pfeuffer[1], Steven J. Ray[1], Gary M. Hieftje[1]; [1]Department of Chemistry, Indiana University

2:40 (528) **Femtosecond Laser Vaporization of Complex Molecules: Nonequilibrium Electrospray Ionization Preserves Noncovalent Interactions**; Robert Levis; [1]Center for Advanced Photonics Research, Temple University

Wednesday Afternoon, *Empire C*
INNOVATIONS IN OPTICAL INSTRUMENTATION
Organizer: Steve Ray; Presider: Dimitri Pappas

1:20 (529) **An Optical Fiber-Based Sensor Array For Multi-Elemental Analysis in Aqueous Environments**; Steven Kopitzke[1], Peter Geissinger[1]; [1]University of Wisconsin-Milwaukee

1:40 (530) **Fiber-Optic Probes with Microscale Optics**; Francis Esmonde-White[1], Cynthia Cipolla[1], Michael Morris[1], Robert Kennedy[1]; [1]University of Michigan, Dept. of Chemistry

2:00 (531) **An Anisotropic Virtually Imaged Phased Array (VIPA) Spectral Disperser for Raman and Brillouin Spectroscopy**; Rajesh Morampudi[1], John Turner[1]; [1]Cleveland State University

2:20 (532) **Low-Frequency Raman Spectroscopy - Enabling Affordable Access to the Terahertz Regime**; James Carriere[1], Frank Havermeyer[1]; [1]Ondax

2:40 (533) **The Multi-channel FTIR, a New Interferometer Solution for Fast and Pulsed Spectral Sensing**; Sascha Pierre Heussler[1], Herbert Oskar Moser[2]; [1]SSLS/NUS, [2]KIT/NES IMT

Wednesday Afternoon, *New York A*
NANOMATERIALS FOR PLASMONICS II
Organizer and Presider: Jean-Francois Masson

1:20 (534) **Role of Plasmon Interactions in Surface-Enhanced Raman Scattering Immunoassays Based on Labeled Gold Nanoparticles**; Marc Porter[1]; [1]University of Utah

1:40 (535) **What is "Robust Surface Chemistry" for LSPR Sensors?**; Amanda Haes[1]; [1]University of Iowa[4]

2:00 (536) **Spatial Control of Light at the Nanoscale Using Plasmonic Nanocrescents**; Cindy Cooper[1], Cara Barnes[1], Christopher Gore[1], Jennifer Shumaker-Parry[1]; [1]University of Utah

2:20 (537) **Gold Plated Filters for Minimizing Time and Complexity of a SERS-based Immunoassay**; Jeremy Driskell[1], David Drake[1]; [1]Illinois State University

2:40 (538) **Patterned Plasmonic Arrays with Differential Resonance for High-Performance SPR Analysis**; Quan Cheng[1], Matthew Linman[1], Abdennour Abbas[1]; [1]University of California Riverside

3:00 – 3:50 pm Exhibit Hall A
DESSERT BREAK AND POSTER VIEWING

Wednesday Afternoon, *Chicago A*
SAMPLING THE WORLD WITH LASER ABLATION AND ATOMIC SPECTROSCOPY
Organizer and Presider: Jhanis J. Gonzalez

3:50 (539) **Ash Composition Analysis of Herbaceous and Woody Biomass Using Laser-Induced Breakdown Spectroscopy (LIBS)**; Tyler Westover[1], Garold Gresham[1], Richard Boardman[1]; [1]Idaho National Laboratory

4:10 (540) **Uranium Isotope Detection in Standard Reference Material Glasses with femto-Second Laser Ablation Multicollector Mass Spectrometry**; Gregory C. Eiden[1], Andrew M. Duffin[1], Garret L. Hart[1]; [1]Pacific Northwest National Laboratory

4:30 (541) **The Effect of Sample Composition on the Interaction between Laser Generated Aerosol and the ICP**; Luca Flamigni[1], Olga Borovinskaya[1], Joachim Koch[1], Detlef Günther[1]; [1]ETH Zurich

4:50 (542) **Preparation of Surrogate Standards for Trace Element Analysis of Biological Tissues via Laser Ablation Inductively Coupled Plasma Mass Spectrometry**; Jenee Jacobs[1, 2], R. S. Houk[1, 2]; [1]Iowa State Univ, [2]Ames Laboratory

5:10 (543) **Diagnostic and Modeling of Laser Induced Breakdown Spectroscopy Based on Optical Tomography**; Igor Gornushkin[1], Sergei Shabanov[2], Ben Smith[3], Nicolo Omenetto[3], Sven Merk[1], Alexander Demidov[1], Ulrich Panne[1,4]; [1]BAM Federal Institute for Materials Research and Testing, [2]Department of Mathematics, University of Florida, [3]Department of Chemistry, University of Florida, [4]Humboldt-Universität zu Berlin, Department of Chemistry

TECHNICAL PROGRAM – WEDNESDAY
Orals 3:50 – 5:30 pm

Wednesday Afternoon, *Empire A*
STUDENT POSTER AWARDS
Organizer and Presider: Mike George

3:50 TBD
4:10 TBD
4:30 TBD
4:50 TBD
5:10 TBD

Wednesday Afternoon, *Empire C*
APPLIED SPECTROSCOPY FOCAL POINT SESSION: NOVEL MICROSCOPIC AND SPECTROSCOPIC TECHNIQUES AT THE NANOSCALE
Organizer: Steve Ray; Presider: Kathleen Gough

3:50 (544) **What Lies Beneath: Broadened Absorption Spectra of Biomolecules Exposed**; Hannah Wagie[1], Bradley Moran[1], Jörg Woehl[1], Peter Geissinger[1]; [1]University of Wisconsin-Milwaukee *(*2012 Applied Spectroscopy Focal Point Author)*

4:10 (545) **Chemical Imaging Beyond the Diffraction limit: Experimental Validation of the PTIR Technique**; Andrea Centrone[1, 2], Basudev Lahiri[1, 2], Glenn Holland[1]; [1]NIST, Center for Nanoscale Science and Technology, [2]University of Maryland, Institute for Research in Electronics and Applied Physics (IREAP)

4:30 (546) **Nano-FTIR: Infrared Spectroscopic Chemical Identification of Materials at Nanoscale**; Florian Huth[1, 2], Alexander Govyadinov[1], Martin Schnell[1], Jesper Wittborn[3], Nenad Ocelic[2], Sergiu Amarie[2], Wiwat Nuansing[1], Fritz Keilmann[4], Rainer Hillenbrand[1], [1]CIC Nanogune Consolider, [2]Neaspec GmbH, [3]Infineon Technologies AG, [4]Dept. of Physics and CeNS, Ludwigs-Maximilians-Universität

4:50 (547) **Whispering Gallery Mode Imaging for Biomarker Detection**; Robert Dunn, Sarah Wildgen, Heath Huckabay; [1]University of Kansas

5:10 (548) **IRENI - Synchrotron-based Wide-Field Infrared Spectrochemical Imaging at the Diffraction Limit**; Kathleen Gough[1], Carol Hirschmugl[2]; [1]University of Manitoba, [2]University of Wisconsin-Milwaukee *(*2012 Applied Spectroscopy Focal Point Author)*

Wednesday Afternoon, *Chicago B*
DROPLETS, DIGITAL MICROFLUIDICS, AND SINGLE CELL CHEMICAL ANALYSIS
Organizers: Steve Ray and Alexander Scheeline; Presider: Alexandeer Scheeline

3:50 (549) **Levitated Drops as Microreactors: How Far Did We Get?**; Alexander Scheeline[1], Edward Chainani[1], Khanh Ngo[1], Woo-Hyuck Choi[1]; [1]University of Illinois at Urbana-Champaign

4:10 (550) **Spectroscopic Analysis in Acoustically Levitated Droplets**; Merwe Albrecht[1], Jonas Schenk[1], Arne Stindt[1], Jens Riedel[1], Ulrich Panne[1, 2]; [1]BAM Federal Institute for Materials Research and Testing, [2]Humboldt-Universität zu Berlin, Department of Chemistry

4:30 (551) **Partial Coalescence of Charged Droplets for Reagent Delivery in Water-in-Oil Microfluidics**; Carina Minardi[1], Mazdak Taghioskoui[1], Kaveh Jorabchi[1]; [1]Georgetown University

4:50 (552) **Bioparticle Capture in a Sawtooth Dielectrophoretic Microchannel**; Paul Jones[1], Mark Hayes[1]; [1]Arizona State University

5:10 (553) **Variability in Single Cell Phytoplankton Fluorescence**; Joseph Swanstrom[1], Tammi Richardson[1], Timothy Shaw[1], Michael Myrick[1]; [1]University of South Carolina

Wednesday Afternoon, *Empire B*
INDUSTRIAL APPLICATIONS OF VIBRATIONAL SPECTROSCOPY
Organizer: Linda Kidder; Presider: Dimuthu Jayawickrama

3:50 (554) **Determination of Polymer Entities in Complex Systems using Near Infrared Spectroscopy And Chemometrics**; Yusuf Sulub, Ph.D.[1], James DeRudder, Ph.D.[1]; [1]SABIC

4:10 (555) **Characterization of Mechanical Deformation in Crystalline Poly(ethylene) Films Using Vibrational Spectroscopy**; Gloria M. Story[1], R. Thomas Cambron[1]; [1]P&G

4:30 (556) **Soil Analysis with Infrared Spectroscopy**; Hui Li[1]; [1]Bruker Optics, Inc

4:50 (557) **Real-Time Monitoring of a Continuous Pharmaceutical Blend Process by FT-NIR Spectroscopy**; Chris Heil[1], Dave Drapcho[1]; [1]Thermo Fisher Scientific

5:10 (558) **Internal Multiple Scattering Hole Enhanced Raman Spectroscopy: Improved Backscattering FT-Raman Sampling in Pharmaceutical Tablets Utilizing Cylindrical -Conical Holes**; Peter J. Larkin[1], Matthew Santangelo[2], Slobodan Sasic[3]; [1]Bristol-Myers Squibb, [2]Pfizer Pharmaceuticals, [3]Vertex Pharmaceuticals

Wednesday Afternoon, *Atlanta*
CELEBRATING 120 YEARS OF THE INFRARED AND RAMAN DISCUSSION GROUP AND THE COBLENTZ SOCIETY
Organizers and Presiders: Michael W. George and Ian R. Lewis

3:50 (559) **Ultrasound Enhanced ATR mid-IR Fibre Optic Probe for Spectroscopy of Particles in Suspensions**; Cosima Koch[1], Maria Reyes Plata Torres[1], Stefan Radel[1], Bernhard Lendl[1]; [1]Vienna University of Technology

4:10 (560) **Validating *in vivo* Transcutaneous Raman Spectroscopy of Bone for Humans**; Francis W. L. Esmonde-White[1]; [1]University of Michigan

4:30 (561) **Gone in 60 Milliseconds:Fast IR with a Planar Array Spectrograph**; Bruce Chase[1], Dan Frost[1], John Rabolt[2]; [1]Pair Technologies LLC, [2]University of Delaware

4:50 (562) **Following Catalytic Processes in both Solution and Solid State with Fast Time-Resolved Infrared Spectroscopy**; Michael W. George[1]; [1]University of Nottingham

5:10 (563) **Infrared Spectroscopic Imaging: the Next Generation**; Rohit Bhargava[1]; [1]University of Illinois at Urbana-Champaign *(*2012 Applied Spectroscopy Focal Point Author)*

Wednesday Afternoon, *New York B*
DISEASE DIAGNOSTICS USING SERS
Organizer and Presider: Duncan Graham

3:50 (564) **Towards Portable Diagnostics: Development of Colloidal SERS Assays**; Patrick Johnson[1], Ashley Driscoll[1], Jing Neng[1], Hao Zhang[1]; [1]University of Wyoming

4:10 (565) **Novel Detection of MRSA using Surface Enhanced Raman Scattering (SERS)**; Mhairi Harper[1], Karen Faulds[1], Duncan Graham[1]; [1]University of Strathclyde

4:30 (566) **Identifying the Genetic Markers of Highly Pathogenic Influenza by SERS**; Richard Dluhy[1]; [1]University of Georgia

4:50 (567) **Challenges in Moving SERS-based Diagnostics from the Analytical Chemistry Laboratory to the Clinic**; Marc Porter[1]; [1]University of Utah

Wednesday Afternoon, *Chicago C*
AMBIENT MASS SPECTROMETRY: FUNDAMENTAL FINDINGS AND THE FUTURE
Organizer and Presider: Jacob T. Shelley

3:50 (568) **Alternative Desorption/Ionization Processes of Low-Temperature Plasma Probe Mass Spectrometry**; Joshua Wiley[1], Jobin Cyriac[1], Jacob Shelley[1], R. Graham Cooks[1]; [1]Purdue University

4:10 (569) **Nanoscale Molecular Cartography: Towards Combined Topographical and Chemical Imaging using Atomic Force Microscopy and Mass Spectrometry**; Olga S. Ovchinnikova[1], Gary J. Van Berkel[1]; [1]Oak Ridge National Laboratory

4:30 (570) **Characterization and Application of Microplasma Devices for Ambient Mass Spectrometry and Surface Analysis**; Joshua Symonds, Reuben Gann, Thomas Orlando; [1]Georgia Institute of Technology

4:50 (571) **Paper Spray Ionization Mass Spectrometry Mechanism: So much more than a Variant of Electrospray**; Ryan Espy[1], Ariel Muliadi[1], Zheng Ouyang[1], R. Graham Cooks[1]; [1]Purdue

5:10 (572) **Paper-SAW: Surface Acoustic Wave MEMS Devices for the Rapid Aerosolization and Ionization of Liquid Samples**; David Go[1]; [1]University of Notre Dame

Wedneday Afternoon, *New York A*
NANOMATERIALS FOR PLASMONICS III
Organizer and Presider: Jean-Francois Masson

3:50 (573) **New Directions in Plasmonic Materials and SERS Applications**; George Schatz[1]; [1]Northwestern University

4:10 (574) **Localized Surface Plasmon Resonance Properties of Gold Nanoplates Coupled with Gold Nanopartcles at Edge Sites**; Francis Zamborini[1], Lanlan Bao[1], Srinivas Beeram; [1]University of Louisville

4:30 (575) **Sensing of Nucleic Acids using Fluorescent Plasmonic Core-Shell Nanoparticles**; Denis Boudreau[1], Olivier Ratelle[1], Marie-Christine Dorais[1], Luc Rainville[1], Danny Brouard[1], Félix-Antoine Lavoie[1]; [1]Département de chimie and Centre d'optique, photonique et laser (COPL), Université Laval

4:50 (576) **Plasmonic Properties of Silver Nanocube Monolayers on High Refractive Index Substrates**; Anatoli Ianoul[1], Adam Bottomley[1], Daniel Prezgot[1], Alyssa Staff[1]; [1]Carleton University

5:10 (577) **Competitive Organothiol and Protein Adsorption onto Gold Nanoparticles**; Karthikeswar Vangala[1], Siyam Ansar[1], Dongmao Zhang[1]; [1]Mississippi State University

TECHNICAL PROGRAM – THURSDAY
Plenary Lectures, Exhibit Hall B
Presider: Michael George

8:00 am – SAS Applied Spectroscopy William F. Meggers Award
(578) Spatial Heterodyne Raman Spectrometer for Wide-Area Standoff Detection; **Mike Angel**, Nathaniel Gomer, Nirmal Lamsal; Univ. of South Carolina, Dept. of Chem. & Biochem

8:30 am – SAS Lester W. Strock Award
(579) Vapor Generation - Make it Your Second Thought for Sample Introduction; **Ralph Sturgeon**; National Research Council of Canada

Thursday Poster Session
9:00 – 10:20 am
Exhibit Hall B

All Thursday posters should be put up between 7:30 – 8:00 am and removed by 5:30 pm

Atomic Spectroscopy: Sample Introduction and New Technology

Board #

1 (580) **Investigating the Performances of Transition Metal Cyanide Complexes for Determination of Cadmium by Vapor Generation ICP-MS**; Zikri Arslan[1], Vedat Yilmaz[1,2], LaKeysha Rose[1]; [1]Jackson State University, [2]Erciyes University

2 (581) **"Microarc" Discharge for Solution Sampling into an Inductively Coupled Plasma Mass Spectrograph**; Jeremy Felton[1], José A. C. Broekaert[2], Steven J. Ray[1], Roger P. Sperline[3], M. Bonner Denton[3], Charles J. Barinaga[4], David W. Koppenaal[4], Gary M. Hieftje[1]; [1]Indiana University, [2]Universität Hamburg, [3]University of Arizona, [4]Pacific Northwest National Laboratory

3 (582) **prepFAST Inline Auto Calibration, Variable Auto Dilution, and Auto QC Dilution for ICP and ICPMS**; Nathan Saetveit[1], Paul Field[1], Austin Schultz[1], Daniel Wiederin[1]; [1]Elemental Scientific

4 (583) **Metal Determination in Cosmetics by ICP – Comparative Study between Borate and Peroxide Fusions using TheOx Electric Fluxer**; John A. Anzelmo[1], Janice Pitre[1], Melanie Bedard[1]; [1]Claisse, Corporation Scientifique

5 (584) **Achieving a Hotter Plasma with an All-Ceramic Torch**; Ryan Brennan, Jerry Dulude, Jol Desmarchelier; [1]Glass Expansion,

6 (585) **Chemical and Petrochemical Applications of Microwave Plasma – Atomic Emission Spectroscopy (MP-AES)**; Doug Shrader[1], Steve Wall[1], Phil Lowenstern[1]; [1]Agilent Technologies

7 (586) **Automated, Syringe-Based Preconcentration, Matrix Removal, and Calibration for ICP and ICPMS**; Nathan Saetveit[1], Daniel Wiederin[1]; [1]Elemental Scientific

8 (587) **Advances in Enhanced Productivity Sample Introduction Accessories for ICP Spectrometry**; Ryan Brennan[1], Jerry Dulude[1], Scott Bridger[1], Vesna Dolic[1]; [1]Glass Expansion

9 (588) **Coupling of an Inert Ion Chromatographic System with ICP-Q-MS for Robust and Accurate Metal Speciation Analyses**; Lothar Rottmann[1], Daniel Kutscher[1], Shona McSheehy[1], Julian Wills[1]; [1]Thermo Fisher Scientific, Bremen

10 (589) **Improved Throughput for Analysis by ICP-OES Using Next Generation Sample Introduction Technology**; Steve Wall[1], Doug Shrader[1], Phil Lowenstern[1]; [1]Agilent Technologies

Atomic Spectrometry: Speciation Analysis and Environmental Applications

Board #

11 (590) **Analysis of Fish Otoliths by Cold Vapor Generation ICP-MS for Mercury- Could Mercury be a Useful Tracer of Fish History?**; Zikri Arslan[1], Mehmet Ates[1], Erdal Kenduzler[2]; [1]Jackson State University, [2]Mehmet Akif Ersoy University

12 (591) **Advancements in ICP-OES Plasma Generation and Application to Environmental Sample Analysis**; Laura Thompson[1], Angela LaCroix-Fralish[1]; [1]PerkinElmer, Inc

13 (592) **Tissue-dependent Metal Ion Affinity for a Datura Innoxia Biosorbent**; Richie Eriacho, Jessica Moore, Debbie Serna, Gary Rayson; [1]Department of Chemistry and Biochemistry, New Mexico State University

14 (593) **Tissue Chemical Variability in Eu(III) Passive Binding Thermodynamics to Datura innoxia Biosorbents**; Gary Rayson[1], Jessica Moore[1], Debbie S[1], Richie Eriacho[1], Fengshan Jiang[1]; [1]Department of Chemistry and Biochemistry, New Mexico State University

15 (594) **Solid Sampling High-Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry to Monitor the Ag body Burden in Individual Daphnia Magna Specimens Exposed to Ag Nanoparticles**; Esperanza García-Ruiz[1], Ana Cristina Lapeña[1], Miguel Angel Belarra[1], Martín Resano[1]; [1]University of Zaragoza

16 (595) **ICP-MS and HPLC-ICP-MS Used as a Tool to Monitor Trends in Inorganic Contaminants in Mussels from a Previously Polluted Fjord**; Daniel Fliegel[1], Astrid J. Meyer[1], Sylvia Frantzen[1], Joar Øygard[1], Kåre Julshamn[1], Amund Maage[1]; [1]National Institute of Nutrition and Seafood Research

17 (596) **Silver Nanoparticle and Ion Toxicity in Saltwater Alga Skeletonema Costatum**; Nicole Hanks[1]; [1]University of Cincinnati

18 (597) **Characterization by HPLC-ICP-MS of Algal Extracts and Water in Evaporation Ponds**; Christopher M. W. Medley[1]; [1]University of Cincinnati

Environmental Analysis

19 (598) **Solid Phase Extraction, QuEChERS Cleanup with LC-MS/MS as an Improved Method for Analyzing Five Estrogens in Wastewater**; Sameera Gunatilake[1], Shelby Steelhammer[1], Todd Mlsna[1], Kang Xia[1,3], Jeong-Wook Kwon[2], Kevin Armbrust[2]; [1]Department of Chemistry, Mississippi State University, [2]Mississippi State Chemical Laboratory, [3]Department of Crop and Soil Environmental Sciences, Virginia Polytechnic Institute and State University

Board #

20 (599) **Pharmaceuticals and Phytosanitary Water Pollution: Combined Raman Spectroscopy and Multivariate Data Analysis**; Ivana Durickovic[1], Mario Marchetti[1]; [1]CETE de l

21 (600) **Quantification of Dicyandiamide (DCD) in Fresh Water Environment**; Shelby Steelhammer[1], Todd Mlsna[1], Dongdi Sun[1], Sameera Gunatilake[1]; [1]Mississippi State Univ.

22 (601) **Interaction Study of Bovine Serum Albumin with Formaldehyde by Flow Injection Chemiluminescence Analysis**; Xijuan Tan[1], Zhenghua Song[1]; [1]Northwest Univ.

23 (602) **Determination of Methane and Formaldehyde Concentrations in Jonesboro, AR**; Sindhu Kaimal[1], Scott Reeve[1]; [1]Arkansas State University

24 (603) **Assessment of possible Impact of Industrial Activities and the Use of Agrochemicals on the levels of Toxic Chemicals in the Natural Environment.**; ElMukhtar Belgasem; [1]Tripoli University

Fuel, Biomass, and Exhaust Analysis

25 (604) **Measurement of Nitro-Compounds in Automobile Exhaust with IR CRDS Method**; Hiroyuki Yamada[1]; [1]National Traffic Safety and Environment Laboratory

26 (605) **Determination of Ester Content in Biodiesel -- Modification in the Existing EN 14103 method**; Dheer Singh[1], Anju Chopra[1], A.K. Tewari[1], M.I.S. Sastry[1], M.B. Patel[1], B. Basu[1]; [1]Indian Oil Corporation Limited

27 (606) **Challenges and Opportunities in On-Line Monitoring of Thermochemical Biomass Processes**; Daniel Carpenter[1], Marc Pomeroy[1]; [1]National Renewable Energy Laboratory

28 (607) **Defining the Relationships between Fuel Composition and Performance Properties Using Compound Profiles and Shape-Based Analysis of GC-MS Data**; Jeffrey Cramer[1], Robert Morris[1]; [1]U.S. Naval Research Laboratory

Polymer Spectroscopy and Materials Analysis

29 (608) **Quantification of Rubber in High Impact Polystyrene by NMR, Raman Spectroscopy and Chemometrics. Confrontation Fitting Method and Chemometrics**; Nadège Brun[1], Patrice Bourson[1], Samuel Margueron[1]; [1]LMOPS - University of Lorraine

30 (609) **Establishment of Patterns and Control of high Temperature Oxidation Flaws of Low-Density Polyethylene with the Raman Spectroscopy**; Vietmann Marie[2], Jumeau Richard[1,2], Bourson Patrice[1], François Lahure[2], Michel Ferriol[1]; [1]LMOPS University of Lorraine, [2]Total Petrochemicals France, Usine de Carling - Saint-Avold

31 (610) **Variable Temperature Raman Spectra, Structural Parameters and Vibrational Assignments of Ethylenediphosphine**; Savitha S. Panikar[1], James R. Durig[1], Victor F. Kalasinsky[2]; [1]University of Missouri-Kansas City, [2]Armed Forces Institute of Pathology

32 (611) **Intermolecular Vibrations of poly-(R)-3-hydroxybutyrate in Low-Frequency Raman and THz Time-Domain Spectra Explored by DFT Calculation with Cartesian Coordinate Tensor Transfer**; Shigeki Yamamoto[1], Yusuke Morisawa[1,2], Hiromichi Hoshina[3], Shinya Ishii[3,4], Harumi Sato[1], Chiko Otani[3], Yukihiro Ozaki[1]; [1]Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, [2]Department of Chemistry, School of Science and Engineering, Kinki University, [3]RIKEN, 519-1399 Aramaki-Aoba, [4]Miyagi University of Education, 149 Aramaki-Aoba

Board #

33 (612) **Raman Spectroscopy and High-Resolution Transmission Electron Microscopy as Complementary Techniques to Investigate Natural nm Thin Graphitic Films**; Daniel Fliegel[1], Mark van Zuilen[2], Richard Wirth[3], Aivo Lepland[4], Yuangao Qu, Anja Schreiber, Alexander E. Romashkin, Pascal Philippot[2]; [1]National Institute of Nutrition and Seafood Research, [2]Equipe Géobiosphère, Institut de Physique du Globe de Paris - Sorbonne Paris Cité, Université Paris Diderot, [3]GeoForschungsZentrum Potsdam, Telegrafenberg, Chemistry and Physics of Earth Materials, [4]Geological Survey of Norway, Leiv Eirikssons vei 39

34 (613) **Raman and X-Ray Diffraction Studies of Cadmium Zinc Telluride (CZT) and Ambient Temperature and Pressure Effected Chemical Contaminants**; Dale L Perry[4], Daniel Sneed[1], Andrew Knudson[2], Lewis Jones[3], John W Farley[1]; [1]University of Nevada, Las Vegas, [2]Sierra College (CA), [3]Morehouse College, [4]Lawrence Berkeley National Laboratory, University of California

35 (614) **Using FT-IR to Investigate the Behavior of Carboxylate Based Monolayers on Titanium Dioxide at High Temperatures**; Catherine G. McKenas[1], Karla S. McCain[1]; [1]Austin College

36 (615) **Electric Field Effect on the Infrared Spectra of Ferroelectric Poly(vinylidene fluoride-hexafluoropropylene) (PVDF/HFP) and Nylon 11 Films**; Hayato Isoda[1], Yukio Furukawa[1]; [1]Graduate School of Advanced Science and Engineering, Waseda University

37 (616) **Thiol on Gold Stability and Impact on Atom Transfer Radical Polymerization (ATRP) of Styrene at Various Temperatures**; Richard Osibanjo[1]; [1]University of California Davis

38 (617) **Reverse Engineering of Polymeric Multilayers using AFM-based Nanoscale IR Spectroscopy and Thermal Analysis**; Mike Lo[1], Tom Eby[2], Usha Gundusharma[2], Khoren Sahagian[1], Curtis Marcott[3], Kevin Kjoller[1]; [1]Anasys Instruments Corp., [2]Kimberkley Clark Corporation, [3]Light Light Solutions, LLC

39 (618) **External Electric Field Effect on the Infrared Spectra of Ferroelectric Vinylidene Fluoride/Trifluoroethylene Copolymer Thin Films**; Kenji Takashima[1], Yukio Furukawa[1]; [1]Waseda Univ

40 (619) **Crystallinity Evaluation of a Biodegradable Polymer by using the new NIR Camera (Compovision) Developed for High Speed Wide Area Measurement**; Daitaro Ishikawa[1], Takashi Nishii[1], Fumiaki Mizuno[2], Harumi Sato[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]Sumitomo Electric Industries, Ltd

41 (620) **Conformational and Structural Studies of n-propylamine from Temperature Dependent Raman and Far Infrared Spectra of Xenon Solutions and ab initio Calculations**; Ikhlas Darkhalil[1], Joshua Klaassen[1], Wouter Herreboutb[2], Johan Domb[2], Benjamin van der Vekenb[2], James Durig[1]; [1]Department of Chemistry, University of Missouri-Kansas City, [2]Department of Chemistry, Universitair Centrum Antwerpen

42 (621) **Local Structure Determination of Thin-Film Boron Carbides**; Wenjing Li[1], Michelle Paquette[1], Sky Driver[1], Sudarshan Karki[1], Bradley Nordell[1], Anthony Caruso[1], Nathan Oyler[1]; [1]University of Missouri-Kansas city

43 (622) **Applications of Headspace GC/MS Methods for Assessment of Polymer Aging**; James Lewicki[1], Rebecca Alba[1], Cynthia Alviso[1], Robert Maxwell[1]; [1]LLNL

Food, Bio-Extract, and Materials Characterization

Board #

44 (623) **Analysis of Inorganic Anions in CVD snd ALD Precursors gor Semiconductor Industry**; Abul Azad[1], Hugh Gotts[2]; [1]Balazs Nanoanalysis, Air Liquide Electronics U.S. LP, 13546 N. Central Expressway, [2]Balazs Nanoanalysis, Air Liquide Electronics U.S. LP, 46409 Landing Pkwy

45 (624) **Optimization and Validation of a Solid-Phase Microextraction Method for Determination of Volatile Organic Compounds from Aspergillus Flavus by Gas Chromatography Mass Spectrometry**; Dongdi Sun[1], Alicia Wood-Jones[2], Todd Mlsna[1], Richard Baird[2]; [1]Chemistry Department, Mississippi State University, [2]Department of Entomology & Plant Pathology, Mississippi State University

46 (625) **Effect of Iron on Volatile Organic Compounds Produced During Pineapple Fermentation Using HS-SPME and GC/MS**; Matthew Essandoh[1], Jon Deweese[1], Todd Mlsna[1]; [1]mississippi State University

47 (626) **Determination of Ascorbic Acid, Sugars, Organic Acids and Total Phenols of Different Cultivars of Citrus Fruits**; Jose-Luis Todoli[1], Silvia Carballo[1], Soledad Prats, Salvador Maestre[1], Amanda Terol[1]; [1]University of Alicante

48 (627) **Wheat Early Generation Desirable Wheat Glycolipid Quality Prediction from 100 mg of Wheat Endosperm as a Boon to Breeding for End Use Quality**; David Wetzel[1], Allan Fritz[1]; [1]Microbeam Molecular Spectroscopy Laboratory and Agronomy Dept., Kansas State University

49 (628) **Flour Stream Purity Determination via Quantitative Near Infrared Chemical Imaging**; Tyler Nickoley[1], Mark Boatwright[1], David Wetzel[1]; [1]Microbeam Molecular Spectroscopy Laboratory, Kansas State University

50 (629) **FT-IR Spectral Studies on the Identification of Organic Foreign Matters in Food**; Joon Shik Park[1], Sung Chel Shin[1], Ju Young Lee[1], Kyeon Yeol Kim[1], Sheen Hee Kim[1], Woo Seong Kim[1], Ki Seoung Kwon[1]; [1]Busan Regional Korea Food and Drug Administration

51 (630) **Application of Handheld and Portable Infrared Spectrometers in Bovine Milk Analysis**; Poliana Macedo dos Santos, Edenir R. Pereira-Filho, Luis Rodriguez-Saona; [1]Universidade Federal de São Carlos, [2]The Ohio State University

52 (631) **Using Infrared Spectroscopy to Classify Types of Grape and Regions in Peru's Piscos**; Marçal Plans Pujolras[1], Beatriz Hatta-Sakoda[2], Juan Carlos Palma[2], Luis Rodríguez-Saona[1]; [1]The Ohio State University, [2]Universidad Nacional Agraria La Molina

Thursday Morning, *Atlanta*
SAS LESTER W. STROCK AWARD HONORING RALPH STURGEON

Organizers: Ralph Sturgeon and Steve Ray; Presider: Steve Ray

10:20 (632) **Finding Metal-protein Binding Constants Under Equilibrium Conditions Using Separation by Ultracentrifugation and Detection by ICP-MS**; James Holcombe[1], Isaac Arnquist[1]; [1]University of Texas at Austin

10:40 (633) **Cooking Solid Samples in a Graphite Furnace. A Story of Metals, Non-Metals and Nanoparticles**; Martin Resano[1], Maria R. Flórez[1], Engracia Mozas[2], Eduardo Bolea, Maite Aramendía[3]; [1]University of Zaragoza, [2]Technological Institute of Aragón (ITA), [3]Centro Universitario de la Defensa, Zaragoza

11:00 (634) **"Cold" Methods for ADME (Absorption, Distribution, Metabolisation and Excretion) Studies of Candidate Drugs using ICP – Mass Spectrometry**; Frank Vanhaecke[1], Björn Meermann[1], Andrei Izmer[1], Deepti Gholap[1], Sylvia Van Dorpe[2], Filip Cuyckens[2]; [1]Ghent University, Department of Analytical Chemistry, [2]Drug Safety Studies, Janssen R&D

11:20 (635) **Matrix Interferences in ICP-AES: How to Recognize and Eliminate Them**; Gary Hieftje[1], George Chan[1], Yan Cheung[1]; [1]Indiana University

11:40 (636) **Electrothermal Vaporization or Atomization on Tungsten Coil for Analytical Atomic Spectrometry**; Xiandeng Hou[1]; [1]Sichuan University

Thursday Morning, *Chicago C*
RAMAN SPECTROSCOPY: A NONINVASIVE METHOD FOR DISCRIMATION OF CELLS AND CELL POPULATIONS I

Organizer and Presider: Michael Blades

10:20 (637) **Single Cell Raman Micro-Spectroscopy – a Powerful Tool in Biophotonics**; Juergen Popp[1, 2], Michael Schmitt[2], Benjamin Dietzek[1], Ute Nerugebauer[1], Christoph Krafft[1], Petra Roesch[2]; [1]Institute of Photonic Technology, [2]Institute for Physical Chemistry and Abbe Center of Photonics, Friedrich-Schiller University Jena

10:40 (638) **Investigation of Single Cell Raman Spectroscopy as a Tool for Monitoring Radiation Therapy Treatment Progression**; Andrew Jirasek[1], Quinn Matthews[1, 2, 3], Julian Lum[3], Alexandre Brolo[2]; [1]University of Victoria, Dept. Physics and Astronomy, [2]University of Victoria, Dept. Chemistry, [3]BC Cancer Agency, Vancouver Island Centre

11:00 (639) **Raman Study of Colorectal Cancer in Live Mouse Model and Cells**; Hidetoshi Sato[1], Akinori Taketani[1], Kosuke Hashimoto[1], Yui Maeda[1], Mika Ishigaki[1], Bibin B. Andriana[1]; [1]School of Science and Technology, Kwansei Gakuin University

11:20 (640) **Multiplexed 3D Raman and SERS Imaging of Cells**; Sarah McAughtrie[1], Katherine Lau[2], Karen Faulds[1], Duncan Graham[1]; [1]University of Strathclyde, [2]Renishaw plc

11:40 (641) **Non-Invasive Single Cell Cytometry Using Label-Free Biophotonic Techniques**; James Chan[1]; [1]University of California, Davis

Thursday Morning, *New York A*
OPTICAL AND PHOTOACOUSTIC TOMOGRAPHY AND MICROSCOPY

Organizer and Presider: Xinmai Yang

10:20 (642) **Photoacoustic Tomography: Ultrasonically Breaking through the Optical Diffusion Limit**; Lihong Wang[1]; [1]Washington University in St. Louis

11:00 (643) **Advanced Image Reconstruction Methods for Photoacoustic Tomography Brain Imaging**; Mark Anastasio, Chao Huang, Lihong Wang; [1]Washington University in St. Louis

11:20 (644) **Photoacoustic Contrast Imaging of Biological Tissues with Nanodiamonds Fabricated for High Near-Infrared Absorbance**; Xinmai Yang[1]; [1]University of Kansas

11:40 (645) **Polarization-Sensitive Optical Coherence Tomography**; Gang Yao[1]; [1]University of Missouri

TECHNICAL PROGRAM – THURSDAY
Orals 10:20 am – 12:00 pm

Thursday Morning, *Empire C*
FROM AG TO AG(RICULTURE): ANALYTICAL CHEMISTRY IN THE MIDWEST
Organizer and Presider: Luisa T. M. Profeta

10:20 (646) **A History of Analytical Chemistry in the Midwest: Regional Performance with Global Impact**; James Spigarelli; [1]Midwest Research Institute (Retired)

10:40 (647) **Identification of Multiple Conformers of Molecules which Associate by Utilizing Rare Gas Solutions with Variable Temperature Vibrational Spectroscopy**; James R. Durig[1], Joshua J. Klaassen[1], Ikhlas D. Darkhalil[1]; [1]University of Missouri - Kansas City

11:00 (648) **Enhanced Detection of Trace Elements in High-Purity Sulfuric Acid Uing Ultrasonic Nebulization with ICP-AES Detection**; Fred Smith[1]; [1]CETAC Technologies

11:20 (649) **Determination of Pollutant Concentration in Spiked Wastewater Samples through Multivariate Regression Modeling of UV-visible Spectral Data**; Amy Fine[1], Bridget O[1], Jemima Ingle[1]; [1]University of Saint Mary

11:40 (650) **Semi-Micro Mid-Infrared Analysis of 100 mg of Composited Wheat Endosperm Enables Protein Content Ranking with a Generational Leap**; David Wetzel[1], Mark Boatwright[1], Allan Fritz[1]; [1]Microbeam Molecular Spectroscopy Laboratory and Agronomy Dept., Kansas State University

Thursday Morning, *Empire B*
HAND-HELD DEVICES FOR PAT AND INDUSTRIAL USES
Organizer and Presider: Connie M. Ruzicka

10:20 (651) **Screening Counterfeit Drugs Using Portable NIR Spectrometer**; Ravi Kalyanaraman; [1]Ravi Kalyanaraman

10:40 (652) **Rapid Screening of Illegal Weight-Loss Substances in Dietary Supplements using a Hand Held Ion Mobility Spectrometer**; Laura Mecker, Jamie Dunn, Connie Gryniewicz-Ruzicka, John Kauffman, Benjamin Westenberger, Lucinda Buhse; [1]US FDA/Division of Pharmaceutical Analysis

11:00 (653) **Implementation of a Portable Raman Device in the Pharmaceutical Laboratory**; Jeff Denault[1], Michael Dotlich[1]; [1]Eli Lilly and Co

11:20 (654) **A Portable Gas Chromatograph for the Monitoring of Biomass Gasification**; Bidhya Kunwar, Todd Mlsna; [1]Mississippi State University

11:40 (655) **Improving Excipient and Raw Material Screening through Portable Near Infrared and Raman Spectroscopic Methods**; Jason Rodriguez[1], Connie Ruzicka[1], Derya Cebeci Maltaş[1], John Kauffman[1], Lucinda Buhse[1]; [1]FDA, Division of Pharmaceutical Analysis

Thursday Morning, *New York B*
NANOPARTICLES AND SERS FOR ANALYSIS
Organizer and Presider: Duncan Graham

10:20 (656) **Plasmonic Nanoparticles in Biosensing and Bioimaging**; Li-Lin Tay[1]; [1]National Research Council

10:40 (657) **New Insights in Single Molecule SERS**; Alexandre Brolo[1], Marica L. A. Temperini[2], Diego P. dos Santos[1, 2]; [1]University of Victoria, Department of Chemistry, [2]University of Sao Paulo, Department of Chemistry

11:00 (658) **Imaging SERS Hot Spots with Super-Resolution Microscopy of Multiple Analytes**; Katherine Willets[1]; [1]University Of Texas at Austin

11:20 (659) **Monolithic Nanoporous Gold Disks as Surface-Enhanced Raman Spectroscopy Substrates**; Wei-chuan Shih[1], Ji Qi[1], Pratik Motwani[1], John Wolfe[1]; [1]University of Houston

11:40 (660) **Optimizing SERS Tags For Their Applications**; Griff Freeman[1], Michael Natan[1]; [1]Cabot Corporation

Thursday Morning, *Chicago B*
ADVANCES IN ANALYTICAL FORENSICS
Organizer and Presider: Greg Klunder

10:20 (661) **Isotopic Determination of Uranium Samples Using Passive Gamma Spectroscopy with Multiple Detectors**; Steven Horne[1], Brian Dickson[1], Sheldon Landsberger[1]; [1]University of Texas at Austin

10:40 (662) **Spectroscopic Examination of the Volatile Organic Compounds Comprising the Bouquet of RDX-based Explosives**; Trocia Clasp[1], Taylor Ingle[2], Janet Jamison[2], Roger Buchanan[3], Tiffani Johnson[1], Scott Reeve[1]; [1]Arkansas Center for Laser Applications and Science (ArCLAS), Arkansas State University, [2]Arkansas Biosciences Institute, Arkansas State University, [3]Department of Biological Sciences, Arkansas State University

11:00 (663) **Towards the Analysis of Forensically Relevant DNA on a Microfluidic Platform**; Claire Lenehan[1], Leigh Thredgold[1, 2], Dmitriy Khodakov[1, 2], Hilton Kobus[1], Adrian Linacre[3], Gunther Andersson[1, 2], Amanda Ellis[1, 2]; [1]School of Chemical and Physical Sciences, Flinders University, [2]Flinders Centre for NanoScale Science and Technology, Flinders University, [3]School of Biological Sciences, Flinders University

11:20 (664) **Accessing the Probative Value of Forensic Evidence with a Ruggedized, Portable Mass Spectrometer Capable of Ambient Ionization**; Christopher Mulligan[1], Kyle Vircks[1], Adam O[1]; [1]Illinois State University

11:40 (665) **Time Dependent Particle Characterization of Residual Materials on Fingerprints**; Jason Guicheteau[1], Ashish Tripathi[2], Erik Emmons[2], Steven Christesen[1], Augustus W. Fountain III[1]; [1]USA RDECOM Edgewood Chemical Biological Center, [2]Science Applications International Corporation

Thursday Morning, *Chicago A*
POLYMERS, POLYMERIZATION AND SPECTROSCOPY
Organizers: Steve Ray; Presider: Bruce Chase

10:20 (666) **Confocal Raman Microscopy to Investigate the Polymerization Kinetics and Properties of Individual Optically Trapped Vinyl-Polymerized Vesicles**; Jonathan Schaefer[1], Joel Harris[1]; [1]University of Utah

10:40 (667) **Real time and *in situ* Monitoring of a Polymerization Reaction by Raman Spectroscopy And Rheological Measurements**; David Chapron[1], Marie-Claire Chevrel[2], Sandrine Hoppe[2], Laurent Falk[2], Alain Durand[2, 3], Patrice Bourson[1]; [1]Université de Lorraine, LMOPS, [2]CNRS, LRGP, [3]Université de Lorraine, LCPM, UMR

11:00 (668) **Evaluation of Millimeter-Scale Alignment of Cylindrical Domains in Polystyrene–Poly(ethylene oxide) Diblock Copolymer Films by Single Molecule Tracking**; Khanh Hoa Tran Ba[1, 2], Jason Finley[1, 2], Daniel A. Higgins[1, 2], Takashi Ito[1, 2]; [1]Kansas State University

11:20 (669) **Orientation and Structure of Individual Electrospun Fibers by Raman Microscopy**; Christian Pellerin[1], Marie Richard-Lacroix[1]; [1]University of Montreal

11:40 (670) **Scanning Angle Total Internal Reflection Raman Spectroscopy Of Thin Polymer Films**; Matthew Meyer[1, 2], Kristopher McKee[1, 2], Emily Smith[1, 2]; [1]Iowa State University, [2]U.S. DOE, Ames Laboratory

TECHNICAL PROGRAM – THURSDAY
Orals 10:20 am – 12:00 pm and 1:20 – 3:00 pm

Thursday Morning, *Empire A*
NOVEL SPECTROSCOPIC APPROACHES IN ANALYTICAL CHEMISTRY
Organizer: Steve Ray; Presider: Gary Rayson

10:20 (671) **Far-Ultraviolet Spectroscopy in the Solid and Liquid States**; Yusuke Morisawa[1, 2], Akifumi Ikehata[3], Noboru Higashi[4], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]Kinki University, [3]National Food Research Institute, [4]KURABO Industries LTD *(*2012 Applied Spectroscopy Focal Point Author)*

10:40 (672) **Calibration Models using Approximate Light Propagation Theories for Decoupling Absorption and Scattering Effects**; Suresh Thennadil[1], Yi-Chieh Chen[1]; [1]University of Strathclyde

11:00 (673) **Tunable Picosecond Spectroscopy for Detection of NO**; Chakree Tangaroon[1, 2], Christopher Lue[1, 2], Scott Reeve[1,2], Bruce Johnson[1, 2], Susan Allen[1, 2]; [1]Arkansas Center for Laser Applications and Science, [2]Department of Chemistry and Physics, Arkansas State University-Jonesboro

11:20 (674) **Discernment of Foreign Mater in Raw Cotton Using Excitation-Emission Spectra**; Gary Rayson[1], Surja Ghale[1], Elizabeth Gámez[1], Dean Anderson[2], Edward Hughes[3]; [1]Department of Chemistry and Biochemistry, New Mexico State University, [2]USDA-ARS, Jornada Experimental Station, [3]USDA-ARS, Cotton Ginning Laboratory, New Mexico State University

11:40 (675) **Quantitative Near Infrared Chemical Imaging Enables Revelation of Milled Wheat Fraction Physical Separation Relative to Particle Size**; Mark Boatwright[1], Elieser Posner[2], Jeff Gwirtz[3], David; [1]Microbeam Molecular Spectroscopy Laboratory, Kansas State University, [2]ESP International, Savyon, Israel, [3]JAG Services

Thursday Afternoon, *Empire B*
NOVEL SAMPLE INTRODUCTION TECHNIQUES AND TOOLS FOR ATOMIC SPECTROSCOPY
Organizer and Presider: Nicolas H. Bings

1:20 (676) **The Use of Laser Radiation to Modulate Electron Temperature in the Inductively Coupled Plasma**; Paul Farnsworth[1], Alisa Edmund[1], Kyli Bishop[1], Nicholas Taylor[2]; [1]Brigham Young University, [2]Pacific Northwest National Laboratory

1:40 (677) **Aerosol and Particle Generation, Transport and Fate in the ICP**; John Olesik[1], Fang Liu[1], Patrick Gray[1]; [1]Ohio State University

2:00 (678) **Graphite Furnace High Resolution Continuum Source Atomic Absorption Spectrometry for the Determination of the Main Components Bi, Sb and Te in Thermoelectric Materials Sampled as Slurries of Nanowires**; José A.C. Broekaert[1], Klaus-Georg Reinsberg[1], Christian Schumacher[2], Katharina Moß[1], William Töllner[2], Sonja Heiderich[2], Kornelius Nielsch[2]; [1]University of Hamburg, Institute for Inorganic and Applied Chemistry, [2]University of Hamburg, Institute of Applied Physics

2:20 (679) **ICP Organic and Inorganic Sample Analysis with a High Temperature Micro Sample Introduction System**; José-Luis Todolí[1], Raquel Sánchez[1], Carlos Sánchez[1], Charles-Philippe Lienemann[2], Marco Grotti[4], Francisco Ardini[3], Jean-Michel Mermet[4]; [1]University of Alicante, [2]IFP Energies Nouvelles, [3]University of Genova, [4]Spectroscopy Forever

2:40 (680) **Alternative Strategies for Sample Introduction: Thermal Inkjet Principle for the Generation of Picoliter Volumes**; Nicolas H. Bings[1], Jan O. Orlandini v. Niessen[1], Jan H. Petersen[1], J. Niklas Schaper[1], Tobias J. Fiedler[1]; [1]Johannes Gutenberg-University Mainz, Institute for Inorganic and Analytical Chemistry, Laboratory for Trace Analysis and Plasma Spectrometry

Thursday Afternoon, *Empire A*
NEW PLASMAS, NEW INSTRUMENTATION AND NEW APPROACHES AT THE FRONTIER OF ATOMIC SPECTROMETRY – THE CODA
Organizers: Carsten Englehard and Steve Ray; Presider: Gerardo Gamez

1:20 (681) **Computational Optimization of Operating Parameters of ICPMS**; Maryam Aghaei, Helmut Lindner, Annemie Bogaerts; [1]PLASMANT, University of Antwerp

1:40 (682) **Simulation of Electron Collision Processes in an Inductively Coupled Plasma**; Ross Spencer[1], David Perkins[1]; [1]Brigham Young University

2:00 (683) **Advances in the Development of a Novel Pulsed Radio Frequency Glow Discharge Plasma Source for Imaging Spectrochemical Elemental Speciation Analysis**; Wolfgang Buscher[1], Tobias Steingrobe[1], Volker Hoffmann[2], Maxim Voronov[2], Gary M. Hieftje[3], Andrew P. Storey[3], Steven J. Ray[3], Carsten Engelhard[1]; [1]University of Muenster, Applied Atomic Spectroscopy, [2]Leibniz Institute for Solid State and Materials Research Dresden, IFW Dresden e.V., [3]Department of Chemistry, Indiana University

2:20 (684) **Analysis of Single Nanoparticles by a New Time-Of-Flight Mass Spectrometer Coupled to Inductively Coupled Plasma Ionization Source**; Olga Borovinskaya[1], Bodo Hattendorf[1], Martin Tanner[2], Sabrina Gschwind[1], Detlef Günther[1]; [1]Department of Inorganic Chemistry, ETH Zurich, [2]Tofwerk AG

2:40 (685) **Rapid Uranium Isotope Measurements of Solids by Resonance Ionization Mass Spectrometry**; Michael Savina[1], Kim Knight[2], David Willingham[1], Brett Isselhardt[2], Stanley Prussin[3], Michael Pellin[1], Ian Hutcheon[2]; [1]Argonne National Laboratory, [2]Lawrence Livermore National Laboratory, [3]University of California at Berkeley

Thursday Afternoon, *Atlanta*
SAS APPLIED SPECTROSCOPY MEGGERS AWARD SESSION HONORING MIKE ANGEL
Organizers: Mike Angel; Presider: Mike Carrabba

1:20 (686) **Multimode Imaging in the Thermal Infrared: An Overview**; M.L. Myrick[1], Stephen Morgan[1], Heather Brooke[2], Megan Baranowski[3], Jessica McCutcheon[1], Wayne OBrien[1], Nicholas Boltin[1], Stephanie DeJong[1], Brianna Cassidy[1], Zhenyu Lu[1]; [1]University of South Carolina, [2]Merck, [3]Sandia National Laboratory

1:40 (687) **The LIBS - Raman Connection: A Perspective**; Richard E Russo[1, 2]; [1]Lawrence Berkeley National Laboratory

2:00 (688) ***in vivo* Subsurface Raman Spectroscopy: Hardly Possible without Optical Fibers**; Francis Esmonde-White[1], Michael D. Morris[1]; [1]University of Michigan

2:20 (689) **UV Raman Studies of Protein and Peptide Structure and Folding Studies**; Sanford Asher; [1]University of Pittsburgh

2:40 (690) **Adsorbate-metal Bond Effect on Empirical Determination of Surface Plasmon Penetration Depth**; Karl Booksh, Laurel Kegel, Nicola Menegazzo; [1]University of Delaware

TECHNICAL PROGRAM – THURSDAY
Orals 1:20 – 3:00 pm

Thursday Afternoon, *Chicago C*
RAMAN SPECTROSCOPY: A NONINVASIVE METHOD FOR DISCRIMINATION OF CELLS AND CELL POPULATIONS II
Organizer and Presider: Michael Blades

1:20 (691) **Non-invasive Identification of Proteoglycans and Chondrocyte Differentiation State by Raman Microspectroscopy**; Katja Schenke-Layland[1, 2], Eva Brauchle[1, 2], Marieke Pudlas[1], Travis Klein[3], Dietmar Hutmacher[3]; [1]Fraunhofer IGB, Dept. of Cell and Tissue Engineering, Stuttgart, Germany, [2]University Hospital of the Eberhard Karls University Tuebingen, Germany, [3]Institute of Health and Biomedical Innovation, Queensland University, Kelvin Grove, Australia

1:40 (692) **Raman Spectral Imaging of Stem Cell Colonies and Tumour Spheroids**; Max Diem[1]; [1]Northeastern University

2:00 (693) **Label-Free Molecular Characterisation of Live Stem Cells by Raman-Micro-Spectroscopy**; Ioan Notingher[1], Flavius Pascut[1], Adrian Ghita[1], Chris Denning[1], Virginie Sottile[1]; [1]University of Nottingham

2:20 (694) **Measurements of Integrin Mobility in the Membrane of Cultured Cells using Single Particle Tracking (SPT) Technique**; Dipak Mainali[1], Aleem Sayed[1], Emily Smith[1]; [1]Iowa State University

2:40 (695) **Chemical Imaging of Live Cells under Autophagy-Inducing Conditions using Raman Microspectroscopy**; Michael Blades[1], Stanislav Konorov[1, 2], Mario Jardon[3], James Piret[3], Robin Turner[2, 4]; [1]Department of Chemistry, The University of British Columbia, [2]Michael Smith Laboratories, The University of British Columbia, [3]Department of Chemical and Biological Engineering, The University of British Columbia, [4]Department of Electrical and Computer Engineering, The University of British Columbia

Thursday Afternoon, *New York B*
APPLICATIONS OF CHEMOMETRICS IN VIBRATIONAL SPECTROSCOPY
Organizers: Barry Lavine and Renee JiJi; Presider: Karl Booksh

1:20 (696) **Sensor Fusion of FTIR and Image Information for Characterization of Microalgae in Response to Ecological Parameters**; Frank Vogt[1], Morgan McConico-Lewis[1]; [1]University of Tennessee

1:40 (697) **Temperature Modeling with Near-Infrared Spectroscopy**; Gary Small; [1]University of Iowa

2:00 (698) **Identification by Transmission Raman of Drug Products and Placebos**; Michael Dotlich[1], Lisa Wenzler[1], Richard Kattner[1]; [1]Eli Lilly & Co

2:20 (699) **Multivariate Curve Resolution Applied To Bilinear Deep-UV Resonance (DUVRR) Raman Spectra of Proteins**; Renee D. JiJi[1], Olayinka O. Oshokoya[1], Carol A. Roach[1], Christopher M. Halsey[1], Mia C. Brown[1], Jason W. Cooley[1]; [1]University of Missouri-Columbia

2:40 (700) **Near Infrared Spectroscopy Applications in Biofuels Characterization**; Edward Wolfrum[1], Amie Sluiter[1], Courtney Payne[1]; [1]National Renewable Energy Laboratory

Thursday Afternoon, *Chicago A*
NEW TECHNIQUES IN THE SEPARATION SCIENCES
Organizer: Steve Ray; Presider: Sarah Staton

1:20 (701) **Universal Anion Detection by Replacement-Ion Chromatography with a Solution-Cathode Glow Discharge Detector**; Andrew Schwartz[1], Zheng Wang[2], Steven Ray[1], Gary Hieftje[1]; [1]Department of Chemistry, Indiana University, [2]Shanghai Institute of Ceramics, Chinese Academy of Science

1:40 (702) **Particle and Molecular Species Separation Via Continuous Electroosmotic Flow with Orthogonal Optical Pressure**; Sarah Staton[1], Alex Terray[2], Greg Collins[2], Sean Hart[2]; [1]National Research Council Post-Doctoral Fellow, [2]Naval Research Laboratory

2:00 (703) **3-D Imaging of Redox Magnetohydrodynamic Flow in Microfluidic Devices by Fluorescence Correlation Spectroscopy and Particle Tracking**; Colin Heyes[1], Feng Gao[1], Adam Kreidermacher[1], Ingrid Fritsch[1]; [1]University of Arkansas

2:20 (704) **Confocal Raman Microscopy for *in-situ* Detection of Polyaromatic Hydrocarbon Accumulation within Single C18 Silica Particles**; Jay Kitt[1], Joel Harris[1], Marc Porter[1], [1]University of Utah

2:40 (705) **Electrophoretic Exclusion: A Microchip Separation Scheme**; Stacy Kenyon[1], Michael Keebaugh[1], Mark Hayes[1]; [1]Arizona State University

Thursday Afternoon, *New York A*
INSTRUMENTATION AND APPLICATIONS: PROBING THE LIMITS IN MOLECULAR SPECTROSCOPY
Organizer and Presider: Linda Kidder

1:20 (706) **Characterization of a Reference-Laser Free Spectrometer**; Kevin Yeh[1, 2], Matthew Schulmerich[1, 2], Rohit Bhargava[1, 2]; [1]University of Illinois at Urbana-Champaign, [2]Beckman Institute for Advanced Science and Technology

1:40 (707) **Mapping 3D Molecular Confromations with Multiple-Mode Multiple-Dimensional Vibrational Spectroscopy**; Junrong Zheng[1], Hongtao Bian[1], Jiebo Li[1], Hailong Chen[1], Xiewen Wen[1]; [1]Rice University

2:00 (708) **IR Microscopy using External-Cavity Quantum-Cascade Lasers**; Robert Shine[1], Miles Weida[1], Dave Arnone[1], Tim Day[1]; [1]Daylight Solutions

2:20 (709) **Use of NMR to Interpret NIR: Application to Biologics Manufacturing**; Maureen Lanan[1], Amr Ali[1]; [1]Biogen Idec

2:40 (710) **Correlation of Quality Measurements to Visible-Near Infrared Spectra of Pasteurized Eggs**; Samantha Hawkins[1], Deana Jones[1]; [1]US. Department of Agriculture-Agricultural Research Services

Thursday Afternoon, *Empire C*
APPLICATIONS AND ADVANCES IN HANDHELD AND PORTABLE SPECTROSCOPY
Organizer and Presider: John Seelenbinder

1:20 (711) **New Frontiers in Handheld FTIR- Instrumentation and Applications**; John Seelenbinder; [1]Agilent Technologies

1:40 (712) **Compact On-Site NMR Assessment of Acyl Group Quality of Combustible and Edible Glycerides**; David Wetzel[1], Marcelo Coronado[1], Mark Boatwright[1], Jeffrey Sherman[2]; [1]Microbeam Molecular Spectroscopy Laboratory, Kansas State University, [2]picoSpin, LLC[4]

2:00 (713) **Opportunities of Portable FT-IR Instrumentation for the Food Industry**; Luis Rodriguez-Saona[1]; [1]The Ohio State University

2:20 (714) **QCL as a Forefront Technology, Rethinking the Limitations of Infrared Spectroscopy**; Frederick G. Haibach[1]; [1]Block Engineering

2:40 (715) **Recent Advances in Laser-Based Mid-IR Devices for Spectroscopic Applications**; Leigh J. Bromley[1]; Patrick Mock[1], Dave Caffey[1], Timothy Day[1]; [1]Daylight Solutions

TECHNICAL PROGRAM – THURSDAY
Orals 1:20 – 3:00 pm and 3:50 – 5:30 pm

Thursday Afternoon, *Chicago B*
APPLICATIONS OF RAMAN SPECTROSCOPY AND MICROSCOPY
Organizer: Steve Ray; Presider: Keith Gordon

1:20 (716) **Chemical Imaging of Heterogeneous and Rough Surfaces by Means of Infrared Microspectroscopy in Specular Reflection Mode**; Valdas Sablinskas[1], Milda Pucetaite[1], Justinas Ceponkus[1]; [1]Vilnius University

1:40 (717) **The use of Raman Spectroscopy in Explaining High Speed Friction of Titanium Alloy Against Tantalum**; Patrice Bourson[1], Jean Jacques Arnoux[2], Guy Sutter[2], Gauthier List[2]; [1]LMOPS University of Lorraine Metz, [2]LEM3 University of Lorraine Metz

2:00 (718) **Depth Profiling in Opaque Materials; Applications of Time-Resolved Raman Spectroscopy**; Ingeborg Iping Petterson, Cees Gooijer, Freek Ariese; [1]Vrije University Amsterdam, LaserLaB

2:20 (719) **Transmission Raman Spectroscopy on Freshly Excised Breast Pathology Specimens**; Marleen Kerssens[1, 2], Pavel Matousek[, 3], Keith Rogers[, 2], Nick Stone[1, 4]; [1]Biophotonics Research Unit GRH NHS FT, [2]Cranfield University, [3]Central Laser Facility, Rutherford Appleton Laboratory, [4]Department of Physics, University of Exeter

2:40 (720) **Cytoplasmic RNA in Undifferentiated Neural Stem Cells: A Potential Label-Free Raman Spectral Marker for Assessing the Undifferentiated Status**; Adrian Ghita[1], Flavius C. Pascut[1], Virginie Sottile[1], Ioan Notingher[1]; [1]University of Nottingham

3:00 – 3:50 pm Exhibit Hall B
BREAK AND POSTER VIEWING

Thursday Afternoon, *Exhibit Hall B*
FACSS INNOVATION AWARDS
Organizer and Presider: Michael George

2012 FACSS Innovation Award winner will be announced at the Friday Morning Plenary

3:50 (721) **Punctuated Microgradients for Electric Field Separations**; Mark Hayes[1], Stacy Kenyon[1], Paul Jones[1]; [1]Arizona State University

4:10 (722) **Far-Field, Sub-Diffraction Fluorescence Lifetime Imaging**; Emily Smith[1, 2], Michael Lesoine[1, 2], Sayantan Bose[1, 2], Jacob Petrich[1, 2]; [1]Iowa State University, [2]The Ames Laboratory

4:30 (723) **Desorption Ionization with the Liquid Sampling-Atmospheric Pressure Glow Discharge Microplasma**; R. Kenneth Marcus[1], Carolyn Q. Burdette[1], Benjamin T. Manard[1], Lynn X. Zhang; [1]Clemson University

4:50 (724) **Advancing Infrared Microscopy Instrumentation by Theory and Computation**; Rohit Bhargava[1], P. Scott Carney[1], Rohith Reddy[1], Kevin Yeh[1], Thomas van Dijk[1], Matthew Gelber[1], Matthew V. Schulmerich[1]; [1]University of Illinois, Beckman Institute for Advanced Science and Technology

TECHNICAL PROGRAM – FRIDAY
Orals 8:00 – 10:30 AM
Empire A

SPECIAL PLENARY SESSION: WELCOMING THREE NEW MEMBER ORGANIZATIONS INTO FACSS
ANNOUNCEMENT OF THE 2012 FACSS INNOVATION AWARD WINNER
Organizer: Steve Ray; Presider: Ian Lewis

8:00 (725) **Sudden Impact: Scholarly Publishing and the Day After Tomorrow**; Michael Blades[1, 3], Rebecca Airmet[3], Peter Griffiths[2, 3]; [1]Department of Chemistry, The University of British Columbia, [2]Department of Chemistry, University of Idaho, [3]Society for Applied Spectroscopy

8:30 (726) **Analysis of Polymer-Surface Coatings Using Infrared External-Reflection Spectrometry**; Takeshi Hasegawa[1]; [1]ICR, Kyoto University

9:00 (727) **Electrophoresis Joins FACSS: History and Newest Results**; Mark Hayes[1]; [1]Arizona State University

9:30 (728) **LIBS in Atomic Spectroscopy: NASLIBS in FACSS**; Richard E. Russo[1, 2], Jhanis Gonzalez[1, 2], Jong Yoo[2], [1]Lawrence Berkeley National Lab, [2]Applied Spectra

(1) **Remote Spectroscopy in the Search for Life on Other Worlds**; Chris McKay[1]; [1]NASA Ames

The search for life on other worlds poses challenges that are well suited to remote spectroscopy. The worlds of particular interest are Mars, Europa, Enceladus, and Titan. On all of these objects the ability to detect and characterize organic materials using stand-off methods would be useful and could bring the cost of missions to these worlds down to the level required for new starts over the next decade or so. Active remote sensing based on Laser Induced Breakdown Spectroscopy (LIBS), Raman, and UV fluorescence provide methods that are finding increasing application in planetary missions. In this talk I review current concepts and future plans for such active remote sensing systems from scale of a few meters to orbital distances.

(2) **Evaluation of a Quadrupole Mass Spectrometer for High Resolution of Light Gases**; William Spencer[1], Kevin Kuchta[2]; [1]SRNS/ SRNL, [2]Extrel LLC

Analysis of methane, ammonia, and water as well as the hydrogen and helium isotopes requires a mass spectrometer that provides high resolution and has an ion source that generates few side reactions. Mixtures of these gases with hydrogen, deuterium, and tritium can lead to very complex and difficult to separate mixtures forming many common isotopologues. For example: 4He and D2; 3He and HD; 16O+, NH2+, CD2+, CHT+,CH2D+, and CH4+ have a common mass resolution problem. The trace isotopes for carbon, nitrogen, and oxygen further complicate the spectrum. SRNL developed a simulator to predict the mass spectrum for potential mixtures and has shown that a mass spectrometer with resolution 3000 resolves most of the isotopologue conflicts. In combination with differences in expected fragmentation patterns, the analyses can be resolved. In practice the lab uses large and expensive dual sector mass spectrometers to make measurements. SRNL has been working with Extrel LLC to evaluate an alternative technique using the Extrel high-quality MAX series quadrupole in combination with a SAES ion getter pump. The gated getter pump can rapidly separate the helium isotopes from the hydrogen ones. Extrel had shown by driving the quadrupole at higher frequency, 2.9 MHz, their system could achieve resolutions greater than 4000 at mass 40 and cover up to the mass 60 range. The quadrupole has large 19 mm x 20 cm rods enabling high resolution with good ion yields. Testing at lower masses found that the quadrupole can separate 16O from CH4+ and partially resolve from NH2+ at mass 16 as well as partial separation of OH+ from NH3+ at mass 17. Good separation was achieved for the 4He from D2 combination but the system could not resolve HD from 3He. The getter worked well for removing the hydrogen isotopes but did not work well for ammonia. Simion™ was used to optimize the ion source for optimal mass resolution and ion yield. The Extrel axial ion source did have some interference from filament reactions. Improved ionization sources as well as higher frequency operation are being designed to further optimize the system.

(3) **Alternative MALDI Matrix Found in Silver Nanoparticles Produced via Soft-Landing Ion Mobility**; Barbara Walton[1], Guido Verbeck[1]; [1]University of North Texas

MALDI is one of the most widely used ionization techniques in mass spectrometry, although one if its biggest drawbacks is matrix interference, particularly in the low mass region. Here, we have shown Soft-Landing Ion Mobility (SLIM) deposited silver nanoparticles have been used as a matrix for low mass peptides without interferences from traditional matrices. Nanoparticle creation and deposition occurred in a SLIM instrument consisting of a laser ablation source and drift tube. Nanoparticles were prepared via laser ablation of a solid silver metal target. The ions produced travel down the drift tube operating at 2 Torr He towards the landing surface. The silver nanoparticles are deposited in the thermal energy regime, < 1 eV , on a gold MALDI plate already spotted with the peptide solutions of interest. Deposition times ranged from 5 to 60 minutes in order to monitor the effect of time on the size and surface coverage of the nanoparticles, and their consequent effectiveness as a matrix. Collected spectra of the Ag nanoparticle deposition showed clear presence of the peptide with limited low mass range interference, while the peptide peaks were non-discernible when analyzing conventionally prepared MALDI samples using CHCA as the matrix. Also observed in the low mass regime of the MALDI spectra was the clustering of Ag_n^+ ions, where n = 2,3, however these clustering peaks did not interfere with the analytes of interest. The ease of this deposition method coupled with the absence of interference makes soft-landing ion mobility nanoparticle deposition a promising new route for MALDI analysis. Laser ablation of a solid gold target to afford similar nanoparticles is currently being studied for use in MALDI matrices as well with hopes of resulting spectra comparable to silver.

(4) **Travelling Wave Ion Mobility-Mass Spectrometry Study of the Influence of Group I Metal-Cation Adduction on Conformation of Isomeric Carbohydrates**; Yuting Huang[1], Eric Dodds[1]; [1]University of Nebraska-Lincoln

Carbohydrates play important roles in biological systems. The study of isomeric carbohydrates remains challenging. Travelling-wave ion mobility-mass spectrometry was used to study the conformation of lithium, sodium, potassium, rubidium and cesium adducts of four isomeric trisaccharides (raffinose, maltotriose, isomaltotriose and melezitose) and five isomeric disaccharides (cellobiose, maltose, trehalose, sucrose and melibiose). The ion mobility drift time (which is related to the shape and charge of the ion) was measured for each carbohydrate as each metal ion adduct. As expected, the size of the metal ion exerted a significant influence on the drift time of the adduct ions. For example, the drift time of adducts of maltotriose varied from 5.89 ms for the [M+Li]+ ion to 6.79 ms for the [M+Cs]+ ion. For a given set of isomers, differences in drift time were also noted for those coordinating the same metal ion. For example, the drift times of maltotriose and melezitose as their [M+Na]+ adducts differed by 0.69 ms. A method to calibrate the travelling wave device was applied to estimate collision cross sections of these adducts from their drift times. The results indicate that the collision cross sections of a particular carbohydrate usually increase with the radii of the coordinated metal ions; however, in some instances the collision cross sections remained similar with addition of a larger metal ion. For example, melezitose had the same drift time of 5.47 ms as the [M+Li]+ ion and the [M+Na]+ ion. The same metal ion adducts of maltotriose followed the more expected trend of increasing drift time with adduction of sodium rather than lithium. Overall, these results suggest that certain carbohydrate isomers will assume a more compact conformation to coordinate a larger metal ion, whereas other carbohydrate isomers do not. This result has analytical implications for distinguishing progressively more complex oligosaccharide isomers by ion mobility spectrometry.

(5) **Hydrogen/Deuterium Exchange Mass Spectrometry Determination of the Allosteric Mechanisms Relating to the Phosphorylation Regulation of Human Liver Pyruvate Kinase**; Xiaohua (Sarah) Zhou[1], Charulata B. Prasannan[1], Maria T. Villar[1], Antonio Artigues[1], Aron W. Fenton[1]; [1]University of Kansas Medical Center

Human liver pyruvate kinase (hL-PYK) catalyzes the final step in glycolysis, the conversion of phosophoenolpyruvate (PEP) and ADP to pyruvate and ATP. The regulation of hL-PYK is vital in controlling the balance between gluconeogenesis and glycolysis to maintain hepatic and in turn blood glucose homeostasis. Protein phosphorylation in response to glucagon is one regulatory mechanism which results in reduce affinity for PEP. This regulatory mechanism

may hold insights that could give rise to the development of anti-hyperglycemic drugs. Phosphorylation occurs at Serine 12 in the N-terminus and results in the interruption of an activating interaction between the N-terminus and the main body. Although the binding site of the un-phosphorylated N-terminus is not known, it is clear that the N-terminus is not interacting with the active site. Therefore, the N-terminus must modify substrate binding in the active site using a long-distance, through-protein mechanism. In this study, Hydrogen/Deuterium Exchange Mass Spectrometry (H/DX MS) has been utilized to identify which region of the protein contributes to this energetic coupling between the N-terminus and the active site. Using the S12D mutant to mimic phosphorylation, we have determined the regions of hL-PYK that change differently upon PEP binding when the S12D mutant is vs. is not present. This required a comparison between the free enzyme, the free enzyme with PEP, the S12D mutant enzyme and the S12D mutant enzyme with PEP. The allosteric specific changes identified by this approach (both total exchangeable backbone amide protons per peptide and rate of exchange) are mapped onto the structure of the protein. Highlighted regions represent areas of the protein that can be targeted for drug design.

(6) **Probing Amino Acid Content of Foodstuffs Using Microwave Hydrolysis Coupled with Desorption Electrospray Ionization Mass Spectrometry**; Jonathan Person[1], Christopher Mulligan[1]; [1]Illinois State University

Profiling of amino acid composition is important in gauging the nutrition value of target foodstuffs. Current methods of amino acid profiling of whole foods, while regarded for their analytical performance, typically require acid hydrolysis for 20-24 hours followed by analysis with HPLC. Given the extensive sample preparation and chromatographic separation, throughput is very low. In an effort to reduce this extensive sample analysis time while maintaining analytical performance, we report the coupling of rapid microwave hydrolysis methods with direct hydrolysate analysis with desorption electrospray ionization mass spectrometry (DESI-MS). Acid hydrolysis can be accomplished in as little as 15 minutes under microwave conditions, including 5-6 minutes of sample cool-down, the hydrolysate is then spotted onto porous Teflon and analyzed via DESI-MS. Soybean meal samples have been investigated with total analysis times of less than 30 minutes when including 5 replicates, and amino acid profiles can be achieved on as little as 50 mg of sample. Precision and accuracy of this method will be reported, and analysis of more complicated foods like peanut butter and infant formula will be discussed.

(7) **Dual Online Extraction Method for H/D Exchange Mass Spectrometry in the Presence of Crowding Agents**; Farai Rusinga[1], David Weis[1]; [1]University of Kansas

The crowded cellular interior, containing about 300 g L^{-1} of macromolecules, is a much different environment for proteins than the dilute buffers used in biophysical studies. Hence, there is considerable interest in understanding the effects of macromolecular crowding on protein structure and dynamics. To this end, synthetic crowders like Ficoll, dextran, and polyvinylpyrrolidone (PVP) are employed to mimic cellular crowding *in vitro*. Hydrogen/deuterium exchange mass spectrometry (HDMS) is a valuable tool for probing protein structure and dynamics, but crowders significantly interfere with LC/MS analysis. To overcome this challenge, we have developed a dual online extraction method using strong cation exchange (SCX) and reverse phase (RP) to remove interference by PVP. HDMS involves replacing amide hydrogens with deuterons (H/D exchange) in D_2O. Hydrogens in folded protein segments exchange more slowly than those in flexible regions. After a predetermined exchange time, deuterium labels are stabilized by acidification to pH 2.5 and chilling to 0^oC (a process called quenching). Proteolytic digestion is used to obtain localized exchange information. Deuterium uptake in peptides is then measured by mass spectrometry (MS). Crowders severely interfere with the peptide MS signal. Our SCX/RP extraction enables rapid removal of crowders under quenched conditions. We have applied an online SCX/RP extraction to 1 µM myoglobin in 150 g L^{-1} of PVP at pH 2.5 and 0^oC, representing a typical quenched H/D exchange sample. Myoglobin was digested online and resultant peptides were trapped on a SCX column. Residual PVP was then washed away with (20/5/5 %) acetic acid/isopropanol/acetonitrile. SCX trapped peptides were eluted with 0.5 M KCl onto a RP desalting trap. An organic solvent gradient eluted the peptide from the RP trap for separation and electrospray MS. The pepsin and SCX columns were reconditioned with 2 M guanidine HCl and 0.5 M KCl (for SCX regeneration). Mass spectra of myoglobin peptides were comparable to those from dilute (without PVP) samples. PVP background was also significantly reduced. These results show that our dual online extraction will enable HDMS studies of the effects of crowding on protein structure and dynamics.

(8) **Multi-analysis Platform Incorporating Raman Microscopy and Multiple Internal Reflection-Infrared Spectroscopy for the *in situ* Analysis of Soft-Landed Clusters**; James Fox[1], William Hoffmann[1], Guido Verbeck[1]; [1]University of North Texas

Over the past decade, the amount of time and effort focused on materials research has increased at an exponential rate, and the impetus for this research lies mainly in the perpetually growing demand for consumer and industrial technology. Many metal compounds of the general structure M_XR_Y (where R is a main group element) have been shown to have many useful catalytic, tribological or electronic properties with could be utilized in current and future technology. However, the number of possible metal/main group combinations and stoichiometries make the process of combing through the possible compounds a daunting task. It is with that in mind that this multi-analysis platform was developed, providing the opportunity to synthesize, modify and analyze such compounds rapidly *in situ*. Utilizing laser ablation, gas-phase metal clusters can be generated in low vacuum, and metal/main group compounds can be synthesized by performing the same ablation in a vacuum chamber back-filled with an appropriate buffer gas. Soft landing-ion mobility is utilized to deposit selected clusters on a substrate of our choosing while also providing structural information on the selected compound. After deposition, Raman microscopy and multiple internal reflection infrared spectroscopy can be employed on the sample in situ for spectroscopic analyses. Additionally, plasma modification and mass spectrometry can also be utilized to further characterize the deposited material. Data will be presented showing the selectivity and qualitatively analytical capabilities of the platform for metal/main group compounds, as well as its effectiveness as a combing device.

(9) **Hydrogen/deuterium Exchange Mass Spectrometry Analysis of Structural Changes in Calcineurin Induced by Calmodulin**; Mohammed Al-Naqshabandi[1], Tori Dunlap[2], Trevor Creamer[2], David Weis[1]; [1]Department of Chemistry, University of Kansas., [2]Center for Structural Biology, Department of Molecular and Cellular Biochemistry, University of Kentucky

Calcineurin (CN) plays essential roles in processes such as T-cell activation, neuronal and muscle development, and cardiac hypertrophy. In its inactive state, an autoinhibitory domain (AID) is bound in the active site. At high calcium concentration, calmodulin (CaM) binds calcium ions, resulting in CaM binding to the unstructured regulatory domain (RD) of CN. CaM binding causes release of the AID from the active site, activating CN. Our previous work on the isolated RD-AID construct from full length CN showed that the RD and AID are completely disordered in the absence of CaM. Upon CaM binding, two regions of the RD become structured.

The data suggest that the structuring causes displacement of the AID from the active site, but CaM has no effect on the AID, which remains unstructured. Therefore the AID must become structured only when it binds to the active site. To better understand the mechanism of activation, it is important to look at the complete complex. To identify conformational and dynamic changes in CN induced by CaM, we have used hydrogen/deuterium exchange-mass spectrometry (HDX-MS). This technique is based on labeling the backbone amide hydrogens of a protein with deuterium. The rate of exchange is a function of the structure and dynamics of the protein. After quenching the exchange reaction to pH 2.5, the protein is digested with pepsin to achieve spatial resolution. The deuterated peptides are separated by HPLC. Deuterium uptake is then measured by MS. Our preliminary results with full-length CN demonstrate that the RD is unstructured in the absence of CaM, while it folds upon binding to CaM. This result confirms our previous work on isolated RD-AID. Additionally, we have observed CaM-induced changes in peptides located in other domains of CN. The data provides new insight into CN regulation and illustrates usefulness of H/DX-MS for protein structure studies.

(10) **Single Cell Identification via Raman Microscopy and Multivariate Analysis**; Yelena Ilin[1], Mary Kraft[1]; [1]University of Illinois at Urbana-Champaign

The ability to distinguish and identify individual cells from different subtypes is critical to a number of medical, engineering, and environmental studies. Such studies include discriminating cancerous and healthy cells at various locations in a tissue, identifying the species of microbes in a co-culture, and detecting the maturation of stem cells. A promising method for cell identification and characterization is Raman microscopy. Unlike other invasive methods, Raman microscopy has the ability to detect changes in the composition of living cells without compromising the cells' function, proliferation, or morphology. Here, we report our efforts to classify individual cells from three different cell lines by multivariate analysis of Raman spectra. Confocal Raman microscopy was used to obtain spectral fingerprints of three different types of cells, both live and fixed, within a monolayer. Partial least-squares discriminant analysis (PLS-DA) was used to construct a model of the cell type-specific variance in the Raman spectra. For validation, we identified "unknown" cells in a separate test set by applying this PLS-DA model to their spectra. Furthermore, the fixed-cell model enabled identifying individual cells seeded in a co-culture. We have also identified various cell components based on peaks in the Raman spectra. This proof of concept demonstrates the feasibility of non-invasive, label-free single cell identification using Raman microscopy. This ability for single cell identification combined with the location specificity of this method will be very useful for correlating cell identity with specific microenvironments. Furthermore, the chemical information encoded in the single cell Raman spectra will provide qualitative information on the aspects of cell composition that differ between various cell types.

(11) **Micro-Raman Spectroscopy to Evaluate the Effect of Oral Cancer Radiotherapy On Tooth Chemical Structure**; Changqi Xu[1, 2], Rachel Reed[1, 2], Ying Liu[1, 2], Jeff Gorksi[1, 2], Yong Wang[1, 2], Mary Walker[1, 2]; [1]University of Missouri-Kansas City School of Dentistry, [2]Deparment of Oral Biology

Radiation therapy is typically used to successfully treat oral cancer. However, there is a significant negative effect of the dose of radiation that an individual tooth receives leading to subsequent dentition breakdown. This unique pattern of tooth breakdown is characterized by enamel shear fracture near the dentin-enamel junction (DEJ). Objectives: To understand radiotherapy-induced effects on the chemical structure of teeth near the DEJ using micro-Raman spectroscopy. Methods: Six paired, extracted human third molars were used with half of the teeth exposed to 70 Gy radiation and the other half to no radiation. Following radiation, the crowns were sectioned buccolingually to produce a 2-mm-thick cross-sectional slice centered on the mesiobuccal and mesiolingual cusps. The sections were then polished sequentially with 600- and 1200-grit SiC paper and ChemoMet polishing cloth (Buehler Ltd). 2D-XY Raman mappings were carried out across the DEJ on the buccal and lingual surface of the exposed sections. Raman images based on the ratio of carbonate (1070 cm^{-1})/phosphate (960 cm^{-1}) and the peak width of 960 cm^{-1} were obtained. Results: Carbonate/phosphate ratios indicated a decrease in carbonate content in enamel near the DEJ after 70 Gy radiation compared to the control group. Changes in the 960 cm^{-1} peak width at the same location indicated the degree of mineral crystallinity in that region decreased after radiation. Calculations based on individual spectra showed that the differences of carbonate content and degree of crystallinity were both significant ($p<0.05$). Conclusions: The preliminary results suggest that radiotherapy has a direct effect on the chemical structure of enamel near the DEJ. These changes could be linked to the dentition breakdown that occurs following radiotherapy. Supported by NIH/NIDCR R01DE21462

(12) **Characterization of Poly-L-lactic Acid Biodegradable Implant Materials by Differential Scanning Calorimetry**; Sudha Muttavarapu[1], John F. Turner II[1]; [1]Cleveland State University

The geometrical shapes of skeletal tissues in the body are important for providing proper mechanical support and locomotion. While the shape of individual bones is governed by genetic and biochemical modulators, bones are constantly undergoing remodeling and bone shapes can be strongly influenced by applied mechanical stresses. It is well known that physical exercise enhances bone mass, however the exact mechanism of localized bone mineral deposition and bone remodeling is unknown. Bone deformation during physical exercise is known to generate electrical potentials within the bone matrix that are theorized to stimulate bone mineral deposition and regulate bone remodeling. In our research, we are quantifying, for the first time, the effect of piezoelectricity on cultured bone tissue in vitro. Our long-term aim is to develop novel piezoelectric bone implants that precisely guide and control bone tissue formation. In our investigation, we employ poly-L-lactic acid (PLLA) as an implantable bone scaffold. The biocompatible PLLA scaffolds can be fabricated with patterned piezoelectric properties. Depending on its density and crystallinity, PLLA is safely biodegraded in the body to lactic acid over periods of several months to years. Because the chemical conformation and long-range crystalline order of PLLA determine its piezoelectricity, non-destructive techniques to characterize the PLLA chemical architecture throughout the cell culture period and during implantation are needed. In our work, we are developing all-optical non-destructive methods based on Raman spectroscopy to simultaneously image the thermal and structural properties of cultured PLLA scaffolds in vitro. In the work shown here, both thermal and structural analysis is achieved by simultaneously performing differential scanning calorimetry and Raman spectroscopy on PLLA. These results provide an optical calibration, based on Raman spectroscopy, for estimating the thermal properties of PLLA scaffolds.

(13) **Wide-field Raman Chemical Imaging of Cold-Drawn Poly-L-Lactide Bioimplants**; Venkata N K Rao Bobba[1], John F. Turner II[1]; [1]Cleveland State University

Poly-L-lactide (PLLA) is a biodegradable and biocompatible polymer commonly used in sutures and implants. Unlike other implantable polymers, PLLA can be endowed with varying degrees of elasticity and piezoelectricity depending on the extent of its long-range molecular order. In its amorphous state, PLLA is isotropic and exhibits no piezoelectric response. By cold-drawing compression

molded plaques, PLLA undergoes molecular ordering. As the draw ratio increases, the mechanical rigidity and piezoelectricity increase up to a draw ratio of 4.5. Greater draw ratios lead to fibrillization and a corresponding decrease in sample crystallinity. By tailoring the crystallinity of PLLA, its degradation rate, Young's modulus, and piezoelectricity can be tailored for a particular application in vivo and lead to greater success rates. Thus, quantification of the crystalline content in PLLA is important for improving the performance of implants. In the work presented here, we have developed a wide-field Raman imaging system based on a narrow passband acousto-optic tunable filter. While AOTF Raman chemical imaging has been reported earlier, our implementation overcomes some of the current limitations and combines novel multivariate strategies with AOTF-based acquisition to provide high resolution images of crystalline content. The multivariate method employs a new Gram-Schmidt orthogonalization method to establish a reference spectrum for automated image analysis based on spectral correlation and is presented here for the first time. In addition to a full theoretical treatment of the multivariate approach, the design of the novel wide-field AOTF Raman imaging system is presented.

(14) **Untangling Fibrillogenesis: A Combined Spectroscopic study of Fibril Formation**; Benjamin Gardner[1], Tanja Deckert-Gaudig[2], Vitali Sikirzhytski[3], Dmitry Kurouski[3], Igor Lednev[3], Volker Deckert[2], Ewan Blanch[1]; [1]University of Manchester, [2]Institute of Photonic Technology, [3]University at Albany

A number of proteins can misfold and form fibrils through the process of fibrillogenesis, which has been implicated in a number of debilitating diseases, including: Alzheimer's disease, Type II diabetes mellitus, Parkinson's and Huntington's disease and CJD. Understanding the structural changes that occur during fibrillogenesis is key to understanding the molecular mechanisms of these diseases, and a requirement for much needed preventative therapeutics to be developed. Insulin is often used as a model protein for studying this process, due to its propensity to form fibrils under a number of conditions, including heating and agitation. To better understand this process we have investigated the fibril formation of the independent chains (21 amino acid A chain & 30 amino acid B-chain), which are normally linked by two disulphide bonds to constitute the mature protein. In our investigation we have combined a number of complementary spectroscopic techniques including: deep UV Raman and conventional Raman Spectroscopy, Raman optical activity (ROA), and Tip enhanced Raman Spectroscopy (TERS). Combining these spectroscopic techniques with AFM imaging, we have identified several notable differences not only in the fibril kinetics, but also divergent and conserved structural transitions. Moreover, TERS has given an insight to spectroscopic differences on the surfaces of the species of fibrils, e.g. differences in alpha helix and beta sheet content. While deep UV Raman provides a sensitive probe of the composition of the fibril core. Overall, this work has been greatly informative about the fibril process and goes a long way to improving the understanding of this complex process, and also highlights the importance of a combined spectroscopic approach to fully understand biological processes.

(15) **Using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy to Monitor Pyridoxal Phosphate in the Active Site of Aspartate Aminotransferase**; Jessica Moore[1], Elyse Towns[1], Joesph Price[1], Mateo Hernandez[1], Michael Toney[1], Don Land[1]; [1]UC Davis

Pyridoxal 5'-phosphate (PLP) is required by many enzymes in amino acid metabolism. Although PLP and PLP dependent enzymes have been extensively studied over the last ~50 years, there are still important unanswered questions regarding control of reactivity and of reaction specificity. Aspartate aminotransferase (AAT) is a prototypical PLP enzyme, binding cofactor that binds PLP via a Schiff base linkage with Lys258. We are attempting to apply attenuated total reflectance Fourier transform infrared spectroscopy to monitor the formation of the Schiff base. This will be extended to studying the protonation states of the Schiff base, and the pyridine ring as a function of the stage of the reaction using inhibitors and alternative substrates. Our goal is to extend these studies to a variety of PLP enzymes so that general principles regarding coenzyme protonation state and reaction specificity can be deciphered.

(16) **A Novel Approach for Non-Invasive Quality Measurements of Intact Salmon using Spatially Offset Raman Spectroscopy**; Nils Kristian Afseth[1], Matthew Bloomfield[2], Jens Petter Wold[1], Darren Andrews[2], Pavel Matousek[2, 3]; [1]Nofima – Norwegian Institute of Food, Fisheries and Aquaculture research, Ås, Norway, [2]Cobalt Light Systems, Harwell Oxford, UK, [3]Central Laser Facility, STFC Rutherford Appleton Laboratory, UK

Numerous feasibility studies have proven the potential of Raman spectroscopy in food analysis. Raman spectroscopy offers a combination of sampling opportunities and chemical specificity that allows for a variety of applications not within the range of standard non-invasive approaches including for instance near-infrared spectroscopy. Major obstacles in Raman food applications have been related to representative sampling, dominating fluorescence interference, and analyses limited to the near-surface regions of biological samples. Recent developments, however, have provided novel approaches for non-invasive sampling, namely spatially offset Raman spectroscopy (SORS). SORS is based on the acquisition of Raman spectra from regions spatially offset on the sample surface from the excitation laser beam, and the technique has already found multiple applications within the medical and pharmaceutical fields. The method also displays a considerable potential within food analysis, an area that so far has not been exploited. Here we explore, for the first time, the possibility of employing SORS in the characterisation of quality parameters of salmon through the skin. Fat content, fat composition and pigmentation are the major quality parameters of farmed salmon, and non-invasive tools for assessing these parameters of live or slaughtered fish would be of major benefit for farming and breeding purposes, and for end-product quality documentation. At present, near-infrared interactance spectroscopy can be used to assess fat content of live salmon, and in this presentation we show that SORS has the potential to provide additional information regarding pigmentation and fatty acid composition. Our studies show that SORS employing 830 nm excitation provides specific and clear spectral signatures of fatty acids and pigments in the salmon muscle both when analysed through light grey skin as well as through dark black skin. SORS also effectively suppresses the broad and dominating fluorescence background of the salmon skin. In the presentation qualitative and quantitative aspects regarding the assessment of fatty acid composition and pigmentation in intact salmon will also be discussed.

(17) **Degree of Conversion of Self-Etch Adhesives on Enamel: A Micro-Raman Spectroscopic Study**; Ying Zhang[1], Yong Wang[1]; [1]University of Missouri-Kansas City

Objective: To investigate the influence of the chemical interaction with enamel on the polymerization of the mild and strong self-etching adhesives. Methods: Two commercial self-etching adhesives Adper Prompt L-Pop (APLP, pH~0.8) and Easy Bond (AEB, pH~2.5) were applied on the prepared enamel surface according to the manufacturer's instruction. The adhesives were also applied on glass substrate as control. Micro-Raman spectroscopy was employed to determine the degree of conversion (DC) of the self-etching adhesives on both substrates. Raman spectral analysis was performed to understand the involved mechanism. Results: The DC of APLP was dramatically enhanced from 9.8% to 84.3% as the substrate was changed from glass to enamel. In contrast, the obtained DCs of AEB

on both substrates showed no significant difference (both appeared to be ~95%). In addition, the DC distributions along the adhesive layers of the APLP and AEB on enamel were also different, showing descending and constant trends (starting from the adhesive/enamel interface), respectively. The Raman spectral analysis disclosed that the chemical interactions of the two adhesives with enamel might have associated with the obtained results. Conclusions: The chemical interactions of the strong and mild self-etching adhesives with enamel affected their photopolymerization differently. The chemical interaction significantly improved the DC of the strong self-etching adhesive APLP rather than the mild one AEB.

(18) **Diffuse Reflectance Adds a New Spectroscopic Dimension for Real-Time Detection of Microcalcification in Breast Needle Biopsies**; Jaqueline S. Soares[1], Ishan Barman[1], Narahara Chari Dingari[1], Zoya Volynskaya[1, 4], Wendy Liu[2, 3], Nina Klein[2, 3], Donna Plecha[2, 3], Ramachandra R. Dasari[1], Maryann Fitzmaurice[2, 3]; [1]George R. Harrison Spectroscopy Laboratory, Massachusetts Institute of Technology, [2]Case Western Reserve University, [3]University Hospitals Case Medical Center, [4]Current Address, Aperio Technologies, Inc.

In this work, we hypothesize and demonstrate that diffuse reflectance spectroscopy provides diagnostic information for detection of microcalcifications, which are an early mammographic sign of breast cancer and geographically target the most clinically significant abnormality within the breast. In particular, microcalcifications are small mineral deposits (calcium oxalate, calcium hydroxyapatite with a range of carbonate substitutions) that range in size from 2-2000 μm with a median of approximately 200 μm. We propose that the size and nature of these clusters produce differential absorption and scattering information from that obtained from normal breast tissue (primarily arising from epithelial and fat cells and collagen fibers). To verify our hypothesis, we collected ex vivo data from 221 tissue sites in fresh breast biopsy tissue cores from 23 patients undergoing stereotactic breast needle biopsies, including 90 normal sites, 56 lesions without microcalcifications and 57 lesions with microcalcifications. Multi-modal spectroscopy employing diffuse reflectance and Raman modalities was employed for measurements and the resulting spectral dataset was compared to the histopathology diagnoses. Using appropriate multivariate chemometric algorithms (principal component analysis in conjunction with support vector machines), we show for the first time that a classification model developed for detection of microcalcifications in breast tissue using only diffuse reflectance spectra shows high predictive power with positive (PPV) and negative predictive value (NPV) of 97% and 88%, respectively. While Raman model is expectedly more specific (PPV = 98%, NPV = 95%), the high diagnostic power obtained using diffuse reflectance creates a new landscape for real-time detection of microcalcifications due to the lower acquisition time and simpler instrument requirements of the latter. We anticipate that this method can be readily translated into existing side-viewing probes for use during core needle biopsies without necessitating extensive optimization of optical components as is typically needed to boost the weaker, if slightly more specific, Raman signals.

(19) **Spectrochemical Imaging at the Infrared Diffraction Limit Reveals Similarities in Brain Tissue from Transgenic Mouse Models of Alzheimer Disease**; Catherine Liao[1], Jillian Lund[1], Margaret Rak[1], Miriam Unger[2], Carol Hirschmugl[2], Benedict Albensi[1], Kathleen Gough[1]; [1]University of Manitoba, [2]University of Wisconsin-Milwaukee

The critical questions into the cause of neural degeneration, in Alzheimer's disease (AD) and other neurodegenerative disorders, are closely related to the question of why certain neurons survive. Answers require detailed understanding of biochemical changes in single cells. Fourier transform infrared microscopy is already an excellent tool for biomolecular imaging in situ; we have conducted large scale survey imaging of brain tissue sections in our lab at U. Manitoba. The sample is illuminated with infrared light; the transmitted light, carrying biospectroscopic information, is then imaged onto a focal plane array (FPA) detector to produce a spectrochemical image that may be processed to reveal many different tissue components. The new mid-infrared beamline IRENI (InfraRed ENvironmental Imaging) at the Synchrotron Radiation Center, University of Wisconsin-Madison, homogeneously illuminates a sample with 12 brilliant synchrotron beams, again imaged onto a FPA, to create sub-cellular spectrochemical images with a pixel resolution of 0.54×0.54 micron^2, an increase of two orders of magnitude over in-house systems. With IRENI's capabilities, it is possible to study changes in individual neurons in situ, and to characterize their surroundings, using only the biochemical signatures of naturally-occurring components in unstained, unfixed tissue. Comparisons among spectra from dried and freshly acquired tissues show that certain restrictions in tissue preparation and storage are critical for preservation of some chemically unstable biomarkers. Recently acquired images of brain tissue from older 3xTg mice, a model for AD, show remarkable compositional similarities to those from TgCRND8, a very different AD model, that suggest similar routes to plaque formation, regardless of genetic predisposition.

(20) **Early Detection of Chytrid Infections in Algal Biomass using Hyperspectral Imaging and Fluorescence Spectroscopy**; Howland Jones[1], Aaron Collins[1], Robert McBride[3], Craig Behnke[3], Thomas Reichardt[2], Michael Sinclair[1], Jerilyn Timlin[1]; [1]Sandia National Laboratories, [2]Sandia National Laboratories, [3]Sapphire Energy

Microalgae have emerged as a promising biofuel feedstock because microalgae can potentially provide higher oil productivity than conventional oil crops while using non-fresh water and less land than other terrestrial energy crops. The cultivation of microalgae at the industrial-scale requires monitoring of algal crops for health and invading predators, such that corrective actions can be performed to prevent crop losses. The current method of detecting predator presence is the use of quantitative PCR (qPCR) analysis. These analyses can be labor intensive, time demanding and expensive; whereas spectroscopic monitoring techniques can be relatively quick and inexpensive. Fluorescence hyperspectral imaging is an ideal tool for examining and following changes in photosynthetic pigments of microalgae and we are using this technique to gain insights into the health of microalgae at the cellular and subcellular level. In addition, the use of Multivariate Curve Resolution (MCR) algorithms to analyze these algal hyperspectral images allows us to discover and extract the endogenous spectral signatures and their associated relative intensities even when nothing is known about the algal culture. We applied fluorescence hyperspectral imaging and MCR to discover the spectroscopic signatures (direct and indirect) associated with Chytridiomycetes (Chytrid) infections of Scenedesmus algal cultures. Chytrids are parasitic fungi that can kill oil-producing microalgae in a matter of hours; therefore the early detection of Chytrids using a field deployable device is desirable to prevent heavy crop loss. Hyperspectral imaging allowed us to understand the spatial location of the spectral signatures within the algal cells and confirm that the spectral signals are indeed related to the Chytrid infections. These spectroscopic signatures can then be used to develop spectroscopic calibration models for the early detection of Chytrid inflections in algal biomass. We will present our hyperspectral imaging results and demonstrate how this signal discovery tool can aid in the development of field deployable spectroscopic measurement devices.

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of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

(21) **Measuring Phytoplankton Community Structure via Fluorescence Imaging Multivariate Optical Computing**; Joseph Swanstrom[1], Shawna Tazik[1], Tammi Richardson[1], Timothy Shaw[1], Michael Myrick[1]; [1]University of South Carolina

Phytoplankton are the oceans net primary producers and play an important role in the global carbon cycle. The amount of carbon exported from the carbon cycle to the bottom of the ocean is related to the phytoplankton speciation and concentration throughout the temporal and spatial community structure of the oceans. Continuous monitoring of the phytoplankton community structure with a rugged and low cost method would allow for high special resolution mapping of the community structure in natural costal or open ocean waters. We are developing a method using multivariate optical computing (MOC) for classifying phytoplankton. MOC is a spectroscopic technique that encodes spectral information of the florescence excitation spectra of target phytoplankton classes into interference filters called multivariate optical elements (MOEs). This report describes the use of a fluorescence imaging photometer that uses a set of MOEs designed for classifying phytoplankton in natural environments.

(22) **Comparison of Various Techniques for Searching for Bio/organic Chemicals Indicative of Life in Na-Sulfate Minerals**; Jill R. Scott[1], Gary S. Groenewold[1], C. Doc Richardson[1, 2], Nancy W. Hinman[1, 2]; [1]Idaho National Laboratory, [2]University of Montana

The presence of bio/organic compounds associated with Na-sulfate deposits found in lava tubes, along with the necessity of oxidizing reduced sulfur to sulfate, suggests that biological activity may be involved in the formation of these secondary minerals in the basaltic subsurface of Craters of the Moon National Monument (COM), Idaho. The secondary Na-sulfate minerals could form by aqueous leaching of sodium ions in conjunction with sulfate ions potentially produced by biooxidation of Fe-sulfide minerals in the overlying basalt. While slightly different, the chemical composition of the COM basalts is analogous to that of their martian counterparts; thus, the potential contribution of biological activity in the formation of sulfate minerals at COM has direct implications for the search for life on Mars. Additionally, the presence of caves on Mars suggests the importance of these environments as a possible location for the growth and preservation of evidence of microbial activity. A key question for detecting the presence of bio/organic compounds in minerals is which method(s) work best. The answer may vary depending on whether the analysis occurs on a rover in a very remote location (i.e., Mars) or in a more traditional laboratory setting as would be the case for samples returned to Earth. Initially, the COM secondary Na-sulfate minerals (thenardite, mirabilite) were examined by laser desorption Fourier transform mass spectrometry (LD-FTMS), Fourier transform infrared spectroscopy (FTIR), and isotope ratio mass spectrometry. LD-FTMS easily detected the presence of the bio/organic compounds with essentially no sample preparation. Recently, the samples have been analyzed with secondary ion mass spectrometry (SIMS) and electrospray ionization mass spectrometry (ESI-MS). The FTIR, LD-FTMS, SIMS, and ESI-MS results will be discussed as well as the pros and cons of these various techniques for detecting potential signs of life.

(25) **GC-MSMS Method for Quantifying 11 Aromatic Amines in Urine of Smokers and Nonsmokers**; Elizaebth A. Cowan[1], Tiffany H. Seyler[1], Jenny G. Kim[1]; [1]Centers for Disease Control and Prevention

Tobacco smoke contains over 4800 compounds and is classified as a Group 1 carcinogen by IARC. Among these compounds, aromatic amines are formed as combustion products during the smoking of tobacco and are detected at high levels in tobacco smoke. Due to the high levels found in mainstream and side-stream smoke (10.59, 8.82, and 0.60 ng/smoked cigarette of o-toluidine, 2-aminonaphthalene, and 4-aminobiphenyl, respectively) aromatic amines pose a threat to exposed nonsmokers as well as smokers. Aromatic amines are known carcinogens; for example, o-toluidine, 2-aminonaphthalene, 4-aminobiphenyl and benzidine are classified as Group 1 carcinogens and o-anisidine and 2,6-dimethylaniline are classified as Group 2B carcinogens. Herein we present the development and validation of a sensitive and robust method for detecting 11 aromatic amines in smoker and nonsmoker urine (o-toluidine, p-toluidine, 2,6-dimethylaniline, o-anisidine, quinoline, 1-aminonaphthalene, 2-aminonaphthalene, 2-aminobiphenyl, 3-aminobiphenyl, 4-aminobiphenyl and benzidine). This is the first time o-anisidine, 2,6-dimethlyaniline, quinoline, and benzidine are measured in the urine of smokers and nonsmokers. Smoking status of each participant was determined by urine cotinine measurement. Previous studies demonstrate the levels of o-toluidine, 2-aminonapthalene and 4-aminobiphenyl are significantly higher in smokers than in nonsmokers. We will present the measurements of all 11 analytes in 50 smokers and 50 nonsmokers.

(26) **Identification of Volatile Biomarker Profiles of Lung Diseases in Canine using Active SPME GCMS**; Shamitha Dissanayake[1], Patty Lathan[2], Todd Mlsna[1]; [1]Department of Chemistry, Mississippi State University, [2]Department of Clinical Sciences, Mississippi State University

The goal of our research is to provide a low cost, efficient, reproducible, quantitative, non-invasive screening method to diagnose diseases at an early stage through the research and development of an analytical system that can provide a rapid and specific assay for diseases. Various challenges associated with the collection and analysis of breath samples with parts per billion concentrations of stress markers and high humidities were successfully addressed with the introduction of novel techniques. Exhaled breath gas samples from canine were collected using a canine mask, two way non rebreathing valve, Teflon connector, Teflon connecting tubes and a Teflon bag. Volatile organic compounds (VOCs), semi VOCs (SVOCs), and water vapor of breath samples were preconcentrated by an Entech 7150 concentrator using a reproducible sample volume. Three different cold traps [tenax (VOC trap), solid phase micro extraction (SPME) (SVOC trap), and silonite coated (water trap)] (liquid nitrogen cooled) were employed in the preconcentration step. Following collection the water trap is heated and flushed before the tenax refocusing step to remove the interference of water. The tenax trap is heated and refocused on to the cold SPME trap. Finally, all the traps are heated and the VOC's released on to the GC column for the chromatographic separation followed by MS analysis. A similar procedure was applied for clinical room air and alveolar gradient was used for quantitative analysis. Optimum instrument parameters were determined using the standards known to be biomarkers of human lung cancer for high throughput screening. Our method has been used successfully to detect the chemical profiles of control (healthy) and diseased animals with further studies underway.

(27) **A High-Throughput Flow Injection ICP-MS Method for Quantitation of siRNA Molecules**; Qiang Tu[1], Fanyu Meng[1], Tiebang Wang[1], Bing Mao[1], Vincent Antonucci[1]; [1]Project Analytical Chemistry, Merck Research Laboratories

Quantitation of siRNA molecules is commonly performed by UV absorption or fluorescence. However, chemical modifications may change the UV absorbance or fluorescence of siRNA molecules, making their accurate quantitation difficult. ICP-AES or HR-ICP-MS can be used for the quantitation of phosphorus, and the number of moles of oligonucleotides can then be calculated using the stoichiometry. But both methods are labor intensive and the

throughput is low. In order to meet the growing demand in pharmaceutical process development to increase sample throughput and turnaround time, a high-throughput flow injection ICP-MS method has been developed for quantitation of siRNA molecules. Specifically, an HPLC system is utilized in automated flow injection (FI) mode and is coupled to an ICP-MS to provide fast and accurate quantitation of phosphorus content in synthetic siRNAs. Isobaric interferences at 31P+ (15N16O+, 14N17O+, etc.) are avoided by monitoring the 31P16O+ molecular ion under optimized conditions in ICP-MS determination. Such approach selectively measures the P content in the sample, which greatly minimizes the interference of non-P containing impurities. Other advantages of this approach include fast run time (< 1 min/sample), excellent sensitivity (LOD=0.8 ppb), low sample consumption (micro liter sample volumes), large linearity range (more than 5 orders of magnitude), and reduced reagent usage. The FI-ICP-MS method provides the capability for accurate high-throughput screening of large amount of siRNA samples in an unprecedented speed.

(28) **Sequestration of Zinc in Activated Macrophages is Essential to Restrict Survival of an Intracellular Pathogen**; Julio Alberto Landero Figueroa[1], Kavitha Subramanian[2], Aleksey Porollo[3], Jospeh A. Caruso[1], George S Deepe, Jr[2, 4]; [1]University of Cincinnati / Agilent Technologies Metallomics Center of the Americas, [2]Department of Molecular Genetics, Biochemistry, Microbiology and Immunology, University of Cincinnati, [3]Department of Environmental Health, University of Cincinnati, [4]Veterans Affairs Hospital, Cincinnati

Macrophages possess numerous mechanisms to combat microbial invasion, including sequestration of essential nutrients, like zinc (Zn). The pleiotropic cytokine, GM-CSF, enhances antimicrobial defenses against intracellular pathogens such as Histoplasma capsulatum (Hc), but the mechanism of action remains elusive. We show that GM-CSF-activated macrophages selectively upregulate an importer Zip2 and amass Zn. Despite increased Zn, metallothioneins sequester and store the labile Zn in a STAT3 and STAT5b dependent manner and the metal is shuttled away from phagosomes into the Golgi. This Zn trafficking is linked with increased exporters ZnT4 and ZnT7, which route Zn into the Golgi. In vivo and in human macrophages, GM-CSF mediates Zn sequestration via metallothioneins. This distinctive GM-CSF strategy starves Hc of Zn, but not iron, copper or manganese, halts replication and fosters fungal clearance without affecting macrophage integrity. These findings illuminate a novel GM-CSF-induced Zn-sequestration network that drives phagocyte antimicrobial effector function.

(29) **Investigating the Commutability of Digested and Dilute-and-Shoot Approach for the Determination of Electrolytes in Human Serum by using Isotope Dilution ICP-MS**; Lee L. Yu[1], W. Clay Davis[1], Yoana Nuevo Ordonez[1], Stephen E. Long[1]; [1]National Institute of Standards and Technology

Electrolytes are necessary for cellular metabolism, for intra- and extra-cellular chemical balance, and for assisting in the neuro-metabolic expenditure of caloric energy. In clinical tests electrolyte levels are measured in blood serum samples. Over the years the National Institute of Standards and Technology (NIST) has developed several standard reference materials (SRM) for validation of clinical measurements of electrolyte in serum. Among these SRMs are 956c Electrolytes in Frozen Human Serum and 909c Human Serum. The determination of electrolytes, specifically K and Ca by ICP-MS, is challenging because of abundance sensitivity issue at K masses and direct isotopic overlap at the most abundant Ca isotope arising from the Ar plasma gas. For certification measurements with the definitive isotope dilution measurements, this problem is compounded by the fact that the analyte must be measured at two or more isotopes. We determined Ca, K, and Mg in SRM 909c Human Serum by using a sector field ICP-MS at the medium resolution mode for Ca and Mg, and high resolution mode for K to alleviate the spectral interferences. Digested and undigested samples of the human serum were measured with the isotope dilution method to investigate the commutability of the complete digestion approach typically used for certification measurement and the dilute-and-shoot approach favored in clinical measurements for its through-put. The results from the two approaches will be compared and the interferences in the ICP-MS measurements will be discussed.

(30) **Metalloproteome of Histoplasma capsulatum: Mn, Fe, Cu, and Zn**; Anna Daigle[1], Julio Landero[1], Kavitha Subramanian[2], George Deepe[2], Joseph Caruso[1]; [1]University of Cincinnati Department of Chemistry, [2]University of Cincinnati College of Medicine[4]

Investigations into the area of proteomics have grown tremendously in the past few decades and have expanded to include metal-containing proteins, known as metalloproteins. Exploring the set of metalloproteins expressed by an organism, known as the metalloproteome, of pathogenic organisms provides valuable information regarding the relationship between pathogen and host as well as an overall greater understanding of the pathogenic organism. Utilizing metal-based purification and identification to study the metalloproteome of a pathogenic organism is currently being applied to *Histoplasma capsulatum* in Dr. Caruso's Metallomics Laboratory. *Histoplasma capsulatum* is a dimorphic fungus which grows into a yeast at 37°C when inhaled, and causes a respiratory infection known as Histoplasmosis. Identification of the metalloproteins within *Histoplasma capsulatum* would allow for better understanding of the microbial growth and toxicity mechanisms that may partially function through metal up or down regulation. This information could potentially lead to treatments that would reduce and possibly eliminate symptoms for individuals infected with the disease. Several analytical instruments including the Inductively Coupled Plasma Mass Spectrometry, High Pressure Liquid Chromatography and Electrospray Ionization/ Iontrap Mass Spectrometry allow for a robust metal-based approach for the identification of metalloproteins within *Histoplasma capsulatum*.

(31) **Isolating a Single DNA Molecule via a Corral Trap**; Xavier Udad[1], Alaknanda Amin-Patel[1], Christine Carlson[1], Jorg Woehl[1]; [1]University of Wisconsin-Milwaukee

Single molecule techniques bring a different aspect to the study of chemical reactions in that they break down a chemical reaction to its most fundamental level. In many experimental schemes, the investigated molecules need to be immobilized so that the data acquisition time can be extended and sufficient signal-to-noise ratios can be achieved. Immobilization can consist of chemical bonding to surface-linked species, physisorption, or dielectrophoretic trapping near electrode surfaces. However, in all of these cases the properties and behavior of the immobilized molecules may be significantly altered due to the proximity of the surface itself, which is an important shortcoming especially in the case of many biophysical processes (e.g., protein folding). We have recently developed a technique for the stable trapping of particles and single molecules such as DNA in free solution in order to overcome these limitations. The trapping idea is based on the fact that DNA molecules are negatively charged when in solution and will therefore be repelled by another object that is also negatively charged. The trap consists of a thin layer of metal decorated with microscopic holes evaporated onto a glass coverslip. A single circular hole can effectively trap a negatively charged DNA molecule by surrounding it with electrons that accumulate at the metal rim when charged by a power supply. The accumulation of electrons creates an electrostatic potential well, and a trapped DNA molecule experiences uniform repulsion in all directions due to the circular shape of the trap.

(32) **Microcolumn Chromatographic-Based Competitive Binding Immunoassays for TBI Biomarkers**; Jeanethe Anguizola[1], Erika Pfaunmiller[1], Michelle Koke[2], Marie Paula Paulemond[3]; [1]University of Nebraska, [2]Nebraska Wesleyan University, [3]Bennett College

A flow injection assay that employs affinity microcolumns and near-infrared fluorescence spectroscopy was developed for the detection of glial fibrillary acidic protein (GFAP), a brain specific protein that is released after traumatic brain injury (TBI). The initial factors considered in the design of this method included the choice of immunoassay format, the length of the antibody immobilized column and the selection of the labeled analyte analog. The final method utilized a sandwich microcolumn prepared with a 100 μm thick layer of a support that contained anti-GFAP antibodies. A competitive binding immunoassay format, based on the simultaneous and sequential injection methods, was employed in this work. In the simultaneous format, the sample containing the unlabeled analyte and the labeled analog were applied at the same time to the column; while in the sequential mode the sample was injected first, followed by the labeled analog. A fixed amount of near-infrared (NIR) fluorescent labeled GFAP plus various amounts of unlabeled GFAP were injected onto the anti-GFAP microcolumn for calibration. The amount of labeled GFAP captured by the microcolumn decreased as the concentration of the unlabeled GFAP in the sample was increased. This led to an increase in the amount of the non-retained, labeled GFAP which was measured with a flow-through NIR fluorescence detector. This method gave results within a few minutes of sample injection and provided a dynamic range up to more than 200 pg GFAP, depending on the assay format. The lower limit of detection for GFAP was estimated to be 2 pg (S/N=3). A recovery study performed using pooled sera spiked with 50 pg GFAP gave a recovery percentage of 102 (+/- 4)% (n=5). This microcolumn-based flow injection immunoassay was found to be a promising approach for the detection of clinically relevant amounts of GFAP in serum following traumatic brain injury.

(33) **Optimization of Protein Entrapment for Preparing High Performance Affinity Supports**; John Vargas[1], Abby Jackson[1], Jeanethe Anguizola[1], Giana Rada[1], David Hage[1]; [1]University of Nebraska-Lincoln

High performance affinity chromatography (HPAC) is a technique that uses biomolecules undergoing specific interactions with target analytes. The stationary phase is usually prepared by covalently attaching a biomolecule, such as a protein or an antibody, to a support like silica. This approach faces challenges like multisite attachment or improper orientation of the binding agent, which may decrease the agent's activity. Entrapment, an alternative approach to covalent immobilization, is a physical process where a macromolecule like glycogen is used as a capping agent to encapsulate the binding agent in the support. In this study, human serum albumin (HSA) was entrapped in hydrazide-activated silica using oxidized glycogen as a capping agent, in which a covalent link was formed between aldehyde groups on the oxidized glycogen and hydrazide groups on the outer surface of support. This process was optimized by altering the purification method of oxidized glycogen from gel permeation chromatography to filtration, as well as increasing the concentration of protein in solution and decreasing the total volume of reaction used for entrapment. The final support was tested by using warfarin (i.e., a drug with known interactions with HSA) as a model analyte for this system. When using a slurry-based entrapment method, the retention factor measured for warfarin on a 1 cm long column containing the entrapped HSA support increased by up to a factor of five when decreasing the reaction volume or when increasing the concentration of HSA. An on-column entrapment approach was also examined, where HSA and oxidized glycogen were reacted with hydrazide-activated silica in a flow-based format. This second approach provided retention factors for warfarin that were up to ten times higher than those obtained by the slurry method. The same approach can also be modified for use with other proteins or supports for use in HPAC or other affinity-based methods.

(34) **Fabrication of an Integrated Microfluidic Device for Single Molecule Trapping**; Christine Carlson[1], Xavier Udad[1], Jörg Woehl[1]; [1]University of Wisconsin Milwaukee

Optical traps or "laser tweezers", which are capable of trapping microscopic dielectric particles through the production of steep electromagnetic field gradients, have been significant in the development of the field of biophysics and the manipulation of microscopic objects. This method of trapping unfortunately has a fundamental size limitation, making it incapable of trapping molecular-scale objects. We have developed a new tool for the trapping and manipulation of nanoscale objects including single molecules, the corral trap, which has distinct characteristics that set it apart from other trapping techniques. In order to increase the versatility of this new trapping tool, steps have been taken to integrate corral traps in a microfluidic cell. The production of such integrated devices based on focused ion beam milling and optical lithography techniques will be presented in detail. Corral trapping in microfluidic devices is expected to have important future applications in areas such as biomedical assays, ultra-sensitive biochemical analysis, and DNA manipulation and screening. Novelty: A novel method for the trapping of single molecules has been successfully used for the trapping of single ssDNA molecules.

(35) **Spectroscopic Studies of the Influence of Membrane Fluidity on Protein Structure**; Michael K. Eagleburger[1], Neeta R. Thawani[1], Elizabeth Reardon[1], Jason W. Cooley[1], Renee D. JiJi[1]; [1]University of Missouri

The ability to study membrane-protein interactions is crucial to understanding the mechanisms behind many natural processes, including membrane protein folding. Previous efforts by our laboratory have established that deep ultraviolet resonance Raman spectroscopy (dUVRR) may be used to study the secondary structure of transmembrane proteins and the membrane proteins have a uniquely enhanced amide I feature. While these studies have yielded important information on the basic interactions of lipid membranes and proteins, they fall well short of mimicking the native complexity of biological membranes. One important component in native membranes is sterols. The most common sterol found in human cells is cholesterol, which is known to decrease lipid fluidity at higher concentrations. Cholesterol has four fused rings with one internal carbon-carbon double bond and an alcohol group. The carbon-carbon double bond of cholesterol has a strong vibrational band that overlaps the amide I band of proteins in dUVRR spectra. Thus in order to mimic the effect of cholesterol on lipid fluidity, an alternative compound, invisible to dUVRR, is needed. The cholesterol analog, 5α-cholestan-3β-ol, lacks the internal carbon-carbon double bond present in cholesterol. Fluorescence anisotropy studies of membrane embedded diphenylhexatriene (DPH) showed that 5α-cholestan-3β-ol reduced the fluidity of phospholipids in a similar manner as cholesterol. Further, dUVRR spectra of the membrane protein gramicidin in liposomes containing up to 25 percent 5α-cholestan-3β-ol showed no additional features arising from the analog.

(36) **Study Of Influence Microwaves Radiation Coupled with HPLC. Effect of Ion Concentration in Mobile Phase.**; Jose-Luis Todoli[1], Silvia Carballo[1], Amanda Terol[1], Juan-Pedro Diaz[1], Soledad Prats[1], Salvador Maestre[1]; [1]University of Alicante

The present work is focused on the study of microwaves radiation with HPLC (High Performance Liquid Chromatography). A set of five vitamins (niacin, pyridoxine, thiamine, riboflavin and biotin) were separated and determined by means of a UV-VIS detector, being the microwave radiation applied to biotin and riboflavin, while the other three vitamins were takes as reference compounds. In order

to perform the separation, a column was placed inside a domestic microwave oven in a hanging position. The column position is an extremely critical point, because it affects the amount of energy absorbed by the mobile phase. In order to avoid magnetron or column damage, a heat well (i.e. water vessels) was used. Results obtained showed that the application of microwave radiation, even at low power levels, gave rise to a significant modification in the characteristics of the separation. It was found that retention times for biotin and riboflavin shortened as the power increased. Furthermore, to compare the effect of microwave radiation with GC oven column heating (HTLC), similar temperature gradients were applied to both MW-HPLC and HTLC for each mobile phase composition. Other experiments were based on the change of the ionic strength of the mobile phase. In this study, the HClO4 concentration in the mobile phase was changed, and it was observed that with the increase in ion concentration, the retention times of vitamins decreased and sensitivity increased as compared with low ion concentration. The extent of this effect was higher with microwave radiations than with traditional heating.

(37) **Redox-Magnetohydrodynamic Pumping, Spatially Separated from Redox Processes at Active Electrodes**; Preston Scrape[1], Ingrid Fritsch[1]; [1]University of Arkansas

In a typical magnetohydrodynamics (MHD) microfluidic pump design, the analyte fluid is placed in a magnetic field, and electrodes in contact with the fluid induce current through it; this current is carried by all charged species in the fluid as an ionic current. The magnetic component of the resulting Lorentz force produces fluid flow. This pumping method requires no moving parts, is multi-directional, and can easily be miniaturized for smaller, more efficient micropumping devices. Addition of redox species to the fluid eliminates bubble formation and degradation of electrodes, which have been common problems in traditional designs of chip-based MHD devices. However, in this "redox"-MHD approach, there are concerns that those redox species may interfere with some analyses. The work to be presented will show localized, directed fluid flow induced by redox-MHD in bulk solution, far from diffusion layers and redox processes at active electrodes. This result suggests that analytes can be spatially separated from redox species, by confining or binding those species to active electrodes, while still allowing redox MHD pumping to occur in the analyte volume. Such a separation would broaden applications of redox MHD for micro total analysis systems (μTAS), and would have implications for studies such as magnetoconvection and ion transport as well. The substrate was a silicon chip patterned with gold electrodes. The major innovation is the use of a magnet much smaller than the distance between electrodes. The magnet produced a magnetic flux density perpendicular to the chip of up to 70 mT. A constant 30 μA current was applied, and the MHD force produced fluid flow up to 16.9 μm/s directly over the magnet, with circulation at the magnet edges to fill the fluid void. This discovery invites further work toward confining redox species to active electrodes while maintaining redox MHD pumping, thus avoiding the problem of redox interference with the analyte. These studies also suggest that magnets and electrodes can be patterned to achieve fluid pumping for the specific requirements of a μTAS device.

(38) **Microfluidics with Magnetohydrodynamic Pumping and Stirring using PEDOT-modified Electrodes**; Christena Nash[1], Ingrid Fritsch[1]; [1]University of Arkansas, [2]University of Arkansas

In redox-magnetohydrodynamics (RMHD), a body force, F_B, which produces fluid flow is defined by a simple right hand rule: $F_B = j \times B$, where the ionic current density, j, generated through oxidation or reduction of redox species at the electrode surfaces, is perpendicular to a magnetic flux density, B. RMHD has complementary features and advantages over existing micropumping approaches. Some concerns have been raised about redox species interfering with detection or degrading biological species. A new approach is being investigated for implementing redox-MHD by using conducting-polymer-modified electrodes to generate j, instead of adding redox species to solution. Recent RMHD studies for both pumping and stirring microfluidics will be presented using the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT). PEDOT was electropolymerized on long microband gold electrodes (100 μm wide and 2.5 cm long) and on ring/disk electrode sets (varying in size) for pumping and stirring respectively. PEDOT was chosen because it can be electrodeposited in aqueous solutions and is biocompatible . To examine RMHD fluid control using the PEDOT-modified electrodes, a cell was constructed with the electrode chip as the floor and a microscope slide as the lid, where the 3 mm height, defined by the thickness of a poly(dimethylsiloxane) gasket between the electrode chip and slide, and with a rectangular opening of 3.2 cm x 1.5 mm containing an electrolyte solution (e.g. 0.1 M sodium chloride). The electrodes were connected to a potentiostat/galvanostat via contact pads on the edge of the chip and the cell was placed on a permanent Nd-Fe-B magnet with a B field of 0.37 T and perpendicular to the chip. Microbeads were added to the electrolyte solution and tracked using video microscopy. Fluid flow patterns and velocities were quantified using particle imaging velocimetry analysis. Fluid speeds as high as 400 μm/s were observed, although over a brief time. We will discuss the implementation of PEDOT-modified electrodes in MHD-induced fluid movement for microfluidic applications.

(39) **Selective Trapping of Single Human Breast Cancer Cells by Insulator Based Dielectrophoresis in a Microfluidic Device**; Sanchari Bhattacharya[1], Tzu-Chiao Chao[1], Alexandra Ros[1]; [1]Arizona State University

Selective trapping of individual cells at specific locations in microfluidic platforms is essential for single cell studies, especially those requiring cell stimulation and downstream analysis. We have previously demonstrated a novel microfluidic device based on direct current (DC) insulator based dielectrophoresis (iDEP) for trapping individual human MCF-7 breast cancer cells. Here, we demonstrate the application of this device for selective trapping of MCF-7 cells from mixtures with human B-lymphocytes. Application of DEP for mammalian cell sorting in microfluidic devices was mainly based on miniaturized electrode designs. However, electrode fouling imposes a limitation on the lifetime of the devices. iDEP devices are cost-effective and robust alternatives. Few studies have been reported on DC iDEP of mammalian cells, mostly in conjunction with AC fields. Our microfluidic devices are targeted for selective capturing of single cells based on their DEP behavior. We employ numerical simulations to compute the trapping condition, in which DEP overcomes electrokinesis. An electroosmotic mobility of 2.2*10-9m2V/sec was determined experimentally in the employed buffer system and used in numerical simulations. The dielectrophoretic mobility was calculated with the 2-shell model resulting in 0.55*10-22m4/V2sec for MCF-7 and 0.09*10-22m4/V2sec for lymphocytes. Due to this larger dielectrophoretic contribution for MCF-7 cells, the simulations predict preferred DEP trapping of MCF-7 cells versus lymphocytes at an applied potential of 240V/cm. This was demonstrated experimentally where single MCF-7 cells were immobilized in the specific trapping regions whereas lymphocytes bypassed this area and were transported downstream. Viability of these cells was studied in the low conductivity buffer used in these experiments, consisting of HEPES (30mM) and Trehalose (120mM). The percentage of viable B-Lymphocytes and MCF-7 cells after 4 minutes of electric field application were 47±6.6% and 57±6.8%, respectively. These values were comparable with cell viability measurements in the absence of an electric field (44±7% and 61±0.8% for B-lymphocytes and MCF-7 cells, respectively), indicating that the cells are not strongly affected

by the electric field. Our ongoing work is dedicated to device optimization, parallelization of the single cell traps, and coupling with mass spectrometric protein analysis.

(40) **Microfluidics Involving Flat Flow Profile and Fluid Stirring Guided by Redox-Magnetohydrodynamics (MHD): toward Lab on a Chip (LOC) Immunoassays**; Vishal Sahore[1], Ingrid Fritsch[1]; [1]University of Arkansas, Fayetteville

Channel-less, flat flow profiles have been achieved using redox-magnetohydrodynamics (MHD) microfluidic pumping between microband electrodes over an interelectrode distance of 5.6 mm and for at least 2.5 cm, with circular stirring of fluid achieved over diameters of 800 μm to 3200 μm using different sized concentric ring/disk electrodes, over a silicon chip placed on a permanent Nd-Fe-B magnet. The absence of velocity gradients due to a flat flow profile and presence of them when stirring at the ring/disk electrodes is anticipated to expedite the assay development and detection process. The goal of the present work is to integrate the unique features of redox-MHD microfluidics for lab-on-a-chip (LOC) immunoassays. Progress made to-date will be described. Redox-MHD involves the addition of chemical species that can oxidize or reduce at the electrodes with a lower overpotential than water and the electrode material, to generate the ionic current density (j) in the presence of a perpendicular magnetic field (B) required for the MHD pumping force (FB = j × B). Redox-MHD has the ability to be used as a non-mechanical, multi-directional microfluidic pumping method that controls fluid flow patterns through the use of placement of electrodes (e.g. microfabricated microelectrode array). Furthermore, it works without requiring channel sidewalls, therefore simplifying device design, and also avoids the problem of bubble generation as well as the electrode degradation. Control of fluid speeds, direction, and patterns for the different electrode geometries will be shown for model redox species.At present, studies that lead toward development of immunoassays involve the formation of a complex assembly using streptavidin-coated superparamagnetic beads and biotinylated alkaline phosphatase (AP). The enzyme-modified beads can be immobilized on the chip surface because of the presence of the external magnetic field. The species p-aminophenyl phosphate (PAPP), a substrate of AP, can be transported in the pumping solution of [Ru(NH3)6]2+/3+ in tris buffer, toward the enzyme-immobilized site using a flat flow profile and circulated at the ring/disk electrodes to react with the AP there. The reaction generates p-aminophenol, PAPR, which undergoes electrochemical detection at on-chip electrodes to give a signal that is related to the concentration of AP attached to the beads.

(41) **CO2-Laser Atmospheric Pressure Ionization of Acoustically Levitated Droplets**; Merwe Albrecht[1], Arne Stindt[1], Ulrich Panne[1], Jens Riedel[1]; [1]BAM Federal Institute for Materials Research and Testing

Once designed for zero gravity experiments, in recent years levitation devices have experienced a renaissance in microfluidics where they serve as wallless reactors and for contactless sample handling. Until now many optical analytical techniques have been employed to interrogate the contents of levitated droplets, however only one approach towards a coupling to mass spectrometry has been successfully conducted utilizing a combination of corona charging, pulsed high voltage electrodes, MALDI matrix addition to the droplet and desorption with an UV-laser [1]. In the presented work we used a single CO_2 laser pulse for vaporization and ionization out of a previously uncharged droplet following the approach of CO_2 MALDI proposed by Hillenkamp 20 years ago [2]. We used water as solvent, glycerol as IR chromophore and amino acids and small peptides as analytes. The droplets were levitated with a home built ultrasonic trap which was set in front of the inlet tube of an atmospheric pressure time-of-flight mass spectrometer in positive ion mode. The CO_2 laser was gated to ~ 20 ms by a mechanical shutter. In order to visualize the laser induced vaporization and plume formation, the experiments were accompanied by high repetition rate shadowgraphy. The resulting spectra resemble results expected for MALDI conditions and show no fragmentation products. This soft ionization is attributed to the low energy coupled to the system by individual photons dictating mere dynamics in the electronic ground state . The observed ions therefore corroborate the lucky survivor mechanism postulated by Karas et al. [3]. This assumption is confirmed due to the fact that only basic analytes such as amino acids and peptides which occur as precharged species produce significant signals. The obtained spectra show also a strong dependency on changes of pH regarding the observed ions and their total and relative intensities.

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(42) **Fluorescence Correlation Spectroscopy (FCS) to Quantify Flow Patterns in Electrochemically-Driven Microfluidic Devices**; Feng Gao, Adam Kreidermacher, Ingrid Fritsch, Colin Heyes; [1]Department of Chemistry and Biochemistry, University of Arkansas

Obtaining high-resolution 3-dimensitonal flow maps from pumpless electrochemically-driven microfluidic devices allow us to study in detail the various forces involved which, in turn, will allow us to design, optimize and fabricate advanced devices for a wide range of (bio)analytical applications. Redox magnetohydrodynamics (MHD) can be used to drive flow, but a detailed description of all the forces involved is not trivial. In addition to Redox-MHD, density gradients caused by the redox reactions also play important roles. Here we show FCS can be used to quantitatively and accurately measure flow speeds and patterns between ~5-50 μm/s in these devices, from which 3-D flow maps can be obtained with a spatial resolution down to 2 μm. We also show that FCS can measure temporal fluctuations in flow speeds which may arise from fluctuations in the rates of oxidation and reduction of the electrolyte species. We discuss the optimal parameters to obtain 3-D flow maps, including the size of the fluorescent polymer beads used in the solution, electrolyte concentration, microfluidic channel dimensions, data acquisition time, and statistical data analysis and compare the results to those obtained by the more common particle image velocimetry (PIV) techniques.

(43) **Using Bead Video Microscopy to Observe Electrochemically Generated Density Gradient Based Fluid Flow in a Microfluidic Setting.**; Adam Kreidermacher[1], Vishal Sahore[1], Ingrid Fritsch[1]; [1]University of Arkansas

Convection caused by density gradients are of interest because they can negatively disrupt fluid flow profiles or be used in a productive way for stirring. Density gradients can be created and controlled in a microfluidic environment by oxidizing and reducing electroactive chemical species at electrodes on a chip in a small volume. Research will be discussed that will focus on the ferrocyanide/ferricyanide redox couple at a gold band electrode on a chip in a cell having dimensions of 5.5 mm x 12.6 mm x 0.810 mm. The generation of density gradients is due to the movement of counter ions to compensate for the oxidized ferrocyanide or reduced ferricyanide at the electrode. Three potassium ions to one ferricyanide ion form a less dense volume element compared to four potassium ions to one ferrocyanide ion, for a given concentration. The electrochemically generated density gradients can produce natural convection from the buoyancy force once the gradients become sufficiently large. This

convection can be monitored using video microscopy of microbeads in the solution to determine the velocity of the fluid movement. In the experimental setup, the chip with the electrode is at the bottom of the cell facing upward into solution. This results in faster convection when ferrocyanide is oxidized because the less dense fluid element rises. The onset of convection occurs at times after the beginning of the applied current or potential that is shorter for higher currents. This can be achieved directly with a higher applied current, or indirectly with an increased ferrocyanide concentration or larger electrodes for a given applied potential. The velocity of the fluid is also higher for conditions that cause shorter times for the onset of convection.

(44) **Direct Quantification of Tenofovir in Simulated Biological Fluids from pH-Sensitive Microparticles using 1H-NMR**; Chi Zhang[1], Tao Zhang[2], Bi Botti Youan[2], Nathan Oyler[1]; [1]Department of Chemistry, University of Missouri-Kansas City, [2]School of Pharmacy, University of Missouri-Kansas City

Recently the use of polymeric nanoparticles as drug delivery carrier for HIV microbicide has gained more attention. Evaluation of the in vitro drug release profile is a critical step during the characterization process of such system. The currently utilized membrane dialysis method has been criticized as it could be affected by the drug partitioning between the donor and receptor compartment. The purpose of our project is to develop a direct method to detect and quantify the amount of tenofovir release in the simulated vaginal fluid (VFS) and semen fluid (SFS) in vitro. We found that solution state NMR was an effective way to detect tenofovir in the two media. Various methodological parameters were validated according to International Conference on Harmonization (ICH) guidelines including linearity, accuracy, precision and so forth. The results indicated that the method was accurate, simple and rapid. The 1H-NMR method validation profile and the drug release evaluation profile are presented in this poster.

(45) **Optimizing Bioassay Performance using Dye Functionalized Whispering Gallery Mode Microresonators**; Daniel Kim[1], Kevin Armendiaz[1], Sarah Wildgen[1], Robert Dunn[1]; [1]University of Kansas [4]

Whispering gallery mode (WGM) resonators enable the label-free detection of analytes based on refractive index changes. We recently coupled fluorescence detection with microsphere resonators to develop an imaging approach for measuring WGM resonances on large fields of resonators. By combining WGM resonators with fluorescence imaging, large scale multiplexing is possible where analyte identity is encoded into sphere size and/or location. To develop point-of-care sensing platforms using this approach, we are currently integrating the resonators with microfluidic devices for sample handling. In these applications, the resonators must be immobilized onto the substrate surface without interfering with the light path of the WGM around the resonator. A glass bonding method will be discussed which effectively immobilizes the small resonators without perturbing the Q-factor of their WGM resonance. The bonding method is also sufficiently strong allowing Langmuir-Blodgett (LB) transfer of films onto the immobilized resonators. Studies using LB films to quantify the effects of the fluorescent dye on resonator Q-factor and for functionalizing the surface of the resonator will be discussed. Finally, LB films are also used to engineer the surface of the substrate and modify the refractive index of the layer between the substrate and the resonator. Studies using these engineered layers to maximize the Q-factor of the resonators will be outlined. Another approach for immobilizing resonators uses tapered microfluidic channels to trap and segregate spheres by size. Progress towards integrating microfluidics with WGM resonators for multiplexed cancer screens will be presented.

(46) **Whispering Gallery Mode Imaging for the Early Detection of Ovarian Cancer**; Sarah Wildgen, Heath Huckabay; [1]University of Kansas

Ovarian cancer is the most deadly of the gynecological cancers even though treatments are extraordinarily effective when the cancer is diagnosed in early stages. Unfortunately, the combination of a lack of early symptoms and inadequate screening methods often leads to late stage detection where interventions are much less effective. This has motivated the long term goal of developing serum screens capable of identifying at-risk populations early in the disease progression. Currently, cancer antigen 125 (CA-125) is a widely used serum marker which is mainly used to confirm a diagnosis, monitor the response to treatment, and detect recurrences of the disease. CA-125 detection alone, however, is not sufficient for an early screen of ovarian cancer. CA-125 is only elevated in about 50% of stage I patients and can be elevated due to other benign conditions. Effective serum screens, therefore, will need to quantify several biomarkers to have the sensitivity and specificity required for an effective early diagnosis. Our group has begun developing sensitive, label-free assays for the multiplexed detection of putative ovarian cancer biomarkers using whispering gallery mode (WGM) resonators. The optical properties of these resonators are strongly linked to refractive index changes, which provide a sensitive mechanism for detecting analyte binding at the resonator surfaces. We have recently demonstrated a fluorescence imaging approach for measuring these resonances which potentially enables large scale multiplexing capabilities. We have demonstrated the multiplexing potential by simultaneously quantifying the putative ovarian cancer markers CA-125, prolactin and osteopontin in buffer. We have also shown that non-specific interactions can be sufficiently reduced to enable measurements in serum by quantifying CA-125 levels in healthy and cancer patient samples. These studies and progress towards developing a deployable screen will be discussed.

(47) **N-linked Glycoengineering for Therapeutics: Rapid Confirmation of Glycan Incorporation**; Melinda L Toumi[1], Heather Desaire[1]; [1]University of Kansas, Department of Chemistry

N-linked glycosylation improves protein therapeutics by enhancing their solubility and bioavailability. However, adding glycans to proteins that are not natively glycosylated can have deleterious effects, such as abrogating the protein's activity. We developed a novel and highly transferrable strategy to append glycans to peptide and protein therapeutics. Using a model protein, luciferase from *Metridia longa,* the efficacy of the approach was demonstrated. First, three unique glycosylation sequons were designed to add glycans to any protein. The sequons were incorporated into the N-terminus of the luciferase sequence, along with a C-terminal 6xHIS tag. The three luciferase mutants were compared to the native, non-glycosylated, luciferase protein. All proteins were expressed using CHO-K1 cells, in T-75 flasks, with ATCC's F-12 media and 150 mM Proline. This model system was used to address these questions: 1) Were the new proteins glycosylated? 2) Was the resulting protein still active? 3) Were any negative effects observable? To answer these questions, several complementary and novel bioanalytical assays were developed. A sensitive and rapid glycan detection assay was developed by cleaving glycans with a glycosidase and adding malononitrile to dervatize the released glycans. Fluorescence was monitored using λ_{ex} of 355 nm and λ_{em} of 430 nm. The modified proteins were determined to have glycans present, whereas the native protein did not. Next, a luciferase activity assay was utilized, and the native protein sample displayed higher enzymatic activity compared to the modified proteins. Finally, Western blot analysis with an anti-6xHIS antibody indicated that the modified proteins were present in lower quantities than the native, unmodified protein, with the modified proteins' concentrations fell below the assay's limit of detection. Thus, the lower activity results for the glycosylated

proteins may be due to decreased titer levels alone and not from glycans negatively impacting enzymatic activity. This research demonstrates a new way to enhance therapeutic proteins by adding glycosylation, and it provides a rapid analysis strategy to measure the success of this glycoengineering approach.

(48) **Extraction and Determination of Oxytetracycline in Muscle and Skin Salmon by Fluorimetry Based on Ionic Pair Formation**; M. Inés Toral[1], Grace Paillavil[1], Nicolas Silva[1], Pablo Richter[1]; [1]University of Chile

This work presents the extraction and determination of oxytetracycline (OTC) in muscle and skin salmon, based on the formation and extraction of ionic pair with crystal violet (CV) evaluated by fluorimetry. A sample of 5.0 ± 0.1 g was weighed and fortified with different concentrations of OTC, 20 mL of buffer Mc Ilvaine/EDTA pH 4 was used as extracting, then was added 2 mL of trichloroacetic acid to precipitate the proteins, the sample was centrifuged and the procedure repeated. Both extracts were mixed, filtered and purified using Sep-Pak C-18 cartridge fitted with methanol/distilled water OTC was percolated with 4 mL of methanolic oxalic acid 1.0x10-2 mol/L. Thereafter ionic pair was formed with CV and extracted with 6 mL of chloroform. The effect of oxalic acid on the fluorescence band of the ionic pair was studied, being found a four times increase, thus simplifying the method, since the percolate can be directly added for ionic pair formation. Through a 22 factorial design, using standard the formation and extraction of the ionic pair was optimized, keeping constant: 6 mL of chloroform, 4 mL of oxalic acid, 50 mL of aqueous phase; analyzing the pH and volume of VC variables, being found to be optimal pH 9.2 and 350 µL of VC. A λex 360 nm was selected, since the ionic pair presents a characteristic band above the blank. In addition excitation and emission slit were optimized, being selected 20-20 nm, for presenting high signals without distortion. Under these conditions, it is possible to construct a calibration curve in enriched muscle and skin salmon, where the linear regression was If = 7.5 x 109 C (mol/L) + 42.4, the detection and quantification limits were 0.08 mg/kg and 0.28 mg/kg, respectively, decreasing considerably the quantification limit in relation to 70 mg/kg obtained by UV-visible molecular spectroscopy. The authors thank the financing of this research to the project FONDECYT 1100103.

(49) **Extraction of Oxolinic Acid and Flumequine from Salmon Muscle and Simultaneous Determination by Fluorimetry**; M. Inés Toral, Karina Seguín, Muriel Andrade, Pablo Richter; [1]University of Chile

This work proposes a method for the extraction from salmon muscle and simultaneous determination at low concentrations of oxolinic acid (OXO) and flumequine (FLU) by derivative fluorescence spectrometry. In this method, the proposed extraction decreases the previous stages of the analytical process. Different salmon muscle samples of 100 mg were crushed, homogenized and fortified individually and/or simultaneously, with OXO and FLU standard solutions to obtain concentrations between 2.8 and 14 mg/kg. Each sample was allowed to stand for 30 min in centrifuge tube of 50 mL. Then 20 mL of acetonitrile was added and stirred in vortex for 20 min and then centrifuged at 5000 rpm for 10 min at room temperature. The supernatant was transferred into 50 mL plastic tubes and 4 mL of hexane was added, stirred in vortex for 3 min and removed the hexane phase, where the fat is extracted. This step is repeated, and then centrifuged at 5000 rpm for 5 min. The fat-free extracts were measured in a fluorescence spectrophotometer to λexc 248 nm and 318 nm, 10-20 nm slit. Using λexc 248 nm, and the first order derivative of the emission spectra, a zero crossing was found at 365.5 nm and 360.5 nm to determine FLU and OXO respectively; however, the recovery percentages were low for FLU and OXO. Moreover, with λexc 318 nm were obtained zero crossing at 366 nm and 360 nm to determine FLU and OXO respectively, under these conditions for FLU a detection limit of 4.0 x10-8 mol/L and a quantification limit of 1.3 x10-7 mol/L were obtained; for OXO a detection limit of 2.7 x10-8 mol /L and a quantification limit of 9x10-8 mol/L were obtained, the recovery percentages were 70% and 71% for FLU and OXO respectively, with a 3% RSD. Based on the results obtained, the latter route was selected for evaluation of analytical signals. The authors thank FONDECYT Project 1100103.

(50) **Modification of Protein Fluorescence by AuNPs: Inner-Filter Effect, Surface Enhancement, and Fluorescence Quenching**; Charles Nettles[1], Dr. Dongmao Zhang[1]; [1]Mississippi State University

Gold nanoparticles (AuNP) can modify protein fluorescence through three different mechanisms: inner-filter effects, fluorescence quenching by Forster resonance energy transfer, and surface plasmon enhancement of fluorescence. The contribution of each effect to experimental measurements of protein fluorescence holds the key to understanding protein-AuNP interactions. Using native and fluorescent labeled protein we investigated the possible significance of fluorescence quenching and/or surface enhancement. This study is important as it provides a guideline for the fluorescent study of protein-AuNP interactions.

(51) **Determination of Protein Glycation Levels by Surface Plasmon Resonance - A Preliminary Study**; Phillip Page[1], Thomas Ryan[1], Mary Murphy[1], Peter McDonnell[2], Tony New[2], Ian Davison[2]; [1]Reichert Technologies, Analytical Instruments Division, [2]Genzyme Corporation, Haverhill Operations, UK

The rise in the number and use of protein-based therapeutics makes it increasingly important to quickly determine the extent of modifications that can occur during formulation and storage. This study was undertaken to determine the feasibility of employing surface plasmon resonance (SPR) to detect the glycation level of bovine serum albumin (BSA) incubated with D-ribose at 37 oC. The first part of this study looked at differences in the immobilization level of control and glycated BSA to the biochip surface. BSA was coupled via formation of an amide bond between lysine residues and a free carboxyl on the surface of the biochip. Reduced immobilization levels were observed for the glycated BSA samples. This result is likely due to glycation reducing the number of available free lysine groups. The binding of control and glycated BSA to a surface immobilized Anti-BSA IgG was also studied. The initial response rates of control BSA and glycated BSA binding to the antibody were found to be a linearly decreasing function of the BSA D-ribose incubation time. The maximum response level of the glycated BSA samples was also greatly reduced. A relatively rapid decrease in the SPR signal was observed during the first hour of incubation. This result could indicate that initial low glycation levels near the BSA binding site(s) have a large immediate effect on the BSA/Anti-BSA interaction. It appears from these initial studies SPR could be used as a relatively simple quick screen for detecting glycation of protein samples.

(52) **Single Molecule Fluorescence Correlation Spectroscopy of Apoptotic Cells using a Red-Fluorescent Caspase Probe**; Michelle Martinez[1], Meicong Dong[1], Michael Mayer[1], Dimitri Pappas[1]; [1]Texas Tech University

Detection of apoptosis in living cells is demonstrated with fast response time and high sensitivity. Fluorescence correlation spectroscopy (FCS) is used to detect caspase activity by identifying the presence of fluorescent single molecules in a single cell. In this work, we demonstrate the use of a new red fluorogenic probe that avoids the spectral overlap of green fluorescent probes, and cell autofluorescence. This new probe, 2SPBO-Casp was synthesized by coupling a water-soluble Nile Blue derivative (2SBPO) to an aspartic acid residue. Upon apoptosis induction, free dye is shown to

accumulate inside the cell after activated caspases within the cell cleave the aspartic acid residues. In previous work in our lab, single apoptotic cells were detected 45 minutes after induction using a rhodamine 110-based probe and single molecule fluorescence. However, significant statistical analysis was needed to exclude false positives. The use of 2SBPO-Casp overcomes the autofluorescence problem of cells and offers a steady fluorescence signal. In our single molecule FCS measurements, Ramos cells were determined apoptotic on the basis of their correlation coefficient value (R2). Cells that contain an R2 greater than 0.65 were identified as highly correlated and therefore determined to be apoptotic. Single apoptotic cells identified by this manner were identified as early as 30 minutes after induction and the number of apoptotic cells reached a peak value at the 3rd hour, which is consistent with other techniques. Overall, this method removes the problem of spectral overlap with cell autofluorescence, but more importantly allows the identification of single molecules in single cells with high sensitivity

(53) **Combining Luminescence and Mid-Infrared Sensors for Advanced Breath Diagnostics**; Paula Fortes[1, 2], Andreas Wilk[2], Ivo Raimundo Jr[1], Boris Mizaikoff[2]; [1]University of Campinas, [2]University of Ulm

Exhaled breath is a highly complex molecular mixture demanding for analytical techniques capable of sufficient molecular discrimination. In addition, advanced breath diagnostic devices should facilitate the quantification of gaseous constituents at ppm-ppb levels [1,2]. While individual analytical techniques such as mid-infrared spectroscopy may provide access to a range of molecules, some IR-inactive constituents require the combination of orthogonal sensing schemes for an extended molecular coverage. The present study combines luminescent sensors (LS) with mid-infrared hollow waveguide (3-20 μm; MIR-HWG) sensing scheme for demonstrating the utility of integrating orthogonal optical sensing techniques [3,4] for non-invasive simultaneous determination of O2 and CO2 (total and 12CO2/13CO2 ratio) in exhaled breath, respectively [5]. The LS sensor is integrated into the MIR-HWG such that a single diagnostic platform is established, ensuring that both sensors simultaneously interact with the same breath gas sample volume. Next to obtaining advanced respiratory data, the determination of O2 is vital to establishing robust calibration functions for CO2 due to potential collisional effects. For data classification and analyte quantification, multivariate data analysis strategies combining thus obtained orthogonal information were used facilitating the evaluation of additional relevant molecular constituents (e.g., volatile organics) next to vital information on total CO2 and O2.

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(54) **Redox Cycling Behavior of Catecholamines on Gold Microelectrode Arrays**; Mengjia Hu[1], Ingrid Fritsch[1]; [1]Department of Chemistry and Biochemistry, University of Arkansas

Detection of neurotransmitters in the extracellular fluid of the brain is of great importance in neuroscience. Techniques such as microdialysis and fast scan cyclic voltammetry are the traditional approaches. The electrochemical method of redox cycling, which is the focus of the presented work, has the ability to recycle electrochemically reversible redox species, thus providing amplified signals and the ability to discriminate between electrochemically reversible and irreversible species. This method also has advantage in that it has low background current which suggests that it could be suitable for the detection of basal level neurotransmitters. Electrochemical redox cycling behavior of three different catecholamines, dopamine (DA), epinephrine (EP) and norepinephrine (NE) was investigated using microfabricated gold microelectrode arrays (MEAs). Redox cycling responses of both individual catecholamines and their binary mixtures will be presented. The redox cycling behavior was studied by cyclic voltammetry and chronoamperometry, and characterized by the amplification (A_f) and collection efficiency (C_e) factors. Because DA and NE are electrochemically reversible, they can be oxidized at electrodes (generator) at a positive potential (+0.55 V vs Ag/AgCl (saturated KCl)), reduced at electrodes (collector) at a negative potential (-0.01 V vs Ag/AgCl (saturated KCl)), and can diffuse back to the generator to be re-oxidized, producing signals at both the generator and collector electrodes. Because EP is electrochemically quasi-reversible, minimal amplification of generator signal is observed, and its collector current is also minimal. Equimolar concentrations of DA and NE mixture show a redox cycling signal that is approximately the summation of the responses from the individual components. When DA or NE was mixed with equimolar concentration of EP, signals without redox cycling almost equal to the sum of individual signals were observed. With redox cycling, the mixtures produce generator signals slightly lower than the sum of individual generator signals. Collector signals are lower than DA or NE individual signals but higher than individual signals of EP. The results are consistent with the disproportionation nature of catecholamines and it might be possible to use this behavior eventually to distinguish the three catecholamines.

(55) **Detection and Identification of Reactive Nitrogen Species using Microchip Electrophoresis with Electrochemical Detection**; Dulan Gunasekara[1, 2], Diogenes do Santos[2, 3], Pann Pichetsurnthorn[2,4], Ryan Grigsby[2], Susan Lunte[1, 2, 4]; [1]Department of Chemistry, University of Kansas, Lawrence, KS, [2]Ralph N. Adams Institute for Bioanalytical Chemistry, University of Kansas, Lawrence, KS, [3]Federal University of Alagoas, Maceio, Brazil, [4]Department of Chemical Engineering, University of Kansas, Lawrence, KS

Reactive nitrogen species such as nitric oxide (NO) and peroxynitrite participate in oxidative stress and nitration/nitrosylation in vivo. These species have been implicated in several cardiovascular and neurodegenerative diseases. The short life time of these molecules makes them difficult to detect, often requiring indirect methods of analysis. Microchip electrophoresis (ME) offers fast and efficient separations; allowing these species to be separated and detected before they significantly degrade. Therefore, ME coupled with both amperometric and laser induced fluorescence detection (LIF) methods were developed by our group for detection of NO in bulk cells. Amperometric detection has an added benefit of detecting other important electrochemically active antioxidants present in the cell. In amperometric studies, the NO peak identification was confirmed based on the migration time using a NO standard and its kinetic profile. However, a dual electrode setup was developed for more reliable identification using a single channel "T" microchip.

This makes it possible to perform voltammetric characterization of the analytes while they are being separated, and thus, a current ratio at different oxidation potentials can be generated to identify different species. ME with dual channels can also be used to obtain similar voltammetric information and therefore, a dual channel chip is being developed for identification and detection of electroactive species in cell lysates. These methods will be utilized to detect and identify NO from stimulated RAW murine macrophage cells.

(56) **Electrochemical Enzyme Linked Bioassay Development on Nanoporous Gold Surface**; Binod Pandey[1, 2], Yih Horng Tan[1, 2], Jay Kishan Bhattarai[1, 2], Kohki Fujikawa[1], Papapida Pornsuriyasak[1], Alexei V. Demchenko[1], Keith J. Stine[1, 2]; [1]University of Missouri-St.Louis, Department of Chemistry and Biochemistry, [2]University of Missouri-St.Louis, Center for Nanoscience

Herein, we report the development of electrochemical bioassays on nanoporous gold (NPG) supports using either antibodies or lectins as recognition elements. Enzyme immobilization on lipoic acid SAMs on NPG surfaces is found to be a successful approach, enabling the square-wave voltammetric detection of p-aminophenol (p-AP), product of the reaction of alkaline phosphatase and p-aminophenylphosphate (p-APP). It was not feasible to detect p-AP on the flat gold surface modified with LPA SAMs, whereas the oxidative current was readily detected on the NPG surface. Two different direct kinetic enzyme based assays using either an antibody or a lectin conjugated to alkaline phosphatase were developed based on the difference in enzymatic reaction rate before and after antigen binding to the antibody or glycoprotein binding to the lectin. The direct kinetic enzyme linked immunosorbant assay, using a single antibody, for the determination of prostate specific antigen and carcinoembryonic antigen has detection limits of 0.75 ng/mL and 0.015 ng/mL for PSA and CEA, respectively. In these assays, a linear response was found up to 30 ng/mL for PSA and up to 10 ng/mL for CEA. This direct immunoassay utilizes a single antibody as opposed to the multiple antibodies used in traditional ELISA and has a good detection limit and a linear response for the determination of biologically significant amounts of these protein biomarkers. We believe this type of immunoassay might potentially be an attractive alternative to the traditional ELISA. Competitive format assays were also performed for both of these biomarkers. Applicability of the immunoassay to real samples was studied using newborn calf serum as a substitute for the human serum matrix. Similarly, enzyme linked lectin sorbent assay (ELLSA) was also developed on the NPG surface in three different formats, traditional ELLSA, kinetic ELLSA and competitive ELLSA. The traditional ELLSA was sensitive for quick glycan profiling of the glycoprotein. Transferrin and IgG were used as two model glycoproteins for the kinetic ELLSA, the binding affinity of the IgG and transferrin to lectin Con A was found to be 650 nM and 105 nM, respectively; competitive ELLSA assays were also performed.

(57) **Electrochemical Detection using an all PMMA Microfluidic Flow-cell with an Integrated Carbon Microelectrode**; Anne Regel[1, 2], Susan Lunte[1, 2, 3]; [1]University of Kansas Department of Chemistry, [2]Ralph N. Adams Institute for Bioanalytical Chemistry, [3]University of Kansas Department of Pharmaceutical Chemistry

Advancements in the miniaturization of analytical instrumentation have led to an increased interest in microfluidic devices capable of utilizing electrochemical detection. Microfluidic devices fabricated using polymers such as polymethylmethacrylate (PMMA) are generally inexpensive and amenable to mass production. However, integrating electrodes into rigid polymers, such as PMMA, is a major fabrication obstacle. To address this problem, we have developed a straightforward method to integrate graphite/PMMA composite electrodes into an all PMMA microfluidic flow cell. The graphite/PMMA composition was optimized and the best electrodes exhibited low noise (70 pA) and high mechanical stability. It was able to withstand a flow rate of 20 µl/min for several hours. Using flow-injection analysis in the microfluidic cell with amperometric detection at 0.5 V (potential vs Ag/Ag/AgCl), a LOD of 50 nM dopamine was achieved. Due to the manual fabrication process, electrode – to – electrode variability required individual calibration of each electrode, but each individual electrode showed good linearity (R^2=0.994) for dopamine in the nanomolar to micromolar concentration ranges.

(58) **Single Cell Analysis by Use of ICP-MS**; Norbert Jakubowski[1], Ulrich Panne[1], Janina Kneipp[1], Heike Traub[1], Kaori Shigeta[1], Daniela Drescher[1], Gunda Koellensperger[2], Evelyn Rampler, Charlotte Giesen[1], [1]BAM Federal Institute for Materials Research, [2]BOKU

Cellular heterogeneity that arises from stochastic expression of genes, proteins and metabolites is a fundamental principle of cell biology, but single cell analysis has been beyond the capability of the quickly growing omics technology. Presently, the best established analytical method for single cell analysis is fluorescence based analysis and cell sorting (FACS) which is most often applied in flow cytometry. Flow cytometry has been fundamental to the discovery and definition of major and minor cell subsets of the immune system and is most often applied in cancer research and more and more for diagnosis in oncology. But this technique is not able to measure the metal content of cells, and thus the multielement capability of ICP-MS looks very promising, because in combination with metal labeling of antibodies (biomarkers) the multiplex and multiparametric capabilities by CyTOF mass spectrometry can be significantly increased compared to FACS, but this instrumental approach is limited to masses above 100 Da. In our research we want to measure the metal heterogeneity of essential elements in single (diseased or healthy) cells together with the distribution of biomarkers by labeled antibodies. For this purpose we have applied two different sample introduction systems for single cell analysis. In the first approach single cells are imbedded into single droplets which are generated by a droplet on demand generator. Major and minor trace elements have been measured in selenium enriched single yeast operating a sector field instrument in a fast scanning mode. First results will be presented. In the second approach single fibroplast cells are grown on microscopic slides and after fixation are ablated by a Newwave 213 nm laser ablation system with the smallest spot size of 4 µm only. Elemental distribution in single cells are measured with a sector field instrument, which is operated in an imaging mode. First results will be presented.

(59) **Elucidation of Selenium Metabolism by Tracer Experiment of Mice Injected with Selenium Stable Isotopes**; Naoki Furuta[1], Yoshinari Suzuki[1], Yoshiteru Hashiura[1], Tatsuya Sakai[1], Takao Yamamoto[1], Takahisa Matsikawa[2], Atsuko Shinohara[2], [1]; [1]Chuo University, [2]Juntendo University School of Medicine

Selenium (Se) is an essential trace element for humans and other animals with a narrow adequate range between deficient and excessive doses, and selenoproteins including glutathione peroxidase (GPx) have important biochemical functions such as reducing the peroxides which are harmful to the living body. To investigate the time-dependent change of Se metabolism, we injected intravenously 82Se-enriched selenite (Se(IV)) or 82Se-enriched selenomethionine (SeMet) into mice fed either Se-adequate or -deficient diets. 4 weeks old mice had received a Se-adequate diets (2.25 µg Se day-1) for 1 week before the beginning a mouse experiment. One group of mice was fed Se-adequate diets (2.25 µg Se day-1) and the other group of mice was fed Se-deficient diets (0.25 µg Se day-1) for the following 4 weeks. And then, 82Se-enriched Se(IV) (2.25 µg 82Se) or 82Se-enriched SeMet (2.25 µg 82Se) was injected intravenously into them. Thirteen different tissues, red blood cells, plasma and urine were collected and weighted just before injection (0), 1, 6, 24, 72 h after injection. Total Se concentration was determined by flow-injection

ICPMS, and Se speciation analysis was conducted by HPLC-ICPMS. Selenium was observed mainly in liver, kidney, red blood cell, plasma and urine. In the liver and kidney of mice injected with 82Se-enriched Se(IV), exogenous 82Se associated with cellular glutathione peroxidase (cGPx) and selenosugar existed. In the case of 82Se-enriched SeMet injection, exogenous 82Se associated with SeMet existed as well as cGPx and selenosugar. Synthesis of cGPx in liver and kidney continued from 6 to 72 h after injection in both cases. We examined time-dependent change of selenoprotein P (Sel-P) in plasma. Hepatic and renal cGPx and plasma Sel-P were synthesized more effectively in the case of 82SeMet injection compared to 82Se(IV) injection. Synthesis of Sel-P in plasma was 1.5 times increased under Se deficient conditions compared to control, but synthesis of cGPx was not increased. That implies that Sel-P is more important to transport Se. Regardless of the Se chemical forms injected into mice, excess amounts of exogenous 82Se were excreted mainly into urine as selenosugar within 6 h after injection.

(60) **New Interface and Collision Cell Design for ICP-MS**; Lothar Rottmann[1], Alexander Makarov[1], Gerhard Jung[1], [1]; [1]Thermo Fisher Scientific; Bremen

New developments in interface design, ion focusing, collision cell technology and software culminate in excellent sensitivity, matrix tolerance, interference removal, high productivity and ease of use for the new Thermo Scientific iCAP Q ICP-MS. The implementation of flatapole technology in the new QCell ensures ultimate interference removal and the proprietary interface design make the iCAP Q ICP-MS well suited even for the most demanding applications. With the incorporation of these new technologies, most environmental, food safety and clinical applications can be performed in a single mode of collision cell operation. Multi-elemental analysis of pharmaceutical samples in compliance with upcoming new USP regulations as well as the speciation analysis of e.g. As and Cr in drinking water, food and beverages using Ion Chromatography coupled to the ICP-MS are further examples of the versatile use of the new iCAP Q ICP-MS.

(61) **A Comparative Study of the Magnetic Data Layers on Terabyte Hard Drives by Glow Discharge Compositional Depth Profile Analysis**; Kim Marshall[1], Gregory Schilling[1], Diane Goodman[1]; [1]LECO Corporation

Glow Discharge Optical Emission Spectrometry (GD-OES) has become an important tool in the arsenal of analytical spectroscopists. Although glow discharge is often used for bulk analysis, its true power lies in its ability to do compositional depth profiling (CDP) of layered and coated materials on a variety of sample types including metals, glasses, and ceramics. In recent years it has become accepted that GD-OES can be utilized for the analysis of surface layers of only a few nanometers in thickness [1]. The precision and apparent accuracy with which these ultra-thin layers can be determined with this technique are impressive. This is particularly so when the speed of the GD-OES analysis is compared to the analysis times of traditional depth profiling techniques like Auger Electron Spectroscopy, Secondary Ion Mass Spectrometry or X-ray Photoelectron Spectroscopy. These methodologies require tens of minutes or even hours for each analysis. Often GD-OES can complete a similar analysis in under a minute. Not only does this mean that the cost of each analysis using GD-OES is greatly reduced but this implies that GDS can be used in process monitoring and control, which is completely out of the question for the other much slower techniques. A comparative study of the magnetic data layers on various terabyte hard disks will be presented. This study provides a framework to ascertain the types of information that can be provided by GDS for process control. On hard disks, all of the magnetic features that are used for data storage reside within the first 50 to 100 nm of the surface. Determining and controlling these extremely thin and complex coatings is key to the quality control of these devices [2, 3]. The precision, accuracy and speed of the data acquired from these surfaces with GDS are exemplary. This work will demonstrate that GDS is well suited for aiding in the process control of such commercial surface coatings.

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(62) **One- and Two-Dimensional Microplasma Arrays**; Jeffrey Hopwood[1], Alan Hoskinson[1], Chen Wu[1], Naoto Miura[1]; [1]Tufts University

Atmospheric pressure microplasmas are a promising technology for low-power optical emission spectroscopy. In this work, we examine a microstrip split-ring resonator (MSRR) discharge operating at 1.8 GHz in helium as an excitation source for gas chromotagraphy of natural gas samples. The plasma requires as little as 0.2 W of microwave power and operates continuously with no electrode damage. With a simple compact spectrometer, we determine static detection limits on the order of 1 ppm for methane, n-butane, carbon dioxide, and hydrogen sulfide. Focused diode laser absorption spectrometry of the microplasma shows that the internal structure of the discharge is surprisingly complex. The dominant feature is a hot core of electrons which deplete metastable atomic states and molecular species. In the second part of the talk, we describe generating arrays of microplasmas from a single power source using a novel energy distribution method that prevents plasma instabilities. Line-shaped arrays of microplasmas over 100 mm in length are demonstrated as well as two-dimensional arrays of steady-state microplasmas.

(63) **the Platelet Secretome**; Christy Haynes[1], Secil Koseoglu[1], Audrey Meyer[1], Sarah Gruba[1]; [1]University of Minnesota

Exocytosis is a fundamental mode of cellular communication, where chemical messenger-filled granules fuse with the cell membrane and subsequently release their content to realize specific functions. Thus, quantitative measurement of chemical messenger storage and release is pivotal to fully understand the inner-workings of cells. Carbon-fiber microelectrode amperometry (CFMA) has been a method of choice for direct measurement of chemical messenger secretion based on its exquisite sensitivity, quantitative capability, and superb temporal resolution (sub-millisecond) in measuring single cell secretion. In this work, CFMA is employed for the first time to investigate the fundamental secretion behavior of individual blood platelets based on the electroactive property of endogenous serotonin molecules. This method reveals how various biophysical characteristics influence exocytotic behavior, and thus, platelet-mediated thrombosis and hemostasis. In addition to granule-stored chemical messenger species, platelets generate and secrete lipid-based species that are critical in the thrombosis cascade; herein, a subset of lipid species are analyzed quantitatively using a targeted UPLC/MS/MS method. Together, these two methods reveal the most detailed analysis to date of the platelet secretome.

(64) **Functionalised Nanoparticles and SERRS for Biomedical Applications**; Duncan Graham[1], Karen Faulds[1], Hainan Xie[1], Sarah McAughtrie[1], Alan Hutton[1], Tara Donnelly[1]; [1]University of Strathclyde

Functionalized nanoparticles have been used in a number of different studies including detection of DNA at ultra low levels, immuno histochemistry and more recently as substrates for surface enhanced resonance Raman scattering (SERRS) based imaging approaches. The advantages of using metallic nanoparticles are that they are very bright in terms of their optical characteristics and also if functionalized in a particular manner to provide a SERRS response give a unique vibrational fingerprint. Here we present the functionalization of gold and silver nanoparticles in such a way that the enhancement effect can be greatly increased through biological

recognition and as such effectively turns on the SERRS effect. This process can give rise to exquisite selectivity in terms of the interaction of the nanoparticles, especially when DNA hybridizations are used and single base mismatches relating to disease states can be analyzed at room temperature. Finally in moving away from the in vitro applications the functionalized nanoparticles can be modified in such a way that they are therapeutically active in vivo and preliminary data relating to in vivo studies of imaging and enhanced therapeutic uses of functionalized SERRS active nanoparticles will also be presented.

(65) **Prospects for *in vivo* Raman Diagnostics**; Nick Stone[1]; [1]University of Exeter / Gloucestershire Hospitals

The primary requirement for successful treatment of cancer is early detection. Rapid advances in laser and detector technologies have made it possible to harness the power of light; to provide molecular and structural information on pre-cancerous tissues from a patient in real-time. This can be achieved in or near the patient during endoscopy, surgery or in the clinic. Biophotonic techniques have demonstrated the potential to revolutionise diagnosis by providing non-destructive, objective measures of tissue disease state. In the longer term this may lead to molecular diagnosis in real-time, able to enhance the selection of personalised medical treatments. With the advent of more sensitive techniques for the detection of many neoplasias, the most important clinical question is 'Will this lesion have a clinical impact on the patient?'. A toolbox of novel Raman spectroscopy techniques, likely to have an impact in the in vivo and near patient environment will be outlined in this talk. They will include endoscopic and needle Raman probes for minimally invasive sampling of disease specific signals; deep Raman techniques for enhanced breast screening and tumour margin analysis and surface enhanced spatially offset Raman spectroscopy (SESORS) for multiplexed detection of disease markers though cms of tissue. The main focus of the talk will be the diagnosis, grading and staging of cancers, however, these techniques may be employed to solve numerous clinical needs.

(66) **Progress toward On-Animal Separation Based Sensors using Microdialysis Coupled to Microchip Electrophoresis.**; Susan Lunte[1], David Scott[1], Simon Pfieffer[1]; [1]University of Kansas

A on-line microdialysis-microchip electrophoresis system is described for in vivo monitoring of nitric oxide metabolites, catecholamines and excitatory amino acids. The directly coupling of microdialysis with microchip electrophoresis leads to a separation-based sensor that is capable of monitoring the in vivo concentrations of several analytes simultaneously. This paper describes progress towards an on-line system that can be employed for the continuous monitoring of fluorescent and electrochemically active analytes simultaneously. The ultimate goal is to miniaturize the entire system for the purpose of on-animal analysis using telemetry for instrument control and data acquisition.

(67) **Simplifying Human Health Problems and their Solutions by Giving more Attention to Chemistry**; Dana Spence[1]; [1]Michigan State

In most university-level general chemistry courses, students are exposed to perhaps the most basic concepts in the chemical sciences. Some of these concepts are so basic, for example, the importance of temperature and pH, that they are applicable to other scientific disciplines. Other concepts that are also important are topics such as molar quantities, polarity, and how molecules move due to diffusion. Ironically, it seems that many times, as we mature as scientists, we forget some of these basic principles. In turn, this investigator believes that certain answers to problems, in particular those problems related to human health, are overlooked because the answers are actually quite simple. In this presentation, results from two different projects in our research group will be provided. One involves diabetes and how a small change in the way insulin replacement therapy may have a profound effect on reducing the complications associated with this near-epidemic disease. The other project involves stored blood and blood banking and how a change in the concentration of just one component in stored blood could significantly reduce the risks and post-transfusion complications associated with receiving stored red blood cells. Of course, facilitating all of these studies is analytical chemistry and novel measurement tools that enable our group and others to perform complex studies related to human health on controlled in vitro platforms. Accordingly, time will be given to describing these devices as well as the human health problems that they are helping to solve.

(68) **Bioanalytical Fluorescence Correlation Spectroscopy**; Dimitri Pappas[1]; [1]Texas Tech University

This talk aims to discuss our recent advances in Fluorescence Correlation Spectroscopy (FCS). We have used FCS for diverse applications such intracellular probes, mapping of microfluidic systems, and energy transfer in nanoparticle-enhanced fluorescence. In our intracellular work, we have shown FCS is a sensitive method of identifying single molecule fluorescence. We have used this approach to identify apoptotic cells via intracellular caspase probes. We have also used FCS to map fluid motion in several microfluidic devices, elucidating mechanisms of mass transport in diverse applications such as microfluidic cell culture and affinity cell separation systems. Lastly, we have employed FCS to understand the light harvesting and energy transfer of phycobiliproteins and nanoparticle-phycobiliprotein conjugates.

(69) **High-Precision Tracking with Non-Blinking Quantum Dots Resolves Nanoscale Vertical Displacement**; Ning Fang[1], Kyle Marchuk[1]; [1]Iowa State University and Ames Laboratory, U.S. Department of Energy

Novel non-blinking quantum dots (NBQDs) were utilized in three-dimensional super-localization, high-precision tracking applications under an automated scanning-angle total internal reflection fluorescence microscope (SA-TIRFM). NBQDs were randomly attached to stationary microtubules along the radial axis under gliding assay conditions. By automatically scanning through a wide range of incident angles with different evanescent-field layer thicknesses, the fluorescent intensity decay curves were obtained. Fit with theoretical decay functions, the absolute vertical positions were de-termined with sub-10-nm localization precision. Attached to kinesin-propelled microtubules, the NBQD's emission intensi-ty profile was used to resolve the self-rotation of gliding mi-crotubules within a small vertical distance of ~50 nm. We demonstrate NBQD's applicability in high-precision fluores-cence imaging experiments.

(70) **Imaging and Tracking Cell Signaling in Membranes**; Yan Yu[1]; [1]Chemistry Department, Indiana University

A major challenge in biological science and engineering is to understand and control how cells communicate. When cells transduce signals, thousands of membrane receptors and signaling molecules reorganize into spatially diverse patterns over many length scales. Such dynamic process is a key element to ensure the spatiotemporal connectivity in cellular signal transduction. In the presentation, I will describe how single-molecule fluorescence imaging and tracking, nanotechnology, and cell biology can be combined to understand T cell signaling during the immune response. Specifically, I will not only elucidate the role of non-muscle myosin IIA in protein translocation, spatial organization, and signaling, but also discuss how to use advanced fluorescence techniques to study molecular mechanisms by which mechanical forces from myosin are directly integrated into T cell signaling pathways.

(71) **Multivariate Curve Resolution Applied to Hyperspectral Images: Progress toward Automated Analyses***; David Haaland[1], Howland Jones[1], Jerilyn Timlin[1], David Melgaard[1], Aaron Collins[1], Michael Sinclair[1]; [1]Sandia National Laboratories

Hyperspectral fluorescence microscopy is a powerful tool in the analysis of biological samples. The resulting digital images can be multiple gigabytes, so rapid and automated analysis methods are needed. We have applied multivariate curve resolution (MCR) to the analysis of these large hyperspectral images. The goal of MCR is to discover the independently varying pure spectra contained in each image and to obtain relative quantitative image maps of each of the fluorescence components. Initially, MCR analyses of the image data required a tedious iterative approach that required an expert's experience and knowledge. Often correlated detector-related read noise and structured noise limited our ability to successfully analyze images of sparse and weak fluorescence samples. Over the years, we have developed a number of approaches to facilitate the automated MCR analysis of hyperspectral images to achieve high quality, robust MCR solutions without the need for user input. We will demonstrate these approaches and automated methods with data obtained from two hyperspectral fluorescence imaging microscopes. The automated approaches we have applied to obtain optimal MCR results are cosmic spike removal, modeling and correcting for detector offsets and structured noise, and automated selection of spatial regions. In addition, spatial compression of the data not only improves computation speed but also serves to reduce the detrimental effects of correlated read noise. After pure spectral components are discovered from MCR analysis of the compressed data, these pure spectra are used to regenerate the composition spatial maps at full spatial resolution. Additionally, time-dependent images of the sample during photobleaching can improve the MCR results since greater discrimination of the fluorophores is achieved because each fluorophore bleaches at a different rate. The result of applying all these approaches has resulted in achieving our goal of automated robust MCR results with little or no user input.

*Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

(72) **Single Molecule Tracking and Imaging Fluorescence Correlation Spectroscopy Studies of Molecular Transport in Reversed Phase Chromatographic Materials**; Justin Cooper[1], Eric Peterson[1], Joel Harris[1]; [1]University of Utah

Reversed phase liquid chromatography (RPLC) has become an indispensable tool in areas such as quality control, pharmaceutics, and other disciplines requiring qualitative and quantitative identification of compounds. This technique takes advantage of the high specific surface areas inherent in porous silica particles to maximize the interaction between analyte molecules and the stationary phase. The separation efficiency and resolution of RPLC are heavily influenced by the rates of analyte exchange between the mobile and stationary phases and of mass transport throughout the intra-particle pore network. In particular, molecular transport in the surface bound state, termed surface diffusion, has been identified as a significant component of the total mass transport rate within chromatographic particles. Intra-particle transport rates have previously been studied indirectly via chromatographic band moment analysis. Fluorescent spectroscopic studies have also provided information on surface diffusion and molecular residence times on planar hydrophobic surfaces. These surfaces are planar analogs of porous chromatographic surfaces, which produce different transport kinetics to those of conventional chromatographic material. We have employed single molecule fluorescence imaging to directly measure the residence times and intra-particle diffusion rates of fluorescent molecules within actual RPLC porous silica particles. The motion of the amphiphilic fluorescent molecules octadecylrhodamine B (R18) and 1,1'-dioctadecyl-3,3,3'3'-tetramethylindocarbocyanine (DiI), were analyzed by single molecule tracking. In addition, a novel imaging variant of fluorescence correlation spectroscopy (FCS), which employs sub millisecond imaging of a small acquisition region on the CCD chip to digitally process the fluorescence emission signal, was developed and used to compare the diffusion rates of molecules both within RPLC porous silica particles and on planar C18-modified interfaces. Measurement of the transport within particles yields information on the total intra-particle diffusion rate, while measurement at planar surfaces provides insight into the surface-specific transport kinetics. Single molecule imaging in conjunction with imaging-FCS has produced the ability to measure and compare transport rates at planar interfaces with those observed directly within RPLC porous silica particles. This comparison has provided unique insight into the contribution of surface diffusion to the total intra-particle mass transport rate and the nature of molecular transport throughout the complex pore network of chromatographic particles.

(73) **Advanced Mid-Infrared Breath Diagnostics**; Boris Mizaikoff[1]; [1]University of Ulm, Institute of Analytical and Bioanalytical Chemistry

Modern trace gas sensing applications demand rapid response times with sensitive and selective detection of target analytes in complex matrices, preferably via direct measurements close to real-time without sample preparation and in a compact device format. The ability to quantify selected constituents in the presence of interferants has importance for a variety of relevant gas sensing applications including breath analysis, process monitoring, homeland security, and environmental surveys.Optical sensor technology based on mid-infrared (MIR) spectroscopy in the spectral range of 3-20 μm provides inherent molecular specificity for discriminating gaseous constituents at ppm-ppb concentration levels. Recently emerging strategies enabling miniaturized and robust MIR gas sensing devices generating rapid, sensitive, and selective molecular signatures take advantage of appropriate waveguide technology, i.e. conventional and substrate-integrated hollow waveguides in combination with compact FT-IR spectrometers and highly efficient IR radiation sources such as broadly tunable quantum cascade lasers (QCLs) [1-9].

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(74) **Sub-Parts-Per-Billion Level Detection of SF6 with a Fiber-Coupled QCL-QEPAS Sensor**; Vincenzo Spagnolo[1], Pietro Patimisco[1], Simone Borri[1], Gaetano Scamarcio[1], Bruce E. Bernacki[2], Jason Kriesel[3]; [1]Dipartimento Interateneo di Fisica, University and Politecnico of Bari, CNR-IFN UOS BARI, [2]Pacific Northwest National Laboratory, [3]Opto-Knowledge Systems Inc.

The detection and quantification of trace chemical species in the gas phase is of great interest in a wide range of applications such as environmental monitoring, industrial process control and medical diagnostics. In combination quantum cascade laser (QCLs), quartz enhanced photoacoustic spectroscopy (QEPAS) offers the advantage of high sensitivity and fast time-response. Very efficient QCL-based QEPAS sensors have been demonstrated for trace detection of several chemical species, such as NH_3, NO, CO_2, N_2O, CO, CH_2O, etc. Small size sensors with simple optical alignment has been realized employing fiber-coupled system between near IR laser source and QEPAS spectrophones, thus the possibility to extend this approach also for mid-IR light sources, considering the small size of the QEPAS module, may allow compact integration also with QCLs. We will report here on the design and realization of optoacoustic sensors based an external cavity QCL laser source emitting at 10,5 µm, fiber-coupled with a QEPAS spectrophone module. SF_6 has been selected as target gas. Single mode laser delivery through the prongs of the quartz tuning fork has been realized using a hollow waveguide fiber with internal core size of 300 µm. To evaluate the performance of the EC-QCL based QEPAS platform we carried out SF_6 concentration measurements at 75 Torr pressure using a 2f wavelength-modulation spectroscopy configuration. A commercial gas dilution system and a certified mixture of 10 ppm SF_6 in N_2 were used to produce the various SF_6 concentrations levels. The SF_6 dilution results have been acquired in scan mode. A 0.1 s averaging time and 30 mW EC-QCL excitation power have been used. Stepwise concentration measurements were performed to verify the linearity of the QEPAS signal as a function of the SF_6 concentration, from 10 ppm down to 9ppb concentration. To determine the best achievable detection sensitivity of the sensor we performed an Allan variance analysis, measuring and averaging its response for a pure N_2 gas sample. Based on the obtained data, the SF_6 concentration that would result in noise-equivalent 1σ sensor readings, at integration time of 2 sec is 0,140 part per billion in volume.

(75) **Atmospheric Trace Gas Monitoring Using Latest Advances in mid-IR Quantum Cascade Lasers**; Mark Zahniser[1], David Nelson[1], J. Barry McManus[1], Joanne Shorter[1], Scott Herndon[1]; [1]Aerodyne Research Inc

Recent advances in infrared laser technology have greatly facilitated field measurements of atmospheric trace gases to identify and quantify their sources and sinks in many environments. The availability of continuous wave mid-infrared quantum cascade lasers, improvements in non-cryogenic infrared detectors, and advances in detection methods using direct absorption techniques with long path length, small volume sampling cells have led to a new generation of smaller, lighter, and more robust instrumentation suitable for measurements from mobile and aircraft platforms, field sites at remote locations, and clinical environments for breath analysis screening. The reliability and reproducibility of these mid-infrared light sources has made long term monitoring and turn-key operation a reality. Trace gas detection in air at the low part-per-trillion levels are now feasible. Fractional precisions of less than 1 part in 10000 allow for isotopologue ratio measurements. Applications to measurements of greenhouse gases methane and nitrous oxide, high precision measurements of carbonyl sulphide (OCS) and formaldehyde (HCHO), and isotopic measurements of CO2, CH4, H2O, will be presented.

(76) **External Cavity Quantum Cascade Lasers for Measurements in Liquids**; Bernhard Lendl[1], Markus Brandstetter[1], Andreas Genner[1]; [1]Vienna University of Technology

Widely tunable External Cavity Quantum Cascade Lasers (EC-QCL) open a broad field of potential applications for absorption spectroscopy of liquids, e.g. in medical diagnosis and process analytical chemistry. There, both tunability and high emission power are crucial, especially when measuring in highly absorbing matrices, e.g. water. The high emission power facilitates large optical pathlengths which brings advantages in terms of robustness (no clogging of transmission cells) and higher signals according to Beer's law. Since the absorption bands in liquids are relatively broad (in the range of tens of wavenumbers) the lasers can be operated in pulsed mode where they offer higher peak pulse power levels and broader tuning ranges compared to mode-hop free operation. Over decades the gold standard in mid-IR spectroscopy has been FT-IR spectrometry. Given the several magnitudes lower spectral power density of the thermal light sources used there EC-QCLs should come along with several spectroscopic benefits. In this context the achievable signal-to-noise ratios (SNR) and the parameters influencing the SNR will be discussed. Furthermore, suitable methods for a comprehensive characterization of EC-QCLs are presented. Two field applications of an EC-QCL based sensor system (200 cm^{-1} tuning range) are presented: Firstly, a mid-IR absorption sensor for routine point-of-care blood analysis was developed and applied in an intensive care environment. Combined with multivariate data analysis the sensor could simultaneously quantify several physiologically relevant blood parameters in human blood plasma, including glucose, triglycerides and albumin. Secondly, the sensor was applied as a realtime analyzer for monitoring the degree of contamination of cleaning water in a cleaning in place (CIP) system. Compared to standard analyzers which are measuring the total organic carbon the QCL-based system not only offered significantly improved time resolution but also information about the type of contamination present in the CIP equipment. Finally, a short outlook on potential new applications of EC-QCLs for measurements in the liquid phase will be given, including the combination of EC-QCLs and evanescent field sensors.

(77) **Tip-enhanced Mid-infrared and Terahertz Photoexpansion Nanospectroscopy**; Mikhail Belkin[1], Feng Lu[1]; [1]The University of Texas at Austin

Mid-infrared absorption spectroscopy in the "molecular fingerprint" region is a powerful technique for chemical analysis. The mid-infrared photoexpansion nanospectroscopy was developed recently to measure absorption fingerprint spectra of samples on nanoscale [1]. In this method, light absorption is detected by measuring associated sample thermal expansion with an atomic force microscope (AFM). This approach results in a simple experimental setup with no optical detectors [1,2]. However, this technique requires using high-power lasers to produce detectable photoexpansion and its sensitivity is practically limited by sample damage threshold to films of ~100-200 nm in thickness. Furthermore, its spatial resolution is limited by thermal diffusion length in samples, which is ~50-100nm in typical chem/bio materials excited with 50ns light pulses [1,2]. Here we demonstrate that the sensitivity of the photoexpansion nanospectroscopy can be dramatically enhanced by moving the laser pulses repetition frequency in resonance with the mechanical frequency of the AFM cantilever [3]. In this case, the AFM cantilever deflection is enhanced by the Q-factor of the cantilever, which may be over three orders of magnitude in air. Furthermore, we show that local light intensity enhancement near the apex of a metal AFM tip can be used to induce over two orders of magnitude higher optical absorption and photoexpansion in the sample immediately below the tip. These improvements allow us to perform photoexpansion nanospectroscopy using low-power compact

semiconductor quantum cascade lasers (QCLs) and achieve very high sensitivity and spatial resolution. We will demonstrate high-quality spectra of polymer films as thin as 10nm and better than 50nm spatial resolution which, in our case, is determined by the dimensions of the intensity 'hot spot' below the tip and is virtually independent of the excitation laser pulse width. The abovementioned sensitivity improvements also allowed us to extend photoexpansion microscopy to the terahertz spectral range using terahertz QCLs. We will present the first terahertz photoexpansion images.

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(78) **Portable and Laboratory Multi-Analytical Techniques to Diagnose Environmental Impacts on Walls and Wall Paintings of Insula IX, 3 (Pompeii, Italy)**; Juan M. Madariaga[1], Maite Maguregui[1], Kepa Castro[1], Ulla Knuutinen[2], Irantzu Martinez-Arkarazo[1], Anastasia Giakoumaki[1], Silvia Fdez-Ortiz de Vallejuelo[1]; [1]University of the Basque Country, Department of Analytical Chemistry, [2]Helsinki Metropolia University of Applied Sciences

Since the time that any archaeological site is brought to light, it suffers deterioration due in part to rainfall, humidity, water infiltrations, etc., but mainly to environmental stressors. Modern analytical techniques, both portable and laboratory, are increasingly used to identify the deterioration compounds promoted by the activity of such stressors (metabolism of microorganisms) or by reactivity between stressors (acidic gases) and original materials that promotes the formation of new compounds (efflorescence or crystallized salts) like bicarbonates, sulphates and nitrates.In the particular case of the Pompeii site, the impacts due to the eruption must be added to the others. The APUV expeditions measured the walls and wall paintings from Insula IX, 3 (Houses 1,2 and 5,24) using portable, non-destructive instrumentation: Raman and DRIFTS for the molecular characterization and XRF for the elemental analysis. Some rooms of greater importance are covered with ceilings but the majority of rooms in both houses are exposed to the open air. Microsamples from the houses and lapili/ash samples were processed with equivalent laboratory instrumentation. Exposed and protected rooms were measured in spring and autumn, considering different orientations to observe possible variations in the salts crystallizations. The CO2 attack on non-protected walls is the greatest decaying phenomena. In protected walls higher sulphur contents (gypsum), from the sulphation of calcite mortars, were observed while a lower amounts were quantified in exposed walls (partial dissolution by rain-washing); apart from gypsum, thenardite, mirabillite, epsomite and hexahydrite were detected; sulphates with higher water content were observed in areas exposed to open air. Additionally, nitrate salts like nitrocalcite and niter were detected only in protected rooms due to its high solubility; the source for potassium was found in the own walls, probably coming from the original mortar manufacturing when using local potassium-bicarbonate type waters. Moreover, changes in pigment coloration were detected (blackening of vermillion and red ochre), due to oxidation processes with years, as well as biological patinas (coming from both microorganisms and non-vascular plants), were also identified. Chemical modeling and chemometrics were used to explain the deterioration process identifying the impacts from the eruption and the environmental stressors.

(79) **Multianalytical Approaches in Art and Archaeology - Conceptions and Misconceptions**; Antonio Candeias[1, 2], Cristina Dias[1,2], Teresa Caldeira[1, 2], Jose Mirao[1, 3], Luisa Carvalho[4]; [1]HERCULES Laboratory, Évora University, Évora, Portugal, [2]Evora Chemistry Centre and Chemistry Department, Evora University, [3]Evora Geophysics Centre and Geosciences Department, Évora University, [4]Lisbon University Atomic Physics Centre, Lisbon University

Heritage research is one of the fundamental pillars for the study and safeguard of cultural heritage and must encompass multidisciplinary approaches. The use of a wide variety of analytical techniques enables the assessment of the material composition of tangible heritage, their causes and processes of degradation and the performance evaluation of new products for conservation-restoration interventions. Nevertheless, there exist a number of factors that may contribute to misdirected research regarding cultural heritage including:- use of heritage artifacts for the sole purpose to show the capacity of an analytical technique without any kind of utility from the standpoint of the piece's history, knowledge or conservation. - use of narrow analytical regime or tendency to focus on specific research details that result in incomplete information that can be problematic when conducting further restoration interventions or historical studies. - time limitation in the realization of research given the current pressure to which researchers are subject to publication, hindering the development of more detailed studies. - excessive sampling of historical artifacts without precise criteria regarding the research objectives or purposes. This contribution is devoted to outlining some of our recent results with the use of multi-analytical methodologies aiming the study of pieces of exceptional cultural and artistic value and/or the development of integrated conservation interventions that can serve as future references and is the result of a joint collaboration between the Jose de Figueiredo Conservation Restoration Laboratory from the Portuguese Institute for Museums and Conservation, the HERCULES laboratory from Evora University and the Lisbon University Atomic Physics Centre. Specific case studies will be used to illustrate projects we have undertaken where the use of a collaborative approach has resulted in the successful characterization of historic building materials, easel paintings, historical textiles, archaeological artifacts and jewelry. Furthermore, we will discuss the use of in-situ analytical techniques (e.g. in-situ Raman spectroscopy, in-situ XRF), micro-analytical techniques (e.g. micro-Raman spectrometry, micro FTIR spectrometry, micro-X-ray diffraction, optical and scanning electron microscopy), advanced microprobes (e.g. PIXE/PIGE and confocal synchrotron induced X-ray fluorescence spectrometry) and high sensitive laboratory analytical techniques (e.g. LC-MS, GC-MS, ICP-MS) within the framework of our research.

(80) **Micro-elemental Analysis and Characterisation of Australian Aboriginal Ochre Pigments and Objects by Synchrotron X-Ray Fluorescence Microscopy (XFM).**; Rachel Popelka-Filcoff[1], Claire Lenehan[1], Erica Donner[2], Enzo Lombi[2], Daryl Howard[3], Keryn Walshe[4], Martin De Jonge[3], David Paterson[3], Allan Pring[4], Jamie Quinton[1]; [1]Flinders University, [2]University of South Australia, [3]Australian Synchrotron, [4]South Australian Museum

Although ochre (Fe-oxide pigments) and other mineral pigments are significant in Aboriginal Australian culture, little is understood about ochre sources and routes of exchange. While bulk geochemical analyses provide data for source characterisation, synchrotron micro-XRF analysis offers insight into the complex mineralogy in this natural material. XFM (X-ray fluorescence microscopy) as performed at the Australian Synchrotron provides spatially resolved analysis, not just composition but also presence and characterisation of individual particles and components. This research analysed both source ochre samples and Aboriginal objects. Source samples comprised two groups: 1. Ochre sources with well-documented

ethnographic information, and 2. Ochre sources with documented strong archaeological data. Furthermore, a bark painting with complex pigment application and a pigment-treated wooden boomerang, (both from Queensland) were analysed directly within the XFM beam. In addition to understanding exchange of the material across the continent, this study will also enhance our knowledge of this inherently complex material. XFM methods characterise the inherent natural variation of ochre, to understand of the formation processes of ochre sources. Analysis of the data with GeoPIXE will lead to quantification of micro-particles and variations within and between sources and attribution of ochre on the objects. With a combination of geochemical and statistical analyses, ancient exchange in cultural ochre can be deduced based on this chemical and mineral signature. Analysis of the experimental data from the painted objects suggests that the artists employed a layering technique and/or mixing of pigments when applying the ochre to the objects. Results were also used to identify the elemental composition of the black pigmentation on the objects, which is often difficult to ascertain. This project is the first comprehensive characterization of Australian ochre and non-dectructive analysis of Australian Aboriginal objects by synchrotron methods.

(81) **Chemical and Architectural Examination of a Tower in Monterubiaglio, Umbria (Italy) Utilizing Portable X-Ray Fluorescence Spectrometry**; Mary Kate Donais[1], Anthony Desmond[1], Bradley Duncan[2], David George[1]; [1]Saint Anselm College, [2]University of Massachusetts, Amherst

The mortar on two faces of a stone masonry tower in Monterubiaglio, Umbria was analyzed utilizing portable energy dispersive x-ray fluorescence spectrometry (pXRF). Based on visual inspection and historical documentation, the lower portion of the tower is known to be of Roman construction technique and the upper is of medieval technique. The two objectives of this research were as follows: 1) to examine the chemical differences between the different mortars on the tower that are associated with these different historic periods of the tower's construction; and 2) compare the Roman mortar to mortars at the nearby Coriglia, Castel Viscardo excavation site to determine whether an association existed between the two locations. No chemical analyses of this tower have been conducted to date. Utilizing Principal Component Analysis (PCA), two data clusters were observed and provided evidence toward the upper and lower mortars on the tower being of different elemental compositions. Examination of the loadings plot for this PCA model indicated elemental associations to each PC which were also observed by overlaying the XRF spectra. Supportive data for associations between the lower, Roman mortar and wall mortars at the Coriglia site also were established through spectral comparisons.

(82) **Microarchaeology of Ceramic and Salt Production Facilities in the Mangrove Forests of Southern Mesoamerica**; Hector Neff[1]; [1]IIRMES, CSULB

Micro-archaeology is the study of the sub-visible portion of the archaeological record, including both microscopic constituents of archaeological deposits and microscopic properties of macroscopic artifacts. The microscopic record requires analytical instrumentation in order to be perceived and measured. Field-portable instruments, such as portable-XRF and portable-FTIR, are keys to progress in this new direction in archaeological research. The present paper illustrates how these instruments are being used to investigate pyrotechnological features associated with prehistoric ceramic and salt production in the mangrove forests of southern Mexico.

(83) **Modified Poteins in Environmental Microbes**; Rachel Ogorzalek Loo[1], Hong Nguyen[1], Deborah R. Leon[2], Bryan Crable[3], Michael McInerney[3], Robert Gunsalus[3], Joseph Loo[1]; [1]University of California-Los Angeles, [2]Boston University, [3]University of Oklahoma

Within the last decade many genome sequences became available for environmental microbes. Because these organisms are genetically distant from well-studied species, we are less able to predict what modifications they might display. Their community lifestyle and unusual metabolisms suggest that they may have much that is new. Unassigned MS/MS data hide clues about how these organisms modify and assemble their proteins. Proteomes of archaea Methanosarcina acetivorans, M. mazei, M. barkeri and Methanospirillum hungatei were investigated to look for unanticipated modifications, along with bacteria Syntrophus aciditrophicus, Syntrophomonas wolfei, and Syntrophomonas fumaroxidans. Trypsin-digested proteins were analyzed by nanoLC-ESI-MS/MS and the resulting data was searched against protein and genome sequence databases with subsequent error-tolerant analyses. Spectra reflecting modified peptides were sequenced de novo, as required, and manually verified. S. aciditrophicus displayed many instances where methionine aminopeptidase or peptide deformylase enzymes appeared "indecisive", yielding mixed populations of initiator Met-on/-off proteins or +/-formyl N-termini. N-terminal heterogeneity appeared to a lesser extent in M. mazei. Data also indicated that ability to predict signal peptides for methanogens is extremely poor. Archaeal surface proteins, such as the Methanosarcinae S-layer proteins MM1976, MA0829, and Mbar_A1758 and M. hungatei flagellin protein Mhun_3140 are extensively modified by O-formylation, O-acetylation, and N-glycosylation. Many peptide variants were observed, including ones displaying tryptophan carboxylation and tyrosine nitration. It is hoped that some of the observed modifications and the proteins that carry them can be linked to an understanding of how important pathways are regulated in these organisms. An unexpected modification was observed in an uncharacterized flavoprotein from Syntrophomonas wolfei. Protein Swol_2052, thought to function as an acyl CoA oxidoreductase, contained an N-terminus that appeared 12-Da heavier than predicted. Possible structures were considered, including modification to a tetrahydropyridine carboxylic acid, consistent with addition of a carbon atom and an 83-Da neutral loss.

(84) **Application of Targeted Metabolomics and Kinetic Flux Profiling to Understand the Physiology of Microbial Consortia**; Shawn Campagna; [1]University of Tennessee, Knoxville

Our lab uses an interdisciplinary approach that relies heavily on liquid chromatography–tandem mass spectrometry (LC–MS/MS) based metabolomics to understand medicinally and environmentally relevant microbial processes. The primary analytical platform is a triple quadrupole MS with an electrospray ionization source, and the targeted methods employed attempt to measure the concentration (pool size) of ~350 analytically tractable, yet chemically diverse, water soluble metabolites that are part of the core metabolome shared by all kingdoms of life. A key feature of these methods is that they are able to detect even highly polar analytes such as nucleotide triphosphates. These methods also measure at least one metabolite from all known carbon and nitrogen utilization pathways, the activated methyl cycle, all amino acid and nucleotide biosynthesis pathways, as well as others; and the average coverage for each major pathway is ~65%. The utility of these metabolomics methods can be enhanced by monitoring the incorporation of stable isotope-labeled nutrient sources, either 15N or 13C, into the metabolome using kinetic flux profiling techniques (KFP). We have found that many microbial systems are able to maintain metabolite concentrations under a variety of conditions, although the flux through pathways may be altered. When coupled, pool size determination and KFP can

be used to determine both the amounts of metabolites within and relative rates of flux through many biochemical pathways in vivo and allow a global snapshot of cellular metabolism to be obtained from a single set of experiments that require less than two hours of instrument time. Several vignettes from our work studying bacterial cell-cell signaling (quorum sensing) and microbial nutrient cycling by marine organisms will be discussed to highlight the utility of applying these metabolomics tools to probe complex biological systems and to provide insight into the mechanisms that consortia of microogranisms utilize to cooperatively and/or competitively dictate resource utilization.

(85) **Targeted Proteomics for the Optimization of Biofuel Pathways in E. coli**; Christopher Petzold[1], Pragya Singh[1], Alyssa Redding-Johanson[1], Tanveer Batth[1], Becky Rutherford[1], Taek Soon Lee[1], Jay Keasling[1], Paul Adams[1]; [1]Joint BioEnergy Institute, Lawrence Berkeley National Laboratory

Successful metabolic engineering of microbes for biofuel production depends on the speed at which biological circuits can be conceived, constructed, and optimized. To this end, metabolic engineers utilize a variety of analytical methods to identify pathway bottlenecks. Protein quantification by using targeted proteomics compliments metabolite and transcript analysis for rapid optimization of engineered pathways. Traditionally, selective protein detection and quantification have been accomplished via immunoblot analysis, which is fast, convenient, and, for a specific protein, easily multiplexed. However, when assaying full pathways custom antibodies must be obtained for every pathway protein resulting in increased development time and experimental costs. Furthermore, obtaining accurate quantitative information can be challenging. Recently, we applied targeted proteomics to metabolically engineered E. coli by using selected-reaction monitoring (SRM) mass spectrometry. This sensitive method is based on two points of selection (linked peptide and a MS/MS fragment masses) to eliminate background signal and noise. With this method entire biofuel pathways can be monitored in one LC-MS/MS run. Our initial efforts were directed at optimizing the mevalonate pathway proteins to produce precursors to isoprenoid-based biofuels. From this analysis, two pathway proteins, mevalonate kinase (MK) and phosphomevalonate kinase (PMK) from S. cerevisiae, were identified as potential bottlenecks. Codon-optimization of the genes encoding MK and PMK and expression from a stronger promoter led to significantly improved protein levels and over 3-fold improved final isoprenoid titer. Complementing analysis of the heterologous pathway is characterization of native E. coli pathways associated with central metabolism. Consequently, we have developed targeted proteomics methods to facilitate quantitative characterization of a variety of metabolic pathways commonly impacted by metabolic engineering. With these methods, we have characterized a variety of pathways and protein expression parameters to improve biofuel production. Overall, our results underscore the importance of targeted proteomics for rapid biofuel pathway optimization.

(86) **Characterization of Natural Microbial Communities using Quantitative Proteomics**; Chongle Pan[1], Zhou Li[1], Nicholas Justice[2], Jill Banfield[2], Bob Hettich[1]; [1]Oak Ridge National Laboratory, [2]University of California, Berkeley

Quantitative proteomics allows measurement of abundance changes of thousands of proteins in a microbial community under different environmental conditions. Here we present optimization and application of different methods for deep quantitative proteomics measurement of a microbial community. We compared the label-free method based on spectral counting, the metabolic labeling method based on 15N labeling, and the chemical labeling method using the TMT or iTRAQ reagents. Each of the methods has unique advantages and disadvantages. The spectral counting method provides the deepest proteome coverage for identification, but its quantification performance is worse than labeling-based approaches, especially the quantification reproducibility. Metabolic labeling and isobaric chemical labeling are capable of accurate, precise, and reproducible quantification and provide deep proteome coverage for quantification. iTRAQ and TMT have the unique advantage of multiplexing more than 4 samples in a single run. Metabolic labeling has the unique advantage of minimizing sample preparation bias from cell lysis to protein extraction. We compared the proteome changes of the AMD community in different environments and growth stages using the label-free approach, the metabolic labeling approach, and the TMT labeling approach. The abundance ratios of thousands of proteins in these comparisons were accurately determined, which informed the metabolic activity changes of different member microorganisms in the community.

(87) **High-Resolution Imaging of Cholesterol and Sphingolipid Distribution in Cell Membranes using Secondary Ion Mass Spectrometry**; Mary L. Kraft[1], Jessica F. Frisz[1], Haley A. Klitzing[1], Kaiyan Lou[1], Joshua Zimmerberg[2], Peter K. Weber[3]; [1]University of Illinois, School of Chemical Sciences, [2]National Institutes of Health, Eunice Kennedy Shriver National Institute of Child Health and Human Develop, [3]Lawrence Livermore National Laboratory, Glenn T. Seaborg Institute

Domains enriched with specific protein species are present in the plasma membranes of mammalian cells. Different lipid species and cholesterol are also hypothesized to be organized into compositionally and functionally distinct plasma membrane domains. In particular, probing the existence and properties of plasma membrane domains that are enriched with cholesterol and sphingolipids, which are often referred to as lipid rafts, have been the focus of intense research. Yet, there is no consensus on the sizes, shapes, and functions of these domains, and even the question of their very existence has not been resolved due to the lack of suitable methods to directly image lipids and cholesterol without the use of potentially perturbing tags. Here we have combined metabolic stable isotope incorporation with high-resolution secondary ion mass spectrometry (SIMS) that is performed with a Cameca NanoSIMS 50 to directly image the sphingolipid and cholesterol distributions in the plasma membranes of intact cells. Specifically, we have used high-resolution SIMS to map the isotope enrichment from metabolically incorporated ^{15}N-sphingolipids and ^{18}O-cholesterol on the dorsal surfaces of fibroblast cells with a lateral resolution of ~90 nm. Statistical methods were employed to definitively determine whether the sphingolipids and cholesterol were heterogeneously distributed and co-localized within the plasma membrane. We expect that this general approach will also enable investigating the distributions of other lipid species in the plasma membrane.

(88) **Real-Time Process Monitoring and Control Solutions Using Mid Infra Red and UV-Vis Spectroscopy**; Kirby Amponsah-Manager[1], Charles Goss[1]; [1]GlaxoSmithKline

In order to produce active pharmaceutical ingredient (API) that meet desired quality at reasonable cost, pharmaceutical processes must be carried out under carefully controlled conditions. To achieve this, off-line chromatographic techniques that have traditionally been the main tools may no longer be sufficient. Growing demands in pharmaceutical process control call for the use of analytical techniques that allow the measurement and control of several critical parameters at many stages in the process. In recent years, many analytical techniques have been embraced to understand, monitor, characterize, measure and control segments of the drug synthesis and development processes. Some of the techniques that have made significant contribution in this regard include spectroscopic techniques such as NIR, mid IR, Raman, UV-Vis, and fluorescence. Others include mass spectrometry and light scattering systems. In this paper, we will discuss how mid IR, NIR and UV-Vis are employed

in-line or online to monitor and control synthetic pharmaceutical processes. Application of these techniques to identify the formation of reaction intermediates, final reaction end point and formation of reaction reaction byproducts will be discussed. We will emphasize the cost savings (time, waste, raw material, safety) and product quality gained in adopting these spectroscopic techniques in the chemistry and development processes.

(89) **Near Infrared Monitoring of the State of Fluid Bed Processes**; Stephen W. Hoag[1], Ravi Kona[1], Bhavesh H. Kothari[1], Raafat Fahmy[1, 2]; [1]University of Maryland, Baltimore, [2]FDA

For fluid bed operations such as granulation and coating, the amount of water and its state during the process is critical to product quality. The ability to measure water during the process is critical for any monitoring system. This presentation will examine a unique monitoring system that incorporates environmental monitoring of the fluidization air at different points in the fluid bed and the use of NIR monitoring of the product and the state of water within the product. The combination of these two measurements provides a very powerful tool for monitoring fluid process and gaining a better theoretical understanding of the processes. In addition, the calculation of the process trajectory will be presented; the process trajectory can be used to identify good from failed batches. If such a monitoring system were connected to a feedback system in process corrections could be used to prevent product failure and take corrective action before the point of product failure is reached.

(90) **Understanding Sampling and the Impact on PAT Method Performance for Solid Dosage Manufacturing**; Gary McGeorge[1], Dongsheng Bu[1], Dimuthu Jayawickrama[1]; [1]Bristol Myers Squibb

Non-invasive spectroscopic methods have become a foundation of the measurement of critical material attributes for oral solid dosage (OSD) manufacturing. Careful consideration of what the measurement is and how to sample one's process are vitally important to the success and validity of the specific control, and ultimately into the overall product control strategy. In this talk we will share our learnings on the topic with specific regard to sampling of powder blends using on-line NIR spectrometers. Here the volume of information will be discussed and its relationship to filtering approaches will be evaluated. This area has seen significant inconsistencies in the literature regarding how to estimate the sample mass being tested in such measurements and it often causes confusion with the health authorities when relating it to the mass of a dosage unit. Moving along in the process we will evaluate options for sampling of tablets using at-line NIR or Raman for both potency and content uniformity assessment. With the capability to test an increased number of tablets it is necessary to redefine the release criteria for content uniformity and link the specification specific sampling plans to a product. We will work though an example product where a modified large-N sampling procedure was adopted and presented to global health authorities. Without such careful consideration in these areas it will not be possible for the pharmaceutical industry to see the real benefits of in-process control and ultimately ensure improved product quality and Real Time Release. These will clearly be even more important as the industry adopts continuous manufacturing.

(91) **Pharmaceutical Process Scale-up Optimization and Control Using PAT**; Neil MacPhail[1], Brandye Smith-Goettler[1], Colleen Neu[1]; [1]Merck and Co., Inc

In the recent history of the pharmaceutical industry, regulatory expectations have evolved with regards to the required level of fundamental process understanding. ICH Q10, highlights a control strategy as a planned set of controls, derived from current product and process understanding, that assures performance and product quality. As a mechanism to understand a number of unit operations process analytical techniques have been developed that not only help to understand the process reproducibility but can also be used to control the quality of products. Utilizing PAT during drug product commercialization allows data capture for process capability measurement, providing confidence that the process is well controlled. The pharmaceutical unit operations that will be discussed during this presentation will include:

1) Blending
2) Lubrication
3) Hot melt extrusion

(92) **The Expanding Role of Raman Spectroscopy at Amgen: Key Advantages and Translation to Diverse Applications**; Dawn Cohen[1]; [1]Amgen

At Amgen, we have the unique opportunity to develop both large and small molecule therapeutics, as well as programs with aspects of both. In the small molecule realm, Raman spectroscopy has long been a champion and continues to establish itself. This success can be attributed to the following key abilities: sensitivity to nonpolar vibrations, ease of implementation in large-scale processes, the ability to probe solid state identity of particles in a slurry in-situ as well as neat, and the serendipitous fact that most API molecules are superior Raman scatters than the excipients of formulation, in conjunction with good selectivity due to different functionality and thus different vibrational frequencies of API vs. excipients. Recent applications where we have capitalized on these abilities will be presented. We have also been exploring the translation of our small molecule successes to large molecule process development. Here, additional advantages of Raman include insensitivity to water (and thus the ability to make sensitive measurements under aqueous conditions), sensitivity to polarizable disulfide bonds and the fact that the cysteine S-H stretch occurs in a region of the spectrum that is relatively clear of interference from other bands. Our initial experiments have been promising. Assessment of cysteine and cystine spectral regions yields real-time kinetic information about biopolymer reduction and related folding. This information is difficult to obtain using other techniques, especially without altering the sample prior to making a measurement. Experimental considerations and the potential of on-line Raman for tracking process dynamics of large molecules will be discussed.

(93) **Raman Spectroscopy of Terrestrial Extremophiles from Hot and Cold Deserts : Analytical Astrobiology and the Search for Life on Mars**; Howell Edwards[1, 2], Ian Hutchinson[2], Richard Ingley[2]; [1]University of Bradford, [2]University of Leicester

The survival strategies of extremophilic organisms in terrestrially stressed locations and habitats are critically dependent upon the production of protective chemicals in response to desiccation , low wavelength radiation insolation , temperature and the availability of nutrients. The adaptation of life to these harsh prevailing conditions involves the control of the substratal geology ; the interaction between the rock and the organisms is critical and the biological modification of the geological matrix plays a very significant role in the overall survival strategy . The identification of the these biological and biogeological chemical molecular signatures in the geological record is necessary for the recognition of the presence of extinct or extant life in terrestrial and extraterrestrial scenarios. Raman spectroscopic techniques have been identified as valuable instrumentation for the detection of life extraterrestrially because of the use of non-invasive laser-based excitation of organic and inorganic molecules and molecular ions with high discrimination characteristics ; the interactions effected between biological organisms and their environments are detectable through the molecular entities produced at the interfaces , for which the vibrational spectroscopic band signatures are unique. A very important attribute of Raman spectroscopy is the acquisition of molecular experimental data non-destructively without the need for

chemical or mechanical pre-treatment of the specimen ; this has been a major factor in the proposal for the adoption of Raman instrumentation on robotic landers and rovers for planetary exploration , particularly for the forthcoming ExoMars mission.In this paper , the merits of using Raman spectroscopy for the recognition of key molecular biosignatures from several terrestrial extremophile specimens will be illustrated . The data and specimens used in this presentation have been acquired from Arctic and Antarctic cold deserts , a meteorite crater , and from hot desert saltpan evaporite locations , from which it will be possible to assess the viability of Raman spectroscopy for the detection of extraterrestrial extremophilic life signatures in forthcoming space missions.

(94) **Raman Spectroscopy in Hypersaline Environments - Importance in Astrobiology**; Jan Jehlicka[1], Aharon Oren[2], Petr Vitek[1], Howell G.M. Edwards[3]; [1]Charles University in Prague, IGMMR, [2]The Hebrew University of Jerusalem, The Institute of Life Sciences, [3]Centre for Astrobiology and Extremophiles Research, University of Bradford

In the frame of forthcoming astrobiological missions it is planned to use a Raman spectroscopic device to identify in situ both minerals and potential organic compounds – possible biomarkers of preexisting life. We report here how Raman spectroscopy can be applied to investigate the characteristics of fossil and recent evaporitic areas on Earth. Firstly, examples of laboratory investigations of pure cultures of halophiles are presented to demonstrate the possibilities for the detection of the major characteristic biomarkers. Secondly, the results of studies of stratified microbial communities within evaporite gypsum crusts in hypersaline saltern evaporation ponds in Eilat (Israel) are presented. Here, the crusts contain vertical layers of orange unicellular cyanobacteria, green filamentous cyanobacteria, and purple sulfur bacteria. Carotenoids and compatible solutes can be detected in the frame of these mats. Thirdly, the performances of miniaturised portable Raman spectrometers are evaluated to estimate the evaporitic mineralogy in dry saline areas (California, USA). Outcrops and complex samples were investigated to estimate the potential of miniaturised spectrometers to work under complex conditions outdoors to detect these compounds using a portable Raman spectrometer and comparisons were made with laboratory instrumentation.

(95) **Requirements for Mobile Raman Instrumentation for *in situ* Analysis**; Peter Vandenabeele[1], Jan Jehlicka[2], Howell G.M. Edwards[3]; [1]Ghent University, [2]Charles University, [3]University of Bradford

When trying to detect biomarker molecules in different matrices by using Raman spectroscopy, different aspects have to be taken into account. One important aspect in this context is the design of the instrument. The instrument should be reliable and stable, though versatile s it should be able to adapt to different situations. Moreover, a high degree of autonomy is expected. The instrument should be light and robust, as it should work under extreme conditions, surviving a long transport phase where it was hibernating. Ideally, the instrument should contain a calibration module. When using Raman spectroscopy, we want the instrument to be able to reach low detection limits of biomarker molecules in a complex matrix; small traces of biomarkers should be picked up. In this presentation, we will discuss the abilities of mobile Raman instrumentation to detect low limits of detection in different matrices – and the influence of the matrix on the achievable limit of detection.

(96) **A Comprehensive Picture of Planetary Materials by Stand-alone Raman Investigation**; Alian Wang[1]; [1]Washington University in St. Louis

Laser Raman spectroscopy has been proposed to be used for planetary surface exploration since 1994. For that purpose, miniaturized and robust Raman spectrometers have been developed in US and in Europe, and were included in the mission proposals for Mars, the Moon, Venus, and asteroids. Flight hardware without the backup of scientific investigations would hardly convey the full power of related technology, thus a broad scope Raman investigation on extraterrestrial materials has been conducted by the Planetary Spectroscopy Research Group at Washington University, since the beginning of this project. We will report a few major results from this investigation, involving mineralogy, mineral chemistry, and mineral crystallinity of the materials from Mars, from the moon, from the terrestrial analog sites, and from simulating experiments. The science payload of a planetary mission normally consist several science instruments. The synergistic application of the data from the full payload is the key to ensure the highest science return from a mission. However, as the PI team of a specific instrument, we also need to extract science information from one system, as much as possible, which is the reason for developing the methodology for Stand-alone Raman investigation.

(97) **Applications of Time-Resolved Stand-off Raman and Laser-Induced Native Fluorescence (LINF) Systems for Planetary Exploration**; Shiv Sharma[1], Anupam Misra[1], Paul Lucey[1]; [1]University of Hawaii, Hawaii Institute of Geophy. & Planetology

At the University of Hawaii, we have developed compact time-resolved (TR) Raman, and fluorescence spectrometers suitable for planetary exploration under NASA's Mars Instrument Development Program. The compact TR-Raman and -fluorescence spectrometers consist of custom miniature volume holographic gratings and custom miniature intensified CCD cameras. These spectrographs have been interfaced with a regular 50 mm camera lens and various diameter (89, 127, and 203 mm) telescopes for remotely interrogating hydrous and anhydrous minerals, biogenic materials, water, water-ice and dry ice, and atmospheric gases. Using a small frequency-doubled 532-nm Nd:YAG pulsed laser (35 mJ/pulse, 20 Hz) and 50-mm camera lens, TR-Raman and LINF spectra of minerals and bio-minerals can be measured within 30 s under super-critical CO2. With the 89-mm diameter telescope these samples can be interrogated to 50 m radial distance during day time and nighttime. With 203- and 127-mm diameter telescopes the system is capable of making Raman measurements of atmospheric gases and biogenic and abiogenic minerals to 125 m radial distance. The LINF system with a 50-mm camera lens is capable of measuring TR-laser-induced fluorescence excited with 355-nm laser in the 340-800 nm spectral range. The TR-fluorescence spectra allow measurement of LINF from rare-earths and transition-metal ions in time domain, and also assist in differentiating between abiogenic minerals from organic and biogenic materials based on the fluorescence lifetime. Biological materials are also identified from their characteristic short-lived (<10 nano s) laser-induced fluorescence lifetime. These instruments are expected to play an important role in planetary exploration in NASA's future Mars Sample Return Mission and lander and rover missions to the Moon, Mars, Venus, and other planetary bodies.

(98) **Non-invasive Chemical Sensing with Temperature-Programmed Microsensors: Overcoming Complex Analytical Problems with Multidimensional Databases**; Baranidharan Raman[1, 2], Douglas Meier[2], Kurt Benkstein[2], Steve Semancik[2]; [1]Washington University, [2]National Institute of Standards and Technology

Complex analytical problems, such as detecting trace quantities of hazardous chemicals in challenging environments, require solutions that most effectively extract relevant information about a sample's composition. In this talk, I will present a chemiresistive microarray–based approach to identifying targets that combines temperature-programmed elements capable of rapidly generating analytically rich data sets with statistical pattern recognition algorithms for extracting multivariate chemical fingerprints. I will describe the chemical-microsensor platform developed at the National Institute of Sensing Technology and discuss its ability to generate orthogonal data through materials selection and temperature programming. Finally, I will discuss recent advances in both devices and algorithms that have been made to deal with practical issues involved in long-term deployment. These issues include identification and correction of signal drift, challenges surrounding real-time unsupervised operation in different background conditions, repeatable device manufacturability, and hierarchical classification schemes designed to deduce the chemical composition of untrained analyte species.

(99) **Sensitive Chemical and Biological Sensing Enabled by Self-Assembled Photonic Crystals and Plasmonic Crystals**; Peng Jiang[1]; [1]University of Florida

We report the achievement of rapid and sensitive detection of various vapors and biological species including proteins, viruses and bacteria by using 3-D self-assembled photonic crystals and 2-D plasmonic crystals created by a simple and scalable bottom-up nanofabrication platform. This platform combines the simplicity and cost benefits of bottom-up colloidal self-assembly with the scalability and compatibility of top-down microfabrication for creating large-area colloidal photonic crystals and a large variety of highly ordered plasmonic nanostructures. Capillary condensation of a condensable vapor in the interstitials of photonic crystals leads to the increase of the effective refractive index of the diffractive medium, resulting in the red-shift of the optical stop bands. The wavelength shift is linearly proportional to the vapor partial pressure for a spectrum of vapors. Optical simulation and theoretical prediction based on Kelvin equation suggest that a liquid film is formed on the walls of the photonic crystals during vapor condensation. We have also demonstrated the capability of this novel methodology in creating highly sensitive and reproducible surface-enhanced Raman scattering (SERS) and surface plasmon resonance (SPR) biosensors over wafer-sized areas. This novel nanofabrication platform is compatible with standard microfabrication, enabling on-wafer integration of plasmonic biosensors with conventional microfluidic devices.

(100) **Bio-Chemical Sensors based on Photonic Crystals**; Marko Loncar[1]; [1]Harvard University, School of Engineering and Applied Sciences

Much of modern technology—from data encryption to environmental sensors to templates for device fabrication—relies on encoding complex chemical information in a single material platform. To address this need, we recently developed a technique for patterning multiple chemical functionalities throughout the inner surfaces of three-dimensional (3D) porous structures. Using a highly ordered, bio-inspired, 3D photonic crystal as a regionally functionalized porous carrier, we generate complex wettability patterns. Immersion of the sample in a particular fluid induces its localized infiltration and disappearance of the bright color in a unique spatial pattern dictated by the surface chemistry. We use this platform to illustrate multilevel message encryption, with selective decoding by specific solvents. Our initial experiments indicate that our system could find use as a colorimetric indicator for liquids based on wettability. Label-free biomedical and chemical sensors are of enormous importance in healthcare, environmental surveillance and national security. Optical cavity-based sensing schemes have demonstrated high sensitivity and integration capability. I will discuss applications of densely integrated photonic crystal nanobeam cavities as high-sensitivity, high-throughput, sensors capable of detecting a few molecules. Furthermore, I will discuss a novel sensing scheme, bistable cavity sensing, that takes advantage of optical nonlinearities to increase the sensitivity of cavity-based sensors.

(101) **Wireless Low Cost Sensors Based on RFID Technology**; Fabio Di Francesco[1], Sabrina Bianchi[1], Matteo Grossi[1], Nicola Calisi[1], Valter Castelvetro[1]; [1]University of Pisa

RFID technology is based on the transmission and reception of radiofrequency signals between a transmitter (reader) and a transponder (tag). The transponder is a device capable to receive input signals from the transmitter and to send back a response. A reader can thus identify, by exchanging electromagnetic signals, a transponder and the devices connected to it. The most widespread and successful application of RFID technology is automatic identification, but in the last few years more and more research projects and commercial companies aim at integrating RFID and sensor systems. The attractiveness of RFID tags comes from their low cost and the possibility of taking multiple concurrent readings by a same reader. These characteristics allow their use for the periodic monitoring of product and object conditions as well as for the realization of wireless sensor networks. Most tags have two main components: 1) an integrated circuit to store and process information, to modulate and demodulate the RF signal and to accomplish other specialized functions; 2) an antenna for signal transmission and reception. Several approaches have been proposed to provide a tag with sensing capabilities, from simple coating of the antenna with a chemically sensitive film to modifications of part of the electronic circuitry to measure variations of electrical resistance or capacitance of a film. In the present work the use of RFID tags coated with thin electroactive films from water borne colloidal hybrid dispersions to produce wireless pH sensors is reported. The active component of the electroactive film is a nanocomposite material consisting of an acrylic polymer matrix loaded with a percolating dispersion of surface-modified multi-walled carbon nanotubes (MWNTs, typically around 0.5 wt %) variously combined with a pH-responsive homo- or block copolymer. The pH-sensitive polymer amplified the changes in resistivity of the electroactive nanocomposite film by enhancing the local perturbations originated from the variable swelling occurring in aqueous solutions at different pH. Possible applications of these sensors in the biomedical field and for food monitoring are discussed.

(102) **Chemical and Biological Sensors: Industrial R&D Perspective**; Radislav Potyrailo; [1]GE Global Research

Sensors with more sensitivity are required today to analyze ultra-trace levels of environmental pollutants, pathogens in water, and low vapor pressure species in air. More selective sensors are wanted to analyze specific biomolecules and analyze ambient urban or battlefield air. Sensors for long-term calibration-free operation are needed for bioprocess monitoring. Battery-free unobtrusive sensors are needed for a variety of applications ranging from industrial to food safety. For these and many other reasons, at GE Global Research we are developing sensors based on several energy-transduction principles that involve radiant, electrical, mechanical, and thermal types of energy. In this talk, we will provide an overview of our fundamental and applied research in this area with several specific examples that will include new sensing materials, new detection concepts, and our strategies of bringing new technologies

from their initial laboratory demonstrations, through the rigorous system optimization, and to final product.

(103) **Non-Invasive Spectral Imaging Advances Preservation of Cultural Heritage**; Fenella France; [1]Library of Congress

The conservation of art and cultural heritage objects requires advances in non-invasive, non-destructive analytical techniques to characterize cultural heritage materials, including substrates (paper, parchment) and media (inks, pigments, colorants). With an integrated 39 MegaPixel camera and LED illumination panels to capture high-resolution images in ultraviolet, visible and near infrared spectrum, researchers can create a spectral map of a manuscript or object that can be linked with other non-invasive analyses . Spectral imaging systems developed for astronomical imaging and remote sensing have been adapted and customized for libraries and museums. The Library of Congress is using hyperspectral imaging to support preservation of cultural heritage materials, It serves as a powerful, non-invasive technique for assessing the preservation, provenance and intellectual composition of heritage items. Advanced spectral imaging allows non-invasive characterization of materials, providing both access and enhanced non-visible and visible information in registered high resolution digital images. This non-contact tool can non-invasively identify and characterize colorants, inks and substrates based on their spectral response, monitor deterioration or changes in parchment, paper, textiles, petroglyphs and other materials due to exhibition and other environmental conditions, and assess previous treatments that modify chemical and spectral responses of cultural heritage materials. The resulting spectral image cube creates a new "digital cultural object" – related to, but distinct from the original. The Library utilizes this system to address challenges associated with characterizing manuscript materials, including: earliest Portolan (nautical) Charts, L'Enfant Plan of Washington D.C., Jefferson's handwritten draft of the Declaration of Independence, James Madison debate papers. It has also been used to illustrate non-invasive characterization of materials, deterioration, and detection of non-visible changes due to exhibition and storage of significant historical documents. The Library spectral imaging program includes development of a spectral reference database and integration of data from other non-invasive analytical techniques to create a full analytical mapping of objects for non-destructive analyses of collection materials. Scriptospatial mapping of data enables direct sharing and visualization of data, with capture of standardized instrumentation parameters and object metadata, while processing of the data cube creates enhanced spectral features captured from the visible and non-visible regions of the spectrum.

(104) **Scales of Production: Provenancing Glass Making in the Hellenistic-Roman World**; Patrick Degryse[1, 3], Dieter Brems[1, 3], Monica Ganio[1, 3], Tom Fenn[1, 3], Kris Latruwe[2], Frank Vanhaecke[2]; [1]KU Leuven - Div. Geology, Centre for Archaeological Sciences, [2]UGent - Analytical Chemistry

The location of primary production of natron glass in the Hellenistic and early Roman world, outside Egypt and Syro-Palestine, is still matter of debate. In this paper, on the basis of trace element (e.g. Zr, Ti…) and Sr-Nd isotope analysis, a database of possible sand raw materials is presented and compared to Iron Age and Hellenistic-Roman glass from around the Mediterranean. It is proven in this work that suitable silica raw materials for glass making are rare, but several regional occurrences can be distinguished chemically on the basis of trace element patterns and varying Nd isotopic composition. Primary production of Iron Age to Roman glass can be proven for both the western and eastern Mediterranean areas on this basis. However, an eastern Mediterranean (Syro-Palestinian and Egyptian) production signature dominates throughout the period studied, while a western Mediterranean signature (North African and northwestern European) is far less common. The largest diversity in primary glass producers occurs during imperial times, when several factories around the Roman world seem to have been active. Moving into late Roman and early Byzantine/early Islamic times, large scale production of glass becomes exclusive to the eastern Mediterranean.

(105) **Raman Spectroscopy in Art and Archaeology : The Illumination of Ancient Mysteries at the Interface between Science and Cultural Heritage**; Howell Edwards[1]; [1]University of Bradford

The major advantages of the adoption of Raman spectroscopy for the analysis of archaeological artefacts and works of art are two-fold : the technique is nondestructive and requires little or no chemical and mechanical pretreatment of the specimen , and the molecular signatures from both the organic and inorganic components can be obtained from the same spectrum , hence affording the opportunity for assessing the interactions and relative stabilities of materials to diverse chemical , biological and environmental changes that have been operating on the specimen often for many centuries.Here the results of several selected case-studies that have been undertaken in collaboration with archaeologists , art historians and conservation scientists will be presented to illustrate the use of the analytical data derived from Raman spectroscopic applications in several scenarios including the following :

- the biodegradation of wall-paintings from prehistoric cave art to the Renaissance–Raman spectroscopy as an early warning device for conservators especially for biological degradation that may be present but invisible ;
- the restoration of severely damaged Renaissance frescoes that have been subjected to deliberate mutilation by gunfire in the Spanish Civil War ;
- the identification of a dragon's blood resin for restoration of a 19th century "goldenised" dish by museum conservators;
- human mummified and skeletal remains from prehistoric, Egyptian dynastic and mediaeval periods over a period of some 4000 years .

In most cases , the information that has been obtained from the Raman spectra of these diverse archaeological specimens and artworks has been novel , often providing an insight into the technologies adopted by ancient cultures and a geographical dimension to the sourcing of original materials , emphasizing the existence of hitherto unsuspected ancient trade routes, and the recognition of the spectral signatures of biological colonisation which demand the urgent intervention of conservation procedures for the protection of archaeological specimens.

(106) **Raman Spectroscopy and X-ray Fluorescence Analysis: Two Complementary Approaches of Interest for Archaeometry Research**; Peter Vandenabeele[1]; [1]Ghent University

Archaeometry is a challenging research field on the border between natural sciences and humanities. When performing research in the cultural heritage field, it is often important to balance the damage the (risk on) damage with the information that is gained from the investigations, as research is performed on precious or unique objects. In order to reach this goal, different approaches can be followed, such as the use of mobile equipment to perform in situ investigations, minimising the (risk on) damage to the artefact. On the other hand, one can try to increase the amount of information that is gained, by using multiple, complementary analytical techniques or by using chemometrical techniques to extract more information from the obtained results. During this presentation, examples will be provided from our recent research of a combined use of in situ Raman spectroscopy with handheld X-ray fluorescence (hXRF) for the non-destructive in situ analysis of art objects.

(107) **Microfluidic Devices for Automated Cell Synchronization and Analysis**; Stephen C. Jacobson[1], Michelle D. Hoffman[1], Seth M. Madren[1], Pamela J. B. Brown[1,2], David T. Kysela[1,2], Yves V. Brun[1,2]; [1]Department of Chemistry, Indiana University, [2]Department of Biology, Indiana University

A detailed understanding of the mechanisms by which bacteria adhere to surfaces is essential to elucidate how biofilms form and bacteria infect. The ability to track these adhesion events at the single cell level with fluorescence microscopy provides insight into the adhesion process and heterogeneity of the process within a given cell population. With microfluidic devices, we are able to precisely control the local environment in which the cells reside and to monitor the behavior of the bacterium Caulobacter crescentus. To improve temporal precision, we moved the cell synchronization step on chip and developed a microfluidic "baby machine." The microfluidic devices have integrated pumps and valves to control the movement of cells and media. Synchronized populations are collected from the device at intervals as short as 10 min and at any time over four days. Our on-chip synchronization method overcomes limitations with conventional physical cell separation methods that consume large volumes of media, require manual manipulations, have lengthy incubation times, are limited to one collection, and lack precise temporal control of collection times. We now have a closed, automated system that streamlines the steps of cell seeding, culture, synchronization, and analysis.

(108) **Single Cell Analysis on Microfluidic Devices**; Christopher Culbertson[1], Metto Eve[1], Lunte Susan[2], Dulan Gunasekara[2]; [1]Kansas State University, [2]University of Kansas

Microfluidic devices have begun to change the way cellular analysis is performed because of their ability to integrate cell transport, manipulation, stimulation, and lysis with the separation and detection of analytes released by the lysis of such cells. The high throughput analysis of single cells is of interest because of even seemingly idendical cells often exhibit heterogeneous behavior when exposed to a stimulus. A better understanding of the heterogeneous nature of cell behavior would help to better understand the etiology of cancers and neurodegenerative diseases. Microfluidics might also be employed in the development of early detection systems for these diseases. Over the past several years , we have developed a variety of methods to analyze the contents of individual cells using a variety of fluorescent reporter molecules. We will discuss these methods and our results in this talk.

(109) **Digital Microfluidic Approaches for Single Cell Genetic Analysis**; Yong Zeng[1]; [1]University of Kansas

Cancer is a complex genetic disease that derives from single cells gradually accumulating mutations. Early-stage genetic biomarkers of carcinogenesis have been challenging to study due to the lack of capabilities of quantitative detection and molecular characterization of mutations at the extremely low frequency. We have developed a digital microfluidic technology as a core platform for high-throughput single cell/copy genetic analysis (SCGA). We demonstrated the feasibility of SCGA for pre-clinical diagnosis of blood cancer by analyzing chromosome breaks associated with lymphoma from chemical-exposed healthy workers. Furthermore, we have adapted the digital microfluidic technology to multi-locus detection and sequencing of genes in single cells for high-throughput analysis of variable regions as well as mutation co-localization. The new capabilities enabled by SCGA allow for the study of early-stage carcinogenesis and rare tumor cells important for metastasis (i.e., circulating tumor cells), thus opening new avenues for cancer biology.

(110) **FTIR Spectroscopic Imaging of Live Cells and Microfluidics**; Sergei Kazarian[1], Ka Lung Andrew Chan[1]; [1]Imperial College London

Fourier transform infrared (FTIR) spectroscopic imaging is a powerful, versatile and label-free method for chemical analysis. The combination of spectroscopy with imaging imaging using focal plane array detectors provides both chemical composition and spatial information about the sample. The potential of this imaging technology for studies of dynamic systems is yet to be fully realised. We will present some of our recent results on the development of applications of FTIR imaging to study fluid flows in microfluidic devices and the imaging of various types of live cells cultured on the surfaces of different ATR elements. Combining chemical imaging with microfluidics enables the detection of chemical species and their spatial distribution inside microfluidic channels. This imaging approach has been shown to be a powerful tool for the in situ study of mixing and chemical reactions in segmented flows. It provides quantitative information such as concentration profiles across the micro channels as well as the concentrations of the reactants and products as a function of time and position. We have demonstrated that it is possible to obtain chemical images of single phase and multi phase fluidic systems, such as laminar flows as well as segmented flows. Chemical imaging of live cells has significant potential for the study of chemicals in living cells without the need of external labelling or dyes. The demonstration of successful culturing of different cell-lines on various ATR elements (Ge, diamond and ZnSe) opens up the opportunity to apply this technology to a wider range of cellular research. Imaging of live cells in micro ATR (single cell level imaging) and macro ATR (for high throughput analysis) will be demonstrated.

(111) **Frequency Modulated Magnetic Traps for Enhanced Biochemical Sensors**; Lane Baker[1], Joe Basore[1], Rashid Zakeri[1]; [1]Indiana University

We report frequency modulation of magnetic fields within fluidic devices. Sandwich assays comprised of a magnetic microparticle for recognition, an analyte, and a fluorescent quantum dot for signal transduction were trapped at structures within a fludic channel. By modulation of the magnetic field, the position of the particle is periodically altered, to add a frequency component to the measurement. Operation of different magnetic structures at different frequencies, results in traps which report unique analytes can be monitored at a single wavelength. We will describe these findings and other recent related results from our laboratory.

(112) **Managing a Global NIR Network: What I Have Learned over 25 Years and Have Yet to Learn**; David Ryan; [1]Solae, LLC

Managing a global NIR (Near Infrared) instrument network with a wide diversity of calibrations has its challenges and rewards. Being competitive in the marketplace requires an ever increasing focus on productivity and product quality. A successfully managed network will make a significant contribution to your organizations bottom line. Like many processes there are more than one approach, however the utilization of basic principles can make the difference between success and failure. We will review network structure, and the relevance of master and satellite instruments given today's technological advances. We will outline solutions to address calibration transfer and instrument matching. A summary of best practice guidelines will provide a roadmap for optimization. Key concepts surrounding the creation of calibration models and there ongoing validation will be outlined. The challenges associated with management of instruments, including responsibilities of production personnel, and solutions to improve management of instruments at remote locations that are rarely if ever visited will be discussed. My goal is to leave you with a summary of what has been applied

successfully, what to watch out for, and what remains to be learned to achieve further improvements.

(113) **The Trials and Tribulations of Applying Quantitative Methods in a Global Environment**; Dimuthu Jayawickrama[1], Gary McGeorge[1], Tim Stevens[1], Boyong Wan[1], John Spirig[1]; [1]Bristol Myers Squibb

To support a global research and manufacturing organization it is often necessary to design methods that are capable of working on a variety of instruments under different conditions. This is often a serious challenge for the pharmaceutical scientist who is interested in generating robust methods that can be implemented as simply as possible. Instrumentation can be one of the most difficult aspects to control, which then requires one to thoroughly understand the performance limitations of instruments and develop approaches to mitigate issues that can arise from instrumental differences. A strategic approach to minimize the effect of instrumentation on calibration methods is to use similar or identical instruments from method development to commercial manufacturing. Even with the use of similar instruments some degree of tweaking to the instrument or method may be necessary in order to achieve desired method transfer. A number of techniques adopted by our group to transfer methods are discussed. For example, using a series of NIR spectral standards and appropriate transfer functions it would be possible to adjust the spectral response of one instrument to match that of another instrument. In some instances a direct transfer (with no adjustments) of methods is possible with the assistance of spectral normalization. This can easily be achieved when the spectral range for calibration is relatively narrow and therefore the impact of the rest of the spectral region on the method may not be significant. A better method for direct transfer would be to use an internal spectral peak to normalize spectra. The pros and cons of each of these transfer techniques will be discussed.

(114) **NIR Calibration Monitoring and Transfer for Pharmaceutical Tablets**; Carl Anderson[1], James Drennen[1]; [1]Duquesne University Center for Pharmaceutical Technology

Experiments were conducted at the Duquesne University Center for Pharmaceutical Technology to develop a system for continuous calibration monitoring and formulate an appropriate strategy for calibration transfer. Indicators of high-flux noise (noise factor level) and wavelength uncertainty were developed. These measurements, in combination with Hotelling's T2 and Q residual, are used to continuously monitor instrument performance and model relevance. Calibration transfer techniques were compared. Using as few as 15 transfer samples, predictive capability of the analytical method was maintained across multiple instruments and major instrument maintenance.

(115) **Data Sampling for Extending the Life of NIR-Based Models**; Jeremy Shaver, Randall Bishop, Neal Gallagher, Barry Wise; [1]Eigenvector Research, Inc

Often, calibration models are constructed from a large fraction of data available. As new process conditions or settings change, such models may need to be updated to account for these changes. When only historical (non-designed) data exists for a given analysis, the question arises: what portion of that data should be used to augment the model? Likewise, when reference measurements are expensive or difficult, down-sampling of the historical data is necessary. There are many published ways to select from historical data. This talk will highlight some of the methods that can be used for both initial model building and model updating. The relationship of these methods to cross-validation will also be discussed.

(116) **Calibration Optimization in Near-Infrared Spectroscopy**; Nanning Cao[1], Charles Hurburgh[1]; [1]Iowa State University

NIR calibration models for composition of grain are typically built from hundreds or thousands of samples over years. To establish a suitable prediction model, a wide range of samples in a calibration set provides more information. However, continuous increase in calibration set size may leads to inadequate models that overfit noise This is a problem encountered in PLS-based NIR models; reduced future prediction accuracy due to overinclusion of noise. The time and money spent on obtaining unnecessary chemical reference values is not cost effective. The development of a selection routine of representative samples for calibration is required to improve both efficiency and robustness of calibration model. In this study of near infrared transmission we attempt to only include only samples contributing useful information without redundancy. Three sample selection methods were used to select optimal sets of calibration samples for whole soybean protein and oil using two Foss Infratec and two Bruins OmegAnalyzerG instruments. When compared to using the complete set of 1500+ calibration samples, concentration prediction errors were reduced with selected sets of several hundred samples. With a uniform distribution of the reference values, models built on calibration sets with only 140 samples (about 2% of the original data pool) for moisture, 100 samples (about 8% of the original data pool) for protein and oil had better prediction performance on an independent test set (a crop year not included in calibration) than using the whole data set. Reference data is costly ($50/sample in this case); optimization can also create significant up-front cost savings to the NIRS user.

(117) **Mechanistic and Analytical Characterizations of Methane oxidation in Ionic liquids by Electrochemistry and *in situ* Infrared Spectroelectrochemistry Techniques**; Xiangqun Zeng[1], Zhe Wang[1]; [1]Oakland University

By taking advantages of the unique properties of ILs as solvents and electrolytes, we have systematically characterized the methane oxidation process in the [C4mpy][NTf2]/Pt and [C4mim][NTf2] under aerobic conditions using an electrode design consisting of a Pt-gauze as the sensing electrode pressed directly onto a thin gas-permeable Teflon membrane with a direct contact to a thin layer of the IL electrolyte. This design allows the methane to be oxidized at the gas/solid/liquid interface (tbp) which minimizes the limitation of high viscosity of ILs and enable us to obtain the benefits of non-volatile ionic liquids in a practical gas sensor application. Our results illustrate promising characteristics for the [C4mpy][NTf2] ionic liquid system with good sensitivity, surprisingly good selectivity, and excellent long-term stability at room temperature as compared to earlier reported atmosphere electrochemical methane sensors. The mechanism of methane oxidation in [C4mpy][NTf2] and platinum under aerobic conditions was systematically characterized by cyclic voltammetry and spectroelectrochemistry (in situ FT-IR) techniques. Our results suggest that the methane oxidation depends not only on oxygen concentration and the Pt electrode potential but also is governed by the properties of IL. The more compact double layer associated with [C4mim][NTf2] prevents methane oxidation whereas the more loosely-packed double layer formed in [C4mpy][NTf2] allows for facile methane oxidation. This mechanism has not been observed in early studies of hydrocarbon electrooxidation, but confirmed by our experimental results. The findings of this work will not only prove useful to improve operating conditions and selectivity leading to practical methane sensors using ILs that is simultaneously robust, sensitive, stable, and selective but also facilitate their potential applications in electrochemical energy conversion such as batteries and electrocatalysis.

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(118) **Facts and Fallacies In Ionic Liquid Luminescence**; Gary Baker[1]; [1]University of Missouri-Columbia

In recent years, ionic liquids have truly surfaced as designer solvents and materials within the physical sciences. Among their numerous attributes, ionic liquids have been reported to possess intrinsic luminescence, although the extent to which this has been demonstrated is certainly laboratory dependent. Likewise, this "autoluminescence" has been the subject of growing controversy, and is equally the bane of researchers seeking to conduct clean spectroscopic measurements—particularly those of the ultrafast time-resolved flavor—on ionic liquid-based systems. American writer James Thurber famously said "There are two kinds of light: the glow that illuminates, and the glare that obscures." In this presentation, we will explore whether, as a community, we have been blinded by the beguiling belief that even as ionic liquids possess no formal fluorophoric unit of note, they might act nevertheless in supramolecular concert to spawn transient fluorophores. To offer some balance to this dialogue, we offer some recent evidence which suggests an alternative explanation for this irregular behavior.

(119) **Exploiting the Versatility of Ionic Liquids and Polymeric Ionic Liquids in Chromatographic Separations and Microextractions**; Jared Anderson[1]; [1]The University of Toledo

Ionic liquids (ILs) are an attractive class of non-molecular solvents whose versatility allows them to be incorporated into various chromatographic and microextraction methods. ILs have negligible vapor pressures at room temperature, possess a wide range of viscosities, can be custom synthesized to be miscible or immiscible with water and organic solvents, and often possess high thermal stabilities. In addition, they can be structurally tuned to modulate desired physico-chemical properties while retaining their unique solvation capabilities. In this talk, ILs and polymeric ionic liquids (PILs) as selective stationary phases in gas chromatography will be discussed. Their application as selective and tunable extraction media for solid-phase microextraction (SPME) and dispersive liquid-liquid microextraction (DLLME) methods in the extraction of a wide class of analytes from environmental (polycyclic aromatic hydrocarbons, borate/boric acid, emerging contaminants), foods (coffee), pharmaceutical (genotoxic impurities), and biological (nucleic acids) samples will be discussed.

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(120) **Microwave-assisted Extractions of Pyrethroids by Ionic Liquids**; Sheila N. Baker[1], Jing Wang[1], Jian Xiong[2], Renee JiJi[2]; [1]University of Missouri, Department of Chemical Engineering, [2]University of Missouri, Department of Chemistry

In this work, we will investigate the use of ionic liquids (ILs) for novel microwave-assisted extractions coupled with chromatographic methods for pyrethroids detection. Pyrethroids will be used as model hydrophobic environmental contaminants in order uncover the structure-property-function relationships of ILs so as to target high yield pyrethroid extractions. Further we will track pyrethroid concentrations over time in nearby waterways and in food supplies.

(121) **Polysaccharide Ecocomposite Materials: Synthesis, Characterization and Applications**; Chieu Tran, Simon Duri[1], April Harkins[1]; [1]Marquette University

A novel, recyclable methods has been developed for the synthesis of nontoxic, biocompatible and biodegradable ecocomposite materials from polysaccharides. Various spectroscopic and imaging methods including FT-IR and NIR spectroscopy and spectroscopic imaging, CP-MAS-NMR, X-ray diffraction, SEM, AFM, TGA, DSC have been used to monitor the synthetic process, to characterize the materials and to determine their chemical and mechanical properties. Novel applications of the synthetic materials including removal of pollutants and bactericide and fungicide will be described.

(122) **Elemental Analysis and Isotope Ratio Determinations of Objects in the Field by Means of a Portable Laser Ablation Sampling Device**; Detlef Günther, Reto Glaus[1], Ladina Dorta[1], Norman Lüchinger[2], Samuel Halim[2], Daniel Tabersky[1]; [1]ETH Zurich, D-CHAB, [2]Nanograde, Spinoff ETH Zurich

LA-ICPMS is a powerful method for direct analysis of solid samples in a quasi-non-destructive manner. One growing field of application is the archaeometric research, where quantitative elemental and isotopic data are crucial to gain insights into provenance and authenticity [1]. To broaden the field of application of LA-ICP-MS to objects outside the laboratory, a portable laser ablation sampling device was assembled using a diode pumped solid state laser and fiber-optics [2]. The ablated materials is sampled on membrane filters at the sample site and subsequently analysed in the laboratory. The analytical performance of this sampling strategy was evaluated by quantifying opaque glass and gold standard reference materials. Main and trace element concentrations were determined to be within 20% of the certified value for most of the elements analyzed. The limits of detection ranged between 0.1 and 10 µg/g, which is about three orders of magnitude lower when compared to other mobile techniques such as X-ray fluorescence (XRF) or mobile laser induced breakdown spectroscopy (LIBS) (LOD: typically 10-1000 µg/g [3]). In addition, the sampling efficiency of our device was shown to be widely independent of the LA frequency chosen. Therefore, sampling at a frequency of one kHz allowed for collecting of sufficient amounts of material within seconds. Furthermore, the determination of trace elements, and Pb and Cu isotope ratios was investigated for ancient Chinese ceramic samples as well as ore materials. Sampling filters were digested and were analysed by MC-ICPMS. The results were compared to data obtained by fs-LA-MC-ICPMS of the same samples. Furthermore the direct analysis of the sampling filters with a LA-MC-ICPMS setup was tested. In addition, simultaneous isotopic and elemental analyses by splitting the carrier gas flow to a MC- as well as a quadrupole-ICPMS will be reported. All laser based techniques require matrix-matched calibration materials for accurate quantification. However, the generation of homogeneous materials is rather difficult. To overcome the lack of calibration materials, flame spray synthesis was used to generate trace element containing nano-carbonate, nano-silicate and nano-phosphate powders. The capability of this technique and some figures of merit on the materials produced will be discussed, in particular to their application in LIBS.

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(123) **Kinetic Model of Atomic and Molecular Emissions in Laser-Induced Breakdown Spectroscopy of Organic Compounds**; Paul Dagdigian[1], Qianli Ma[1]; [1]Johns Hopkins University

A kinetic model has been developed to predict the relative intensities of atomic and molecular emissions in laser-induced breakdown spectroscopy (LIBS). This model includes a comprehensive set of chemical processes for neutral and ionic chemistry in the plasma, as well as excitation and de-excitation of the upper levels of the observed spectroscopic transitions. The relative excited-state concentrations predicted by this modeling are compared with experimental measurements of the time dependence and relative intensities of the emissions for 1064 nm ns laser irradiation of residues of organic molecules deposited on aluminum substrates. The model reasonably predicts the relative intensities and time dependence of the atomic and molecular emissions. Significantly, the model reproduces the vastly different temporal profiles of the atomic and molecular emissions. The latter are found to extend to much longer times after the laser pulse, and this appears to be due to

the increasing concentration of the molecules versus time. From the simulations, the important processes affecting the CN and C2 concentrations are identified. The differing time dependence of the atomic and molecular features has implications for the optimum gate width in observing these features in LIBS measurements.

(124) **High Spatial and Depth Resolution Sampling in Ultrafast LIBS**; Vassilia Zorba[1], Yuan Lu[1], Xianglei Mao[1], Richard Russo[1]; [1]Lawerence Berkeley National Laboratory

Ultrafast laser-based schemes are used to identify the limits of detection in Laser Induced Breakdown Spectroscopy (LIBS) at small spatial and depth material sampling lengthscales. The LIBS spectral emission and laser-induced plasma properties were studied in different classes of solid samples. Configurations used include single and double-laser pulse geometries in the optical far-filed as well as near-field laser ablation. Sub-micron spatial resolution in LIBS was systematically achieved in the optical far-field. In addition, nm-scale depth resolution was achieved using fs-laser irradiation, an important aspect in thin film and interfacial layer analyses. Finally, we demonstrate the use of double-laser pulse configurations as secondary excitation sources that offer significant spectral emission intensity and sensitivity enhancements in the sub-micron spatial scale, and assist towards further minimizing the requirements for ablated mass in laser-ablation based chemical analysis beyond the attogram scale.

(125) **Temporal Evolution of the LIBS Spectra of a Representative Nitro Compound**; Jonathan Merten[1], Nathan Bullock[1], Cheyenne Sheppard[1], Matthew Jones[1], Christian Parigger[2], Susan Allen[1]; [1]Arkansas State University, [2]University of Tennessee Space Institute

LIBS has been investigated extensively for the detection of explosives, normally by the measurement of N, O and C lines and their ratios. There have been fewer studies on the potential of molecular fragments (e.g. CN, C2, NO) for explosive identification. Even less information is available regarding the temporal evolution of these molecules' emission within the plasma. We have investigated the early (first two microseconds) evolution of the CN and C2 spectra from LIBS plasmas formed on 3-nitrobenzoic acid (NBA), a simulant for energetic nitro compounds. This is available in pure, solid form and contains a nitro-substituted benzene ring. It should be noted that molecular LIBS is interesting for other applications, for example, detection of biological samples or isotopic analysis. We have measured the integrated CN violet band areas as a function of time during the first two microseconds of plasma evolution. This behavior is compared to that of graphite/NH4NO3 admixture plasmas. In addition to the spectral evolution, time resolved atomic excitation and vibrational temperatures are compared. The CN violet spectra are generally well-fit by a single vibrational temperature at times >1μs. Early spectra, however, are not well fit by varying the equilibrium temperature. These results may indicate non-equilibrium conditions or differences between rotational and vibrational temperatures. Alternatively, an optically thick plasma may cause the discrepancies between computed and measured spectra. We will describe the results of experiments currently underway to distinguish between these possible scenarios. Approved for public release.

(126) **High-resolution Optical Diagnostics of Uranium Transitions in a Laser Induced Plasma: A Time-Resolved Line Profile Study**; Nicholas Taylor; [1]Pacific Northwest National Laboratory

Accurate, precise, and rapid measurement of isotopic composition is of great analytical interest. Among the analytical tools available, optical spectroscopy provides an attractive pathway to achieve these goals. At low pressures, optical spectroscopy can achieve high isotopic selectivity and sensitivity at high speeds, while laser-induced sample vaporization eliminates complicated sample preparation associated with mass spectrometry techniques. Initial modeling and literature results suggest that optical measurements of uranium isotope ratios can be performed in a laser-induced plasma under ambient conditions, which could dramatically increase the range of applications for the technique. Unfortunately, the literature data available on many of these optical transitions is limited at best. We present an experimental study of the temporal evolution of uranium neutral and ionic spectral line profiles in a laser-induced plasma under various buffer gas environments at a range of pressures up to ambient conditions. In contrast to laser-induced breakdown spectroscopy, the current study measures line profiles using high-resolution laser spectroscopy with absorption and/or fluorescence detection. As a result, high spectral and temporal resolution is achieved throughout the plasma evolution, including long delays when emission intensities are reduced below noise levels but ground state populations remain significant. The transient behavior of the laser-induced plasma is evaluated for atom and ion lifetimes and transition linewidths, including the time-dependent Lorentzian line broadening and line shifting mechanisms.

(127) **Laser Ablation Imaging Mass Spectrometry Incorporating Separations**; Kermit Murray[1], Sung-Gun Park[1]; [1]Louisiana State University

Imaging mass spectrometry using laser desorption or ablation typically involves the direct creation of ions from a prepared tissue section followed by mass spectrometry separation or, in some cases, ion mobility separation coupled with mass spectrometry. We are developing methods that go beyond this approach and incorporate an additional separation step between laser material removal and mass spectrometry analysis. Biomolecules in tissue sections are ablated, captured in a solvent stream and separated by liquid chromatography or capillary electrophoresis before ion formation in an electrospray source mass spectrometer. In the laser ablation sampling system for on-line electrospray analysis, mouse brain tissue sections are deposited on a conductive microscope slide and mounted on a xyz stage. The sections are ablated in transmission (back side irradiation) mode using a wavelength tunable pulsed infrared optical parametric oscillator. The ablated material is captured in an exposed flowing solvent stream either on an exposed section of a microfluidic chip or the exposed section of a silica capillary tube. The exposed solvent flow capillary is easily coupled to a capillary LC column using a flow injection valve to transfer the captured material. The use of a microfluidic chip adds more possibilities for sample treatment and separations, including electrophoretic injection and separation. We are currently optimizing the chip-based capture and separations system and incorporating the capture and imaging components.

(128) **MALDI Imaging Mass Spectrometry of Three-Dimensional Cell Culture Systems**; Amanda Hummon[1], Haohang Li[1], Eric Weaver[1]; [1]University of Notre Dame

3D cell cultures have increased complexity compared to simple monolayer and suspension cultures, recapitulating the cellular architecture in the body. For example, many colon cancer cell lines form rounded heterogeneous spheroid structures that mimic the pathophysiological properties of tumors when grown under appropriate cell culture conditions. Classical imaging methodologies, like immunohistochemistry, are commonly used to examine the distribution of specific species within the spheroids. However, there is a need for an unbiased discovery-based methodology that would allow examination of protein/peptide distributions in 3D culture systems, without a need for prior knowledge of the analytes. We are developing MALDI imaging mass spectrometry protocols to examine protein distributions in 3D cultures models. Using the colon carcinoma cell lines, we have grown spheroids measuring 1 mm in diameter for MALDI IMS imaging. We detect changes in the spatial distribution of proteins across the spheroids by IMS and are currently

identifying the individual species present. To do so, we are using a combination of the MS/MS capabilities of our MALDI TOF-TOF to sequence peptides in a de novo fashion and LC-MS/MS of homogenized cultures. Once we have established the most successful approach to determine protein identification in a 3D culture tissue slice, we will expand our studies to genetically manipulated spheroids to examine cancer-relevant changes to signal transduction pathways.

(129) **Multidimensional Approaches to Glycopeptide Analysis**; Eric Dodds; [1]University of Nebraska - Lincoln

In the fullest sense, glycoproteomic analysis should not only identify glycosylated proteins and characterize the complement of modifying oligosaccharides, but should also establish site-specific covalent relationships between carbohydrate structures and the proteins they modify. This can be accomplished for isolated glycoproteins on an individual basis through adoption of standard peptide-level proteomic approaches; however, large-scale, systems-oriented glycoproteomics remains largely unrealized and represents a grand challenge in post-genomic science. Taking into consideration the many levels of glycoproteomic depth (including possibility of multiple heterogeneously glycosylated sites per protein), the need for integration of orthogonal analytical dimensions is readily apparent. Fortunately, glycoproteomic complexity can also be viewed as an analytical advantage, as glycopeptides have a diverse and distinguishing array of physicochemical characteristics which influence chromatographic retention, exact mass, gas-phase dissociation, and ion mobility. This presentation will describe our ongoing efforts to develop integrated high-dimensional glycopeptide analytics which incorporate chromatographic enrichment and separation strategies, accurate mass measurement, multiple tandem mass spectrometry strategies (including application of both collision-induced dissociation and electron transfer dissociation), and ion mobility spectrometry. This fusion of dimensions will accelerate our progress towards the goal of truly systems-oriented, site-specific glycoproteomics.

(130) **A "Radical" Approach to the Characterization of Disulfide Bonds within Peptides and Proteins –Application of Gas-Phase Ion/Radical Reactions**; Yu Xia, Lei Tan, Kirt Durand, Craig A. Stinson; [1]Purdue University

Disulfide bond formation in proteins, being an important post-translational modification, is essential for proteins to maintain their biologically active structures. Characterization of a peptide or protein containing disulfide bonds requires obtaining sequence information and the correct assignment of the connectivity of each disulfide bond. Collision-induced dissociation (CID), although is very powerful in protein/peptide identification, often fails to provide structural information necessary for characterizing disulfide-linked peptides. Several alternative mass spectrometric methods are currently under investigation to meet the challenge, including electron capture /transfer dissociation (ECD, ETD), UV photodissociation, and ion/ion metal transfer reactions, etc. In this study, atmospheric pressure (AP) ion/radical reactions were utilized for disulfide peptide sequencing and characterization. The AP ion/radical reactions were facilitated by allowing radicals generated from a low temperature helium plasma to interact with peptide ions formed from nanoelectrospray ionization (nanoESI) in front of the atmospheric inlet of a mass spectrometer. The reaction products were analyzed in an on-line fashion by tandem mass spectrometry. A series of peptides containing disulfide bonds was investigated. Efficient disulfide bond cleavage was observed for peptides either having intra- or inter-chain disulfide bonds. The reaction mechanism was hypothesized to be dissociative addition of OH to a disulfide bond, leading to the formation of sulfinyl radical (-SO•) and sulfhydryl (-SH). Given the cleavage of the disulfide bond from ion/radical reactions, subsequent CID provided rich sequence information for peptides containing single intra-chain disulfide bond. The utility of ion/radical reactions was further demonstrated using bovine insulin, having three disulfide bonds. Collisional activation of the [M+5H+OH]5•+ insulin ions provided 76% sequence coverage as compared to 23% from CID of the intact [M+5H]5+ ions. The gas-phase structure and reactivity of the newly-generated peptide sulfinyl radial ions were further investigated by unimolecular dissociation and ion-molecule reactions. It was observed that sulfinyl radical could cleave a disulfide bond. This result suggested that disulfide bond scrambling could happen in the presence of the sulfinyl radical after the initial radical attack. Similar radical mediated chemistry was observed for ETD of peptides containing multiple disulfide bonds, which warranted caution for disulfide bond connectivity assignment.

(131) **Reporter Peptides for an Expedited Disulfide Shuffling Analysis: How to Guarantee Aberrant Assignments are not Artifacts of Sample Preparation**; Daniel F. Clark[1], Eden P. Go[1], Heather Desaire[1]; [1]University of Kansas

Disulfide bonds are an important post-translational modification that play a large structural role in proteins by imposing conformational constraints. Disulfide bonds are of particular importance because protein pharmaceuticals are becoming more prevalent in medicine and ensuring the correct conformation is imperative for proper efficacy and safety. Extreme care must be exercised because disulfides can easily be changed from native to a shuffled form through improper handling during expression, purification, or formulation. Incorrect disulfide bonds commonly result in decreased protein activity and could cause detrimental effects. Disulfide bonds are typically analyzed by employing a bottom-up approach. However, this approach could increase the possibility of disulfide shuffling. We present a method for checking disulfide shuffling during enzymatic deglycosylation and proteolytic digestion by enlisting the aid of reporter proteins or peptides to be present during sample preparation. Disulfide bonded peptides are well known to preferentially undergo disulfide scission when subjected to electron transfer dissociation (ETD). We make use of this knowledge to quickly identify the disulfides by searching for the peptide masses in the ETD MS/MS spectra. Lysozyme was carefully chosen as the reporter protein because it has approximately the same cysteine content as our analyte protein (5.4% to 3.7% of amino acids respectively) and none of the cysteine-containing peptides in lysozyme have isobaric masses with any of the cysteine-containing peptides in the analyte protein. Data shows that despite the required elevated temperatures for the extended amount of time for deglycosylation and proteolysis, disulfide shuffling remains at a minimum under the optimal conditions used. Native disulfide-bonded tryptic peptides from lysozyme are still easily detected in the gp120-lysozyme medley. Thus, not only was there no detectable shuffling within lysozyme, but there was no shuffling between cysteine-containing peptides from gp120 and lysozyme. This research solves a critical problem in MS analysis of disulfide-bonded peptides: When aberrant disulfide bonds are detected, it has been difficult to determine if the scrambling was present in the protein or introduced during sample preparation. Introducing a "reporter protein" of known disulfide connectivity allows one to verify that scrambling did not occur during sample preparation.

(132) **SAM-Spec® - Innovative and Flexible PAT Systems**; Richard Escott, Fabien Chauchard; [1]Indatech

SAM-Spec® is an optical technique based on Spatially Resolved Spectroscopy(1,2) which has been developed from medical device R&D. The capability provides both spatial and spectral information from the measurements, which can then be used to characterise materials and products. It is an optical method based on the physics of light propagation, enabling simultaneous chemical and physical properties to be measured using:

- Scattering coefficient : μs'= a□-b (a~Density, b~ Particle Size)
- Absorption coefficient : μa=c*k1…i(l) (Beer's law)

The system commonly uses a UV/NIR light source for irradiation, and measurements are performed at several set distances away from the point of incidence to enable physical characterisation. Absorbance spectra also provide chemical characterisation capabilities from the same measurements. Symmetrical data acquisitions enable physical changes to be assessed eg, uniformity, homogeneity and integrity. SAM-Spec® (Spatial Advanced Measurement by Spectroscopy) can be seen as a hybrid approach between image analysis and spectroscopy, using fibre optic technology ideally suited to on-line applications. The flexibility of the technique allows many configurations to be utilised depending upon the application and the process interface required. These can vary from simple enhancements with existing spectrometers, to specifically customised systems using for example probes, cells and hyperspectral cameras. The technology is ideally suited to on-line process monitoring and control for: blending, granulation, fluidised bed dryers(3), crystallisations, separations, high throughput tablet control etc: and examples of these applications will be given to illustrate the current capabilities.

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(133) **PAT for a Continuous Process: Strategy, Challenges and Development**; Peter Hamilton[1, 3], Luke Bellamy[2], Ralph Caricofe[1], Rahn Mckeown[1], Darryl Ertl[1], David Littlejohn[3]; [1]GlaxoSmithKline R+D, [2]GlaxoSmithKIlne GMS, [3]CPACT/ WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde

Traditionally, the pharmaceutical industry has operated largely using batch processes that are outlined by standard operating procedures with product quality testing at the end of each manufacturing stage. Using this approach, a pass/ fail response for the unit operation is relayed to the process operators that determines if they can proceed to the next stage. This is commonly a slow process requiring hours or even days for results to be obtained. Furthermore, this approach provides no information about the process itself. More recently, however, phrases like Quality by Design (QbD), six sigma and lean manufacturing have emerged, and the industry has responded by investing in new and innovative ways to manufacture their products and implement process control in-situ. In this time, Process Analytical Technology (PAT) has become a well established term within the sector, especially since the FDA's 2004 PAT initiative was established. Whereas PAT has made great strides in improving process understanding and control, the full extent of it capabilities are yet to be achieved. For example, in batch processing, success is being realized as more and more examples of PAT for real-time release are being accepted by the FDA for measurement of critical quality attributes such as loss on drying or blend uniformity. However, as the industry continues to make steps towards continuous manufacturing, the need for accurate and representative PAT measurements is greater than ever. In this study, PAT was evaluated for a late phase compound with intended secondary manufacturing via a continuous process (from granulation to tabletting). The initial aim was to analyze and control three critical quality attributes (CQAs) in situ: content uniformity, % wetness and particle size of the granulated product containing API and two excipients, however, the scope was extended to implement PAT into the entire line. A cross site, multidisciplinary team including formulators, engineers and PAT scientists determined the initial strategy regarding aspects such as analyzer type, locations and integration into each unit operation. Development work was then carried out using NIR and Raman spectrometries and particle size analysis techniques as proof of concepts for each CQA to be tested in-line.

(134) **Assessment of Continuous Reactor Technologies for the Cooling Crystallisation of L-Glutamic Acid**; David Littlejohn[1], Laura Palmer[1], Denise Logue[1], Naomi Briggs[1], Alison Nordon[1], Alastair Florence[1], Jan Sefcik[1], Lihua Zhao[1], Visal Raval[1]; [1]University of Strathclyde

The EPSRC CMAC Centre is researching technologies to facilitate a change in the way crystalline products are manufactured, by switching from batch to continuous processing. Continuous manufacturing initiatives should allow for the production of optimised particles, in more rapid, cost effective and sustainable ways. In order to make progress in continuous manufacturing, it is useful to compare the performance of different types of reactor technologies. In this study, two continuous reactors were evaluated: a CoFlore reactor from AM Technologies and an oscillatory baffled reactor (OBR) from NiTech Solutions. With the CoFlore system, free moving agitators in each stage of the reactor mix the reactant stream, when the reactor body is subject to agitation. This promotes good mixing behaviour, whilst reducing back-mixing and eliminating the need for agitator shafts and mechanical seals. In the OBR, the frequency and displacement of a series of baffles along the reactor length can be adjusted to ensure efficient mixing is achieved during crystal formation. In the current work, L-glutamic acid (LGA) was selected as a model compound for a comparison of the performance of the reactors. The effects of varying reactor parameters on the polymorph, yield and particle size of LGA were assessed. Particle size was measured by laser diffraction, and physical form was characterised by microscopy and X-Ray powder diffraction (XRPD). Non-invasive Raman spectroscopy with a Kaiser Raman PhAT probe was investigated for process monitoring in each of the reactors. Raman peaks that can be attributed to the solute, and the alpha and beta polymorphs of L-glutamic acid have been identified. The study has shown that some reactor parameters are more influential on the crystallization process than others. Comparisons with crystallization in a conventional batch reactor have revealed interesting differences in the extent to which control of crystal formation in the different reactors can be exercised.

(135) **Understanding Pharmaceutical Transformations Using Raman Spectroscopy: Influence of Polymeric Excipients**; Alan D. Gift[1], Jacob A. Hettenbaugh[1], Leslie A. Southard[1], Amanda L. Riesberg[1]; [1]University of Nebraska at Omaha

Drug tablets containing anhydrous active pharmaceutical ingredients (APIs) that can potentially transform to the hydrate form during manufacturing processes. The ability to understand and manipulate these transformations is important to maintain control of the solid state form of the API. The influence of polymeric excipients on the hydrate transformation of two model APIs, caffeine and carbamazepine, was investigated. Anhydrous API was added to aqueous solutions containing different polymeric excipients, and transformation to the hydrate form of the API was monitored using in-line Raman spectroscopy. The collected spectra were correlated to a partial least squares (PLS) regression model to quantify the extent of transformation of the API. The results showed that both polyacrylic acid and polyvinyl alcohol inhibited the transformation of caffeine and these inhibition effects were dependent on pH of the solution and percent hydrolysis of the side chain respectively. The results also showed that hydroxypropyl methylcellulose and polyvinylpyrrolidone inhibited the transformation of carbamazepine and these inhibition effects were dependent on the chain length of the

polymer. The observed inhibitory effects of these polymers are attributed to polymer adsorption to the API crystal surface.

(136) **A Novel Approach to in- and at-line Transmission Raman Spectroscopy**; Frank Roche[1], Manu Toivainen[1, 2], Jussi Tenhunen[2], Mikko Juuti[2]; [1]GMS Technical, GlaxoSmithKline, UK, [2]VTT Technical Research Centre of Finland

Transmission Raman (TR) spectroscopy provides a fast and robust method for measuring the chemical composition of a wide variety of materials. In transmission measurement mode, the measured sample is illuminated at a distance with a relatively high power laser light source, such as a semiconductor laser with 785/820nm wavelength, 500-1200mW in power consumption, and the irradiance of transmitted Raman-scattered light usually measured at spectral range between 200-1700 1/cm. The potential for quantitative measurements makes transmission Raman spectroscopy the preferred solution in pharmaceutical industrial on-line applications such as tablet API concentration measurement in tablets with continuous inspection. Transmission Raman is the only known working method of vibration spectroscopy for high throughput on-line API concentration uniformity characterization of pharmaceutical tablets. The diffuse reflection mode associated with NIR does not provide a representative enough sampling from the bulk of the tablet (only the upper 100 µm are measured) whereas in transmission mode, attenuation due to absorption at wavelengths longer than 1200 nm is too high for high speed measurement. It can be also stated that NIR spectra do not provide enough selectivity at wavelengths shorter than 1200nm, as most of the absorption peaks are too broad and wide. Utilization of MIR (mid-infrared) would be even more difficult due to poor light transmission through tablets. A recently developed new-type transmission Raman spectroscopic instrument was utilized and a transmission Raman probe accessory were developed for use in on- and at-line tablet inspection test measurement applications. For the undertaking of such tests, Transmittance Raman probes with newly invented illumination and detection units were built. A multivariate calibration model (spectral matched filtering) was devised to provide estimates for the API (paracetamol) levels of the tablets during each experiment performed. Results were derived which showed that this technology has the ability to increase the intensity of the collected Raman signal by factor of at least 20 fold (compared to conventional transmittance Raman technology). It was also demonstrated that this technique can be applied to real on- and / or at-line tablet inspection systems when combined with a suitable tablet presentation system. The accuracy of the transmission Raman system developed is also suitable for low level API control, which will also be presented in the paper. The measurement of API concentration can be detected accurately by the Raman method developed and within the specifications required. Therefore, the development undertaken delivers a novel approach for transmission Raman measurement concept and technique for the tablet QA inspection and release. Finally, application possibilities of this flexible QA method for new Transmission Raman instrument will be outlined.

(137) **Low-frequency Raman and THz Studies on Higher-Order Structures of Polymers**; Yukihiro Ozaki[1], Shigeki Yamamoto[1], Yusuke Morisawa[1, 2], Hiromichi Hoshina[1, 3]; [1]Kwansei Gakuin University, [2]Kinki University, [3]RIKEN, [4]Miyagi University of Education

Low-frequency vibrational bands observed in Raman and THz spectra can be sensitive not only to the local structures of molecules, but also to their higher order structures which would be governed by weak chemical interactions among the molecules, for example, the hydrogen bonds and Van der Waals interactions. These weak intermolecular interactions could be important when the polymer molecules are gathered, interacted with each other, and organized to make the crystalline structures. This low-frequency region below around 300 cm-1 is called Terahertz (THz) region in a field of the THz time-domain (TD) spectroscopy. Although assignments of the vibrational modes in the THz region are desired in order to understand the weak interactions mentioned above, it was quite difficult because these bands are usually highly delocalized in the molecules, and to be mixtures of some fundamental vibrations. The assignments and the interpretations of the vibrational bands in the THz region can be more rigid and reliable by comparing the experimental low-frequency Raman and THz-TD spectra, and also comparing them with the computed spectra. Here, we present our recent experimental and theoretical studies on the low-frequency Raman and THz spectra of polymers, such as poly-(R)-3-hydroxybutyrate (PHB), polyglycolic acid (PGA), polylactic acid (PLA), nylons, polyethylenes, and so on. The quantum mechanical calculations of the spectra were applied to the polymers with the aid of the Cartesian-coordinate tensor transfer (CCT)[1,2] method, which enabled the high-level of the calculations and to include the explicit consideration of the intermolecular interactions. The results obtained here confirmed a sensitivity of the vibrational bands in the THz region to the higher-order structures of the polymers and the roots of their intermolecular interactions.

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(138) **Towards Raman Spectroscopy on a Microchip**; Imran Akca[1], Nur Ismail[1], Lantian Chang[1], Kerstin Worhoff[1], René M. de Ridder[1], Markus Pollnau[1]; [1]University of Twente

In numerous applications, Raman spectroscopy is utilized to monitor unique Raman scattering in order to identify specific molecules or structures. We aim at developing a low-cost, compact, hand-held apparatus for Raman spectroscopy of the skin and tooth. A critical function of this system is spectral separation of the Raman-scattered signals. In our case, the core element of such a device is an arrayed-waveguide grating (AWG). Two silicon oxynitride single-mode channel waveguide geometries are designed for Raman spectroscopy of the skin and tooth. For tooth measurements we design the AWG to have a central wavelength of λc = 901 nm and a free spectral range of ~22 nm, with a resolution of 0.2 nm. The skin application requires the AWG to be polarization insensitive, to have a central wavelength λc = 881 nm, and to have a minimum resolution of 5.5 nm. For the Raman measurements light from a Ti:Sapphire laser at 785 nm, after passing through a laser-line filter, is reflected from a dichroic mirror and focused onto a sample with a microscope objective. The backscattered light from the sample is collected by the same optics; the Rayleigh component is again reflected by the dichroic mirror, which transmits the Raman wavelengths. An edge filter removes the residual light at the laser wavelength, and the light is focused into the input channel of the integrated spectrometer using a x50 microscope objective. The output channels of the AWG are imaged onto an electron-multiplying CCD through a camera lens. The set-up is tested by measuring the Raman spectra of silicon and cyclohexane. The preliminary dental measurements show excellent agreement between the spectra of healthy and carious tooth enamel measured with our integrated device and spectra recorded using a conventional Raman spectrometer.

(139) **Studies of Photopolymer Heterogeneties by Confocal Raman Microscopy**; Céline Dietlin[1], François Courtecuisse[1], Bandar El Fouhaili[1], Céline Croutxe-Barghorn[1], Xavier Allonas[1]; [1]Laboratory of Macromolecular Photochemistry and Engineering, ENSCMu, UHA

Photopolymers are used in a wide range of industrial applications (graphic arts, microelectronic, coatings…). Oxygen inhibition is most of the time an issue in free radical photopolymerization performed in

air. As a result, the structure of the cured polymer coating shows heterogeneities across the depth of the film: a gradient of conversion is created leading to poor final surface properties (scratch or chemical resistance). The depth characterization of photopolymer films by Confocal Raman Microscopy (CRM) is important to assess the extent of the effect of oxygen inhibition but also to correlate the curing state of the sample with its mechanical properties. Nevertheless the depth profile determination could be tricky for thick samples due to optical issue like refraction effects. An adequate preparation of the sample combined with the use of an immersion objective allows us to study these specific samples by CRM. After detailing the procedure used, some examples of the studies performed with this setup will be shown such as the influence of the photoinitiator nature or additives known to reduce oxygen inhibition on the through cure of acrylate coating.

(140) **The Key Role of Surface Chemistry in Surface Enhanced Raman Spectroscopy: From Label-Free DNA Analysis to Drugs of Abuse**; Steven Bell[1], Maighread McCourt[1], Evanthia Papadopoulou[1], Alan Stewart[1], Shuai Zheng[1]; [1]Queen

Successful SERS detection relies on the target of interest coming into close contact with an appropriately enhancing substrate. Since numerous very effective enhancing materials are known, the main challenge in SERS is to understand and control target adsorption onto the surface, both to promote detection of compounds of interest and to reject interfering compounds. In some cases, such as single- and double-stranded DNA, we have shown that promoting adsorption is simply a matter of not introducing competing ions and that SERS spectra can be recorded at nanomolar concentrations using conventional colloids without any need to thiolate the DNA to promote adsorption or to introduce dye labels.[1] This method can be used to detect single base substitutions in oligomers [2] or hybridisation. [3] Alternatively, for targets which do not spontaneously adsorb, it may be useful to chemically modify the surface, for example using self-assembled monolayers of appropriate thiols. Mixed thiols are particularly promising since their composition can be controlled [4] to tune the surface properties and they can act cooperatively to bind targets such MDMA ("ecstasy").[5].

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(141) ***In vivo* and *in vitro* Glucose Sensing in Complex Biological Environments by Surface-Enhanced Raman Spectroscopy**; Richard Van Duyne[1]; [1]Northwestern University

Surface-enhanced Raman spectroscopy (SERS) is a highly sensitive and selective technique which allows for the detection and characterization of low-concentration analytes in complex biological environments, both *in vivo* and *in vitro*. Due to the rising incidence of diabetes, one of the primary *in vivo* small molecule targets is glucose. It is projected that the number of people with diabetes in the U.S. will double or even triple by 2050. Although various *ex vivo* and implantable blood glucose monitoring instruments exist, most are severely inaccurate in measuring hypoglycemic blood glucose values (<80 mg/dL). Combining SERS with spatially offset Raman spectroscopy (SESORS) allows for highly accurate (particularly at hypoglycemic values), reproducible, quantitative, *in vivo*, transcutaneous glucose sensing. The latest progress on *in vivo* glucose detection by SESORS will be presented, demonstrating the reliability, accuracy, and long-term stability of our implantable silver film over nanospheres (AgFONs) substrates for *in vivo* glucose sensing in multiple animal subjects. To accurately determine the enhancement factors (EFs) for our glucose detection system, which includes a mixed decanethiol-mercaptohexanol (DT/MH) partition layer on the AgFONs, we have interrogated the normal Raman limits of glucose detection from 0 to 123 mg/dL (0 to 6 mM). The results demonstrate remarkable accuracy and consistency, with exceptional values for the root-mean-square error of calibration (RMSEC) (4.6 mg/dL) and the root-mean-square error of prediction (RMSEP) (5.0 mg/dL). We are also continually working towards optimization of FON substrates to achieve the highest EFs possible for the detection of small molecules and analytes. We are now able to achieve reproducible EFs of up to 10^8. Finally, we are combining microfluidics with SERS, using both SERS nanoantennas (gold nanoparticle cores coated with a Raman reporter molecule, and encased in a protective silica layer) and FONS as the enhancing substrates, for the interrogation of various molecules in blood.

(142) **New and Improved Mass Spectrometric Reference Materials**; Richard M. Essex[1], Jeffrey J. Morrison[1, 2]; [1]New Brunswick Laboratory, [2]DHS National Technical Nuclear Forensics Center

The USDOE New Brunswick Laboratory has been tasked with management of a program to provide analytical reference materials to enhance the traceability, accuracy, and precision of nuclear forensic measurements. This program is sponsored by the DHS National Technical Nuclear Forensic Center and has been pursued in cooperation with DOE Laboratories, NIST, and FBI as well as international partners. Creating mass spectrometric calibration standards and new isotopic tracers specific for nuclear forensic analyses has been one of the program focus areas. Toward this end, certified attributes for selected U isotopic reference materials are being expanded. Included are new high-accuracy high-precision values for a 4% U-235 enriched UO2 fuel pellet standard (CRM 125-A) which is also being characterized a radiochronometric standard. The certified isotope amount ratios for a 4.5% U-235 enriched U nitrate solution (CRM U045) and a 63% U-235 enriched U3O8 oxide material (CRM U630) are being expanded to include the n(U-232)/n(U-238) and n(U-233)/n(U-238); ratios that can be particularly valuable for forensic material characterization. To refine nuclear forensic analytical capabilities for material characterization and radiochronometry, a suite of desirable isotopic tracers has been identified. These tracers include a >99% enriched 134Ba that is being produced in an isotope separator at INL, a Th-229 tracer that has been produced and is being characterized for certification, and an Am-243 tracer solution that is being produced and characterized at NPL in the UK. Several other tracer materials have been identified as priorities and are in various stages of planning. An ultra-pure U-233 tracer solution (>99.99% U-233 enriched) is tentatively planned for production in FY 2014. A Pa-231 calibration material has been proposed as a priority nuclear forensic reference material and the production feasibility for of a Np-236 tracer is being evaluated. The laboratory uses of these materials include mass spectrometer calibration, highly reliable concentration measurements, and

improved radiochronometry. From a broader perspective, the availability of new reference materials identified by the analytical community will expand and improve currently analytical capabilities. More importantly, these materials will provide a level measurement quality assurance and traceability that is essential for analytical results associated with nuclear forensics.

(143) **Identification of Uranium Ore Concentrate Species by Near Infrared Spectroscopy**; Gregory Klunder[1], Jonathan Plaue[1], Paul Spackman[1], Patrick Grant[1], Martin Robel[1], Lars Borg[1], Rachel Lindvall[1], Ian Hutcheon[1]; [1]Lawrence Livermore National Laboratory

One of the first steps in uranium production is the mining and processing of uranium ore to provide Uranium ore concentrates (UOC), commonly referred to as Yellow Cake, a reference back to early mines when processed uranium samples were yellow. Today, the colors of the UOCs vary from yellow to dark brown which can be an indication of the type material and the process procedure. Although the visual evaluation of the sample color is the simplest detector, it suffers from being very subjective and does not provide chemical information. Nuclear forensic analysis of UOC samples relies on a number of differe nt analytical techniques to provide information about the samples to identify the process, materials, and origin. Recently, we've been investigating visible and near-infrared (NIR) spectroscopy as a rapid non-contact and non-destructive method to interrogate the sample. Vibrational overtone and combination bands of C-H, O-H, and N-H are detected in the spectral range from 1000 – 2500 nm, and use to identify uranium species that result from ammonium or sodium hydroxide processing, such as ammonium diuranate or ammonium uranium carbonate. In addition, electronic transitions from various uranium oxide species, U3O8, UO2, UO3 and UO4 have been identified. In this study, we have measured visible and NIR reflectance spectra from a number of different UOC samples and compared the results to the x-ray diffraction and infrared. The spectra were evaluated using chemometric analysis and the samples separated into groups with similar chemical features. The results of this study and the applicability of this technique for UOC characterization will be discussed. This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

(144) **Geochemistry of the Trinity Nuclear Test: Investigation of Trinitite Glass at High Spatial Resolution**; Jeremy J. Bellucci[1], Antonio Simonetti[1], Christine Wallace[1], Elizabeth C. Koeman[1], Peter Burns[1]; [1]University of Notre Dame

This study documents the first geochemical investigation of trinitite glass to date. Major and trace element abundances were determined *in situ* for 11 samples of trinitite utilizing electron microprobe and laser ablation ICP-MS (LA-ICP-MS) analyses, respectively. The spatial distribution (relative to ground zero) of these samples has been determined using the specific activity of ^{152}Eu, and yield distances between 51 and 83 m away. The major element compositions of the trinitite glass exhibit large variations (e.g., FeO wt. % = 2.1-8.3), and these define trends that can be attributed to mixing between natural minerals (K-feldspar, Calcite, Quartz) and an unknown component, possibly of anthropogenic origin. These minerals are typical components of arkosic sand, which is the predominant surface deposit at the White Sands Proving Ground, site of the Trinity test. The range in trace element abundances is also large (e.g., U [µg/g] = 0.6-45). Normalized trace element patterns can be divided into 5 categories: 1) Zr- rich (n=31), 2) Nb and Ta rich (n=4), 3) Nb and Ta depleted (n=4), 4) "average" and U depleted (n=37), and 5) "average" and U enriched (n=31). The trace element patterns are largely influenced by the absence or presence of trace mineral phases in the arkosic sand, specifically: zircon and mafic minerals (e.g., ilmenite), or represent complete homogenization of the arkosic sand during melting. Trace elements potentially of anthropogenic origin are Co, Cr, Cu, Ga, and Pb. Uranium seems to have two sources in trinitite: zircon and the U tamper used in the Gadget device. Lastly, samples originating further away from the blast tower are enriched in volatile elements (e.g., Co, Cu, and Pb) relative to those originating from closer to ground zero, which could be a function of temperature.

(145) **Computational Age Dating of Special Nuclear Materials**; Ding Yuan[1], Paul Guss[1]; [1]National Security Technologies

Conventionally, parent-daughter nuclide ratios are the keys for age dating of special nuclear material (SNM). The drawback of the ratio method is that there are a large number of ratios for any given decay chain. For SNM, which contains nuclides of different decay chains, the dating task becomes even more complicated. In recent years, we have developed an integrated multi-chain Constraint Progressive Reversal (CPR) method for SNM age dating. The CPR method employs a precise decay forward and inverse calculation algorithm and tracks every single nuclide in a full decay chain or multiple decay chains associated with a specific SNM sample. With this comprehensive bidirectional calculation approach, it is possible to identify the likely 'end-of-enrichment date' on the timeline of the SNM, which in turn would allow inferring the likely age of the sample. Because this approach naturally integrates all possible ratios, it significantly reduces uncertainties associated with manual ratio selections. The computational approach we developed permits visualization of the decay dynamics and other chronological events, such as those associated with end of enrichment, secular equilibrium, beginning of accumulation, and total depletion of the physical sample. By using this comprehensive computational approach, a very complex system of equations can be visually analyzed, and thus can be adopted for age dating of 'pure' SNM or spoof detection of mixed SNM. We shall describe the computational essence, algorithm advantages, software implementation, and present age dating and spoof detection examples of this approach. Key Words: radioactive decay, special nuclear material, nuclear forensics, age dating, spoof detection. This manuscript has been authored by National Security Technologies, LLC, under Contract No. DE-AC52-06NA25946 with the U.S. Department of Energy and supported by the Site-Directed Research and Development Program and NA-22.

(146) **Nuclear Forensics: Separation and Measurement of Lanthanoid Isotopic Ratios in Spent Research Reactor Nuclear Fuel**; Nicholas Sharp[1], William McDonough[1, 2], Alice Mignerey[1], Donna Beals[, 3]; [1]Department of Chemistry and Biochemistry, University of Maryland, [2]Department of Geology, University of Maryland, [3]Savannah River National Lab

Nuclear power reactors are typically benchmarked by models such as ORNL ORIGEN-ARP, however it is uncertain if these models will accurately define a research reactor's spent nuclear fuel composition. In the event of nuclear material being taken from a research reactor it is important from a nuclear forensics perspective to be able to determine characteristics useful for identifying which reactor the material came from. These characteristics include neutron fluence and energy spectrum. A reactor's neutron fluence and burnup can have a significant effect on the lanthanoid elements' isotopic ratios, thus measuring these ratios can indicate a reactor's operating charateristics. Lanthanoid isotopic ratios can be precisely measured via multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), however this requires the lanthanoids to be efficiently separated using column chromatography to remove isobars. This work focuses on the separation procedure from Dy-La in spent research reactor fuel using a two stage column separation, the first involving AG50W x8 400 mesh resin with HCl and HNO_3 to separate the lanthanoids from the short-lived fission products, notably ^{137}Cs and ^{90}Sr. Results have shown rapid elution of these two elements

resulting in their complete separation from the lanthanoids. The lanthanoids are then quantitatively collected with ^{90}Y as a high-dose, short term contaminant and $^{147,145}Pm$ as a long term source of activity. The separation of the lanthanoids is accomplished by using the same resin as before but treated with NH4OH to convert the resin from H^+ to NH_4^+ form and using α-hydroxyisobutyric acid buffered to pH 4.7 as the eluent. To date the separation of the elements Dy, Tb, Gd, Eu, Sm, and Nd have been accomplished with contamination from adjacent elements on the order of 1 part in 10,000 (1 ε). The analysis procedure using a Nu Plasma MC-ICP-MS for Nd isotopic ratios has been constrained to a ± 0.28 ε at the 2 σ level which will ensure detection of altered isotopic ratios greater than 5% deviation from natural values. Work is being done to develop analysis routines for the other lanthanoids.

(147) **The Application of Combined Radiogenic and Light Stable Isotope Studies to Forensics, Ecology and Archaeology.**; Gareth Davies[1], Janne Koornneef[1], Laura Font[1], Jason Laffoon[1,2]; [1]VU University Amsterdam, [2]Leiden University

The mantra, "you are what you eat" is at the basis of much new research in ecology, archaeology and forensic science. Light stable isotopes such as C-N provide information about diet (dominantly C3 or C4 plants, vegetarian, meat or fish). The hydrological cycle controls the isotopic fraction of H & O and these isotopic systems are becoming widely used to provide regional provenance information based on major precipitation belts. When combined, the light stable isotopes can be used to recognise immigrants to a community but with limited further provenance information. Radiogenic isotope systems such as Sr-Nd-Pb are widely used as provenance indicators of geological process and Sr isotopes in particular are starting to be extensively applied in archaeology to determine if individuals are immigrants to a local population. In this presentation we will outline how new chromatographic and mass spectrometric techniques, coupled with technological developments, which now allow the precise isotopic analysis of sub nanogram amounts of Sr-Nd-Pb. The introduction to modern mass spectrometers of improved electronics and the use of 1012 and 1013 ohm resistors have greatly improved signal to noise ratios. For example, TIMS analysis of 100 mV of 88Sr yield 2 SE errors of <0.00002 (using a Triton Plus). Increased sensitivity in inlet systems to multi-collector inductive coupled plasma (using a Neptune) allows determination of sub nanogram Pb isotope ratios. These levels of sensitivity and precision have opened up a series of new provenancing tools. In a forensic science context a person's movement over time can provide vital information for. Combination of isotopic data from tissues with different elemental turnover times potentially provides such a time line. Validation work will be presented on the use of Sr and Pb isotopes in human hair as a provenance indicator for movement in the recent weeks to years and these data are compared to isotopic data from human teeth providing a direct comparison to provenance during a person's youth. Specific examples will also be presented of how a combination of stable and radiogenic isotopes has been combined to provide refined provenance information in an ecology and archaeological context.

(148) **MC-ICPMS: Enhanced Ion Yields for Measuring "Almost Nothing in Not Very Much" and for Those Hard to Measure Elements**; Charles Douthitt[1], Johannes Schwieters[1], Nicholas Lloyd[1], Claudia Bouman[1]; [1]Thermo Fisher Scientific

Significant improvements in analytical performance of the Thermo Fisher model Neptune-Plus high-resolution multiple-collector inductively coupled plasma mass spectrometer (HR-MC-ICPMS) include improvements in sensitivity and enhancements to the dynamic range. Improvements to the pumping system and cone design lead to increased ion yields, in some cases up to 4% (relative to nominal values around 0.1%). Significant increases in sensitivity have been observed for both wet plasmas (from solutions) and dry plasmas (from laser ablation of solids). The enhancements to sensitivity, when combined with the many favorable characteristics of MC-ICPMS, open up a challenging class of analytical problems which require analysis of low concentrations in small samples ("measuring nothing in not very much"), as demonstrated by the accurate and precise quantitation and measurement of isotope ratios of sub-fg levels of Pu in 100-µL samples. Other recent examples will be shown, including high precision measurement of Nd in seawater at low (5 ppb) concentrations. The increase in sensitivity also leads to improvement to counting statistics, leading to higher precision and, in some cases, allows measurements to be moved from SEMs into Faraday cups, also resulting in higher precision. This will be illustrated by measurements of the variation of 235U/238U caused by mass dependent fractionation, a measurement which also exploits the large dynamic range of the Neptune-plus. The high mass resolution capability of the Neptune-Plus HR-MC-ICPMS (to remove polyatomic interferences) combined with the enhanced sensitivity (to compensate for the reduction in sensitivity that accompanies increase in resolution) allow exploration of the measurement of S isotopes for elemental and isotopic analysis. Using high mass resolution and amplifiers with 10e12 ohm resistors for isotope dilution measurements, researchers report 50 times higher detection efficiency and 100 times better precision for sulfur and δ34S than the single-collector high-resolution sector field type ICPMS (HR-ICP-SFMS). Reduction of blanks by >1order of magnitude relative to ID-TIMS suggests that ID-HR-MC-ICPMS is the best method for measurement of very low concentrations of S. Coupling GC with MC-ICPMS has allowed, for the first time, compound specific δ34S isotope analysis (CSIA) of volatile organic molecules, and the technique is currently being extended for more general use in the meas urement of S isotope systematics.

(149) **Bringing Speciation Tools (GC-MC-ICPMS) in Geochemistry for Fast and Precise Lead Isotope Ratio Determination in Complex Matrices. Application to Crude Oil Exploration.**; Christophe Pecheyran[1], Georgia Sanabria Ortega[1], Olivier F. X. Donard[1], Sylvain Bérail[1], Mike Lewan[3], Alain Prinzhoffer[2]; [1]University of Pau, LCABIE/IPREM, [2]Ipex co., [3]U. S. Geological Survey

Pb isotope ratio determination in geological samples by MC-ICPMS needs careful Pb isolation in order to achieve the highest accuracy and precision required for reliable data interpretation. We have developed a new method inspired from the speciation toolbox to determine Pb isotope ratios without using the cumbersome ion-exchange-matrix separation. After sample digestion, Pb is simply ethylated and separated from the bulk matrix (e.g. black shale, asphaltene, crude oil and kerogen) by extraction in isooctane, and the Et4Pb formed is injected in a gas chromatograph coupled to the MC-ICPMS. By this method, the total time of the procedure (sample preparation and analysis) is reduced at least 15 times compared to the conventional-continuous sample while providing similar precision and accuracy. We will see how this methodology can be applied to crude oil dating, which is a key parameter governing the probability of success in petroleum exploration, taking the Illinois basin as a case of study.

(150) **Automated Sample Preparation for Radiogenic Isotopes: Removing an Analytical Barrier to Generating Sr, Nd and Pb Isoscapes**; Paul Field[1], Gwyneth W. Gordon[2], Stephen Romaniello[2], Daniel Wiederin[1], Ariel Anbar[2,3]; [1]Elemental Scientific, Omaha, NE, [2]School of Earth & Space Exploration, Arizona State University, Tempe, AZ, [3]Department of Chemistry, Arizona State University, Tempe, AZ

Beginning in the 1960s, gas-source MS led to the emergence of light stable isotopes as a powerful tool in hydrology, paleothermometry and climate science. The use of gas-source GC-IRMS proliferated in

the 1980s and 1990s with the development of automated sample preparation and introduction systems (EA, TC-EA, TOC, etc.). These systems generated large datasets of H, C, N and O isotope values in natural materials that, in turn, allowed development of predictive isoscapes for source attribution of unknown samples of water, plants, animals and humans. Radiogenic isotope variations are unrelated to light stable isotope variations, so radiogenic isoscapes provide independent information about a sample's origin. In addition, radiogenic isotope values can persist even through sample degradation or processing at high temperatures that can modify the light stable isotope signature of a sample. Although MC-ICP-MS has dramatically improved high-precision radiogenic isotope sample throughput, promising applications in isoscapes and source attribution remain hampered by the tedious manual drip chromatography required for sample purification. The time has arrived for automated sample preparation to expand the utility of high-precision isotope analyses in forensic anthropology, nuclear forensics and food authentication applications, where large data sets are required. We have developed protocols to automate ion exchange purification of radigenic isotopes using the new prep*FAST*-MC™ (ESI, Nebraska, Omaha). The system is not only inert (all-Teflon® flow paths), but is also very flexible and can easily facilitate different resins, samples and reagent types. When programmed, it utilizes a wide range of volumes/flow rates to automatically load samples, wash column, condition column and elute fractions. Reproducibility, reliability, recovery, blank and carry over will be evaluated for Sr and U isotopes in natural samples. Unattended, the automated low-pressure ion exchange chromatography system can process up to 60 samples overnight and reduce the need for expensive laminar-flow hood space and cleanlabs.

(151) **Classification of Prostate and Breast Tissue Data from High-Resolution Fourier Transform Infrared (FT-IR) Spectroscopic Imaging**; Rohith Reddy[1], David Mayerich[1], Michael Walsh[1], Matthew Schulmerich[1], Paul Scott Carney[1], Rohit Bhargava[1]; [1]University of Illinois at Urbana Champaign

Fourier transform infrared (FT-IR) spectroscopic imaging provides spatially resolved chemical information on a microscopic scale. Chemical information from mid-infrared wavenumbers has been shown to be valuable in determine tissue cell types and in performing prostate and breast cancer detection. Our goal is then to use the spatial distribution of tissue cell types to perform improved diagnosis of cancer. However, this step is limited by the spatial resolution provided by current imaging systems. Recent work has demonstrated high-definition imaging, where data of significantly higher spatial detail than previously possible was obtained by making minimal modification to commercial FT-IR imaging instruments. These design improvements were based on an understanding of the optical system derived from rigorous modeling of light propagation through the instrument. Here, we extend this work by demonstrating that it is possible to identify previously obscured tissue types by performing histological classification. These features and based on bio-chemically derived spectral features (metrics) and can improve cancer detection accuracy. We present image classification results where classification of high-definition imaging results in an accurate labeling of terminal ductal lobular units (TDLUs) which are obscured when using conventional imaging. Modeling light-sample interaction in FT-IR spectroscopic imaging has provided important insights into the nature of data obtained from FT-IR imaging instruments. Recent work has shown there can be large variability between spectra from different points on a sample that is expected to consist of the same essential chemical constituents. Spectra at the edges of tissues are characteristically and consistently different from chemically similar tissue in the middle of the same sample. Here, we explain these differences when using a prostate epithelial tissue sample and present simulation and experimental results from spectra at an air-tissue edge. Furthermore, we perform histological classification of tissue samples using spectral metrics and also show that an appropriate selection of localized metrics can make our data robust to the spectral distortions caused by scattering at the tissue boundary.

(152) **Standoff Raman Spectroscopy of Large Areas Using Defocused Excitation with a Spatial Heterodyne Raman Spectrometer**; Nathaniel Gomer[1], S. Michael Angel[1]; [1]University of South Carolina

We have developed a new type of Raman spectrometer for planetary applications called the Spatial Heterodyne Raman Spectrometer (SHRS). The SHRS is similar to a Michelson interferometer used in a conventional FT Raman spectrometer, but the SHRS uses stationary diffraction gratings in place of mirrors and requires no moving parts. The SHRS measures all wavelengths simultaneously and can be coupled with a pulsed laser source and gated detector for measurements in high ambient light conditions. The SHRS system boasts an expanded etendue because it does not have an entrance slit and has a large acceptance angle (up to 10 degrees). This allows the system to maintain high sensitivity when making standoff measurements of large area samples using defocused laser excitation. This is important for photosensitive samples where a larger laser spot size might reduce photodegradation. It is also useful for heterogeneous samples where measuring a larger area would be more representative of the sample as a whole. This paper will include an overview of the system configuration and show results using larger laser spot sizes on various types of samples.

(153) **TEA CO2 Laser-Induced Gas Plasma Spectroscopy (LIGPS): A Breakthrough Method in LIBS**; Ali Khumaeni[1], Zener Sukra Lie[1], Hideaki Niki[1], Kazuyoshi Kurihara[2], Kiichiro Kagawa[3]; [1]Program of Nuclear Power and Energy Safety Engineering, Graduate School of Engineering, University of Fukui, [2]Department of Physics, Faculty Education and Regional Studies, University of Fukui, [3]Research Institute of Nuclear Engineering, University of Fukui

A novel method realizing a breakthrough in LIBS has been developed using a TEA CO2 laser-induced gas plasma. In this method, a TEA CO2 laser (10.64 μm, 200 ns, 750 mJ) was focused on a metal surface at 1 atm to induce a "gas plasma", without ablating the metal surface; the metal only works as the source of electrons initiating the gas plasma. This phenomenon never occurs in the case of standard LIBS method, in which a pulsed Nd:YAG laser is employed to produce a "target plasma". The characteristics of the gas plasma are quiet different from the standard LIBS plasma (target plasma). Namely, the plasma is much bigger in diameter (high heat capacity) and is much more stable; the emission lifetime is much longer (several tens of μs); and the background emission is much lower. These characteristics are very favorable as an excitation source for spectrochemical analysis. By devising many unique sampling techniques, we have proved that the LIGPS method can be applied for highly sensitive and direct elemental analysis on many kinds of samples including powder, organic solid, dust, liquid, and so on. The problem of the LIGPS method, which cannot be employed for metal analysis, has been easily overcome using scratching technique utilizing fine diamond powder. As a result, this method can be applied for any kinds of samples. By using the LIGPS method, the weak points of the standard LIBS method can almost be solved. Thus, we can say that this technique is breakthrough of LIBS.

(154) **Variable Temperature Study of the Infrared Spectra by Utilizing Xenon Solution and Microwave Spectroscopy for the Conformational Analysis of Cyclohexylisocyanate**; Xiaohua (Sarah) Zhou[1], James R. Durig[1]; [1]Department of Chemistry, University of Missouri-Kansas City

The microwave spectrum of cyclohexylisocyanate, *c*-$C_6H_{11}NCO$, has been investigated from 10,000 to 21,000 MHz and forty-four

transitions for the more stable *equatorial-trans* conformer were assigned. The rotational constants of the ground vibrational state have been determined: A = 3546.87(28), B = 936.12(1) and C = 839.06(1) MHz. By utilizing these rotational constants along with ab initio MP2(full)/6-311+G(d,p) predicted structural values, adjusted r_0 parameters have been obtained for the *equatorial-trans* conformer. Variable temperature (-100 to -55°C) studies of the infrared spectra (3500 to 400 cm^{-1}) of cyclohexylisocyanate dissolved in liquid xenon have been recorded as well as the infrared spectra of the gas and solid. Additionally, the Raman spectrum (3600 to 100 cm^{-1}) of the liquid has also been investigated. These spectral data indicated the present of two conformers in the fluid states which are the *equatorial-trans* and *axial-trans* forms. The second part of the conformational name refers to the relative position of the NCO moiety relative to the alpha hydrogen. By utilizing seven conformer pairs, an enthalpy difference of 442±44 cm^{-1} (5.29 ± 0.53 kJ/mol) was obtained with the *equatorial-trans* conformer the more stable form. To aid in the vibrational assignment, ab initio calculations have been carried out by the perturbation method (MP2) to second order with full electron correlation by using a variety of basis sets up to 6-311+G(2df,2pd). These results are compared to the corresponding quantities of some similar molecules.

(155) **Pulsed EPR Studies of Photosystem II Elucidating the Mechanism of Solar Water Oxidation**; Ruchira Chatterjee[1], Sergey Milikisiyants[1], Christopher Coate[1], K. V. Lakshmi[1]; [1]Rensselaer Polytechnic Institute

The solar water-splitting protein complex, photosystem II (PSII), catalyzes the light-driven oxidation of water to dioxygen in Nature. The four-electron water oxidation reaction occurs at the tetranuclear manganese-calcium-oxo (Mn_4Ca-oxo) cluster that is present in the oxygen evolving complex (OEC) of PSII. The mechanism of light-driven water oxidation has been a subject of intense interest and the OEC of PSII has been studied extensively by structural methods. While the recent X-ray crystal structures, single crystal EXAFS and EPR spectroscopy investigations provide a model for the geometry of the catalytic Mn_4Ca-oxo cluster, there is limited knowledge of the protein environment that surrounds the catalytic site. One of the key questions is the exact location of substrate water molecules within the OEC. It is also suggested that the binding and activation of the substrate water molecules at the Mn_4Ca-oxo cluster in the OEC of PSII is facilitated by key amino acid residues that could be ligated to the catalytic cluster. In this study, we use -dimensional (2D) hyperfine sublevel correlation (HYSCORE) spectroscopy to probe the magnetic interactions of the paramagnetic manganese-calcium-oxo (Mn4Ca-oxo) core with surrounding protons and nitrogens in the S2 state of PSII. Compared to one-dimensional techniques, two–dimensional HYSCORE spectroscopy has superior resolution for multinuclear systems since the nuclear frequencies corresponding to different electron spin manifolds are dimensionally separated. We also demonstrate the use of two biomimetic dimanganese model complexes, $[H_2O(terpy)Mn^{III}(\mu\text{-}O)_2Mn^{IV}(terpy)OH_2](NO3)3$ (terpy = 2,2':6',2''- terpyridine) and $[(bipy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bipy)_2](ClO_4)_3$ (bipy = 2,2'-bipyridine) to model the magnetic interactions of the manganese ions of the OEC of PSII. From our study, we can draw important conclusions about the coordination of the (i) substrate water molecules in the OEC of PSII by quantitatively characterizing the magnetic interactions of water molecules that are directly bound to Mn(III) and Mn(IV) ions in the model complexes (ii) surrounding amino acid residues in the S_2 state of PSII.

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(156) **Discovering Protein Linear Interaction Motifs with Proteome-Scale H/D Exchange Mass Spectrometry**; David Weis[1]; [1]University of Kansas

Many protein-protein interactions are mediated by flexible linear segments. Knowledge of the structure of the bound segment can provide valuable insight into the development of small molecule inhibitors of the interaction. However, discovery of such linear interaction motifs remains challenging, particularly because the interactions are often transient. Amide H/D exchange is particularly sensitive to the subtle structural transitions that such peptides experience. Here, we describe a high-throughput, one-pot approach to screen libraries containing thousands of endogenous peptides, obtained from proteolysis of cell lysates, for binding against a target protein of interest. We have used the binding of ribonuclease S (RNase S) to the linear ribonuclease S peptide (S peptide) as a model system to establish the feasibility of this approach. Free S peptide is unstructured but folds upon binding to RNase S. Following lysis of *S. cerevisiae*, the soluble proteome was digested separately with trypsin, GluC, and chymotrypsin. A peptide library was prepared by combining the individual digests. The library was then spiked with S peptide and subjected to H/D exchange both with and without RNase S. The multi-protease approach produced a complex library of peptides. To minimize deuterium loss that would arise from a long gradient separation, independent samples were analyzed separately using short, segmented gradients that focused on different parts of the elution profile. Despite the complexity of the sample, the deuterated MS features of S peptide were readily identified. S peptide became significantly protected from H/D exchange in the presence of RNase S while control peptides showed no RNase S-induced protection. The same level of protection was observed when S peptide was screened for binding to RNase S in the absence of the peptide library. Taken together, these results demonstrate that H/D exchange can be used to detect the binding of a single peptide to a target protein a highly complex, proteome-scale peptide library.

(157) **Protein Dynamics and Interaction Probed by Hydrogen Exchange Mass Spectrometry**; Igor Kaltashov[1]; [1]University of Massachusetts-Amherst

Mass spectrometry is now an in indispensable tool in the armamentarium of molecular biophysics, where it is used for a variety of tasks ranging from covalent structure determination to studies of higher order structure, conformational dynamics and interactions of proteins and other biopolymers. This presentation will focus on recent advances in this field (with particular emphasis on native electrospray ionization mass spectrometry and hydrogen/deuterium exchange) and evaluate current challenges and reviews possible future developments. Several examples will be considered to highlight the potential of mass spectrometry in such areas as conformational stability and aggregation of therapeutic proteins, as well as protein/ligand and protein/receptor interactions.

(158) **Biophysical Characterization of Virus Particles as Gene Delivery Vehicles**; Brian Bothner; [1]Montana State University

Adeno-associated viral (rAAV) vectors can mediate safe gene transfer for the long-term correction of genetic diseases in animal models and efficiently deliver corrective genes for the treatment of human diseases. They are safe and persist in humans following delivery to lung, sinus, skeletal muscle, brain, and liver tissue. The ability to efficiently transduce different cell/tissue populations for corrective gene delivery has generated significant interest in understanding the mechanism of cellular entry and the biophysical properties of the capsids. We are using a range of biophysical and biochemical approaches to characterize the stability and dynamics of empty and DNA containing AAV particles. Protein dynamics are an important component of the entry process for this virus, so

understanding the relationship between particle stability and function is critical to use as a gene or drug delivery vehicle.

(159) **Covalent Labeling and Mass Spectrometry for Studying the Structures of Protein-Protein Complexes**; Richard Vachet[1], Yuping Zhou[1], Jia Dong[1], Vanessa Mendoza[1]; [1]University of Massachusetts Amherst

Amyloid fibril formation from normally soluble proteins is implicated in several human diseases including Alzheimer's, Parkinson's, type II diabetes, and dialysis-related amyloidosis (DRA). The main pathogenic process underlying DRA is the formation of fibrils by β-2-microglobulin (β2m), and evidence suggests that Cu(II) could play a key role in this process. Like other amyloid systems, β2m fibril formation proceeds by partial protein unfolding, subsequent oligomerization, and eventual elongation to form mature fibrils. While many aspects of general amyloid formation are understood, molecular-level information is lacking for the early oligomeric protein forms that precede the insoluble amyloid fibrils; however, this information is critical for the rational development of therapeutics against amyloid diseases like DRA. Because these oligomers are kinetic intermediates and are usually present as mixtures, obtaining residue-specific information for these protein-protein complexes is challenging with existing methods. To address these challenging measurements, we are investigating new mass spectrometry (MS)-based tools based on covalent labeling. To gather insight into the structures of the homooligomeric complexes of β2m, we are exploring the use of pseudo-specific covalent labels such as diethylpyrocarbonate (DEPC) that can react with several solvent exposed amino acid side chains. In this presentation, it will be shown that DEPC can react with approximately 30% of the solvent exposed amino acids in the average protein, thereby providing good structural resolution. Because the DEPC modifications of some residues (e.g. Ser, Thr, and His) can undergo hydrolysis before detection, we find that the use of fast proteolytic digestions and middle-down sequencing can ensure the detection of modified amino acids and increase the effective structural resolution obtained with this covalent labeling reagent. Using the data obtained from the DEPC labeling along with MS detection, we have been able to develop structural models for both the dimer and tetramer of β2m. These oligomers appear to be on the pathway to the insoluble amyloid fibrils, and thus structural information about them could guide the development of inhibitors of their formation.

(160) **Top-Down Mass Spectrometry and Supercharging for Characterizing Protein Assemblies**; Joseph Loo[1], Jiang Zhang[1]; [1]University of California, Los Angeles

The application of mass spectrometry (MS) for studying proteins and protein complexes has utility in biology, biochemistry, and biomedical research. The assessment of protein interactions can address the functional role of proteins and protein complexes. Developments in protein MS and tandem MS (MS/MS) to define the structures of proteins and protein complexes, including the sites of ligand bonding will be discussed. Collisionally activated dissociation (CAD) with high resolution time-of-flight and Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry of gas-phase stable noncovalent complexes resulting from electrostatic interactions can be used to probe ligand binding sites (e.g., nucleotides, metals). Electron transfer dissociation (ETD) and electron capture dissociation (ECD) is particularly useful for elucidation of disulfide bonds in large proteins, especially if the electrospray ionization (ESI)-based multiple charging is enhanced (e.g., supercharging). Supercharging can be a valuable tool in protein ESI-MS to extend the working m/z range of mass spectrometers. We have shown previously that sulfolane and other reagents (3-nitrophenyl alcohol, etc) potently supercharge proteins in ESI-MS. Supercharged proteins undergo more efficient fragmentation and potentially yield novel sequence information that is valuable for elucidating the structure of large proteins. CAD and ECD fragmentation is enhanced for supercharged disulfide-bonded proteins (e.g., lysozyme, etc), showing more facile cleavage of disulfide bonds, and allowing partial or full disulfide bonded sequence to be deduced. Moreover, ECD and ETD can be used to probe the binding sites of weakly-bound ligands and the topology of protein-protein complexes (e.g., hemoglobin).

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(161) **Controlling Oxygen via Microfluidic Devices for Cells and Tissues in vitro**; David Eddington[1]; [1]University of Illinois, Chicago

My lab has designed, fabricated, and validated a suite of devices to easily and accurately regulate oxygen levels in cellular cultures within standard culture formats such as multiwell plates, Boyden chambers, and 3D cell matricies. Oxygen can be delivered or extracted to the cells via simple diffusion and is rapid due to the microscale distances separating the oxygen microchannels from the cell cultures. This oxygen can also be patterned onto anatomical regions of tissue, in gradients across a substrate, or cyclic profiles of high or low oxygen. In addition, due to the rapid equilibration time, intermittent hypoxia profiles or ischemia reperfusion studies are easy to perform in a format compatible with fluorescence microscopy for real time analysts of cell or tissue function. We are applying these devices with researchers studying topics varying from insulin release from islets under hypoxia, strokes in acute brain slice preparation, wound healing, and ROS signaling pathways.

(162) **Polystyrene-based Microfluidic Devices for Integrating Cell Immobilization with Analysis**; R. Scott Martin[1]; [1]Saint Louis University

Recent work from our lab has involved the use of epoxy-based encapsulation of materials to integrate fluidic interconnects and electrochemical detection with other processes such as microchip electrophoresis. This general encapsulation approach allows the electrode material to be polished before each use and also enables the use of different electrode materials. This includes a palladium electrode for coupling microchip electrophoresis with electrochemical detection as well as a carbon fiber electrode (as a working electrode) and a platinum electrode (as a counter electrode). More recently, we have extended this approach to the development of polystyrene-based devices. This talk will show some of this recent work and demonstrate how the polystyrene devices are much more robust for both the immobilization of PC 12 cells and the analysis of catecholamines released from these cells upon stimulation.

(163) **Microchip Electrophoresis Based Methods to Monitor Nitric Oxide Metabolism and Reactive Nitrogen Species**; Susan M. Lunte[1], Christopher T. Culberston[1, 2], Dulan Gunaserkera[1], Francassi daSilva[1], Tom H. Linz[1], Eva Metto[2]; [1]Ralph N. Adams Institute for Bioanalytical Chemistry, Kansas State University, [2]Dept of Chemistry, Kansas State University

Nitric oxide (NO) is a highly diffusive, reactive species that exhibits a short half-life under physiological conditions. It is involved in many important biological processes including immune signalling, smooth muscle relaxation and neurotransmission. While NO is required for proper biological functions, large amounts of NO produced over a long period can result in the formation of reactive nitrogen species (RNS) such as dinitrogen trioxide (N^2O^3) and peroxynitrite (ONOO-). These RNS can deplete glutathione and cysteine, nitrate tyrosine residues on proteins as well as cause other nitrosylation and oxidation reactions in cells. Therefore, large quantities of NO production for extended periods of time have been implicated in the pathology of several neurodegenerative diseases as well as programmed cell death. The detection of NO detection and RNS has been accomplished using electrochemical or spectroscopic

methods. Fluorescence detection using NO-selective fluorescent probes is popular due to its high sensitivity, relative simplicity and low cost. However, these methods can suffer from cross reactivity of probes with other RNS and dehydroascorbic acid. In the case with the amperometric biosensors, interference of endogenous electroactive compounds can make detection and accurate quantitation difficult. Therefore, utilizing a separation method prior to detection allows the compounds of interest to be isolated from potential interferences. Microchip electrophoresis (ME) is ideal for such analyses due to its fast and efficient separations, low volume requirements, compatibility with high pH conditions and ultimately its compatibility with single cell chemical cytometry systems. In this presentation, the development of ME devices for detection of NO, RNS and methylarginines in model reactions, cell lysates, single cells and human plasma will be presented.

(164) **Monitoring Bacterial Production of Pyocyanin using Microfabricated Electrochemical Sensors**; Edgar Goluch[1], Thaddaeus Webster[1], Nil Tandogan[1], Pegah Abadian[1]; [1]Northeastern University

We have integrated a miniaturized pseudo-reference electrode made from palladium with a gold working electrode inside of a nanofluidic cavity. The performance of these devices was compared against gold electrodes with standard commercial Ag/AgCl reference electrodes. The fabricated devices were then used to selectively detect production of pyocyanin by four Pseudomonas aeruginosa strains in growth media. Much interest in recent years has been placed on using electrode assemblies in microfluidic channels to perform real-time electrochemical measurements. However, the scale down of reference electrodes for microfluidic systems faces many challenges, such as the IR drop that occurs when reference electrodes are downstream or far away from the working electrode or dissolution of electrolyte from the reference. Palladium was chosen for its ability to adsorb molecular hydrogen from the solution, allowing stable potential measurements without the need for special electrolytes, a desired trait in reference electrodes. Optical lithography was used to simultaneously create dozens of devices on a three-inch silicon wafer. The small dimensions of the nanochannel prevent cells from entering and interacting directly with the electrodes. Further, confining the electrodes inside a nanocavity, away from the bulk sample reservoir, decouples the measurements from external flow conditions. To show their utility in biological systems, the fabricated sensors were used to detect pyocyanin with square wave voltammetry. The devices were able to selectively detect pyocyanin produced by four different PA strains grown in trypticase soy broth for 46 h at 37 °C. Fluid samples were loaded directly onto the devices without any pretreatment. Wildtype PA14 produced the highest concentration of pyocyanin, followed by pelA, which cannot form dense biofilms, and phzS and phzM mutants, which cannot produce pyocyanin. The ability to detect low concentrations of pyocyanin electrochemically opens the possibility for real-time studies of P. aeruginosa. Furthermore, the small size of the devices allows integration inside microfluidic systems to provide label-free chemical analysis of biologically relevant systems. The group is also developing devices to trap individual bacterial cells and expose them to dynamic chemical gradients using nanofluidic channels. In the future, the electrochemical sensors will be combined with the microchamber devices.

(165) **Effects of Confinement on Macromolecular Transport in Nanochannels Studied by Fluorescence Correlation Spectroscopy**; Dane Grismer[1], Paul Bohn[1]; [1]University of Notre Dame

As lab-on-a-chip technology continues to transition from fluidic manipulations in two-dimensional planar geometries to three-dimensional stacked geometries, the need for a more comprehensive understanding of nanoscale behavior becomes apparent. Of particular interest are the effects of confined environments on molecular transport, specifically, in rectangular nanochannels of approximately attoliter volume. Confinement occurs when the container size is of the same magnitude as important scaling lengths of macromolecules. Translational diffusion in this restricted space results in an increased frequency of wall collisions, Ω_W, and the corresponding cumulative effect on surface adsorption events can no longer be discounted when modeling molecular motion. As optically-accessible vessels, horizontally-aligned nanochannels of nanometric height are ideal structures to study confinement effects on macromolecular transport. A Fluorescence Correlation Spectroscopy (FCS) setup is used to take precise *in situ* measurements of the translational diffusion rates. As a platform for single-molecule studies, the need for averaging from ensemble data is eliminated. Varying the degree of confinement and relating it to subsequent changes in molecular motion adds valuable insights into our understanding of transport at the nanoscale. Of particular significance are the subdiffusive tendencies of large, flexible molecules compared to small molecules, which show little to no deviation from bulk behavior. Consideration is taken when using the autocorrelation function to analyze data, as confined diffusion approximates two-dimensional diffusion, rather than the traditional three-dimensional free diffusion assumption.

(166) **NIR in Enabling Real-Time Release**; Gary McGeorge[1]; [1]Bristol-Myers Squibb

In order to move towards a Real-Time Release testing environment within the pharmaceutical manufacturing space it is important to understand the relationship between the critical quality attributes relating to raw materials, in process samples or finished products and the NIR spectra that are obtained from them. By creating this understanding in a holistic manner it will be possible to continue to embed NIR as an indispensible tool to support the modernization of manufacturing. In this talk we will present a variety of applications and case studies whereby NIR spectroscopy was leveraged to model the properties of raw materials, intermediate materials or finished tablets. In addition the relationship of these measurements to the process will be highlighted. Two examples will be given that focus on the role of FT-NIR to understand the dissolution performance of tablets. The results will advertize the flexibility and power of NIR since there were two completely mechanisms for the dissolution variation; polymorphism and compositional non-uniformity.

(167) **A Novel Sample Selection Strategy by Near Infrared Spectroscopy (NIRS)-based High Throughput Tablet Tester for Content Uniformity in Early Phase Pharmaceutical Product Development**; Zhenqi Shi[1], James Hermiller[1], Thomas Gunter[1], Xiaoyu Zhang[1], David Reed[1]; [1]Eli Lilly and Company

Pharmaceutical manufacturers have started to explore utilizing fast, non-invasive spectroscopy method (such as Near Infrared Spectroscopy, NIRS) to monitor content uniformity (CU) among solid oral dosage units, with the goal of potentially replacing traditional random sampling followed by HPLC. Meantime, pharmaceutical researchers have become aware that utilizing NIRS to replace the traditional CU test often requires substantial effort to create a robust calibration dataset representative of the variation of interest, which is not commonly available in early R&D as the formulation and process parameters are still being optimized and finalized. Even with the advent of continuous manufacturing, the creation of a robust NIRS calibration dataset is still considered time and labor-consuming in early R&D. Therefore, the capability of NIRS is often overlooked in early R&D, and used typically for collecting information only. This study proposes a new sample selection strategy via NIRS to simplify the traditional CU test in early R&D with improved statistical confidence. This strategy originated from the prescreening of a large amount of tablets by a near infrared

spectroscopy (NIRS)-based high volume tablet tester to the selection of extreme tablets with highest, medium and lowest content of API for further HPLC test. A qualitative NIR model was used to translate spectral information to a concentration-related metric, i.e., scores, which allowed the selection of those extreme tablets. This sample selection strategy of extreme tablets was shown to provide equivalent representation of CU in the process compared to randomly sampling in the traditional CU test. Since it only requires reference tests on three extreme samples per stratified location, the time and labor-saving nature of this strategy is advantageous for CU test in early R&D. The extreme sampling approach is also shown to outperform random sampling with respect to statistical confidence for representing the process variation. In addition, a chemometric approach utilizing only pure component raw materials to simplify the development of an NIRS model with sensitivity to API concentration variation in the process is discussed with the advantage of not requiring tablets at multiple API levels. Prospective applications of this sample selection strategy for both batch and continuous processes will also be addressed.

(168) **Use of NIR Hyperspectral Integrated Computational Imaging for Quality Control of Pharmaceuticals**; Brittney Metts[1], Robert Lodder[1, 2]; [1]Department of Chemistry, University of Kentucky, [2]College of Pharmacy, University of Kentucky

We will be using hyperspectral integrated computational imaging (HICI) to determine the purity of various pharmaceutical samples. Near-IR wavelengths were chosen due to the excellent absorbance ranges for organic functional groups. By employing HICI both spatial and spectral features of the sample can be encoded. Factor analysis will be done on the spectra obtained to determine the regions with the most variability correlated to the sample property of interest. Once the region (wavelength or wavenumber) of best variability is determined, it can be used to set up a linear concentration calibration to determine the quality of the pharmaceutical in question.

(169) **Developing Content Uniformity Thresholds Independent of Scale of Scrutiny of a NIR Spectrometer**; Sameer Talwar[1], Zhenqi Shi[2], Steven Short[3], Carl Anderson[1], James Drennen[1]; [1]Duquesne University, [2]Eli Lilly, [3]Merck

The objective of this study was to investigate the relationship between the near infrared (NIR) spectrometer interrogated sample size and the content uniformity of an analyte of interest in a pharmaceutical sample. This work should provide direction for development of uniformity thresholds using any spectrometer, independent of its spot size. The effect of scale of scrutiny of a spectrometer on estimated content uniformity was displayed using single-point NIR spectroscopy. A three component direct compression system was blended to different times/degrees of homogeneity (270, 180, 90, and 30 seconds), with 270 seconds required for the powder blend to reach homogeneity, as predicted by NIR. The powder batches were subsequently compressed and tablets were analyzed using a different NIR spectrometer with a unique spot size. The decrease in blending time was well correlated to an increase in tablet variability. However, the variance in predicted concentration in tablets was observed to be smaller than seen for the powder mixture, which was attributed to the higher scale of scrutiny of the tablet spectrometer. Investigations of the effective sample size using Monte Carlo simulation based photon migration predicted a 45 times higher sample size being interrogated using the tablet spectrometer compared to blend spectrometer, based on different sample density and collection optics. Further, near infrared chemical imaging (NIR-CI) was used to estimate the content uniformity as determined with different spot sizes, and which is expected to provide content uniformity thresholds that are consistent irrespective of scale of scrutiny of a spectrometer. A PLS-DA model was used to generate a predicted concentration image of the chemical components in a tablet. Different spectrometer spot sizes were simulated by randomly selecting groups of pixels on the predicted image. The relative standard deviation (RSD) of the predicted concentration of the chemical components within each simulated spot size was then calculated. The profile of RSD vs. spot size is referred to as the threshold curve, which provides content uniformity thresholds for a specific spot size/scale of scrutiny. The threshold curve was validated by projecting the variability in the four blend and tablet batches with varying homogeneity onto the curve.

(170) **Distribution Analysis of Dissolution Process for Pharmaceutical Tablets by using a Developed Portable NIR Imaging Device**; Daitaro Ishikawa[1], Koudai Murayama[2], Takuma Genkawa[5], Kimie Awa[4], Yoko Torigoe[1], Sergei Kazarian[3], Makoto Komiyama[2], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]Yokogawa Electric Co., [3]Imperial College London, [4]Dainippon Sumitomo Pharma Co., Ltd.; [5]University of Tsukuba

In a previous study, we investigated the effectiveness of a newly developed portable NIR imaging device (Distribution NIR spectrometer; D-NIRs) for PAT using dried tablets. However, in practical use, these tablets are dissolved by penetrated liquid as the oral medication. Thus, an investigation of the dissolution process of tablets is needed, especially, the imaging of that process is very important to visually recognize how the active pharmaceutical ingredients (API's) dissolve. Therefore in this study, the distribution analysis of dissolution processes of API's in tablets was carried out using D-NIRs. The device has three main parts, that is, a spectrometer (Polychromator type NIR spectrometer; P-NIRs), an imaging unit and a source unit. Although P-NIRs is a typical polychromator type spectrometer, it uses high density photo diode array (640 element and 20μm pitch), which was developed to measure high speed and high spectral resolution measurement. The light source is a halogen light from three different directions; it is connected by fiber to the imaging unit. Moreover, as the main feature, line scanning method by galvano-mirrors is accepted for high speed imaging. The simplified tablets, which include ascorbic acid and other contents, were dissolved. The NIR spectra and imaging of the samples were obtained by D-NIRs; the spectra were measured over the wavelength region from 950 to 1700 nm with 1nm interval. In addition, the set of spectra were measured over the 5×5 mm region per each sample with spatial resolution of 1 mm or less. The feature peaks of ascorbic acid in this region were appeared bands at around 1203, 1350 and 1519nm so on. It is important to note that a change in these peaks spectra of ascorbic acid was confirmed from the imaging made by second derivative. This result demonstrated that the visually evaluation of dissolution process of API's is possible by using the new NIR imaging device.

(171) **Signal Processing of Spectral Information for Chemometrics: from the Big Picture to Key Details**; Leslie Collins[1], Kenneth Morton[1], Peter Torrione[1]; [1]Duke University

This talk focuses first on the general problem of pattern recognition, and then we will consider specific critical details that must be considered to develop robust signal processing techniques for processing spectral information. The key components of a pattern recognition system, including feature development, feature selection, data reduction, classifier design, and cross validation will be presented with a focus on processing spectral data. Mathematical details regarding commonly used chemometric techniques will be provided in parallel with illustrative examples. Finally, several specific processing details that when ignored can degrade processing system robustness will be highlighted and discussed.

(172) **Determination of Isotope Ratios in Ambient Air at Atmospheric Pressure for Nuclear Forensics using LIBS**; François Doucet[1], Rick Kosierb[2], Paul Bouchard[1], Mohamad Sabsabi[1]; [1]NRC-CNRC, [2]CNSC-CCSN

Field portable technologies and methods are sought to provide simple, inexpensive, and fast analysis of materials in the mining, construction, and other industries. However, the level of portability needed for this particular application imposes some restrictions on the choice of many of the core components used in a low cost LIBS handheld sensor. This means that relatively low-performance components, such as a low-energy laser source and a low cost, low resolution spectrometer, and working conditions in ambient air at atmospheric pressure, must be considered to fulfil these conditions. In addition, the market price of such a portable device should be affordable or as low as possible to increase the breadth of potential end users and allow the deployment of multiple units for security enhancement. The present paper describes the determination of isotope ratios using Laser-Induced Breakdown Spectroscopy in air at atmospheric pressure for partially resolved uranium-235/uranium-238 and hydrogen/deuterium isotope shift lines in such conditions. Using a Partial Least Square (PLS1) regression, it is possible to build a model that enables the accurate determination of the isotopic ratio under conditions where the application of traditional univariate approaches for hydrogen and uranium would not be achievable without the use of ultra high resolution spectrometer. In addition, the application of PLS1 regression to determine the uranium-235/uranium-238 and deuterium/hydrogen isotopic ratios between 0 and 1 mass fraction was also successfully demonstrated. The performance obtained with such a LIBS sensor will be discussed for nuclear forensics.

(173) **When Chemometrics Becomes an Added Value for Quantitative LIBS : Example of Soils Analysis**; Bruno Bousquet[1], Josette El Haddad[1], Lionel Canioni[1]; [1]Univ. Bordeaux, LOMA, UMR 5798. CNRS, LOMA, UMR 5798

This presentation will be focused on quantitative LIBS with calibration. The advantage of using chemometrics compared to regular univariate approach will be emphasized. More specifically, in our work a 3-layer artificial neural network was exploited. The choice of the input data is critical to obtain the best performance of the network. These input data are selected from a series of criteria set by the analyst either after a simple reading of the spectra or after a preliminary multivariate analysis to retrieve to most relevant data in the original LIBS spectra. This approach is thus an extension of the classical univariate calibration curve and so it also needs a set of samples with known concentrations before running the model to predict the concentrations of unknown samples. This application of chemometrics to quantitative LIBS will be illustrated on soils analysis. LIBS measurements were realized with a mobile LIBS system on real soil samples prepared as pressed pellets. We will present our results on quantitative LIBS for different chemical elements, with a special emphasize on lead. The use of artificial neural network was demonstrated to provide significant improvement compared to the classical approach of calibration curve. The reference values of concentrations used for the calibration were obtained with ICP-AES. We will finally discuss about the well-known matrix effects which have major influence on quantitative LIBS analysis and we will suggest future directions for the LIBS technique.

(174) **Quantitative LIBS Analysis of Standard Reference Materials of Various Categories under Low Pressure Conditions**; Soo-Jin Choi[1], Kang-jae Lee[1], Jong H. Yoo[1, 2], Jack J. Yoh[1]; [1]Seoul National University, [2]Applied Spectra Inc

We carried out quantitative analysis of LIBS signal from Standard Reference Materials (SRM). A Q-switched Nd:YAG laser which operates at 1064 nm with a pulse duration of 5-7 ns and output pulse energy of 70 mJ at 10 Hz is focused onto the surface of a target placed inside of a vacuum chamber. The gate delay is varied from 0.3 to 1 μs, and the gate width is set to 1.05 ms. The targets were mounted on a XYZ stage inside the chamber of 760 to 10-3 torr to utilize the pressure dependence of the plasma. In order to minimize error due to a matrix effect, we used 21 SRMs that belong to different categories of food, clay, sludge, steelmaking alloy, geochemical and agricultural materials. Further, principal component analysis (PCA) was used for rapid identification and discrimination of the unknown materials.

(175) **Laser ablation Methods for Analysis of Urinary Stones: Comparison Study Based on Calibration Pellets**; Karel Novotný[1], Kateřina Stepánkova[1], Michaela Vašinová Galiová[1], Viktor Kanický[1], Jozef Kaiser[1, 2], David Hahn[1, 3]; [1]Department of Chemistry, Faculty of Science, Masaryk University, [2]X-ray micro CT and nano CT research group, CEITEC - Central European Institute of Technology, Brno University of Technology, [3]Department of Mechanical & Aerospace Engineering, University of Florida

Methods based on laser ablation, such as Laser-Induced Breakdown Spectroscopy (LIBS) and Laser-Ablation Inductively Coupled Plasma Mass/Optical Emission Spectrometry (LA-ICP-MS/OES) are particularly suitable for urinary stones bulk and micro analysis. The aim of this study is to demonstrate the calibration capabilities and limitations of these techniques. There are no commercially available standards, which would correspond to urinary calculi matrix. Internal standardization is also difficult, mainly due to different crystalline phases in one kidney stone. Calibration pellets were prepared from human urinary stones with phosphate, oxalate and urate matrix. For this comparative study the most frequently used laser-ablation based analytical techniques were chosen, such as LIBS and LA-ICP-MS . Moreover some unconventional techniques such as simultaneous LIBS – LA-ICP-OES and laser ablation (LA) – LIBS were also utilized.

(176) **Assuring Ehylene Purity: Reliable Sub-PPM Measurement of Ammonia and Water With Online TDL Analyzers**; Mohamad Dabboussi[1], Greg Lankford[1], Xiang (Sherry) Liu[1], HsuHung (Steven) Huang[1], Kuan-Ting (Gary) Yeh[1], Wnehai Ji[1], Alfred Feitisch[1], William Jenko[1]; [1]SpectraSensors, Inc.

Accompanying the ever-increasing performance of polymerization catalysts used to produce polyethylene (PE) is a general increase in catalyst sensitivity to impurities in ethylene feed. These can impact the length and branching of polymer chains as well as interchain bonding, which in turn determine important properties such as crystallinity. Furthermore, impurities may poison catalysts irreversibly, necessitating their premature replacement. Thus, the economics of polyethylene production do not merely depend on the cost of ethylene feed. The amount and quality of PE produced by a given amount of catalyst also is critically important, and the purity of ethylene feed directly impacts both. Methods of measuring ethylene purity include gas chromatography for acetylene, ion mobility for ammonia, and a variety of sensors that indirectly respond to water including vibrating quartz crystals (VQC) and aluminum oxide (AlO3) capacitance probes. Each of these suffer from limitations ranging from long response times (GC) to response drift, long wet-up or dry down times, sensitivity to contamination, and loss of responsiveness due to poisoning of or physical/chemical changes in the sensor element (VQC and AlO3). Modern TDL (tunable diode laser) analyzer technology overcomes all of these shortcomings by measuring an intrinsic property of water, acetylene, or ammonia molecules: their response to light from a laser at specific wavelengths determined by the chemical bonding between constituent atoms. Being governed by the laws of nature, this effect does not change over time. And because the interaction is

instantaneous and highly selective, TDL spectroscopy responds quickly to concentration changes and is not affected by contaminants. Employing a patented differential spectroscopy technique, the same technology employed to measure NH3 and H2O in ethylene has been deployed globally to measure H2O at sub-ppm levels in dryer outlets for natural gas processing and liquefied natural gas operations.

(177) **Small Optical Sensors for Oxygen Monitoring in Challenging Environments**; Brian Marquardt[1], Lauren Hughs[1], Charles Branham[1], Wesley Thompson[1]; [1]Applied Physics Laboratory, University of Washington

As continuous manufacturing processes gain popularity, the need for online measurement technologies becomes more urgent. The ability to sense low concentrations of oxygen in a flowing system is of considerable interest to a variety of industries. Currently available oxygen measurement technologies are inadequate or ill-suited to the demanding requirements of continuous manufacturing processes. Still optical oxygen sensors have the potential to meet these development challenges because of their high sensitivity, fast response, and non-consumptive measurement technology. We present an optical oxygen sensor that utilizes a phosphorescent porous transition metal complex that is highly photostable, and responds quickly to changes in oxygen concentration. Our research has combined these metal complexes with low cost fiber-optic platforms and highly permeable membranes to produce a sensor that is small, inexpensive and robust. Chemically inert coatings and matrix materials have extended the application of this sensor to use in solvent degassing for pharmaceutical processes; where even very low concentrations of oxygen can lead to catalyst fouling and undesirable side-products. The novel O2 sensor has also been used for monitoring bio-fuel fermentations via a NeSSI-built fast-loop sampling system. In this application, the sensor was able to track small changes in the nearly anoxic fermentation broth, and alert technicians to potential upsets in real time. The small format and fast response of the sensor also make it well suited for medical applications, where it has been tested for monitoring blood oxygen concentration in an arterial catheter. A discussion of the performance and analytical merits of the sensor will be presented with emphasis on the industrial, environmental and medical applications of the device.

(178) **Mid-Infrared Light Emitting Diode-Based In Situ Gas Phase Diagnostics for Microelectronics Thermal Deposition Processes**; James Maslar[1], William Kimes[1]; [1]National Institute of Standards and Technology

The development and demonstration of in situ gas-phase optical diagnostics for microelectronics thermal deposition processes is potentially beneficial for a number of reasons. Such diagnostics can be utilized for advanced process control to enhance process productivity, e.g., through improved yields, reduced tool downtime, and reduced reactant waste. In addition, gas-phase diagnostics can provide data for validation of equipment-scale process models. Fourier transform infrared (FT-IR) spectroscopy has been demonstrated to be sensitive to a variety of species present during many thermal deposition processes. However, FT-IR spectrometers are relatively large and expensive and the measurement times associated with traditional FT-IR spectroscopy are long compared to the time scales associated with many deposition processes. Hence, the development of optical systems that are more compact, less expensive, and capable of higher temporal resolution than FT-IR spectroscopy is of interest. Mid-infrared light emitting diodes (LED's) can potentially be used to assemble such an optical system. The purpose of this work is to investigate the performance of optical systems based on mid-infrared LED's for characterizing gas-phase processes during microelectronics thermal deposition processes. The atomic layer deposition (ALD) of metal oxides and metal nitrides using metal alkylamido compounds, e.g., tetrakis(dimethylamido) titanium (TDMAT) and tetrakis(ethylmethylamido) hafnium, and water (for oxide ALD) or ammonia (for nitride ALD) was selected for this investigation. Direct absorption measurements were performed utilizing various LED's with different emission wavelengths to probe different gas phase species present during these deposition processes. Measurements were performed in a custom-built, single-wafer, warm-wall reactor with an optical path length of ~100 mm. The performance of this technique when probing species with broad absorption features, e.g., the unresolved C-H stretching modes of TDMAT, and species with narrow absorption features, e.g., the resolved N-H stretching modes of ammonia, will be discussed.

(179) **Spectroscopic Analysis of Solvent Exchanges: Distillate Line versus Distillate Vessel**; John Wasylyk[1], Robert Wethman[1], Ming Huang[1], Richard Schild[1], Thomas Raglione[1]; [1]Bristol-Myers Squibb Co

Solvent exchanges are routine in the synthesis of pharmaceutical compounds and other chemical manufacturing operations. Solvent exchanges are required in-between reactions when different solvents are required for each step and the product is not isolated. Solvent exchanges also play a crucial role in crystallization where achieving the desired crystal form, morphology and/or size are often times dependent on a specific solvent system or solvent ratio. Spectroscopy can be used to replace the traditional gas chromatography methods and enable rapid on the floor analyses for the operator. Two approaches can be taken to determine solvent exchange endpoints. One approach is via in-line or off-line analysis by sampling directly from the reactor vessel. The second approach is to analyze samples either in-line or off-line from the distillate line. The latter approach is often easier to implement due to the ease of accessing the distillate line. Sampling from the distillate line can be correlated from available modeling software such as DynoChem. Once correlations are established between reactor vessel and distillate lines, sampling from either the vessel or distillate line can effectively be used. Furthermore, samples from the distillate line are free from the reaction products, starting materials, catalysts, reagents, etc. making the chemometric models easy to develop and apply and results very reliable.

(180) **Monitoring Emulsion Polymerization by Raman Spectroscopy**; Serena Stephenson, Kishori Deshpande, Ravindra Dixit; [1]The Dow Chemical Company

As a technique based on light scattering rather than light absorption, Raman spectroscopy is uniquely suited for analysis of multi-phase liquid streams where boundary layers causes issues due to refraction when using absorption spectroscopy. Demonstration of the capability of a Raman spectroscopy for tracking un-reacted monomer and co-monomer during an olefin-based polymerization reaction in a batch reactor configuration has been achieved. Discussion of the analytical setup, model building, and batch trials will be included.

(181) **Deep UV Raman Measurements of Energetic Materials and their Photochemical Products**; Sanford Asher[1], David Tuschel[1], Luling Wang[1]; [1]University of Pittsburgh

We have measured deep UV resonance Raman spectra of explosive molecules with the objective of determining the optimal stand-off methods to identify and quantitate them in environmentally complex samples. We will discuss Raman cross sections of both solution and solid samples and the role of photochemistry in modifying their spectral signatures.

(182) **Ultraviolet Resonance Raman Cross Sections of Solid State Explosive Materials**; Erik Emmons[1], Ashish Tripathi[1], Jason Guicheteau[2], Augustus Fountain[2], Steven Christesen[2]; [1]SAIC, [2]U.S. Army Edgewood Chemical Biological Center

Knowledge of resonance Raman cross sections of explosives is important for benchmarking standoff explosive detection systems

based on deep ultraviolet Raman spectroscopy. Most Raman cross section measurements in the literature have focused on liquids, gases, and ions in solution, while solids have received relatively little attention. Explosives are nearly always encountered in the solid phase, however, and the cross section in general depends on the phase of the material. We are undertaking a program to measure resonance Raman cross sections of solids in the deep ultraviolet ($\lambda <$ 262 nm) using the internal standard technique. Nitro- and nitrate-based explosives have previously been shown to exhibit significant resonance enhancement when excited with these wavelengths. Due to the very short penetration depths (~tens of nm) under resonance conditions, it is necessary to use nanoparticles of explosives when performing the measurements to avoid biasing the results due to absorption. We are using different techniques including spray drying, inkjet printing, and deposition of sublimating materials on surfaces to co-deposit these nanoparticles with the internal standard and measure the cross sections. Results will be presented for explosives such as sodium nitrate, ammonium nitrate, RDX, HMX, TNT, and PETN.

(183) **Wide-Area Standoff Raman Spectroscopy Using a Spatial Heterodyne Raman Spectrometer**; Mike Angel[1], Nathaniel Gomer[1], Nirmal Lamsal[1]; [1]Univ. of South Carolina, Dept. of Chem. & Biochem

Raman spectroscopy is a valuable tool for molecular analysis and is currently being investigated for a wide range of applications, including planetary applications. NASA has stated a desire for small, space-flight capable instruments with minimal or no moving parts to analyze minerals and detect organic molecules and biomarkers on other planets. Raman spectroscopy is an ideal technique for this application and a standoff instrument would allow a much larger range of samples to be investigated. We have developed a new type of Raman spectrometer for planetary applications called the Spatial Heterodyne Raman Spectrometer (SHRS). The SHRS interferometer uses stationary diffraction gratings in place of mirrors and requires no moving parts. The SHRS also does not require long focal length optics to achieve high spectral resolution, which makes the SHRS intrinsically small. The SHRS system boasts an expanded etendue because it does not have an entrance slit and has a large acceptance angle (from 0.5° up to 10°). The expanded etendue allows the system to maintain high sensitivity when making standoff measurements of extended-area samples using defocused laser excitation. The SHRS also measures all wavelengths simultaneously and can be coupled with a pulsed laser source and gated detector for measurements in high ambient light conditions. This paper will discuss a UV SHRS and will focus on wide-area measurements and issues using UV excitation.

(184) **Detection of Hazardous Chemicals in Glass and Plastic Bottles with Standoff Time-Resolved Raman System**; Shiv Sharma, Anupam Misra, John Porter, David Bates; [1]University of Hawaii, Hawaii Institute of Geophy. & Planetology

We present time-resolved (TR) Raman spectral data on standoff detection of hazardous chemicals using a portable standoff TR-Raman system utilizing a 203 mm diameter telescope. Some of these chemicals are used in the synthesis of homemade explosives (HMEs). These TR-spectral data show that good-quality Raman spectra of chemicals such as ammonium nitrate, potassium nitrate, potassium perchlorate, sulfur, nitrobenzene, benzene, acetone, and various organic and inorganic chemicals could be easily obtained from remote distances, tested up to 120 meters, with a single-pulse laser excitation and with detection time less than 1μs. The system uses a frequency-doubled Nd:YAG laser (532 nm, 100 mJ/pulse, 15 Hz, pulse width 10 ns) capable of firing a single or double pulse. In standoff TR-Raman detection, the double-pulse sequence simply doubles the signal to noise ratio. Significant improvement in the quality of Raman spectra is observed when the standoff detection is made with 1 s integration time. The system uses a 50-micron slit and has a spectral resolution of 8 cm-1. The HMEs chemicals could be easily detected through clear and brown glass bottles, PP and HDPE plastic bottles, and through fluorescent plastic water bottles. Standoff Raman detection of HME chemicals from a 10 m distance through non-visible concealed bottles in plastic bubble wrap packaging is demonstrated with 1 s integration time. Possible applications of the standoff TR-Raman system for homeland security and environmental monitoring will be discussed.

(185) **Standoff Raman using Tunable Laser Excitation in the UV and NIR**; J. Chance Carter[1], S. Michael Angel[1, 2], Paul Steele[1], Christine N. Paulson[1]; [1]Lawrence Livermore National Laboratory, [2]University of South Carolina

Standoff Raman systems are being developed for a variety of applications including planetary measurements and high explosives detection in ambient light conditions. In the systems to be described, a tunable pulsed laser source (UV and NIR wavelengths) is directed onto samples at standoff distances (e.g. 10s of meters) and Raman scattered light is collected using a telescope which is fiber-coupled to a spectrograph equipped with a gated ICCD detector. The instrument development and testing will be discussed along with specific issues related to standoff detection.

(186) **Photoexcitation Infrared Spectroscopy of Bulk-Heterojunction Films**; Yukio Furukawa[1], Jun Eguchi[1], Hiroki Yoshida[1]; [1]Waseda University

Infrared spectroscopy is a powerful tool for investigating carriers generated by chemical doping and photoexcitation in conjugated polymers. A blend between a conjugated polymer and [6,6]-phenyl-C61-butyric acid methyl ether (PCBM) shows high performance as an active layer in organic photovoltaic solar cells. In a photovoltaic solar cell, excited states are generated on conjugated polymer chains upon photoexcitation. After fast photochemical processes such as charge separation, long-lived free positive carrier (positive polaron) and negative carrier (the anion of PCBM) are formed. These long-lived positive and negative carriers are recombined into neutral species in micro- to millisecond time scales. Recombination dynamics of these photogenerated long-lived carriers can be studied by infrared spectroscopy. In this paper, we present a study of recombination dynamics of photogenerated carriers in a blend of a conjugated polymer, regioregular poly(3-alkylthiophene) (P3AT) or poly(p-phenylenevinylene) (PPV) derivative, and PCBM by difference infrared spectroscopy. Steady-state photoinduced infrared absorption from a conjugated polymer and PCBM was measured by the difference FT-IR method. The observed absorption was attributed to photogenerated positive polarons (positive carriers in a conjugated polymer). The temperature effect of the absorption intensity was measured from the range from 77 to 300 K. The data were analyzed on a simple bimolecular recombination reaction of a positive and a negative carrier; it is assumed that the rate constant of the bimolecular recombination is expressed by an Arrhenius-type activation energy. We obtained two kinds of activation energy from observed temperature dependence of photoinduced absorption intensity. For a blend film of regioregular poly(3-hexylthiophene) (P3HT) and PCBM, we obtained the activation energies of 18 and 81 meV. The activation energy of 81 meV is associated with the inter-chain recombination process, in which polaron hopping between polymer chains plays an important role. This activation energy is probably significant in polymer solar cells.

(187) **Understanding the Electronic Structure of Thiophene Systems and Donor Acceptor Copolymers using Spectroscopic and Computational Chemistry**; Keith Gordon[1]; [1]University of Otago

Spectroscopic methods in concert with computational chemistry may be used to probe the electronic structure of conducting materials,such as thiophenes and donor-acceptor copolymers. We have used these methods to study dimerisation of 3' styryl substituted terthiophene units and to explain the lack of reactivity of the resulting regiospecific sexithiophene structures. Using density functional theory (DFT) calculations we show that alkoxy groups at the outer thiophenes enhances reactivity and polymer species may be formed from such terthiophenes. We have also used these methods to study a series of copolymers that contain alternating electron-donor and acceptor units were studied using both Raman spectroscopy and density functional theory (DFT) calculations. Each of the polymers in the series uses a carbazole donor unit and the acceptor unit is varied. The acceptors used are DBT (bis(2-thienyl)-2,1,3-benzothiadiazole)), FL (fluorene), SeBT (benzoselenadiazole) and BT (benzothiadiazole). The nature of the electronic transitions present in these copolymers has been determined using resonance Raman spectroscopy with time-dependent density functional theory. These that the lowest energy transitions have electron density from a delocalised orbital to one strongly localised at the electron acceptor moiety.

(188) **Nanoscale IR Spectroscopy of Organic Semiconductors**; Curtis Marcott[1], Michael Lo[2], Kevin Kjoller[2]; [1]Light Light Solutions, [2]Anasys Instruments

Organic photovoltaic (PV) materials, such as poly(3-hexylthiophene) (P3HT) and P3HT doped with (6,6)-phenyl-C_{61}-butyric acid methyl ester (PCBM), have been heavily researched in harnessing solar power as a source of alternate energy. Local material variations, i.e., phase separation, can contribute to the overall solar conversion efficiency of the solar cell. Using instrumentation that combines a tunable IR laser source with detection via an atomic force microscope (AFM-IR), high spatially resolved chemical analysis of P3HT and P3HT/PCBM samples is performed. Spectral changes within 100 nm are observed when a series of spectra is collected across a flat area of P3HT. Phase separation of the P3HT and PCBM within a surface defect can be detected by comparing the spectra of interest with the pure component spectra. Surface topology is also correlated with both chemical information and relative mechanical stiffness.

(189) **Raman Spectroscopic Study of the Interaction between poly(3-hexylthiophene) and Metal Oxide**; Jun Yamamoto[1], Yukio Furukawa[1]; [1]Waseda University

In organic electronic devices such as organic thin film solar cells fabricated with regioregular poly(3-hexylthiophene) (P3HT), device performance is improved by inserting the ultrathin metal-oxide layer (buffer layer) between the indium-tin oxide (ITO) anode electrode and the P3HT layer. The buffer layer may lead ohmic contact between the ITO electrode and the P3HT layer. However, the role of the buffer layer has not been fully clarified yet. Raman spectroscopy is a powerful tool for elucidating the structure of organic semiconductor polymers and carriers generated by doping: a positive polaron (charge, +e; spin, 1/2) and a positive bipolaron (charge, +2e; spin, 0). In this paper, interaction between P3HT and metal oxide such as molybdenum oxide (MoO3), vanadium oxide (V2O5), nickel oxide (NiOx), etc. has been studied by Raman spectroscopy. A thin film of P3HT was formed on an ITO-coated glass substrate by the spin-coating method; a MoO3 layer was then formed on the layer by vacuum evaporation. A MoO3 layer was formed on an ITO-coated glass substrate; a P3HT layer was then formed on the layer. The Raman spectra of these bilayer samples, glass/ITO/P3HT/MoO3 and glass/ITO/MoO3/P3HT, were measured with excitation at 780 nm. The observed spectra were assigned on the basis of those of positive polarons and positive bipolarons, which were generated by FeCl3 doping. The observed spectra were attributed to the superposition of the spectra due to P3HT and positive polarons. Thus, interaction between P3HT and MoO3 leads to the formation of positive polarons. The localized electronic states associated with polarons will improve ohmic contact between the ITO electrode and the P3HT layer. Polarons were also formed from interaction with V2O5, and were not formed from interaction with NiOx.

(190) **Optical Spectroscopy of Active Organic Electronic Devices**; Richard McCreery[1, 2], Rajesh Kumar[2], Rajesh Pillai[2], Nikola Pekas[1], Lian Shoute[2]; [1]National Institute for Nanotechnology, [2]University of Alberta

Three terminal molecular electronic devices containing a conducting polymer can undergo “dynamic doping” to effect a large change in conductivity. Similar “resistance switching” memory devices (RRAM) have been reported, but the mechanism and characteristics of the resistance change are often unclear. We use Raman and UV-Vis spectroscopy to probe polymer structure and doping in polythiophene-based RRAM devices, in order to establish the mechanism and dependence on device structure. Using a 3-terminal configuration with a partially transparent “gate” electrode permits acquisition of high quality Raman spectra through a Raman microscope operating at 780 nm. The neutral and “polaron” forms of polythiophene have distinct Raman features which can be correlated directly with the conductivity of the memory devices. Spatially resolved Raman mapping provided a complete picture of the dynamics of “switching” between the neutral (insulating) and polaron (conducting) forms. Oxidation of the polymer to its conducting polaron state occurs throughout the polymer film, even in locations remote from the positively biased electrode. We attribute this “remote” oxidation to conduction within the polymer causing a moving “front” of polarons. The mechanistic insight available from Raman spectroscopy will permit improvements in switching time and retention, and progress toward integration of polymer-based RRAM with conventional microelectronic formats will be described.

(191) **Biological Analysis using SERS - The Strathclyde Story**; Duncan Graham[1]; [1]University of Strathclyde

SERS has been researched at the University of Strathclyde for over 2 decades and has predominately focused on biological applications whilst examining the fundamental principles. This presentation will be a journey through the Strathclyde approach to SERS with a heavy emphasis on nanoparticle assembly using functionalised nanoparticles to enhance the SERS approach. Functionalized nanoparticles have been used in a number of different studies including detection of DNA at ultra low levels, immuno histochemistry and more recently as substrates for surface enhanced resonance Raman scattering (SERRS) based imaging approaches. The advantages of using metallic nanoparticles are that they are very bright in terms of their optical characteristics and also if functionalized in a particular manner to provide a SERRS response give a unique vibrational fingerprint. Here we present the functionalization of gold and silver nanoparticles in such a way that the enhancement effect can be greatly increased through biological recognition and as such effectively turns on the SERRS effect. This process can give rise to exquisite selectivity in terms of the interaction of the nanoparticles, especially when DNA hybridizations are used and single base mismatches can be analyzed at room temperature. Dye oligonucleotide silver nanoparticles (DOSN) have also been used to detect double stranded DNA through triplex formation to switch on the SERRS and a distance relationship between nanoparticles and SERRS response established for the first time. This approach has been extended to look at DNA-protein interactions, peptide-protein interactions and sugar-protein

interactions. This presentation covers the full range of design, the optical properties and finally the biological properties of functionalized nanoparticles in relation to their assembly and how that relates to the provision of new biological knowledge.

(192) **Successful Application of Raman Spectroscopy in Pharmaceutical Discovery Research**; Don Pivonka ; [1]Incyte Pharmaceuticals

Over the last 20 years, the ever changing synthetic and computational technologies within discovery research have created a range of opportunities for Raman spectroscopy to contribute to the discovery process. For example, synthetic technologies such as resin bound solid phase synthesis, combinatorial chemistry, microwave based synthesis, and radio chemistry have proven to exhibit many unique and previously unmet analytical opportunities for application of Raman spectroscopy. In this lecture, a variety of "success" stories will be presented for Raman applications in support of these technologies. One of the premier applications of Raman spectroscopy in pharmaceutical research lies at the heart of the discovery process. In this application, Raman spectroscopy has been used to complement computational chemistry by aiding the understanding of how both the physical structure and the electronic properties of a molecule are related to its biological activity, i.e., the structure-activity relationship (SAR). In SAR investigations, Raman spectroscopy has been developed as a tool for identification of the molecular subcomponents within a compound series, which play an active role in binding kinetics. Raman spectroscopy has also exhibited utility in uncovering electronic trends, within both pendant functional groups and the molecular backbone scaffold, which foster the binding process. The ability of Raman spectroscopy to complement computational chemistry by differentiating electronic from geometric parameters in ligand-receptor interactions will be specifically addressed. While examples used to present the SAR component of this talk will focus on pharmaceutical discovery, the technology involved can be readily applied to a wide range of chemical composition vs. physical property attributes throughout the chemical industry. Finally, the presentation will include a discussion of potential future advancements and applications.

(194) **Development and Implementation of Spectroscopy Methods for Quantitative and Qualitative Analysis of Pharmaceutical Reagents**; Bernard Agyei[1], John Wasylyk[1], Ming Huang[1], Robert Wethman[1], [1]Bristol Myers Squibb

Off-line spectroscopy is a prevalent technique used for rapid evaluation of pharmaceutical raw materials and is suited for qualitative and well as quantitative purposes. Qualitative analysis is generally used for rapid material confirmation by comparing the Raman or NIR spectra that of an established reference spectra. Quantitative methods are applied to both incoming reagents as well as prepared reagent solutions where a specific concentration is required by the process. The type of analysis and the level to which the method must be qualified in order to meet each goal depends on the level of sensitivity required. Specificity, linearity, precision and accuracy must be established regardless of the spectroscopic technique used for quantitation. Furthermore, robustness testing adds an additional level of reliability to the method when analyzing varying grades of reagents from multiple sources. Issues concerning cross-contamination from either the source of the material or from sampling techniques can impact the results and can often times be identified by the spectroscopy method. This study demonstrates the applicability of the off-line spectroscopy as a tool for identification and quantification, as well as challenges faced, when developing methods for rapid analysis of pharmaceutical raw materials and reagents.

(195) **Probing Degradation Pathways of Noradrenaline Pharmaceutical Formulations via Thermal, Light and Oxidative Stress**; Janet de los Reyes[1], Channa A. Wijesinghe[1], Molesworth Samuel[1]; [1]Hospira, Inc

Forced degradation is an important approach to aid in the understanding of pharmaceutical formulations. It provides insights into possible degradation products that can be formed during exposure to various stress conditions. Ultimately, it provides information that can be used to control manufacturing conditions, storage conditions and packaging configurations so that the end users will receive the finished pharmaceutical products at their highest level of quality. In this study, degradation of noradrenaline in pharmaceutical formulations was induced via thermal, photochemical (light exposure), and oxidative stress. Multiple formulations were prepared containing different concentrations of metabisulfite, a common antioxidant used in pharmaceutical formulations including a formulation without metabisulfite. Formulations were filled into both clear and amber vials and were either headspaced with nitrogen or air prior to stoppering and capping. Degradation pathways were probed and many degradants were identified through the utilization of multiple analytical techniques including chiral HPLC and UHPLC coupled with multiple detectors including photodiode array and quadruple ion trap mass spectrometry. Nine prominent degradation products were linked to light-induced degradation. However, the presence of the antioxidant, metabisulfite, significantly altered the impurity profile by reducing the number of degradants to two (excluding the sulfonic acid derivative impurity that can only be observed in the presence of metabisulfite). The formation of the D isomer, an inactive isomer to L-noradrenaline, is linked to thermally-induced degradation more so with the non-metabisulfite containing formulation. Additionally, it was observed that the formation of the sulfonic acid derivative impurity in the metabisulfite-containing formulations was enhanced by thermal stressing. In addition to the sulfonic acid derivative and the D-noradrenaline, four degradants, including 3,4-dihydroxybenzaldehyde were observed to be thermally induced. Formation of noradrenalone is linked to oxidation as it was prominent during oxidative degradation as well as the air-headspaced non-oxidative degradation samples. Multiple competing degradation pathways of noradrenaline exist for each of the specific formulations evaluated. Within the experimental design of this study, these pathways have been probed to help gain understanding of the variables that can adversely affect product integrity.

(196) **Applications of Raman Spectroscopy in Formulation Development**; Kei Moriyama[1], Yulian Lin[1], Junichi Jinno[1], Toru Nishibayashi[1]; [1]Formulation Research Institute, Otsuka Pharmaceutical Co., Ltd

Raman spectroscopy is one of the promising methods for the chemical and crystallographical analysis of active pharmaceutical ingredients (API) and formulations because of the high sensitivity and specificity to drug-like compounds, and the high resolution in chemical imaging. A lot of novel analytical techniques of API and formulations arise from raman spectroscopy coupling with chemometrics, for example, quantification of amorphous in a crystalline form, chemical imaging of a tablet surface or cross-section, and monitoring of crystal transition under the change in temperature or humidity. Here we report our recent attempts to develop such methodologies as above in order to understand the quality and the function of formulations more precisely.

(197) **Isolation of Single Isomers using Supercritical Fluid Chromatography and Determination of Absolute Configuration of Warfarin using Vibrational Circular Dichroism**; Hiroyuki Yamashita[1], Tatsuhiro Tokunaga[1], Toshikazu Adachi[1], Masamichi Yuda[1], Toshio Teramura[1]; [1]Astellas Pharma Inc

Given the differences in biological effect of individual isomers, the pharmaceutical industry is increasingly frequently implementing measures to produce not a racemic mixture but a single isomer in drug development. Supercritical fluid chromatography (SFC) is one such tool developed to acquire a single isomer from a racemate. However, efficient synthesis and conduct of structure-activity-related studies requires not just obtaining an isomer but also determining its absolute configuration (AC). Vibrational circular dichroism (VCD) is one method of determining the AC of a chiral compound in solution. The oral anticoagulant warfarin is a racemate, demonstrating structural diversity depending on solvent environments, with a closed-ring cyclic hemiketal form reported in organic solvents. Here, we attempted to acquire individual isomers of warfarin using SFC and determine their ACs using VCD. Column and modifier screening were conducted on SFC using a racemate of warfarin to determine peak separation conditions. We prepared two single isomers from the racemate and analyzed their VCD spectra in CDCl3 and DMSO-d6 solution. We also calculated VCD spectra of each different form, namely an open side chain form (R form) and cyclic hemiketal forms (RS and RR forms). Observed VCD spectra were then compared with the calculated one to determine ACs of each peak. SFC screening clearly demonstrated that individual isomers could be prepared using an OD-H chiral column with MeOH as a modifier, and total sample preparatory yield was 79%. Comparison of VCD spectra revealed the first peak on SFC to be the R form and the second the S form. Our findings further suggested that warfarin exists almost exclusively in its cyclic hemiketal form in organic solvent. Taken together, these results showed SFC and VCD to be useful in improving drug discovery efficiency, and AC determination of a compound in solution was found to be possible using VCD, regardless of whether or not the compound exhibited structural diversity by solvent.

(198) **Photochemical and Oxidative Degradation of Formulated and Unformulated Phytonadione and Elucidation of Degradants**; Tristan Walters[1], Tristan Walters[1]; [1]Hospira, Inc. McPherson, KS

Phytonadione, also known as Vitamin K1 is an artificially produced, naturally occuring compound most notably found in plants where it serves in Photosystem I as an electron acceptor. As a pharmaceutical product, phytonadione is used as a cofactor to induce production of coagulant factors such as prothrombin. Phytonadione is extremely light sensitive and moderately oxygen sensitive. In this study, phytonadione was exposed to light in pharmaceutically formulated and unformulated suspensions filled in clear and amber vials; the headspace of some solutions were nitrogen protected and others were exposed to atmosphere. Light exposure was performed at both ambient light conditions (at approximately 600 lux over multiple days) and an accelerated exposure in a photostability light chamber (per ICH Q1B). The formulation evaluated consists of an emulsifier, acetate buffer, and a surfactant. In addition to these excipients, the formulated product used in this study will include EDTA, a well characterized chelator. The unformulated product contained only the chemicals necessary to obtain satisfactory dissolution and buffer. The goal of this study was two-fold. The first objective was to compare the photochemical reactions between formulated and unformulated phytonadione. The second objective was to compare the products of light exposure of solutions headspace-protected by nitrogen with those that are not. Degradation profiling was determined using various methods such as UPLC-PDA, UPLC-MS, and UPLC-MS/MS. Unique degradation pathways related to both light stress and oxygen in the vial headspace have been observed and characterized. Results demonstrate considerable degradation within all of the previously mentioned variables. One of the prominent degradation products observed in the study has been linked directly to the reduction of the quinone moiety to the corresponding quinol. This degradant has a distinguishable single λmax at approximately 233nm. This is a stark difference from phytonadione which has multiple (three) relative maximums at approximately 245, 271, and 331nm. Nitrogen-headspaced vials were observed to prevent certain pathways of degradation from occurring (complex oxidation), however, oxidation as well as with non-oxygen dependant degradations resulted in the formation of several impurities. Overall, the formulated products with both atmospheric and nitrogen headspaces tend to have less degradation than their counterparts.

(199) **Building Robust Transmission Raman Models: What if my Material Suppliers Change?**; Andrew Owen[1], Hilary Jeffreys[2], Steven Brown[2], Matthew Bloomfield[1], Pavel Matousek[3], Darren Andrews[1]; [1]Cobalt Light Systems, [2]Actavis UK Ltd., [3]Science & Technology Facilities Council

The profit margins of generic pharmaceutical companies are inextricably linked to the supply of their raw materials. Solid dosage formulations may have only a few weight percent of active ingredient, so the unit price paid for excipients greatly affects the final selling price. As manufacturing processes must be insensitive to changes in supplier, any method chosen to measure the content uniformity (CU) of the product must also be insensitive. Transmission Raman spectroscopy (TRS) has generated a great deal of interest as an alternative method for CU. It offers significantly faster lot release than chromatography techniques and simpler, more robust models than near infrared (NIR) techniques, with no compromise in accuracy. A comprehensive design of experiments (DoE) matrix was assembled for a tabletted formulation. The API concentration range spanned 75% to 125% of the nominal target dose. Both lactose monohydrate and microcrystalline cellulose (MCC) are included in the excipient blend and two suppliers for each were used to construct the tablet set. Tablets manufactured with the existing excipient suppliers were analysed alongside tablets reflecting a change in either lactose or MCC supplier, or both, fully accounting for future supplier changes. Subtle differences in the spectra related to fluorescence or particle size are shown to be effectively modelled, creating a simple, robust calibration model.

(200) **Raw Materials ID through Containers Using Spatially Offset Raman Spectroscopy**; Matthew Bloomfield[1], Guy Maskall[1], David Crawford[1], Pavel Matousek[2], Darren Andrews[1]; [1]Cobalt Light Systems, [2]Science & Technology Facilities Council

The correct identification of raw materials delivered to any manufacturing facility is an important process, none more so than in the pharmaceutical industry where it is a regulatory requirement. For many of the high value pharmaceutical markets 100% verification of incoming goods is mandatory, which puts a significant burden on analytical resources. Spectroscopic techniques are increasingly popular for identifying materials due to their speed, convenience and accuracy. As instrumentation becomes increasingly easy to use and robust it is being adopted by users with no spectroscopic experience whatsoever. It has emerged that the most versatile technique is Raman spectroscopy due to its high chemical specificity and simple operation. A significant limitation of spectroscopic techniques for verification is that the packaging is often not transparent, which precludes the use of NIR, FT-IR and conventional Raman. This means that the samples need to be measured in a powder sampling booth where the containers can be opened in safety then sampled, resealed and the booth cleaned. This can be extremely expensive and time-consuming. This report focuses on the application of Spatially Offset Raman Spectroscopy (SORS) to accurate, robust ID through the packaging supplied to the end user. SORS allows high quality Raman spectra to be measured through opaque containers such as

sacks, bottles, tubs and bulk containers made out of paper, plastic, glass or multiple layers. We present data on the spectral quality and reproducibility of SORS measurements on common pharmaceutical incoming goods such as MCC, lactoses, Mg stearate and APIs when measured through their original packaging. Using a SORS-optimised analysis routine we demonstrate the very high selectivity and discrimination of the matrix of materials.

(201) **Parallel Determination of 17alpha-Ethinylestradiol and Desogestrel Content in Pharmaceutical Formulations by UV-visible Derivative Spectrophotometry.**; M. Inés Toral, Fallon Nacaratte[1]; [1]University of Chile

The 17alpha-Ethinylestradiol (EE2) is a semi-synthetic estrogen drug used as contraceptive or to reduce symptoms associated with menopause. Desogestrel (DSG) is a progestin synthetic drug derivated from progestogenic activity, used in inhibiting ovulation. The combination of EE2 and DSG produces a synergistic effect in their mechanisms of action on the body, which makes the formulation of an efficient contraceptive. For this reason, was developed a parallel method for determination and validation of 17alpha-Ethinylestradiol and Desogestrel by derivative spectrophotometry. The method was applied in formulations pharmaceuticals.To develop the method, was carried out a solubility study and spectral behavior for both drugs, acetonitrile was selected, because the resolution of spectra are better for both analytes. Furthermore, the forced degradation was studied and only was found that in acid-base conditions a band shift occurs for both analytes. For the selection of spectral variables were selected a $\Delta\lambda$= 190-350 nm, second derivative, a smoothing factor of 8•103 and scale factor of 1•104. The analytical signal was evaluated by the graphic method for EE2 and zero crossing method for DSG, the wavelengths were 288 nm and 220, respectively. The determination ranges were found to be between 1.5•10-6 to 5.0•10-4 mol/L and 1.7•10-7 to 1.0•10-3 mol/L for DSG and EE2, respectively. A study of interferents was carried out using excipients; it was found that only polyvidone (solubility universal) interferes between $\Delta\lambda$ 190-250 nm, where DSG is determined. For this reason, a parallel method was proposed for the determination. In the method, the samples were divided in two parts, one was used to determinate EE2, which was diluted with acetonitrile; the second sample was diluted in deionized water, filtered and the solid was diluted in acetonitrile. The method was applied to Ciclidon® and Dal®, Gynopharm Chile was found a content of 0.148 ± 3•10-3 mg of DSG, 0.03 ± 6•10-4 mg of EE2 and 0.148 ± 7•10-4 mg of DSG, 0.02 ± 3•10-4 mg of EE2, respectively. The results show a good accuracy and good repeatability. This work was financed by FONDECYT Project Nº 1100103.

(202) **Analysis of the Binding of Second-Generation Sulfonylurea Drugs to Human Serum Albumin by High Performance Affinity Chromatography**; Ryan Matsuda[1], Jeanethe Anguizola[1], K.S. Joseph[1], David Hage[1]; [1]University of Nebraska-Lincoln

High performance affinity chromatography (HPAC) was used to examine the binding of second generation sulfonylurea drugs (e.g., gliclazide and glibenclamide) with their transport protein human serum albumin (HSA) at various stages of glycation. Glycation is a type of non-enzymatic modification found in proteins that is caused by elevated levels of glucose in blood, as occurs in diabetes. Type II diabetes, the most common form of this disease, is often treated by using sulfonylurea drugs such as gliclazide and glibenclamide. Frontal analysis was used to estimate the number of binding sties and association equilibrium constants for these drugs with normal HSA and glycated HSA. The results showed that both gliclazide and glibenclamide were binding to normal HSA and glycated HSA at two groups of high and low affinity sites. Zonal elution competition studies were used to examine the effect of glycation on three specific regions of HSA: Sudlow sites I and II and the digitoxin site. An overall increase in affinity for the tested drugs was seen at both Sudlow sites I and II as the level of glycation for HSA was increased. As the level of glycation was increased, a decrease in binding affinity may have occurred for the digitoxin binding site. These results illustrate how HPAC can be used as a tool for studying drug interactions with modified protein complexes and as a potential tool for personalized medicine.

(203) **Analysis of Free Fractions for Drug Enantiomers by Multi-Dimensional High Performance Affinity Chromatography using Ultrafast Extraction Combined with a Chiral Stationary Phase**; Xiwei Zheng[1], Michelle Yoo[1], David Hage[1]; [1]Chemistry Department, University of Nebraska, Lincoln

A multi-dimensional system based on high performance affinity chromatography was developed to measure the free fractions of drug enantiomers and to study their binding with serum transport proteins. *R/S*-Warfarin and the protein human serum albumin (HSA) were used as models to test this approach. Ultrafast extraction based on an immobilized HSA microcolumn was first used to separate the free and protein-bound fractions of *R*- and *S*-warfarin in the presence of a sample that contained soluble HSA. The extracted free fraction of *R/S*-warfarin was then delivered to a larger HSA column, which was utilized as a chiral stationary phase. It was found that the free fractions of *R*- and *S*-warfarin that were determined by this method gave good agreement with those measured by ultrafiltration. It was also found that this approach provided a fast estimate of the association equilibrium constants for drug-protein interactions, giving results consistent with the literature and reference methods. This method could be used at clinically-relevant concentrations of warfarin and HSA and made it possible to simultaneously determine the free fractions and equilibrium constant values for both warfarin enantiomers. This approach is not limited to warfarin or HSA but could easily be extended to other chiral drugs and serum proteins or used for the high-throughput screening of drug-protein interactions.

(204) **Quality Evaluation of Pharmaceutical Tablets by using the New NIR Camera (Compovision) Developed for High Speed Wide Area Measurement**; Kimie Awa[1, 2], Daitaro Ishikawa[1], Fumiaki Mizuno[1, 3], Takashi Nishii[1], Yoko Torigoe[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]Dainippon Sumitomo Pharma Co., Ltd., [3]Sumitomo Electric Industries, Ltd

This study reports the validity of the newly developed NIR camera (Compovision) designed for high speed measurement under various practical situations. Compovision was developed by Sumitomo Electric Industries, Ltd., and the imaging system used consists of Compovision including a beam splitter, the movable sample stage and halogen lamps. It can measure transmittance and diffuse reflectance NIR spectra. The camera can detect 320 pixels with all spectral regions of 1000 - 2300 nm at one line. The reflectance of whole spectral region from the object is separated to 237 bands, and the new InGaAs detector with high sensitivity developed by Sumitomo Electric Industries, Ltd. detects their 320 pixels × 237 bands data at one time. It is possible to carry out the imaging of the area of 30 cm2 within several seconds (i.e. Compovision can obtain the spectral data of approximately 100,000 pixels in a few seconds), in the case of the 1 mm spatial resolution, by these innovations of this system, and it is just beginning to be applied to the high speed total test at line of the factories. Two kinds of sample tablets were prepared for determination of their quality. One of them was made by direct compression from the powder of ascorbic acid, lactose corn starch and mg-stearate, and after that mg - stearate was added in an arbitrary. On the other hand, film-coated tablets which were different coating time were made by splay coating method. Those tablets contained polyethylene glycol, hypromellose, titanium oxide and talc as the coating reagents. The NIR image consisted by the diffuse reflectance spectra in the 1000 - 2300 nm region were measured by

using Compovision. All the spectral data were collected with a 6 nm spectral resolution. The data were collected by the NIR analysis program, and converted into text files per pixel for spectral analysis. The irregular part of the coating could confirm by the NIR image which used the feature wavelength of the coating reagent, clearly. This result suggests that Compovision is effective for evaluation of the tablet quality at line.

(205) **A Study on Penetration depth of Near-Infrared Diffuse-Reflectance Light from Bilayer Tablets by using a Compact NIR Photo-Diode Array Spectrometer**; Koudai Murayama[1], Daitaro Ishikawa[2], Takuma Genkawa[3], Yoko Torigoe[2], Makoto Komiyama[1], Yukihiro Ozaki[2]; [1]Yokogawa Electric Corporation, [2]Kwansei Gakuin University, [3]University of Tsukuba

In this study, we prepared bilayer tablets with various layer thickness, and investigated penetration depth from the bilayer tablets of diffuse-reflectance(DR) NIR light. For this purpose, in the DR NIR spectra were measured in very short-time by using a newly developed high-speed, high-sensitivity and compact process-NIR spectrometer (P-NIRs) with a high-density photodiode array sensor. To separate incompatibility APIs or combine a fast dissoluble medicine and a sustained release medicine, the pharmaceutical tablets are multi layered tablets and coated tablets. Investigations of penetration depth of DR NIR light from the tablets are necessary for the NIR measurement of inside medicine of multi layered tablet and coated tablets by a DR method. The first layer of bi-layered tablet samples contained ascorbic acid, and the second layer did not do it. The first layers consist of mixed powder of talc, lactose, microcrystalline cellulose and coloring material. The second layers consist of mixed powder of talc, lactose, microcrystalline cellulose and ascorbic acid. The layer thickness of the first layer and second layers were different.We acquired the DR measurement spectra of these tablets in several ten of milli-seconds by using P-NIRs with an optical fiber probe. The DR measurements of test samples were measured for the DR light from the first and second layer each. The acquired spectral data were transformed by using suitable pre-processing method. NIR spectra of samples with the different layer thickness were measured, and the penetration depth into the first layer of DR NIR light were investigated. We have succeeded the diffuse reflection measurement of the pharmaceutical bi-layered tablets in a very short time by using P-NIRs. And the result of this investigation showed about the penetration depth into the tablets of DR NIR light.

(206) **A Survey of Metal Contamination in Pharmaceutical Excipients**; Gang Li[1], John Kauffman[1]; [1]Division of Pharmaceutical Analysis, FDA

The current pharmacopoeial method for determination of heavy metal contamination is a sulfide precipitation preceded by a digestion step, and the allowable limits for toxic metals in pharmaceutical materials can be ten or more parts per million. The US Pharmacopoeia (USP) is currently revising both the methods and the limits for heavy metals, metalloids and residual catalysts, and the International Conference on Harmonization of Technical Requirements for Human Drugs (ICH) has initiated a working group to harmonize the limits across the three ICH regions (Europe, Japan and US). These activities are expected to result in revised limits on metals in pharmaceuticals which could be significantly lower than the current limits. Data on the prevalence of metal contamination in pharmaceutical materials are sparse, and as a result there is uncertainty surrounding the impact of the anticipated new limits on pharmaceutical manufacturers and on the availability of drugs. The FDA Division of Pharmaceutical Analysis has surveyed the metal contents of pharmaceutical excipients. The survey included the analysis of the toxic metals cadmium, arsenic, lead and mercury as well as common catalytic metals such as the catalysts that are covered by the current European Medicines Agency (EMA) guideline on residual metal catalysts and reagents and the USP draft chapter <232>. Analyses of pharmaceutical excipients were performed using inductively coupled plasma mass spectrometry (ICP-MS). The analytical methods developed for this survey were capable of accurately analyzing the elements of interest in pharmaceutical excipients, and in general low metal levels were found in the excipients. This poster will present the results of this survey and provide some example calculations for total metal levels in pharmaceutical finished products based on the measured metal concentrations in the excipients.

(207) **Tip-Enhanced Raman Scattering (TERS) for Nano-Bioanalytical Applications**; Jennifer A. Dougan[1], K. L. Andrew Chan[1], Sergei G. Kazarian[1]; [1]Imperial College London

Tip-enhanced Raman scattering (TERS) spectroscopy is a powerful technique which allows for investigation of surfaces and materials at nanoscale spatial resolution. This spatial resolution is achieved by the combination of scanning probe microscopic and surface enhanced Raman scattering (SERS) spectroscopic techniques. Typically, in TERS experiments, surface enhancement of the Raman effect is achieved by surface coating a standard AFM tip with a plasmonic substrate - most commonly through gold or silver sputtering - to produce an "active" TERS tip. The tip is then employed as the enhancing surface providing information-rich vibrational spectra from the sample *via* laser light-tip-sample interactions. Spatial resolution is afforded by the distance-dependent nature of the SERS enhancement and spatial control of the AFM tip. This technique has been applied to a wide range of sample types. Indeed, this laboratory has previously reported spatial resolutions of 14 nm for single walled carbon nanotubes, SWCNTs, (inverted configuration) and the ability to discriminate between a mixture of similar SWCNTs. [1] Furthermore, SWCNTs have also been studied in top-illumination mode, producing spatial resolution of 20-50 nm (upright configuration). [2] Methodologies which allow for comprehensive charactersisation and interpretation of substrate-sample interactions are essential for the development and application of bio-nano-analytical tools. TERS presents an attractive option for such investigations. Here we demonstrate our recent investigations using TERS spectroscopy for substrates and samples towards bio-nano-analytical applications. A number of parameters have been investigated for rational TERS experiment design, including the optimisation of tip preparation, sample and instrument configuration.

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(208) **Tip and Tricks for Successful Tip-Enhanced Raman Imaging**; Emmanuel Leroy[1]; [1]HORIBA

Tip-enhanced Raman has become a hot topic of research in molecular spectroscopy, and the number of publications continues to grow steadily, however most of them are limited to single spectra or line profiles. Crafting suitable tips is certainly challenging, but making the step from spectral acquisition to hyper-spectral TERS imaging also requires taking care of many details. We'll cover recent tip manufacturing techniques for reliable enhancement, and the hardware requirements and techniques to successfully and efficiently generate images.

(209) **Adding Tip-enhanced Raman Spectroscopy Functionality to the "NanoBits" Toolbox Concept for Atomic Force Microscopy**; Gerardo Gamez[1], Victor LeNader[1], Pierre Brodard[2], Malte Bartenwerfer[3], Johann Michler[1]; [1]EMPA, Swiss Federal Laboratories for Materials Science and Technology, [2]College of Engineering and Architecture of Fribourg, [3]OFFIS, Institute for Information Technology

The atomic force microscope (AFM) has become a standard and wide spread instrument for characterizing nanoscale devices and can be found in most of today's research and development areas. NanoBits (www.nanobits-project.eu) is a collaborative project, funded by the European Commission, which aims to provide exchangeable and customizable scanning probe tips that can be attached to standard AFM cantilevers offering an unprecedented freedom to adapt to specific applications (analogous to screwdriver or drill bits, hence the name). For example, the size and shape of the tips can be adjusted to allow characterizing three dimensional high-aspect ratio and sidewall structures of critical dimensions, such as from nano-optical photonic components and semiconductor architectures which is a bottle-neck in reaching more efficient manufacturing techniques. It is thus an enabling approach for almost all future nanoscale applications. Raman spectroscopy allows obtaining valuable information from materials, such as composition, stress, and crystallinity, in a non-destructive manner. However, in typical Raman spectroscopy the spatial resolution is limited to several hundred nanometers and scattering signals can be very low. Tip-enhanced Raman spectroscopy (TERS) permits to go beyond these limitations, thus allowing characterization of nanostructures. In this study, the possibilities of developing a set of NanoBits to allow TERS are being explored. The methods to fabricate the TERS NanoBits and the resulting spectra will be presented.

(210) **Thermogravimetric Analysis and Atomic Force Microscopy Characterization of Concanavalin A Immobilization on Nanoporous Gold**; Yih Horng Tan[1, 2], Binod Pandey[1, 2], Kohki Fujikawa[1], Alexei V. Demchenko[1], Keith J. Stine[1, 2]; [1]Department of Chemistry and Biochemistry, University of Missouri – Saint Louis, [2]UM-St. Louis Center for Nanoscience, University of Missouri – Saint Louis

Immobilization of proteins from solution onto functionalized surfaces has attracted tremendous amounts of attention, primarily due to the great interest in the development of biosensor devices. Nanoporous gold (np-Au), made by dealloying low carat gold alloys, is a relatively new nanomaterial finding application in catalysis, sensing, and as a support for biomolecules. In this study, thermogravimetric analysis was applied to measure the loading of thiol derivatives, including octadecanethiol (C_{18}-SH), 8-mercaptooctyl α-D-mannopyranoside (αMan-C_8-SH), and 3-mercapto-triethyleneglycol (HO-PEG_2-SH), into monoliths of np-Au. Modification with a 1:4 molar ratio mixture of the mannoside derivative (αMan-C_8-SH) with either octanethiol or HO-PEG_2-SH was also investigated. TGA analysis of the mass loss from np-Au removed after different time periods of formation of C_{18}-SH SAMs revealed a different rate of SAM formation depending upon whether static incubation or flow-through conditions were used. The np-Au monoliths modified with αMan-C_8-SH bind lectin Concanavalin A (ConA), and the additional mass due to bound protein was clearly seen in the TGA analysis. A comparison of TGA traces measured before and after exposure of HO-PEG_2-SH modified np-Au to ConA solution shows that the non-specific binding of ConA was minimal. In contrast, np-Au modified with octanethiol showed a significant mass loss due to non-specifically adsorbed ConA. A significant mass loss was also attributed to binding of ConA to bare np-Au monoliths. TGA also revealed a mass loss due to the binding of ConA to np-Au monoliths modified with pure αMan-C_8-SH. The use of mass losses determined by TGA to compare the binding of ConA to np-Au monoliths modified by mixed SAMs of αMan-C_8-SH and either octanethiol or HO-PEG_2-SH revealed that binding to mixed SAM modified surfaces is specific for the mixed SAMs with HO-PEG_2-SH but shows a significant contribution from non-specific adsorption for the mixed SAMs with octanethiol. TGA data also provide evidence that ConA bound to the αMan-C_8-SH modified np-Au can be eluted by flowing a solution of methyl α-D-mannopyranoside through the structure. The presence of ConA proteins on the modified np-Au surface is confirmed using atomic force microscopy (AFM). The results highlight possible application of modified np-Au monoliths to glycoscience and glycotechnology.

(211) **Influence of Tip-Sample Contact on Vibration Ring Down of AFM Cantilevers**; Ehsan Rezaei[1], Joseph Turner[1]; [1]University of Nebraska-Lincoln

Several material characterization techniques associated with the atomic force microscope (AFM) rely on the dynamics of the cantilever as it vibrates while in contact with the sample. In this talk, we focus on the ring down characteristics of an AFM cantilever that is excited with a short pulse while in contact with a sample. The equations of motion are first derived and examined with respect to a linear viscoelastic contact. The response of the lowest several modes is illustrative of the linear contact. Next, the role of a nonlinear contact is examined with respect to the excitation amplitude, the temporal pulse width, and the applied static force. Finally, application of this analysis is discussed for a variety of materials including polymer blends and biological materials.

(212) **Polarized Resonance Micro-Raman Spectroscopy of Pentacene**; David Tuschel[1]; [1]HORIBA Scientific

Pentacene is one the organic compounds showing great promise for its use in molecular electronic devices, particularly organic field effect transistors. Attempts to understand the conduction mechanism and the role that chemical bonding and crystal structure play in that process can be assisted by the use of resonance Raman spectroscopy. In particular, Franck-Condon processes can be probed through the resonance Raman effect. We have probed individual grains of pentacene obtaining micro-Raman spectra from a single location using different excitation wavelengths. Variation of the Raman spectra from a single location reveals the coupling between the phonons and electronic transitions at different excitation wavelengths. Furthermore, we have obtained polarized (parallel and perpendicular) micro-Raman spectra of individual grains at various orientations with respect to the incident polarization. We will discuss our results with respect to the significance of resonance micro-Raman spectroscopy for molecular electronic device characterization and the monitoring of crystal structure.

(213) **Micro-Raman and micro-XRF Mapping of Metal Oxide Grain Chemistry using Multivariate Statistical Analysis**; Robert Davis[1], Eric Telfeyan[1]; [1]GE Global Research Center

The analysis of heterogeneous samples is often time consuming due to the high sampling density required to actually assess the material and the time required to processing the resulting large data sets. In this work both Raman and X-ray fluorescence (XRF) spectroscopies are utilized to generate a comprehensive chemical map of a complex mineral cross-section non-destructively. Data processing of the collected Raman and XRF spectra is aided by the use of multivariate statistical analysis (MVSA), allowing for rapid identification of unique grain chemistries, not possible in traditional univariate approaches. Micro-XRF imaging of the mineral cross-section yielded both bulk and trace elemental composition with high spatial resolution. Micro-Raman analysis provides complimentary information on the molecular bonding, phase, crystallinity and orientation of mineral grains. The combination of these two techniques allows for the rapid and precise identification of mineral grain chemistry with a lateral resolution of several micrometers. The

advantages and disadvantages of using MVSA for data processing in these types of systems are also discussed.

(214) **A Near-field Scanning Optical Module for Inverted Microscopes**; Taher Ababneh[1], Jorg Woehl[1]; [1]University of Wisconsin-Milwaukee

Optical imaging techniques have played a major role in evolving biological and physical sciences. However, there are fundamental limitations of conventional microscopy. The diffraction of light limits standard optical microscopy to a spatial resolution comparable to the wavelength of light. As a result, optical microscopes are restricted in their ability to resolve fine features and details. Near-field scanning optical microscopy (NSOM) is a cutting-edge imaging technique which has achieved an optical resolution beyond the diffraction limit and promises direct manipulation of single molecules on surfaces. By using a very small light source with a diameter much smaller than the wavelength of the light, resolutions better than the diffraction limit can be achieved. The probe must be very close to the surface; much closer than the wavelength of the light. This region is the "Near-Field" and hence the name of the technique. Typically, excitation light is delivered to the aperture through an optical fiber. The aperture can be a metal-coated tapered fiber with a nanometer-size opening at its end which is held at a constant distance of typically 10 nm from the sample surface during the xy-scan. The resolution of NSOM depends on the size of aperture used and the distance to the sample, but not on the wavelength of light. We demonstrate the construction of a near-field optical module for a confocal microscope. Several hardware requirements are implemented in order to bring the tip into the general vicinity of the sample (coarse approach), fine position the tip using a piezoelectric scanner, attain the proper tip-sample working distance using shear-force feedback and maintain the vertical position of the tip using a feedback loop control system. In addition to the hardware requirements, a computer system that drives the scanner, measures data and converts the data into an image is used. The details of the technique, optimal experimental parameters and imaging results will be discussed.

(215) **Design and Application of a Multiple-Source Fluorometer for Lanthanide-Sensitized Luminescence**; Guoying Chen[1, 3], Guyu Liu[2], Feng Qin[2]; [1]USDA, Agricultural Research Service, Eastern Regional Research Center, [2]Shanghai Institute for Food and Drug Contro

A fluorometer was developed for lanthanide-sensitized luminescence (LSL) using multiple excitation sources, a xenon flashlamp and UV LEDs. The photodetector was a photomultiplier tube module gated to reject time-domain background noises including matrix interferences. Significant improvement in analytical performance was achieved over commercial desk-top fluorescence spectrometers. Target analytes are mainly two classes of antibiotics: tetracyclines and fluoroquinolones, in food, biological, or environmental matrices. LSL's excellent specificity enabled measurement without prior HPLC separation. For real food samples, limit of detection (LOD) was typically in ng/g level, and linear range extended to three decades. Reproducibility is usually <2% relative standard deviation. It was highly portable at 4.6 kg and 15 W power consumption.

(216) **Photon Trapping Spectroscopy: Design, Fabrication, and Testing of an Automated System of Real-Time Monitoring**; Ryan Schmeling[1], Peter Geissinger[1], Joseph Aldstadt[1]; [1]University of Wisconsin Milwaukee

We are developing a novel approach to ultra-trace analysis by molecular absorption spectroscopy. In Photon Trapping Spectroscopy (PTS), a high-finesse optical cavity is created by use of a flat, rotating mirror of high reflectivity. Light from a dye laser (488 nm) enters the cavity by transmission through a highly-reflective dielectric mirror, in the same way as in Cavity Ring-Down Spectroscopy (CRDS). However, unlike CRDS, the cavity exit mirror contains a slit (1.0 mm diameter) that is rotated at high speed on an axle, thereby transmitting a fraction of the trapped light to a photomultiplier tube detector. In this approach, absorbance data can be recorded directly. In previous prototypes the instrument was manually aligned and the data was manually reduced. In the current prototype instrument FPGA (Field-Programmable Gate Array) hardware and LabVIEW software are used to automate the process of data collection and reduction. This allows for real time monitoring of the cavity for alignment purposes. Results will presented for the monitoring of gas-phased nitrogen oxides at parts per billion levels in ambient air.

(217) **Measurement of Heterogeneous Rate Constants Using Photomicroscopy**; Walter Bowyer[1], Tessa Sullivan[1], Gabriella Mylod[1], Alexa Hill[1], Katherine Delaney[1]; [1]Hobart and William Smith Colleges

Electrochemical techniques provide a wide arsenal for measuring heterogeneous kinetics at electrode surfaces. However, the range of techniques for measurement of rates at other surfaces is more limited. We are applying photomicroscopy to measure rates of reaction where metal is consumed by a reactant. Here we describe applications to two systems. First, indium mediated allylation is an extremely versatile reaction that is regio- and stereoselective and proceeds in aqueous solutions. We apply photomicroscopy to measure the kinetics of the reaction of allyl chlorides at the indium surface. We now report absolute heterogeneous rate constants that range from 3E-5 to 3E-4 cm/sec. To demonstrate the potential for broader application of our technique, we report preliminary measurements on the dissolution of gold metal.

(218) **Evaluating Optical Point Spread Function Fitting Methods**; Bradley M. Moran[1], Peter Geissinger[1], Jorg C. Woehl[1]; [1]University of Wisconsin Milwaukee

The ability of an optical imaging system to produce accurate image representations of a sample is of utmost importance for scientific investigation. In many situations the features under study in a system exceed the diffraction limit of light, and when imaged, appear as blurred intensity distributions rather than distinct sharply defined objects. Many factors, such as limitations of optics, rate of detection, detector pixel size, optical reflections and other sources of noise contribute to this deviation from optical clarity. By determining the point spread function of the imaging system, these aberration effects can largely be accounted for. Once the point spread function is computed, it can be used for image deconvolution, leading to enhanced or even super resolution. In this study, six methods of modeling the PSF are assessed for their robustness, using both generated and experimentally obtained images. Conclusions about the accuracy and efficiency of method are specified.

(219) **Construction of a Continuous Wave – Stimulated Emission Depletion Microscope: Applications in Analytical Chemistry**; Bhanu Neupane[1], Yaqing Zhao[1], Paul Tyrlik[1], Gufeng Wang[1]; [1]North Carolina State University

We report the construction of a sample-scanning, continuous-wave (CW) stimulated-emission depletion (STED) microscope. Measurement of the point spread function of 45 nm fluorescent microspheres shows that the lateral resolution of the microscope is ~80 nm, corresponding to a ~3.5 fold improvement over conventional confocal fluorescence microscopes. As an application of such microscopy, we report the study of nanoparticle self-assembling at the liquid-liquid (L-L) interface. In recent years, nanoparticle self-assembling has gained much attention because it offers new routes to fabricate nanoscopic materials with unique electronic, optical and magnetic properties. It is also important to probe fundamental phenomenon relevant to analytical chemical science, such as adsorption, desorption, partition, crystallization and phase transitions. Although electron microscopic techniques allow the study of particle self-assembly at the solid-liquid interface in great detail, such kind of

study at the liquid-liquid interface is not feasible. Our home-built STED microscope reveals that 500 nm microspheres self-assemble into crystalline structures, whereas 200 nm particles form random aggregates at the oil-water interface. The size-dependency originates from the direct competition between inter-particle interactions and thermal activity. We believe that this kind of study will provide more insight for the understanding of interfacial phenomena.

(220) **From RS to SORS to SERS to TERS: which Raman Spectroscopy for me?**; Renata Lewandowska[1]; [1]HORIBA Jobin Yvon

The Raman Spectroscopy has found its place as an important analytical tool after years of the exclusion as "academic" technique. The intense developments made easier – or simply possible – the use of different types of Raman Spectroscopy. The Resonance Raman Spectroscopy, the plasmon enhancement techniques as SERS or TESR (or others), SORS, Transmission Raman, ROA, to name a few make their way independently from the "classical" Raman Spectroscopy and become the new techniques on their own. However, as it is usual in a relatively new field, the Raman Spectroscopy – or probably more exactly, the Raman Spectroscopies – suffers from some misunderstandings and common (and sometimes false) beliefs which make a choice of an appropriate technique and the required parameters of the system difficult. With my academic and industrial experience and without a reference to any particular existing Raman spectrometer, I would like to re-explain - and demystify sometimes – some definitions and opinions concerning the Raman Spectroscopy. Firstly, I would like to compare different Raman techniques, to point out their main field of applications, their possibilities, advantages, difficulties and limits. Then, I will focalise on the experimental questions like the difference between the dispersion and the resolution, the sensitivity, the use (and abuse) of NIR and UV excitations, the spatial resolution, the role of data treatment, the possibility of quantification using Raman data, the reference samples, the reliable comparison of the systems and other key parameters in Raman Spectroscopy.

(221) **Extreme Surface Analysis of Polyethylenes by Attenuated Total Reflection Far-ultraviolet Spectroscopy — Comparison with Atomic Force Microscope Measurement**; Erika Tanimura[1], Yusuke Morisawa[1, 2], Harumi Sato[1], Naomi Kariyama[3], Noboru Higashi[3], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]Kinki University, [3]Kurabo Industries Ltd

Technology of surface modification of polymers has become increasingly important along the spread of the use of polymers. As a technique for the surface analysis of polymers at molecular level, attenuated total reflection (ATR) infrared (IR) spectroscopy has been widely used. In the measurement of ATR-IR, however, analysis depth reaches to several micrometers. Because the depth is proportional to the wavelength, the light penetrates only tens of nanometers by use of the light in the far ultraviolet (FUV) region. Thus, it is possible to obtain the information localized to the more extreme surface by using ATR-FUV than ATR-IR. In this study, we originally developed a FUV spectrometer for investigating extreme surface of polymers by using ATR technique. To test the instrument, we studied electronic state of several kinds of polyethylenes. In addition, we used an atomic force microscope (AFM) to examine the state of the polyethylene surface. The results from AFM experiment were compared with those obtained from the ATR-FUV spectra. Trapezoidal internal reflection element (IRE) made by sapphire was put in as the incident angle of 70 degree. Measurement range was 145-250 nm. We measured 5 high density polyethylenes (HDPE), 6 linear low density polyethylenes (LLDPE) and 7 low density polyethylenes (LDPE) made by Japan polyethylene corporation. As to AFM measurements, probe area is 4 μm square. In the spectrum of the polyethylenes observed, the peak of absorption band was appeared at around 156 nm. The intensity of the band was varied in the different measurement even for the measurements of the same polyethylene. In ATR-FUV, analysis depth of the evanescent wave for polyethylenes was estimated to be about 50 nm. To examine the relationship between structure and spectra of the extreme surface at this depth, we compared the spectra with the surface pattern obtained from AFM. We measured at three different points for each sample. From the data from the AFM measurements, we quantified the surface asperities of each sample. As a result, we realized that the spectral intensity of ATR-FUV shows the sensitive changes on the surface asperities of about 50 nm depth in each polyethylene.

(222) **AlO Flame Emission Spectroscopy**; Christian Parigger[1], Alexander Woods[1], Jonathan Height[2], Burl Donaldson[2], Walter Gill[2]; [1]University of Tennessee Space Institute, [2]Sandia National Laboratories

Flame emissions from solid propellant plumes show diatomic molecular aluminum monoxide superposed to black- and/or grey-body radiation [1]. Accurate line-strength files allow us to infer temperature from AlO spectra collected at various locations in the plume [2]. The background radiation is modeled with constant, inverse to wavelength, and inverse to wavelength-squared, emissivity [3,4]. We present results from our recent flame pool experiments, discuss our AlO and continuum radiation modeling [5], and also show time-resolved flame spectra following laser-induced optical breakdown of aluminum particles.

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(223) **LIBS: Measurement and Analysis of TiO Spectra**; Alexander C. Woods[1], Christian G. Parigger[1], James O. Hornkohl[2, 3]; [1]University of Tennessee/UT Space Institute, Center for Laser Applications, [2]Hornkohl Consulting

Recent interest in the titania (TiO_2) nanoparticle for thin film applications poses questions concerning the behavior of Ti containing particles emanating from a plasma. We discuss our efforts in predicting diatomic molecular spectra for selected titanium monoxide (TiO) bands. The titanium monoxide (TiO) molecule provides insight into the environment in which TiO_2 is generated. Previous work involved the calculation of predicted spectra for the TiO γ ($A^3\Phi$—$X^3\Delta$), γ′ ($B^3\Pi$—$X^3\Delta$), and E-X $\Delta v=0$ transitions. These synthetic spectra are used to infer temperature by nonlinear fitting to TiO molecular transitions measured in the laboratory. The excitation source consists of a Nd:YAG laser with nanosecond pulse duration implemented in a typical laser-induced breakdown spectroscopy (LIBS) setup.

(224) **Simplification and Standardization of Method Development in Analytical LIBS**; Emily Schenk, B.Sc.[1], Jose Almirall, Ph.D[1]; [1]Department of Chemistry and Biochemistry, Florida International University

Laser-induced breakdown spectroscopy (LIBS) is an analytical tool that is increasing in popularity, progressing from the research realm

to real-world application. A disadvantage of analytical LIBS is the many parameters that must be optimized during method development. An approach to the standardization of LIBS method development and optimization is considered in order to simplify the process. Several parameters pertaining to both the laser used to generate the transient plasma and the manner in which the emission is detected that can be manipulated during method optimization. Here, standardization is considered for several matrices using different irradiation wavelengths. The matrices evaluated include cotton, glass and soil due to differences in physical properties of the materials resulting in different responses to ablation. The irradiation wavelengths included in this work consist of UV (266 nm), VIS (532 nm) and IR (1064 nm) Nd:YAG lasers. This paper presents a method and experimental support for the use of "universal LIBS parameters" during method development for most any matrix under consideration. Potential parameters were evaluated on the basis of analytical merit, i.e. the influence on sensitivity and precision, in addition to the resulting conditions of the plasma, i.e. plasma temperature and electron density. Laser parameters, especially the power density, are important to generating a LIBS plasma above the breakdown threshold of the material and critical to analytical conditions. A uniform power density of approximately 1.2 x 1011 W/cm2 was observed for the matrices in question, analyzed using different laser wavelengths, all of which produced the lowest limits of detection with the best precision with similar plasma conditions. Additionally, crater morphology and useful ablation efficiency (intensity/mass) were evaluated as a method to assess the quality of laser-sample interactions to determine optimal operating conditions. These conditions were attributed to LIBS parameters such as laser focusing depth, laser focusing properties, and duration of ablation (number of shots fired). The ability to establish universal LIBS parameters provides a more standardized approach to analytical LIBS method development, regardless of matrix and irradiation wavelength and a addresses the need for simplification of the analytical LIBS technique overall.

(225) **Ablation Chamber for Simultaneous DP-LIBS and Laser Ablation ICP-OES/MS**; Karel Novotný[1], Lucie Krajcarová[1], Aleš Hrdlička[1], Viktor Kanický[1], Jozef Kaiser[2], Radomír Malina[2], David Hahn[3]; [1]Department of Chemistry, Faculty of Science, Masaryk University, [2]X-ray micro CT and nano CT research group, CEITEC - Central European Institute of Technology, Brno University of Technology, [3]Department of Mechanical & Aerospace Engineering, University of Florida

A special interaction chamber was designed to be compatible with the New Wave UP MACRO Laser Ablation System and to fulfill all demands for simultaneous measurements double pulse laser-induced breakdown spectroscopy (DP-LIBS) and laser ablation coupled to ICP optical emission or mass spectrometry. For single pulse LIBS only two orthogonal fused silica windows are used, the first from the top for the ablation laser beam and the second one from the front for collecting the light of plasma. For DP-LIBS the third window from the side is needed being orthogonal to the previous two. For Laser ablation ICP OES/MS a flow of transporting gas has to be implemented. The inner space of the chamber was optimized for low volume and quick flush of gas, which is crucial for the method. The gas enters the chamber through three oblique jets on the top and leaves to the ICP on the back side. The chamber is equipped with a vertically adjustable sample holder to adapt various sample heights and exchangeable inner rings allowing to various sample diameters to be altered and to minimize the inner volume.

(226) **Effects of Excitation Wavelength on LIBS Plume Morphology using Focused Shadowgraphy**; Amina Hussein[1, 2], Prasoon Diwakar[1], Sivanandan Harilal[1], Ahmed Hassanein[1]; [1]Center for Materials under Extreme Environment, School of Nuclear Engineering, Purdue University, [2]Department of Physics, McGill University

Pulsed laser ablation has numerous scientific and industrial applications, however its underlying physics and various interaction processes are not fully understood. The complexity of laser ablation process becomes elevated when considering expansion into an ambient environment. The presence of an ambient gas during laser-plasma expansion leads to shockwaves formation, internal plume structures, plume splitting, and confinement. We investigated the generated shockwave dynamics in laser ablation plumes in one atmosphere air using focused shadowgraphy. Current research specifically focuses on the dynamics of plasma generation and its expansion at the earliest time of its evolution (first 10s of nanoseconds). The purpose of the present work is to investigate the effect of laser wavelength and energy on plasma plume formation and its expansion dynamics. For generating plasmas, 6 ns pulses from a Nd:YAG laser emitting at 1064 nm, 532 nm, and 266 nm are focused onto Al target. A frequency doubled Nd:YAG laser emitting at 532 nm is used as a probe for recording the shadowgraphic images. Distinctive plume morphologies observed in shadowgram images indicate that different mechanisms govern laser ablation at each wavelength (inverse bremsstrahlung, photoionization, etc.). Laser wavelength has distinctive effect on laser energy absorption, material ejection, and secondary shockwave formation. Higher energies at all wavelengths result in faster plume expansion caused by extensive plasma heating. Simple models using Taylor-Sedov solution are used to model plume expansion dynamics at different wavelengths and energies to benchmark our experiments. A comprehensive analysis of different mechanisms involved during pulsed laser ablation is presented.

(227) **Effect of Spectral Interference on Uranium Lines in Laser-Induced Breakdown Spectroscopy**; Inhee Choi[1], Xianglei Mao[1], Dale L. Perry[1], Richard. E. Russo[1]; [1]Lawrence Berkeley National Laboratory

The performance of laser-induced breakdown spectroscopy (LIBS) has been evaluated for determination of appropriate uranium lines for real-world samples such as uraninite in air at atmospheric pressure. NIST Standard Reference Material (SRM)s were used to evaluate the spectral interferences on detection of uranium lines. The background from continuum and molecular emission significantly influence the uranium detection. Time-resolved dependence of LIBS plasmas from uranium was characterized. Additionally, the isotope shifts of uranium atomic and ionic lines have been demonstrated for two different levels of uraninum standard samples. Data show the LIBS technique in air at atmospheric pressure can be applied for isotopic analysis of spectral emission of U I (423.167 nm) and U II (424.437 nm) lines with reasonable spectral resolution.

(229) (**Wavelength Effect on Detection Limits in nano- and femtosecond-LA-ICP-MS**; Nicole L. LaHaye[1], Prasoon K. Diwakar[1], Sivanandan S. Harilal[1], Ahmed Hassanein[1]; [1]Purdue University

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is a widely used technique in solid sample mass analysis. Laser ablation (LA) is preferable to other techniques because it allows direct analysis of solid samples without preparation and requires smaller sample size. LA as a sample introduction technique, however, faces several challenges in accuracy and precision of results, in particular elemental fractionation, defined as the change in elemental ratio as a function of time or preferential ablation of particular elements in the sample. The use of femtosecond (fs) lasers

in sample ablation is preferable to nanosecond (ns) lasers due to the lack of melting and thermal effects, which can increase elemental fractionation and cause collateral damage to the sample. This paper explores the effect of wavelength (fs: 800nm and 400nm; ns: 1064nm, 532nm, and 266nm) and energy on signal intensity, reproducibility, and detection limits. Wavelength has a profound effect in ns-LA—shorter wavelengths produce less heating and melting effects and also reduce plasma shielding, producing less elemental fractionation—but wavelength effects in fs-LA have not been studied in detail. Four different NIST glass standards were used to produce calibration curves and determine the detection limits of six elements (Fe, Cu, Sr, Pb, Th, and U). Though wavelength is not generally believed to have an effect in fs-LA-ICP-MS because the short pulse duration does not allow for plasma shielding, our results show an increase in signal intensity for shorter wavelengths, allowing for lower detection limits. Elemental ratios vary significantly as a function of wavelength in ns-LA but stay constant in fs-LA, demonstrating the important effects that wavelength has on elemental fractionation in ns-LA-ICP-MS.

(230) **Fluorescence Imaging of Analyte Profiles in an Inductively Coupled Plasma with Laser Ablation as a Sample Introduction Source**; Lance Moses[1], Paul Farnsworth[1]; [1]Brigham Young University

The locations of aerosol vaporization, atomization, and ionization, relative to the sampling cone of an inductively coupled plasma mass spectrometer largely determine the efficiency of transmission through the vacuum interface between the plasma and the mass analyzer. Due to diffusion, ions created too far upstream from the sampling cone may not be detected, nor will the contents of particles that are not completely vaporized before reaching the sampling cone. Optimal instrument sensitivity is achieved when ions are created on the plasma axis, close to the sampling orifice. In a 2006 paper, Mills et. al.1 studied the effects of power, nebulizer gas flow rate, and matrix additions on ion production and transmission in a solution based ICP-MS instrument. Using an iCCD to collect laser induced fluorescence, Mills et. al. obtained high resolution images mapping the relative densities of Barium species in the ICP. Maps of ion densities as a function of nebulizer flow rate provided direct information about the influence of nebulizer flow on ion distributions in the plasma. Fundamental differences between solution based systems and laser ablation-ICP-MS (LA-ICP-MS) systems, namely aerosol properties and gas environment, motivate similar work to be done using laser ablation as the sample introduction source. Using methods similar to Mills et. al., we have mapped barium ion densities between the load coil and the sampling cone of an ICP-MS as a function of nebulizer gas flow rate and nebulizer gas composition. In this poster, we will present the first results of our mapping experiments.

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(231) **From Sample to Signal: A Comprehensive Study of the Influence of Laser Parameters on fs-LA-ICP-MS**; Prasoon Diwakar[1], Nicole LaHaye[1], Jhanis Gonzalez[2], Dayana Oropeza[2], Richard Russo[2], Ahmed Hassanein[1], Sivanandan Harilal[1]; [1]Purdue University, [2]Lawrence Berkeley National Laboratory

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has become a widely used analytical technique for elemental and isotopic analysis of solid samples for a variety of applications. The technique allows analysis of any sample in atmospheric pressure conditions with minimal or no sample preparation making it very suitable for rapid chemical analysis of major and minor constituents in the sample. Additionally, the technique offers high sensitivity, large dynamic range and miniscule sample intake (minimum damage to the sample). The technique has been constantly evolving since its inception in 1980s and recent research has focused on improving the quantitative aspect of the technique which includes the improvement of the sensitivity, precision and accuracy of the technique. One of the major challenges for LA-ICP-MS has been matrix –dependent fractionation effect which occurs due to non-stochiometric sampling during ablation process. Matrix-matched standards are required for calibration to account for fractionation effect but such references and standards are not readily available which calls for need of laser ablation process which can eliminate or minimize elemental fractionation. Laser parameters, typically wavelength, pulse width, irradiance, repetition rate, pulse energy are the critical parameters which influence the laser ablation process and thereby influence the LA-ICP-MS signal. In recent times, femtosecond laser ablation has gained popularity owing to reduction in fractionation related issues and improved analytical performance which can provide matrix-independent sampling. The advantage offered by fs-LA is due to shorter pulse duration of the laser as compared to phonon relaxation time which results in ablation of the sample before thermal diffusion in the sample lattice minimizing thermal effects. It has been shown that fs-LA-ICP-MS shows improved analytical performance as compared to ns-LA-ICP-MS, but detailed mechanisms and processes are still not clearly understood. Improvement of fs-LA-ICP-MS over ns-LA-ICP-MS elucidates the importance of laser pulse duration on the ablation process. In this study, we have systematically studied the influence of laser pulse width (40 fs- 6 ns) and energy on LA-ICP-MS signal intensity and repeatability using brass sample. Experiments were performed using single spot ablation mode as well as rastering ablation mode and the Cu/Zn ratio was monitored. Initial results show slight pulse width effects in fs regime, while the effect becomes more pronounced when moving from femtosecond to picosecond and nanosecond regime. Optimum Cu/Zn ratio and RSDs (< 2%) were obtained in 200-400 fs regime for the given experimental condition (spot size- 100μm, laser wavelength- 800 nm, energy >100μJ, Ar flow rate- 1 lpm). Experiments were also performed to assess the influence of wavelength (1030 nm, 800 nm, 343 nm), spot size and laser frequency on LA-ICP-MS signal from brass and NIST glass standards (NIST 610, NIST 613). The results of this study provide a comprehensive picture and additional insight into complex laser ablation mechanisms influenced by critical laser parameters pursuant to quantitative matrix-independent LA-ICP-MS analysis of solids.

(232) **Use of Liquid Standard Addition into a Laser Ablation Stream for Elemental Analysis of Samples to Avoid the Need for Matrix-Matched Standards**; Melissa Zwilling[1], Jose Almirall[1]; [1]Florida International University

Elemental analyses of solid samples are often performed via laser ablation methods. These methods can include LIBS, LA-ICP-MS, and LA-ICP-OES. Although effective, these methods require the use of a matrix-matched standard to account for particle-plasma interactions such as variations in electron density, temperature, and time to reach local thermal equilibrium in the plasma. These alterations are directly related to the type of matrix being analyzed, resulting in the need for a matrix-matched standard. However, standards can be costly and difficult to find, especially if the composition of the sample matrix is unknown. Therefore, a method is needed for determining the concentration of a solid sample without the need for a matrix-matched standard. Here, we introduce a nebulized solution of known elemental concentration into a stream of laser ablated particles prior to ionization and detection. The concentration of the solution is increased in consecutive trials, resulting in a standard addition method for determining the concentration of an unknown solid. This method will be applied to an LA-ICP-OES system using samples of forensic interest such as float

glass and latex paint samples. Houk et al [1] has demonstrated that a similar method resulted in comparable accuracy and precision between samples with and without matrix-matched standards. Two separate methods will be used to determine the mass of the ablated sample. The ablated mass will be measured directly with a piezobalance and compared to calculations of mass using the density of known solid samples and the crater volume as determined with a Keyence digital microscope. These methods may be applied to any laser ablation system, and assist in the quantitative analysis of materials without the need for a matrix-matched standards.

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(233) **Bioimaging of Trace Metal Distribution in Rice Seeds (Oryza sativa) by LA-ICP-MS**; Priyanka Basnet[1], Dulasiri Amarasiriwardena[1]; [1]School of Natural Science, Hampshire College

Rice is a staple food source in many parts of the world and a major source of carbohydrates, proteins and nutritional elements (i.e., zinc) but it also tends to bio accumulate toxic elements such as arsenic and lead [1]. Laser ablation inductively coupled mass spectrometry (LA-ICP-MS) has been elegantly used for variety of solid, biological and environmental matrices [2]. In this study, a method was developed to determine the trace metal spatial distribution within the tissues of rice (*Oryza sativa*) seed using LA-ICP-MS. Rice seeds were prepared by embedding onto resin blocks and were dissected to thin sections for LA-ICP-MS analysis. Trace metals, ^{66}Zn, ^{75}As, ^{111}Cd, ^{121}Sb and ^{208}Pb, were analyzed by ablating three lines across the seed. Carbon (^{13}C) was used as an internal standard to account for the difference in the amount of sample ablated. For quantification purposes a suite of multi-elemental spiked cellulose standards (0-39.9 µg/g) was prepared and linear calibration functions were obtained. The optimized laser conditions were used to ablate both standards and samples: 60% energy, 10 Hz rep rate, 50µm spot size and a speed of 50µm/s using 213 nm UV laser. Zinc concentrations were highest in the embryo followed by the endosperm. Rice grown in Sb contaminated rice fields from China demonstrated elevated Sb, Cd and Pb in various grain tissue regions with a general order of Zn>Sb>Pb~Cd>As. The ablated seeds from a contaminated field showed clear presence of Sb with highest concentrations located in the husk (8.6µg/g), followed by bran (3.8µg/g) and endosperm (1.2µg/g). Quantified bio images of trace metal distributions in rice seeds from several origins will be presented. Our approach offered insightful tissue level trace metal distributions in rice grain, which can be beneficial for research on seed development and rice cultivation.

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[2] Durrant SF, and Ward, NI, (2005) *J. Anal At Spectrom.*, 20:821–829.

(234) **Analysis of Laser-Induced Aerosols in LA-ICP-MS: Role of Wavelength in Elemental Fractionation**; Peter deVietien[1], Prasoon Diwakar[1], Sivanandan Harilal[1], Ahmed Hassanein[1]; [1]Center for Materials under Extreme Environment, School of Nuclear Engineering, Purdue University

Laser ablation (LA) inductively coupled plasma mass spectrometry (ICP-MS), particularly with nanosecond lasers, has become a widely used analytical technique for elemental and isotopic analysis of solid samples for a variety of applications. Femtosecond LA has shown superior results as compared to nanosecond LA sample introduction and analysis in ICP-MS. Owing to its lower cost and field portability, ns lasers are still preferred over fs laser counterpart for sample introduction in ICP-MS which provides motivation for research in understanding fundamental processes in ns-LA-ICP-MS. Elemental fractionation has been one of the major challenges in LA-ICP-MS which can occur during three stages: ablation, transport, and during ionization. This study focuses on fractionation effects occurring during laser ablation, particularly the effect of ns laser wavelength on fractionation. An Nd:YAG ns laser operating at 1064, 532, and 266 nm wavelengths was used to ablate a brass sample, with varying transport gas flow rates (0.4-1.8 L/min) and varying laser pulse energies (0.1-8 mJ). These range of parameters affect the ICP-MS signal intensity at each wavelength studied and predicting an optimum range for both energy and flow rate. The signal intensity of the ICP-MS increases with decreasing wavelength indicating higher sensitivity at shorter wavelengths. Our results indicate that lower laser energy and fewer number of laser shots are required to obtain stoichiometric Cu/Zn ratio for shorter wavelengths. White light interferometry was used to determine aspect ratio of the craters. The role of various parameters including wavelength, laser pulse energy, aerosol flow rate, crater aspect ratio, and particle size distribution is discussed in detail along with theoretical predictions that provide more insight into the causes of elemental fractionation in ns-LA-ICP-MS.

(235) **Density and Temperature Evolution of nano- and femtosecond Laser Ablation Plumes in Vacuum and Ambient Air Environment**; Justin R. Freeman[1], Brandon Verhoff[1], Prasoon K. Diwakar[1], Sivanandan S. Harilal[1], Ahmed Hassanein[1]; [1]Purdue University

Laser-induced breakdown spectroscopy (LIBS) is a widely used technique for elemental detection of unknown materials through analysis of spectral emission features of the produced plasma. The advantage of LIBS over other detection techniques is that it offers in situ material analysis with minimum sample preparation and provides near real-time results. However, there are some issues in using LIBS, such as elemental fractionation and matrix effects, that must be carefully understood in order to provide accurate results. Methods studied to overcome these issues include using different laser-target heating geometries, double-pulse ablation schemes, different wavelength lasers, and shorter laser pulses. Recent advancements in femtosecond (fs) laser technology have led to the development of fs LIBS, which offers several advantages over conventional nanosecond (ns) LIBS. Femtosecond LIBS plasmas provide reduced continuum and atomic plume due to of lack of plasma heating by the laser beam, thereby offering improved spectral quality, especially at earlier times of the plasma lifetime. However, more systematic studies on fs-produced plasma properties are necessary for optimizing laser-produced plasma applications. We compared the spatial and time evolution of electron density and temperature for ns and fs LIBS plumes by employing optical emission spectroscopy. For producing the LIBS plumes, 800 nm 40 fs pulses from a Ti:Sapphire laser or 1064 nm 8 ns pulses from a Nd:YAG laser were focused on a brass target in vacuum or in ambient air environment. Brass is an often studied target material because of its binary composition of copper and zinc, each displaying significantly different melting temperatures of 1068 °C and 420 °C, respectively. For comparing ns and fs LIBS plasmas, similar laser fluence levels are used, though the power densities differ by five orders. Because of the substantial difference in pulse durations and subsequent laser heating and ablation mechanisms of the two lasers, marked differences between the two laser-produced plasmas are seen. The Boltzmann method and the Stark Broadening method are used to estimate plasma temperature and density, respectively. The advantages and disadvantages of using fs LIBS over ns LIBS are discussed in detail.

(236) **Time Resolved Powerchip Laser Diagnostics: Beyond the McWhirter Criterion**; Jonathan Merten[1], Ben Smith[2], Nicolo Omenetto[2]; [1]Arkansas State University, [2]University of Florida

The McWhirter criterion was initially put forth as a necessary "but not a sufficient condition for a plasma to be in LTE." [1] Cristoforetti et al. have recently reminded the LIBS community of the importance of further evaluating the plasma's spatial and temporal gradients for LTE, pointing out that the gradients must be gentle enough that electron collisions can counteract the perturbation inherent in plasma evolution. [2] These additional considerations are particularly relevant in rapidly evolving powerchip laser (PCL) plasmas, which generate a few nanoseconds of relatively weak continuum followed by a brief (~100 ns) period of atomic emission. Powerchip Nd:YAG lasers have been commercially available for several years now, but have not become popular in the LIBS community. They can produce pulses of several tens of microjoules with sub-nanosecond pulse widths at repetition rates up to several kilohertz thanks to their passive Q-switches and thermally efficient diode laser pumping. Their high beam quality and short pulse width allow focused irradiances in excess of 10 GW/cm2. Unfortunately, the passive Q-switches in powerchip lasers result in pulse to pulse jitter of ~7 μs, making standard time-resolved measurements impossible. We have circumvented this problem with a low insertion delay ICCD and a 70 ns optical delay line. We present here the first time-resolved measurements (8 ns resolution) of PCL LIBS plasma evolution, including temperature and electron number densities. We evaluate the plasmas for LTE both in terms of the McWhirter criterion and the temporal gradient parameters presented in Cristoforetti et al. Experiments are carried out in argon, air and helium atmospheres, a novelty in this type of plasma. The results have implications for the extension of calibration-free LIBS to these diminutive plasmas and may be relevant to the other low energy, pulsed solid-state lasers making their way into LIBS research.

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(237) **Effect of Electrode Characteristics and Ambient Gas on the Sensitivity of Aerosol Measurement using Spark Emission Spectroscopy**; Prasoon Diwakar[1], Pramod Kulkarni[2]; [1]Center for Materials under Extreme Environment, School of Nuclear Engineering, Purdue University, [2]Centers for Disease Control and Prevention (CDC), National Institute for Occupational Safety and Health (NIOSH)

Spark emission spectroscopy is pulsed microplasma analytical technique which offers simple, robust and low-cost approach for near real-time analysis of elemental composition of aerosols. An aerosol preconcentration method that allows near-real-time measurement of aerosols using spark plasma spectroscopy at absolute mass detection limits in the range of 11 pg-5 ng has been developed at NIOSH (Diwakar and Kulkarni, J. Anal. At. Spectrom., 27:1101, 2012). The method involves collection of aerosol on a tip of 500 μm tungsten electrode, followed by ablation and atomization by a pulsed spark plasma and detection of emission spectra. Effect of electrode size (100, 250, 500 μm) and material (W, Pt, Rh), and the type of carrier gas (He, N, Ar) on the sensitivity and detection limits of our method was further investigated in this study. Results suggest that the smaller diameter electrodes result in a greater analyte signal enhancement; the 100 μm electrode gave an enhancement of a factor of 2 over 250 μm electrode. Carrier gas perhaps had the strongest influence on the signal. For a 100 μm electrode, the absolute analyte signal intensity increased by a factor of 2.5, 4, and 10, compared to that in air, when the carrier gas was He, N, and Ar respectively. Ar resulted in maximum enhancement in signal intensity (factor of 10) resulting in improved sensitivity of the technique; however also resulted in higher background intensity. No significant effect on signal intensity was observed for different electrode materials. Detection limits in sub-picogram levels can be achieved for many elements by employing 100 μm electrode in Ar carrier gas. Measurements of electron density and excitation temperature are presented and atomic emission enhancement mechanisms are discussed.

(238) **Signal Enhancement Effects by Co-Existing Carbon in Inductively Coupled Plasma Mass Spectrometry and Inductively Coupled Plasma Optical Emission Spectrometry**; Daisuke Suzuki[1], Yoshinari Suzuki[1], Naoki Furuta[1]; [1]Chuo University

It is well known that signals of elements, such as arsenic (As) and selenium (Se), whose ionization energy (I.E.) is about 10 eV are enhanced by co-existing carbon in analysis with using inductively coupled plasma (ICP). This phenomenon has been considered to be caused by charge-transfer (CT) reaction from C^+ or CH^+ to analyte. However, it is difficult to explain that the signal enhancement is caused by CT only. Because, the signal enhancement has been observed not only in ICP mass spectrometry (ICP-MS), but also in ICP optical emission spectrometry (ICP-OES). In this study, carbon and analyte were separately introduced to ICP via pneumatic and ultrasonic nebulizers, respectively, and two samples were merged in front of a plasma torch. Finally, we quantified the change of sample introduction efficiency, plasma temperature, and other factors due to co-existing carbon in ICP-MS and ICP-OES. While the carbon solutions or mixed solutions (carbon and analyte) were introduced into ICP by a flow injection method via a pneumatic nebulizer, an analyte solution or ultrapure water were continuously introduced into ICP via an ultrasonic nebulizer, respectively. As, Se, and Cu were measured at m/z = 75, 82, and 63 in ICP-MS, and 189.042, 196.060, and 324.754 nm (all atomic lines) in ICP-OES, respectively. We tried to explain the signal enhancement by the change of sample introduction efficiency, plasma temperature, and other factors. As other factors, CT was considered in general. To evaluate this CT effect, we checked whether the signal enhancement occurred or not by co-existing bromine (I.E.: 11.81 eV) instead of carbon (I.E.: 11.26 eV). As the result, As, Se, and Cu signals were not enhanced by co-existing bromine. So, we concluded that CT is not a main factor for the signal enhancement by co-existing carbon. Instead of CT, the change of sample introduction efficiency, plasma temperature, and other factors will be discussed in this presentation.

(239) **Comparing Theory and Experiment for Analyte Transport in the First Vacuum Stage of the ICP-MS**; Matthew Zachreson[1], Ross Spencer[1]; [1]Brigham Young University

The Direct Simulation Monte Carlo algorithm as coded in FENIX has been used to model the transport of trace ions in the first vacuum stage of the inductively coupled plasma mass spectrometer. Haibin Ma of the Farnsworth group at Brigham Young University measured two radial trace density profiles: one .5 mm upstream of the sampling cone and the other 10 mm downstream. We have been comparing simulation results from FENIX with the experimental results. We find that gas dynamic convection and diffusion are unable to account for the experimentally-measured profile changes from upstream to downstream. Including three-body recombination, however, makes it possible to account for the way the profiles change. This and other results, both from the simulation and from a fluid code, will be presented.

(240) **Glow Discharge Imaging Spectrometry with a Tilting Interference-Filter Spectrometer**; Andrew Storey[1], Steven Ray[1], Carsten Engelhard[-2], Volker Hoffmann[-3], Wolfgang Buscher[-2], Maxim Voronov[-3], Gary Hieftje[1]; [1]Indiana University, [2]University of Münster, [3]Leibniz Institute for Solid State and Materials Research Dresden

Glow discharge spectrometry has been applied widely to bulk and depth analyses of solid samples. Recently, several modified spectrometers have been utilized also for imaging the emission from a glow discharge, to provide information about the lateral distribution of elemental composition. Many recent related efforts have focused on improving analytical performance of the glow discharge sources and application of the methods to laterally heterogeneous samples. A simpler imaging instrument is explored here that uses a tilting interference filter for spectral discrimination to yield both spatial and spectral information about solid samples. Similar instruments have long been applied in astronomy for monochromatic imaging of faint cosmic phenomena and also in time-resolved fluorimetry. Tilting-filter spectrometers boast higher optical throughput and better spatial resolution than many other spectral-imaging techniques. The method will be evaluated in terms of its figures of merit based on experimental data and theory, imaging data from heterogeneous samples, and where this method fits into the spectral-imaging toolbox for glow discharge spectrometry. The potential for three-dimensional elemental profiling by the combination of this spectral-imaging technique and quantitative depth profiling will be discussed. A three-dimensional optical profiling instrument has been used to characterize the glow discharge craters generated from laterally heterogeneous samples sputtered with pulsed radio-frequency and direct-current glow discharges.

(241) **Depth Profiling Characterization by a novel plasma TOF MS technique**; Philippe Hunault[1], Christophe Morin[1], Agnes Tempez[-2], Patrick Chapon[-2]; [1]HORIBA Scientic Elemental Analysis - Edison, NJ - USA, [2]HORIBA Jobin Yvon SAS - Longjumeau France

Plasma Profiling Time of Flight Mass Spectrometry couples a plasma source fed with pure Ar and created under a pulsed RF potential with an orthogonal time of flight mass spectrometer (TOFMS). This depth profiling technique allows fast (minutes) and direct analysis of ultra-thin to -thick conductive and non-conductive layers with nm depth resolution. Transient signals generated by the pulsed RF potential are monitored. The more intense signals detected in the plasma extinction phase (once the RF is turned off—the so-called afterglow region) are extracted for high sensitivity. Applications range from thin film analysis for composition, contamination detection, and doping level to characterization of diffusion mechanisms. Various examples from photovoltaics, photonics corrosion science materials will be given and compared to other surface techniques.

(242) **Glow Discharge Analytical Plasmas with OES or TOF MS Detection for Depth Profile Characterization of thin Film Solar Cells**; Philippe Hunault[1], Christophe Morin[1], Agnes Tempez[-2], Celia Olivero[-2], Sebastien Legendre[-2], Patrick Chapon[-2]; [1]HORIBA Scientific Elemental Analysis, [2]HORIBA Jobin Yvon SAS

Technologies for PV evolve very rapidly with a marked trend towards thin films. The driving force for the researches is the cost and thin films technologies have the needed cost reduction potential. The films can be Si based with various dopants, CdTe, CIGS, organic films. Hybrid configurations are also subject to intense researches with layers made for instances from Si nanowires coupled to organic layers, nanoparticles deposited inside layers etc. Researches are also made on alternative substrates (compared to bulk glass) to create flexible cells. However if the materials evolve and change rapidly the needs for characterisation and control are now well identified. Thin film technologies involve a number of operations to be performed and key parameters to be followed carefully (including time, temperature etc – any variation to the optimum conditions inducing major defects in the final product). Therefore rapid measurement to assess performances and provide immediate feedback to the process, capability to look at thin/thick films (a "thin" film is less than 1 micron ; cells have now a total thickness of 3-5 microns with most layers being less than 1 micron thick) and capability to look at major and traces or follow up of gradients are crucial. Glow Discharge Optical or Time of Flight spectrometries rely on the controlled erosion of a representative part of the material (2-8mm diameter) by a dense RF plasma and provide the distribution of species as a function of the penetration depth. Ultra Fast techniques (3 minutes only are needed to sputter out for instances all layers of chalcopyrite solar cells) they nevertheless offer nanometre depth resolution and are therefore ideal to detect composition changes, interface contamination or gradients. Various examples taken from cooperative works will illustrate the capabilities of these techniques for PV thin films.

(243) **Metastable Atom Formation in a Millisecond Pulsed Glow Discharge**; Kyler Robinson[1, 2]; [1]OSU-UML, [2]University of Tulsa

The glow discharge plasma is a common ion source for analytical applications such as mass spectrometry and optical emission spectroscopy. Several modes of operation exist for the plasma, including direct current, radio frequency, and pulsed. Although each has their own distinct advantages, this study has focused on pulsed plasmas. Glow discharges that are pulsed create three distinct temporal regions: the prepeak, the plateau, and the afterglow. Studying the temporal regions gives insight to excitation and relaxation processes of the gas-phased plasma species. While much work has been performed on pulsed glow discharges in the past decade, the temporal evolution of the distribution of plasma species has not been researched thoroughly in plasmas other than argon. In order to understand the processes better it is necessary to examine the characteristics of different plasma gases- such as krypton and xenon. In this study the spectroscopic spatial and temporal characteristics of krypton and xenon millisecond glow discharge plasmas will be presented over the pulse cycle.

(244) **Mechanisms for Population Inversion in the Prepeak of Pulsed Glow Discharge Plasmas**; Tim Gustafson[1, 2]; [1]OSU-UML, [2]Oklahoma State University

Pulsed glow discharges are characterized by three different temporal regions: prepeak, plateau, and afterglow. Several reports have demonstrated how each temporal region is dominated by differing ionization mechanisms. The majority of these reports have focused on elucidating the ionization mechanisms of the plateau and afterglow regions. It has been found that ionization during the plateau region is the result of a mixture of electron ionization, charge exchange, and Penning ionization. In the afterglow region, applied power is terminated and ionization is accomplished from collisions with metastable atoms by Penning ionization. To date, researchers have attributed ionization in the prepeak to electron ionization. However, the population inversion during the prepeak between doubly charged and singly charged working gas ions, observed by several research groups, cannot be accounted for by electron ionization. This study continued the examination of the Auger effect as a possible mechanism for this population inversion. The prepeak has been observed in different inert gas plasmas to document the population inversion in each. The prepeak in argon, krypton, and xenon has been compared with helium to test the Auger effect as the mechanism responsible for the population inversion.

(245) **Advances in Detectors for FTIR Imaging**; Christopher Lynch[1], Richard Spragg[, 2], Andrew Turner[, 2], Robert Hoult[, 2], [1]PerkinElmer LAS Shelton CT, [2]PerkinElmer LAS Seer Green UK

Applications of FTIR imaging with MCT array detectors have grown over the past ten years. However the available wavelength range has

been restricted. Staring 2-dimensional arrays have photovoltaic detector elements with a cutoff above 900cm-1. The linear arrays used in the alternative pushbroom scanning systems employ photoconductive elements that have allowed them to reach approximately 700cm-1. Recent developments have extended this limit to around 500cm-1, increasing the range of applications. This extended range is of particular interest for measurements of minerals and of crystallinity in a variety of materials. We describe and illustrate the performance of an imaging system with an extended range array. Among the applications facilitated is imaging of the crystallinity in bone using splitting of the phosphate band near 580cm-1. With earlier imaging systems crystallinity had to be estimated from intensity ratios within the unresolved bands around 1050cm-1. The lower absorbance of the 580cm-1 band allows measurements on samples where the absorbance at 1050cm-1 is too high. MCT arrays have normally been used for imaging in both the mid-IR and the near IR. We have investigated a customized InGaAs array for imaging in the near IR to 4000cm-1. As well as removing the need for cooling with liquid nitrogen this provides a factor of two sensitivity improvement over MCT , allowing images with the same signal-to-noise performance to be obtained in a quarter of the time.

(246) **Evaluation of Thermal Infrared Sources for AC Imaging Applications**; Nick Boltin[1], Scott Hoy[1], Stephanie DeJong[1], Stephen Morgan[1], Michael Myrick[1]; [1]University of South Carolina

We have been working on infrared reflectance imaging using a low-cost microbolometer-array camera. This requires AC modulation of an infrared light source combined with lock-in detection. This presentation will focus on the characteristics of IR light sources that are applicable for AC-modulated imaging. These characteristics include: total power, spectral distribution(focusing on 7 -14 micron wavelength), cost, availability and/or ease of construction, voltage and current, modulation power, and angular distribution. Some of the sources we have explored are: a large area hot plate, Hawkeye Technologies IR-18 and IR-12K, and a custom fabricated source from metal wire.

(247) **A New Truly Easy-to-Use Dedicated Infrared Microscope**; Thomas Tague[1], Sergey Shilov[1], Fred Morris[1], Matthias Boese[1]; [1]Bruker Optics, Inc

A new stand-alone infrared microscope (LumosTM) has been developed for the rapid analysis of small samples. The new microscope was developed with the intent of providing state-of-the-art microanalysis capabilities with a truly easy-to-use user interface. The visual image quality of the Lumos is excellent so the important first step in the analysis, visualization, is easily accomplished. The Lumos utilizes a unique objective design, where the numerical is low for sample viewing and high for the infrared data collection. This makes it very easy to locate and view the sample without sacrificing infrared performance. The novel Wizard user interface controls all aspects of the microscope and guides the user through the analysis process. The sample stage, sample focus assembly, condenser, aperture, polarizers, and ATR mode are controlled in the software providing true "point and shoot operation". The motorized stage has encoded sample plates to allow for automatic recognition of microsampling accessories, such as well plates, rotating inserts, etc. ATR microanalysis is accomplished by simply clicking on the area of interest in the software to center it and selecting ATR. The ATR crystal is automatically lowered and ideal contact made with the sample without any user intervention. Area reflection, transmission, and ATR images are collected by simply drawing the desired analysis and starting the desired acquisition. The image processing software interface provides research quality analysis tools with an intuitive interface. The Lumos incorporates an integrated rugged interferometer that is extremely efficient. The close proximity of the interferometer to the sample provides unmatched throughput and sensitivity. The patented "RockSolidTM" interferometer is permanently aligned and proven to be durable. The reference laser is a diode laser yielding an expected lifetime of over ten years for the entire system. The Lumos also has a unique ability to readily analyze samples with traditional sampling accessories. A port is provided to attach accessory modules from Bruker's Alpha FTIR Series. Standard ATR, transmission, reflection, and even gas cell analysis can be readily conducted with the Lumos. Lastly, the Lumos comes with a comprehensive validation package to support any range of validation requirements.

(248) ***In-Situ* FT-IR Reaction Monitoring Using Standard Detector**; Matthias Rolland[1], Marc-André Laliberté[1], Mathieu Côté[1], Frederic Despagne[1]; [1]ABB Inc.

The MB-Rx is an in-situ chemical reaction monitor designed for laboratories and pilot plants. It provides chemists with real-time insight into chemical or biochemical reaction kinetics and key parameters (intermediates, products, by-products). The MB-Rx allows an easy and simple uninterrupted access to in-situ reaction monitoring thanks to the DTGS detector that does not required liquid nitrogen or expensive sterling cooler. Three different pre-aligned probes, achieving a limit of detection of 0.1% acetone in toluene, are available to monitor a wide variety of chemical compound syntheses. This poster will focus on the following three syntheses:

- Artificial flavor, used as aroma in alcohol-free drinks, ice, candies, gelatins and other products of current life;
- Carbamates, used in the production of paints, solvents, pharmaceutical products and insecticides;
- Polyurethanes, used for their resistance to high and low temperatures, chemicals, sunlight degradation or mechanical stress and for their excellent insulation properties regarding electricity, temperature and noise.

Using the MB-Rx for those chemical syntheses offer direct benefits such as increasing the profitability of the artificial flavor synthesis by optimizing the reaction instead of perfecting the purification process. Also, MB-Rx can reduce the safety concern of human manipulations of the precursors during carbanates synthesis or can improve the quality of the polyurethanes by matching their properties to the targeted applications. MB-Rx shows direct advantages than can be applied for other chemical syntheses.

(249) **Adaptable Infrared Surface Plasmon Resonance Spectroscopy Accessory**; Nicola Menegazzo[1], Laurel Kegel[1], Yoon-Chang Kim[1], Derrick Allen[1], Karl Booksh[1]; [1]University of Delaware

A second generation prototype enabling surface plasmon resonance (SPR) spectroscopic measurements in the infrared (IR) range is described. The new design (v2) uses the optical train (optics and detector) within conventional FT-IR spectrometers by confining dimensions of the accessory to space available within the sample compartment of the spectrometer The v2 accessory builds upon knowledge gained from a previous version that was based on a modified commercial variable angle spectroscopic accessory and addresses observed limitations of the original design - improved temporal stability and measurement acquisition speed, crucial to biomolecular binding studies, as well as optical flexibility, a requirement for investigations of novel plasmon-supporting materials. Different aspects of the accessory, including temporal stability, mechanical resilience and sensitivity to changes in refractive index of a sample were evaluated and presented in this contribution.

(250) **Increasing the Resolution and Capabilities of the Czerny-Turner Imaging Spectrograph though a Novel Design Variant**; Jason McClure[1]; [1]Princeton Instruments

Traditional Czerny-Turner (CT) type imaging spectrographs suffer from optical aberrations that reduce spectral resolution and diminish the usable portion of the instrument's focal plane array detector. The

CT type spectrograph is by far the most commonly used research instrument for dispersive optical spectroscopy and over the past 20 plus years has seen little to no improvement. Image aberrations inherent to this type spectrograph are well understood and impart distortions to recorded spectra that affect resolution both spatially and spectrally. Understanding the effect these aberrations have on spectral data, however, are typically left as an exercise for the researcher. We present the discovery of a novel variant to the traditional CT spectrograph, the Schmidt-Czerny-Turner (SCT) anastigmatic imaging spectrograph. The SCT spectrograph is shown to be free from all the offending image aberrations of its predecessor. The three major offending image aberrations present in the traditional CT type spectrograph, Spherical, Coma, and Astigmatism are discussed with respect to the effects they have on spectral data. Results are discussed in comparison to traditional CT spectrographs of nearly equivalent f/# and focal length where standard spherical and toroidal optics are implemented. With a focal length and aperture ratio of 320 mm at f/4.6 respectively, this novel design exhibits a 7-fold gain in fluence at the focal plane extremities and a 30% increase in spectral resolution. The scope of experiments and techniques now made possible by the Schmidt-Czerny-Turner spectrograph are also discussed.

(251) **Sensei: Innovative Optical Dispersive Spectrometer Design Platform which Increases Throughput >10 Times without Sacrificing Spectral Resolution**; Jeffrey Meade[1], Bradford Behr[1]; [1]Arjae Spectral

High-resolution optical dispersive spectrometers have been limited in optical throughput due to a fundamental design in spectrometers; i.e. the entrance slit, or in scanning monochrometers, the exit slit. In all spectrometers, the slit rejects most of the light in order to achieve high spectral resolution, bringing the total optical efficiency of a high-resolution dispersive spectrometer down to <1% in most applications. Arjae Spectral has introduced spectrometers which present a new approach for improving spectral resolution. Arjae's spectrometer platforms (currently Raman and hyperspectral) have been designed to incorporate a high throughput virtual slit (HTVS), a patented innovation. These spectrometers use a larger input aperture (for maximum throughput) in combination with a series of specially configured mirrors, lenses, and other elements to preserve total flux, allowing the delivery of dramatic performance improvements. The HTVS innovation modifies the shape of the beam in the spectrometer with close to 100% total optical efficiency. This technological breakthrough reproduces the high-resolution effect of a conventional slit by reformatting the shape of the beam while maintaining the focal ratio. However, unlike previous optical image reformatters, this device operates in pupil space, making it robust and manufacturable as it does not use complex moving parts. The net benefit is that the classic trade-off between resolution and throughput in a dispersive spectrometer is eliminated using HTVS technology. Arjae's Sensei™ spectrometers achieve both high spectral resolution and high optical throughput simultaneously over a large spectral bandwidth. Two configurations of the spectrometer have been demonstrated; one in the visual bandpass and one in the NIR bandpass. The two spectrometers are well-suited for Raman spectroscopy with peak throughput efficiencies at 600 nm and 950 nm respectively. The VIS spectrometer operates over the wavelengths 480-680 nm (+2030 to -4090 cm-1 shift from 532 nm) with a spectral resolution of 0.24 nm (<7 cm-1 at 600 nm), while the NIR spectrometer operates over the wavelengths 730-1100 nm (+960 to -3640 cm-1 shift from 785 nm) with a spectral resolution of 0.75 nm (<9 cm-1 at 950 nm). Results have shown a 10-15x increase in collected Raman signal compared to similarly classed Raman spectrometers.

(253) **An Integrated *in situ* Raman and Turbidity Sensor for High Level Waste Tanks**; Christina Gasbarro[1], Job Bello[1], Anton Smirnov[1], Samuel Bryan[2]; [1]EIC Laboratories, Inc., [2]Pacific Northwest National Laboratory

Stored nuclear waste must be retrieved from storage, treated, separated into low- and high-level waste streams, and finally put into a disposal form that effectively encapsulates the waste and isolates it from the environment for a long period of time. Before waste retrieval can be done, however, waste composition will need to be characterized so that proper safety precautions can be implemented during the retrieval process. In addition, there is a need for active monitoring of the dynamic chemistry of the waste during storage since the waste composition can become highly corrosive. This work describes the development of a novel, integrated fiber optic Raman and light scattering probe for in situ use in nuclear waste solutions. The dual Raman and turbidity sensor provides simultaneous chemical identification of nuclear waste as well as information concerning the suspended particles in the waste using a common laser excitation source.

(254) **Persistent Nanoparticles - Where Do They Accumulate**; Detlef Günther, Tobias Walser[2, 3], Wendelin Stark[2], Stefanie Hellweg[3], Ludwig Limbach[2], Karin Birbaum[1], Robert Brogioli[1]; [1]Laboratory of Inorganic Chemistry, D-CHAB, ETH Zurich, [2]Institute for Chemical and Bioengineering, D-CHAB, ETH Zurich, [3]Institute of Environmental Engineering, D-BAUG, ETH Zurich

More than 100 million tons of municipal solid waste are incinerated worldwide every year and little is known about the fate of nanomaterials during incineration. 10 kg cerium oxide nanoparticles added to 7 t waste and 1 kg sprayed into the furnace were given into a full-scale incineration plant. Residues from the combustion process were filtered efficiently from flue gas and found to contain some loosely bound nano-cerium oxide, while the persistent nano-cerium oxide did not become part of the residues and did not show any physical or chemical changes [1]. Respiration is a route of entry to the human body for released nanoparticles. Uptake studies of lung fibroblasts treated with persistent cerium oxide using four different size fractions, and concentrations ranging from 100 ng/g to 100 mg/kg, show that the amount of incorporation is size dependent, while particle number density or total particle surface area are of minor importance. We found that diffusion (20-50 nm) or sedimentation (250-500 nm) limits the transport of nanoparticles to the fibroblast cells [2]. As released nanoparticles may enter the food chain, we studied the uptake of ceria in maize. Different exposures of cerium oxide demonstrated that the absorption or incorporation of CeO2 nanoparticles does occur at concentration levels of < 50 mg cerium/kg leaves. The uptake was not dependent on open or closed stomata. We observed no translocation of the nanoparticles [3]. Results presented will demonstrate that nanoparticles persist in the environment presenting a challenge where analytical science is crucial and some new strategies for nanoparticle detection will be discussed.

(1)Walser et al., Persistence of engineered nanoparticles in a municipal solid waste incineration plant. Nature Nanotechnology 2012, doi:10.1038/nnano.2012.64

(2)L. K. Limbach et al., Oxide nanoparticle uptake in human lung fibroblasts: Effects of particle size, agglomeration and diffusion at low concentration. Environ. Sci. Technol. 2005, 39, 9370-9376
(2)K. Birbaum et al., No evidence for cerium dioxide nanoparticletranslocation in maize plants. Environ. Sci. Technol. 2010, 44, 8718-8723T.

(255) **Elemental Mass Spectrometry from Laboratory to Clinic**; Barry Sharp[1]; [1]Loughborough University

ICP-MS is the most powerful technique yet developed for elemental analysis. This arises largely because the ICP is a'hard' ionisation

source that yields almost 100% ionisation efficiency for most elements in the periodic table, compared with at best 0.1% for molecular ionisation sources such as the electrospray. However, this performance is gained at the cost of destroying all the molecular information as molecules are broken down to their constituent atoms in the source. This problem is overcome by coupling the technique to powerful absolute or procedural separation schemes and it is through this means that its power can be used to advance understanding in the bio- and bio-medical sciences. A key property of ICP-MS is that its response is, to a first approximation, independent of chemical form and therefore when used as a detector following separation there should be a mass balance between the total elemental signal and the summed signal from separated components. Here data will be presented demonstrating the use of ICP-MS for predicting the clinical outcomes for patients undergoing Pt-based chemotherapy. In the UK, about 65% of cancer patients receive Pt-based drugs for both curative and palliative intent. Cisplatin, and the more recent variants oxaliplatin and carboplatin are used to treat a wide variety of tumours, but the clinical pathway is often dominated by toxic side effects that prevent patients from receiving their intended doses. Current clinical practise is based on a standardised dose predicated on body surface area but this is sub-optimal for individual patients. Thus, there is a critical need to develop personalised dose models to improve outcomes, to avoid unnecessary suffering and to reduce healthcare costs. We have developed 4 assays based on ICP-MS that allow: the number of Pt-DNA adducts (DNA is the target molecule) per nucleotide pair to be quantified; the speciation of the major adduct forms namely those with guanine and adenine bases; the partitioning of the drug in the major cell compartments; and quantification of DNA through its P content. Patient data will be presented that indicate how these assays may be used to predict clinical outcomes.

(256) **Single-Cell Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for Deep Profiling of the Human Hematopoietic System**; Sean Bendall[1], Erin Simonds[1], Garry Nolan[1]; [1]Stanford University[4]

Classical four-color fluorescence flow cytometry helped define the major cell subsets of the immune system that we understand today (i.e. T-cells, B-cells, macrophages). Machines with eight or more colors brought characterization of rare immune subsets and stem cells. With intracellular staining, higher parameter measurements lead to examination of regulatory signaling networks and patient stratification with clinical outcomes. However, this progression has now been stymied by the limit of fluorescence parameters measurable, realistically capped at 12-15 due to boundaries in instrumentation and spectral overlap considerations in fluorophore-based tagging methods. Now, a novel combination of elemental mass spectrometry with single cell analysis (mass cytometry - CyTOF) offers examination of 30-50 parameters (theoretically up to 100) without fluorescent agents or interference from spectral overlap. Essentially, heavy metal isotopes as reporters replace fluorophores. By then exploiting the resolution, sensitivity, and dynamic range of elemental mass spectrometry, on a time-scale that allows the measurement of 1000 individual cells per second, this device offers a much-simplified alternative for ultra-high content cytometric analysis. Using mass cytometry (Science, May 2011) combined with novel single-cell visualization methods (SPADE - Nature Biotechnology, Oct 2011) we examine healthy human bone marrow, measuring 34 parameters simultaneously in single cells (binding of 31 antibodies, viability, DNA content, and relative cell size). The signaling behavior of cell subsets spanning a hematopoietic hierarchy defined by this profiling was monitored with 18 simultaneous functional markers and a battery of ex vivo stimuli and inhibitors. We then go on to investigate how this cellular behavior changes during leukemogenesis – Acute lymphoid leukemia (ALL) and acute myeloid leukemia (AML). We will also provide examples of how high dimensional mass cytometry analysis can reveal previously unappreciated levels of organization in virus-specific memory T cell compartments (Immunity, Jan 2012). Together, these collective works expose unappreciated layers of human hematopoietic organization, and provide an opportunity to reevaluate diseases and pharmacological therapeutics as specific perturbations to this inherent order.

(257) **Mass Spectrometric Studies in (pre)clinical Research on Cancerostatic Metallodrugs**; Gunda Koellensperger[1], Gerrit Hermann[1], Stephan Hann[1]; [1]BOKU

In recent years, the mechanisms of metallodrug-induced cell death were extensively studied using biological/biochemical methods, i.e. addressing the involvement of metallodrugs in biochemical processes and signaling pathways in preclinical (cell models) and clinical samples. As a drawback, the biochemical methods do not allow characterizing metallodrug metabolites or metallodrug-biomolecule adducts at molecular level. Hence, the knowledge on intracellular chemistry of these drugs is still based on solution chemistry, studied by spectroscopic techniques in an environment mimicking biological situations. Elemental speciation analysis offers an outstanding tool-set capable of sensitive and selective quantification of metallodrugs and their metabolites capable of dealing with preclinical relevant concentration levels (cell model experiments involve typically drug concentrations in the < sub μM range). Therefore our major aim was the development and application of elemental speciation analysis addressing the assessment of the intracellular chemistry of metallodrugs in cancer cells. Consequently, we could relate quantitative investigations to the activity profile and resistance mechanisms of the drugs. The analytical methodologies were based on complementary inorganic and organic mass spectrometry in combination with chromatography. Investigations concerned primarily the clinically established cisplatin, however also other candidate anticancer drugs were studied in our group.

(258) **Metallomics Approaches – Powerful Methods for State of the Art Clinical, Biomedical and Environmental Research**; Joseph Caruso[1], Karnakar Chitta[1], Edward Merino[1], Julio Landero[1], Phanichand Kodali[1], Kavitha Subramanian[1], Adeoye Opeolu[1], George Deepe[1]; [1]University of Cincinnati

Metallomics studies extend to various trace metal species and their interactions with each other in animals or plants. In our labs the metallomics approaches involve combinations of chromatography, elemental mass spectrometry and molecular mass spectrometry. In this presentation, the metallomics approach allows us to study up or down regulation of zinc metalloproteins as we develop a viable model to explain how zinc assists the macrophage (white blood cell) in eliminating a lung pathogen – Histoplasma capsulatum, Hc. We utilize LC-ICPMS in tandem with ESIMS to search the Zn proteome in the macrophage and in Hc. Macrophages and their importance to human life as 'pathogen sensors' play important roles in the initiation of inflammatory responses, elimination of pathogens, and manipulation of the adaptive immune response and these are well known. Not as well known are the effects of metal ions, metal species and metalloproteins on the ability of particular macrophages to do their critical work. Although arsenic toxicity is well known, little is known about how its effects are exerted at the proteome level. Protein phosphorylation is an important post-translational modification involved in the regulation of cell signaling. In this study we identify phosphorylation in arsenic toxified cells with and without the presence of selenium - a well known as an arsenic antagonist. We find these identifications are markedly different between As toxification only or when in the presence of SeMet. For the latter we see major enhancements for cell health. Further, we see that

cytotoxicity, in the presence of SeMet, is reduced as are reactive oxygen species, ROS.

(259) **It's Raman, Just Stick a Probe in Your Batch, Right? Why Sampling is Critical.**; Ian Lewis[1], Kevin Davis[1], Sean Gilliam[1], Maryann Cuellar[1], David Strachan[1], Pat Wiegand[1], Joe Slater[1], Herve Lucas[2], Carsten Uerpmann[2], ; [1]Kaiser Optical Systems, Inc., [2]Kaiser Optical Systems, SARL

While the demonstration of new Raman applications remains important to the understanding of the wider applicability of Raman spectroscopy for industrial analysis a critical element is often overlooked – appropriate sampling. Burdensome sampling approaches requiring either extensive sample work-up or extractive sample can render the most promising laboratory analytical method inappropriate for real-time industrial process sampling. Each sample's chemical phase presents it's own unique challenges and thus different approaches are required to optimized in situ instrumentation to ensure robust Raman spectral analysis. In this presentation new developments in probe technology, micro-sampling, and alterative excitation wavelengths will be given. The presentation will include a selection of applications, the challenges associated with those applications, and the solutions developed for several different industrial market segments.

(260) **Advances of VOA in Pharma and Don**; Rina K. Dukor[1]; [1]BioTools, Inc

The top billion-dollar drugs such as Herceptin, Lipitor, Plavix, Epogen and Procrit are unique in that their active pharmaceutical ingredient (API) is either a chiral small molecule or is composed of a biologic such as protein. Both types of pharmaceuticals are the fastest growing in research & development and require additional characterization that is not needed for traditional small molecule API. For biopharmaceuticals, the stability of secondary and higher order structures and effects of formulation or addition of excipients, storage and delivery methods are critical to document and understand. For chiral drugs, absolute configuration and optical purity must be determined prior to any regulatory approval. Vibrational spectroscopy - IR, Raman, Vibrational Circular Dichroism (VCD) and Raman Optical Activity (ROA) - is uniquely positioned for the task. It has no limits on upper concentration and Raman especially is good for measurements in water. It allows measurements in states of solution, solid, gel, sprays, or with protein on a patch. ROA and VCD are measured as a difference in scattering (Raman) or absorbance (IR) of left and right circularly polarized radiation. This difference adds a 'chiral' dimension or in other words an increased sensitivity to spatial orientation that provides for answers not obtained with other methods. VCD and ROA have now gained significant use and credibility through the pharmaceutical industry, in large part due to several early adapters that include Don Pivonka! VCD has become a technique of choice for determination of absolute configuration, as it requires no crystallization, no separation, and no shift reagents and provide the easiest, fastest and most precise method for the task. For biologics, both VCD and ROA, have several advantages for elucidation of secondary and higher order structure. In this lecture, we will briefly discuss the instrumentation and provide examples of the use of VCD and ROA in (bio)pharmaceutical industry.

(261) **Otimising Image Fidelity in 3D Confocal Raman Imaging**; Neil Everall[1]; [1]Intertek-MSG

Confocal Raman microscopy is an established technology for mapping and imaging the chemical and physical structure of complex materials. It is particularly useful for the analysis of transparent or semi-transparent samples, for example by non-destructive depth profiling. It is well known that the correct choice of microscope objective is critical in order to preserve the depth resolution and spatial accuracy of depth profiles; in particular, using the standard metallurgical objectives that are routinely supplied with Raman instruments yields incorrect depth scales, poor depth resolution, and degraded spectral S/N compared with a properly corrected objective [1,2]. When depth profiling geometrically simple systems such as planar laminates it is possible to estimate the true structure using fairly simple numerical treatments, but with more complicated structures this is harder to do. Furthermore, modern confocal Raman microscopes can image structures in 3D on reasonable timescales, so it is becoming increasingly important to know how to optimise and interpret the resultant volumetric images. This presentation will consider the accuracy and quality of 2D and 3D Raman images of complex structures including laminates, coated fibres, polymer blends and dissolving beads. It will show that by using a properly corrected objective the true structure of the sample is revealed, while the image obtained with a metallurgical objective is badly distorted, often in a non-intuitive way. The size and shape of objects is displayed incorrectly, the degraded resolution makes it more difficult to resolve spatial variations in composition and structure, and the decreased spectral S/N unnecessarily lengthens the data acquisition time compared with a corrected objective.

[1] N Everall, Analyst 135, 2512 (2010)
[2] N Everall, J Lapham, F Adar, A Whitley, E Lee and S Mamedov. Appl. Spectrosc. 61, 251 (2007)

(262) **Electrospun Nanofibers: A Challenge and an Opportunity for Raman Spectroscopy**; Bruce Chase[1], John Rabolt[1], Wenqiong Tang[1], Wenwen Liu[1]; [1]University of Delaware, Department of Materials Science

The last decade has seen a tremendous resurgence in the production of nanofibers by electrospinning. Polymeric fibers with diameters ranging from 50 nanometers to 10 microns can be readily produced with potential applications in the fields of bioscaffolds, filtration, catalysis, and many others. The performance of these nanofibers is often dependent on the mechanical properties of the fibers and the non-woven mesh, with the fiber properties being driven by the molecular level strudture, orientation and morphology. Raman scattering is an ideal probe to follow the development of these molecular level properties in electropsun fibers.

(263) **Enhanced Transmission Raman Spectroscopy**; Michael Pelletier[1]; [1]Pfizer Worldwide Research & Development

The small probe volumes typical of traditional Raman analyzers can cause substantial error in the quantitative analysis of most pharmaceutical tablets due to the inherent compositional heterogeneity of these tablets. Transmission Raman spectroscopy can provide improved accuracy for pharmaceutical tablet analysis by probing a larger volume of the tablet. Photon migration leads to a much longer excitation pathlength through the tablet, causing excitation of a greater tablet volume. Ordinarily the greater pathlength through the tablet would lead to greater sensitivity, but this is not the case for transmission Raman spectroscopy. The efficiencies for getting light into the tablet, and for collecting the Raman photons that are generated are usually poor, leading to greatly reduced sensitivity compared to traditional backscattering measurements. An "optical diode" using a multi-layer dielectric mirror has been reported that recycles lost photons, increasing both sensitivity and volume sampling homogeneity. This talk will describe a different approach for increasing the sensitivity and volume sampling homogeneity of transmission Raman spectroscopy based on spatial coherence rather than the angular dependence of mirror reflectivity. Photons from the tablet that are not confocal with the excitation or collection apertures, or not within the solid angle of collection, are reflected back onto the tablet regardless of their wavelength. Benefits include achromatic performance and ease of implementation. Results using commercially-available, over-the-counter pharmaceutical tablets will be presented.

(264) **A New *in vivo* Raman Probe for Enhanced Applicability to the Body**; Paul Pudney[1], Eleanor Bonnist[1], Peter Caspers[2, 3], Jean-Philippe Gorce[1], Chris Marriot[1], Gerwin Puppels[2, 3], Scott Singleton[1], Martin van der Wolf[2, 3]; [1]Unilever Discover, [2]River Diagnostics BV, [3]Erasmus MC

This talk describes a new in vivo Raman probe that allows investigation of areas of the body that are otherwise difficult to get access to. It is coupled to a previously described commercially available in vivo Raman spectrometer which samples the skin through an optical flat. In the work presented here the laser light emerges from a smaller pen shaped probe. It thus works on the same principles as the original spectrometer with its relative performance in terms of signal to noise of the spectra and spatial resolution obtained being only slightly diminished. It allows the window to be placed against the subject in more curved and recessed areas of subject's body and also for them to be more comfortable whilst the measurements take place. Results from three areas of the body that have been very difficult to study before are described, these being the mouth, axilla and scalp. Results from the scalp and axilla strata cornea (SC) show significant differences from the 'normal' SC of the volar forearm. For instance the scalp is observed to have lower amounts of natural moisturising factors (NMF) compared to the volar forearm within the same subjects. Also for both the axilla and scalp the lipids show a change in order as compared to the lipids in the volar forearm and also differences from each other. The potential significance of these observations is discussed. Further we show how we can probe the mouth, in this case observing the presence of the astringent tea polyphenol epigallocatechin gallate within the oral mucosa.

(265) **Bioanalytical Use of Symmetrical and Asymmetrical NIR Dyes**; Gabor Patonay[1], Maged Henary[1], Garfield Beckford[1], Eric Owens[1], Andy Levitz[1]; [1]Georgia State University

Near-Infrared (NIR) absorbing carbocyanine dyes are increasingly used as reporting labels, probes, imaging agents or markers in analytical, biological and medical field. NIR dyes can be useful for studying and characterizing biomolecular interactions or developing bioanalytical methods. NIR dye characteristics such as spectral dependence on microhydrophobicity can be utilized for this purpose. NIR dyes are known to bind biomolecules which often results in significant spectral changes and fluorescence enhancement of the NIR dye. Due to this microenvironmental sensitivity of NIR dye spectra NIR dyes can be used for reporting about enzymatic, DNA or other biomolecule to biomolecule interactions. NIR dye microenvironmental sensitivity greatly depends on its structure. Most of the applications reported in the literature have used symmetrical carbocyanines in the past. Asymmetric carbocyanines have not been utilized extensively due to their more complicated synthesis. During these studies we present here we have systematically synthesized several asymmetric NIR dyes and their symmetric analogues with different solubility in aqueous environment. Aqueous solubility was modulated by adding water soluble moieties to the carbocyanines. Microenvironmental sensitivity of these dyes was characterized and their binding properties to biomolecules were determined. According to our studies water soluble asymmetric dyes exhibit higher microenvironmental sensitivity than their water soluble symmetric counterparts. The results of these studies are useful in determining what NIR dye structures exhibit high binding constants and how to optimize detection of the biomolecule NIR dye complex. Carbocyanines that are insensitive to environmental changes are useful for biomolecule reporting applications such as labels while environmentally sensitive carbocyanines are useful for biomolecule characterizations, measuring enzymatic reactions or biomolecular interactions such as protein-DNA interactions. NIR dyes that contain alkenesulfonato moieties have significant fluorescence in aqueous buffer solution. This property allows for the characterization of the alkenesulfonato monooxygenase enzyme. After enzymatic cleavage of the alkenesulfonato moiety the fluorescence decreases. The reduced fluorescence can be measured by binding the alkene NIR dye to biomolecules and measure the fluorescence enhancement. This presentation gives examples of these specific applications illustrating the utility of carbocyanines. One possible utility is determining viability of bacterial and yeast cells using NIR fluorescence.

(266) **Enhancing the Electrical Properties of 2-D single-walled Carbon Nanotube Networks**; Marcus Lay[1], Pornnipa Vichchulada[1], Nidhi Bhatt[1], Darya Asheghali[1]; [1]University of Georgia

Single-walled carbon nanotube (SWNT) soot contains up to 40 wt% impurities (such as amorphous carbon and residual metal catalyst), in addition to large SWNT bundles during the growth process. Therefore, the formation of purified suspensions of SWNTs is of great scientific and practical interest. Most purification methods involve the use of oxidizing acids that damage their sp2 network, and thus the conductivity. The Lay research group is developing an effective non-oxidizing purification method that uses low-power probe sonication for unbundling and dispersing SWNTs into aqueous suspensions. Next, the suspensions are treated with iterative centrifugation cycles at low centrifugal force, which results in suspensions of unbundled, high-aspect ratio SWNTs. Even after this purification and separation, the polydispersity of SWNTs limits their performance in electrical applications. As produced, bulk SWNT samples contain a mixture of chiral vectors and diameters, resulting in inter-nanotube electronic behavior varying from metallic to semiconductive electronic transport. A powerful tool for overcoming this major obstacle is the use of SWNT networks. We are developing a network deposition method that allows the formation of arbitrary densities of high-aspect ratio SWNT deposits at room temperature. As the density of SWNTs is strictly controlled, the electronic properties of these transparent and flexible networks are tunable from metallic to semiconductive behavior. Therefore, this deposition method greatly improves the level of control and reproducibility with which SWNT-based electronic materials may be formed. A drawback to the use of such networks is the high electrical resistance (R) that often exists in them, which is caused by several factors. There is a R at the metal/SWNT interface due to poor contact between sp2-hybridized C and metal. This results in increased capacitance at the junction. Further, a Schottky barrier exists between the semiconductive SWNTs and the metal electrode. Additionally, R at the tunnel junctions between overlapping SWNTs is increased by residual surfactants, and Schottky barriers between semiconductive and metallic SWNTs. An approach using low-temperature annealing will be compared to an electrochemical approach used to reduce the non-optimal level of electrical R in SWNT networks.

(267) **High Throughput Identification of Promiscuous Inhibitors Among Screening Libraries with the Use of an Intrinsically Fluorescent Probe**; Megan M. McCallum[1], Premchendar Nandhikonda[1], Leggy A. Arnold[1], Ajit Jadhav[2], Adam Yasgar[2], David Maloney[2], Leggy A. Arnold[1]; [1]University of Wisconsin - Milwaukee, [2]NIH Chemical Genomics Center

Testing small molecules for their ability to modify cysteine residues of proteins in the early stages of discovery using high throughput screening is expected to increased efficiency and success to identify promising reversible inhibitors. With the use of a novel fluorescence-based high throughput assay, these compounds can be identified rapidly, in parallel, for small molecule libraries using sub-milligram quantities. Thiol-containing molecules have an essential role in many biochemical and physiological reactions due to the ease of which they are oxidized and form new bonds. Glutathione is the most abundant non-protein thiol as it is found in the millimolar range

in most cells. Therefore, it is important to determine the reactivity of the small molecules toward thiols to circumvent unwanted side-effects of potential drug candidates. Currently, there are no established pre-clinical high throughput assays for the assessment of compound reactivity towards glutathione. With the use of intrinsically fluorescent thiol-containing molecules, the electrophilic and alkylating properties of library compounds can be sensitively and selectively determined.

(268) **Probing DPPC/GM1 Model Membranes with Single Molecule Orientations of Acyl-Linked Fluorescent Lipid Analogs**; Kevin Armendariz[1], Robert Dunn[1]; [1]University of Kansas

There has been a long standing interest to describe the effect of various biological components on membrane structure and function. Historically, gangliosides have received significant attention as they have been implicated in cell signaling and membrane trafficking. Gm1 is the most well studied ganglioside, due in large part to its natural affinity for binding to cholera toxin and the presence of Gm1 in detergent resistant membrane fractions. Many standard techniques provide an important ensemble averaged view of the effect of minor components, such as Gm1, on membrane structure. However, the recent evolution of several single molecule techniques has begun to provide molecular level structural information of biological and model membranes. Here we use single molecule fluorescence measurements to probe the effects of ganglioside Gm1 on molecular level membrane structure. Defocused polarized total internal reflection fluorescence microscopy is utilized to quantify the orientation of acyl-linked fluorescent lipid analogs doped into supported monolayers of DPPC and Gm1. These results are compared to a macroscopic view of membrane structure provided by bulk fluorescence measurements. Interestingly, single-molecule measurements reveal significant changes in the molecular level membrane structure at low, biologically relevant, Gm1 concentrations which are not observed in bulk fluorescence measurements.

(269) **Improving PDQ Database Search Strategies to Enhance Investigative Lead Information for Automotive Paints**; Barry Lavine[1], Nikhil Mirjankar[1], Mark Sandercock[1, 2]; [1]Oklahoma State University, [2]National Centre for Forensic Services

New techniques for pattern recognition assisted infrared (IR) library searching of the Paint Data Query (PDQ) database have been developed to determine the model, and year of an automobile from a paint sample recovered at a crime scene. Modern automotive paints have a thin clear coat which on a microscopic fragment is often too thin to obtain accurate chemical information. The small size of the fragment also makes it difficult to accurately compare it with manufacturer's paint color standards. Fortunately, adhesion between paint layers is usually very strong and so both primer layers are often transferred during a collision if the clear coat and color coat layers are also transferred. As the primer layers and clear coat layer are usually unique to the automotive manufacturing plant where these layers were applied, combining chemical information obtained from the Fourier Transform (FT) IR spectra of the two primer layers and from the clear coat layer should make it possible to rapidly and accurately identify the make, model, and specify certain years of manufacture of an automobile from its paint system alone. Applying mid-level and high-level data fusion techniques where data (e.g., spectra) from multiple sources (e.g., IR spectra of clear coat and primer paint layers) are combined and class membership information is extracted, search prefilters have been developed to differentiate between similar but nonidentical FT-IR paint spectra, and to determine the make and model of the vehicle from which an unknown paint sample originated. Even in challenging trials where the clear coat and undercoat layers evaluated were all the same make (General Motors) with a limited production year range, the respective manufacturing plants were correctly identified using only chemical information. The development of search prefilters and library searching algorithms for the PDQ database, which is the focus of this presentation, is needed to extract investigative lead information from clear coat and primer layer paint smears.

(270) **Nonparametric Permutation Hypothesis Testing: Application to Forensic Physical Evidence**; Michael Sigman[1], Liqiang Ni[2]; [1]University of Central Florida, Department of Chemistry, [2]University of Central Florida, Department of Statistics

Parametric statistical tests often rely on the assumption of normality which frequently does not hold for experimental data and the robust nature of the statistical test is relied upon to insure reliable results. Nonparametric tests free the analyst from rigid distributional assumptions. The nonparametric permutation test exhibits excellent discriminating power for forensic evidence analyses, while rigorously holding the Type I error at the nominal level. The nonparametric permutation test has been applied to multivariate data sets comprised of laser induced breakdown spectral profile representations of glass and paint samples. Multiple spectra from each of two samples are compared through a similarity metric (i.e., Fisher transformations of Pearson product moment correlation coefficients). The difference between the sums of the similarity metric within spectral groups and between spectral groups, Wn, is calculated for all n permutations of the set of spectra. The fraction of Wn greater than or equal to the original spectral grouping, W0, is a measure of the p-value for the test. Results from laboratory tests of glass and paint analyses show that the test is sensitive enough to detect within-sample variations at a prescribed significance level (i.e., alpha = 0.05). A methodology will also be described which combines the nonparametric permutation test with a Wilcoxon rank sum test to allow the nonparametric permutation method to be applied to casework samples. This work was supported under award number 2006-DN-BX-K251 from the Office of Justice Programs, National Institute of Justice, Department of Justice. Points of view in this document are those of the authors and do not necessarily represent the official position of the U.S. Department of Justice. Ni's research was supported in part by grant DMS-0885409 from the National Science Foundation.

(271) **Chemometrics and Databases for Comparisons of Spectral Data from Trace Evidence**; Stephen L. Morgan[1], Edward G. Bartick[2], John G. Goodpaster[3], Molly R. Burnip[1], Eric J. Reichard[3], Kevin Roberts[2]; [1]University of South Carolina, [2]Suffolk University, [3]Indiana University-Purdue University Indianapolis

Trace fiber investigations where the hypothesis of a common source for two fibers could not be rejected and evidence was found to have probative value. Testimony of FBI examiner Paul Stombaugh before the Warren Commission concerned some fibers stuck on a jagged edge of Oswald's rifle stock: "there is no doubt in my mind that these fibers could have come from this shirt." However, the next statement--"There is no way, however, to eliminate the possibility of the fibers having come from another identical shirt"—epitomizes the problem of class evidence. The goals of our work include: (a) assess error rate performance in trace fiber evidence examinations based on UV/visible microspectrophotometry and infrared spectroscopy; (b) create a database of fiber characteristics, including UV/visible spectra, to establish a performance baseline relevant to discussions of fiber discrimination; and, (c) intra- and inter-laboratory consistency, and improvements in forensic laboratory practice. Statistical evaluation of trace evidence data from UV/visible or IR spectroscopy have great utility for assessment of assessing similarity or dissimilarity of spectra when comparing questioned and known trace evidence samples. The use of statistical hypothesis testing with both univariate and multivariate data, coupled with good experimental design, permits the investigator to exercise control over errors in statistical decision arising from measurement uncertainties. We have

employed both univariate and statistical significance in discrimination of UV-visible and infrared spectra from a wide variety of textile fibers and other materials. Statistical methods, coupled with informative graphics for comparing grouped data distributions, can produce reliable statistical support of inclusion and exclusion decisions.

(272) **Automated Analysis of Gamma-Ray Spectra for Detection of Radioisotopes**; Gary Small[1]; [1]University of Iowa

The U. S. Environmental Protection Agency National Decontamination Team (EPA-NDT) as part of the Airborne Spectral Photometry of Environmental Collection Technology (ASPECT) program provides the only operational airborne 24/7 emergency response radiological and chemical mapping capabilities available in the United States. This program employs downward-looking remote sensing technology to collect spectral signatures using the infrared and gamma spectral regions to provide first responders with detailed plume information at the scene of catastrophic contaminant releases. Previous work in our laboratory has developed a series of automated signal processing and pattern recognition tools for use in identifying chemical signatures from the multispectral and hyperspectral infrared data collected by the ASPECT aircraft. In the work presented here, these concepts are applied to the automated and selective detection of radioisotopes from an analysis of gamma-ray spectra. Gamma-ray spectra present several challenges to the development of a reliable detection algorithm. The signal received is highly dependent on the aircraft altitude because of Compton scattering due to interactions between the upwelling gamma rays and atmospheric species. Spectral intensities and bandshapes change as a consequence of this inelastic scattering phenomenon. This complicates the assembly of training data for use in the application of supervised pattern recognition methods. Relatively low signal-to-noise ratios are also observed, thus requiring the use of signal processing methods to help extract radioisotope signatures from background noise. In this presentation, a novel spectrum simulation methodology is used to develop training sets for use with supervised classifiers such as support vector machines and piecewise linear discriminants. Various signal processing and background suppression strategies are also incorporated to help improve the reliability of isotope detection. Presented results will focus on the detection of cesium-137 and cobalt-60 at several survey sites.

(273) **Bayesian Regression: Is it Worth the Trouble?**; Steven Brown; [1]University of Delaware

While there are many ways to regress one set of multivariate measurements x on a response y, one that has relatively little exposure in chemometrics involves Bayesian statistics. In a Bayesian regression, the aim is to find the posterior conditional probability p(y|x) from the priors p(y) and p(x|y) using Bayes rule:

$p(y|x) = p(x|y)p(y)/p(x)$

In principle, this regression has the advantage of allowing information about the distribution of the response y to be used, which could lead to results that are superior to those from PLS and PCR, and it gives distribution information, not parameters, as outputs. However, getting p(x|y) from a set of spectra is less than straightforward, because Bayesian statistics takes the view that parameters carry error, while data does not, and many distributions must be specified or approximated. That can be troublesome when the number of spectral variables is large and the number of samples is small, as is usually the case in data examined by chemometrics. This talk considers some of the assumptions that underlie analysis of spectral data using a Bayesian approach and show the consequences of noise in the measurements as well as correct and incorrect assumptions regarding the prior distributions. Comparisons to conventional methods are made for several datasets.

(274) **Quantification of Drug Delivery by Capillary Electrophoresis**; Michael Heien[1], Nicholas Laude[1], Saliya Ratnayaka[1]; [1]University of Arizona

The effects of lipid composition and macromolecules on the loading efficiency of pharmaceutical compounds and other small molecules within large unilamellar vesicles are investigated by means of capillary electrophoresis with electrochemical detection. A hybrid capillary electrophoresis microfluidic device is used to separate and lyse individual vesicles prior amperometric detection of the contents at a carbon-fiber microelectrode. This system is capable of quantifying zeptomole amounts of material loaded in artificially prepared liposomes and giving information on the mobilities and size distribution of liposomes. Systems such as commercially available anticancer drugs with liposomal delivery systems will be studied using this system in order to study factors which may improve the efficiency of drug delivery. By modifying the lipid composition of the liposomes or incorporating macromolecules such as dextrans or proteins into the liposomal core, the loading efficiency of the drug may be improved. In addition this system offers could be a platform for studying components of biological systems.

(275) **High Sensitive Approaches for the Fluorescence Imaging Detection of Human Serum Proteins after PAGE**; Jin Ouyang[1], Jing Zhang[1], Na Na[1]; [1]College of Chemistry, Beijing Normal University

Proteomics plays an important role in disease diagnosis. Although the progression in the proteomic technologies would largely contribute to the development of mass spectrometry for low-abundant proteins, the key step frequently used for the analysis of complicated samples is the gel electrophoresis. To improve the sensitivity of the detection of human serum proteins after native polyacrylamide gel electrophoresis (PAGE), we have introduced several fluorescent probes for protein imaging. For example, a series of small organic molecules were synthesized and subsequently utilized as fluorescent bio-probes in protein detection, 9, 10- bis [4-(3-sulfonatopropoxyl)-styryl] anthracene sodium salt (BSPSA) and 9, 10-bis□4-[2-(N, N, N-triethylammonium)ethoxyl]-styryl□ anthracene dibromide (BTEAESA) displayed bright aggregation-induced fluorescence emission, while 2, 5-dihydroxy -4'- dimethylaminochalcone (DHDMAC) emitted with obvious blue-shifts after sinking into the hydrophobic cavities of proteins. In addition to the semiconductor quantum dots (QDs) imaging1,2, we also found that the biocompatible and environmentally-friendly carbon QDs and silicon QDs performed excellently in protein imaging3. Interestingly, biomolecules-stabilized noble metal nanoclusters (DNA-Ag NCs and BSA-Au NCs) could also be applied to visualize proteins due to their photostabilities, ultrafine sizes and nontoxicities4,5. Furthermore, colloidal Au and Ag nanoparticles (NPs) were indicated to producing greatly enhanced fluorescence emission after binding to the in-gel proteins with nearly no backgrounds, while no signal was generated in the absence of either proteins or gels. As demonstrated, these fluorescence imaging methods are much simple, fast and sensitive, showing potentials in clinical diagnosis.

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(276) **Surface Electrophoresis of ds-DNA Molecues**; Arnab Ghosh[1], Venu Korampally[1], Keshab Gangopadhyay[1], Shantanu Bhattacharya[2], Shubhra Gangopadhyay[1]; [1]Department of Electrical and Computer Engineering, Univ of Missouri, Columbia, [2]Department of Mechanical Engineering, IIT Kanput, India

Some of the widely used methods for fractionation of ds-DNA are slab-gel electrophoresis, zone electrophoresis, capillary electrophoresis in micro-capillaries, micro-fabricated channel arrays, etc, but larger DNA fragments above 10 kbp can't be resolved very well with the above bulk electrophoresis techniques. A new technique called Surface electrophoresis emerged which utilizes electrostatic interactions between nucleic acid molecules and surfaces using its inherent chemical, topological, or structural properties. We have fabricated a gel free micro-channel device made up of poly-dimethyl siloxane for surface based electrophoresis of DNA molecules[1]. Our surface electrophoresis device has certain advantages like small fractionation lengths, quick separation time, and very low applied electric potential. We have demonstrated the fractionation of a 1kb ds-DNA ladder in 9-10 minutes within 4-5 mm fractionating distance, with a 24 Volts applied electric potential. The concentration of DNA we use for fractionation is very high, and so essentially we are studying the bulk phenomenon of DNA molecule translation. To further improve the fractionation process we are exploring the use of a TiO^2 based photonic crystal surface for electrophoresis of DNA molecules. The TiO^2 photonic crystal surface will enhance the fluorescence signal from the labeled DNA molecules many folds, which will allow us to image and study the motion of low concentration of DNA molecules. Also the photonic crystals have a periodic grating structure on their surface, which would further improve the fractionation efficiency. We have fabricated the TiO^2 photonic crystal which has almost 25-30 folds fluorescent enhancement over a plain glass slide.

(277) **Dielectrophoretic Manipulation of Erythrocytes for Blood Typing**; Adrienne Minerick[1], Kaela Leonard[1]; [1]Michigan Technology University

Human blood is of incredible diagnostic interest because it is easily obtainable and can provide a plethora of information about a person's general health such as protein, iron, vitamin and electrolyte levels. The goal of this research is to expand blood diagnostic capabilities by using dielectrophoresis as a means to provide an ABO-Rh blood type classification from blood. Prior results from our lab suggest that the dielectric properties (permittivity and conductivity) of human erythrocytes change dependent upon ABO-Rh antigen expression. The Clausius-Mossotti factor is directly dependent upon the dielectric properties and thus alternating current dielectrophoresis is a mechanism by which ABO-Rh blood types can be identified by quantifying red blood cell behaviors. Additional prior results with β(1-3) galactosidase treatment demonstrated cleavage of the ABO antigens without harming the erythrocyte and verification of the galactose residues in the supernatant. Treatment yields immunologically bare erythrocytes whose membrane surface is bereft of the ABO antigens. Previous experiments done in a 0.9S/m conductivity buffer have shown that the range over which the crossover frequency occurs for ABO-Rh blood types in their native state is 17MHz, whereas the range over which the crossover occurs for the modified samples is 5MHz. This uniformity in cross over frequency is an indication that the ABO antigens influence crossover frequency of the red blood cells. Further experiments at lower medium conductivities of 0.01S/m and 0.1S/m have been conducted over a large frequency range In addition to measuring the crossover frequencies of blood samples, the dielectrophoretic spectra as a function of frequency have been constructed using a novel intensity profile approach. This approach allowed typical dielectrophoretic traces to be plotted versus frequency for each ABO-Rh blood type, both native and modified samples. In this manner, not only could the crossover frequencies of the blood types be compared, but also the curvature of their traces, giving a more accurate method of distinguishing between blood types.

(278) **Determination of Aptamer-Protein Binding Affinity using Open-Channel Separation Techniques**; Wenwan Zhong[1], Samantha Schachermeyer[1], Jonathan Ashby[1]; [1]University of California, Riverside

Capillary electrophoresis is a great tool for measurement of protein affinity with other molecules, such as small molecules, DNA, other proteins, and nanoparticles. CE offers two biggest advantages compared to others: it does not request immobilization of the interactive parties, and its open channel imposes negligible interference to the complex. However, it cannot tolerate high levels of salt in its running buffer. There is concern that proteins may not have the proper conformation if not present under physiological conditions. This also would be a problem for measurement of affinity between protein and aptamer. Aptamers typically require Mg2+ and Na+ to fold properly and acquire good affinity to the protein target. Addition of those cations at mM concentration would make it challenging to analyze those by CE. Our group has been developing a new method for affinity measurement in another open-channel separation system: asymmetrical flow field flow fractionation (AF4). AF4 can use 1x PBS containing 1 mM Mg2+ as the carrier fluid, which allows proper folding of the aptamer, and can separate the free aptamer from the protein-bound one for affinity calculation. We tested our method on several binding pairs, and evaluated the performance of the AF4-based affinity measurement with the CE-based approach. AF4 requires higher amounts of samples, but it is more suitable for interactive systems that requires high salt binding environment.

(279) **Fifty Years of LIBS and No Limits for Analysis**; Matthieu Baudelet[1], Yuan Liu[1], Matthew Weidman[1], Michael Sigma[2, 3], Martin Richardson[1]; [1]Townes Laser Institute, College of Optics and Photonics, UCF, [2]Chemisty Department, UCF, [3]National Center for Forensic Science, UCF

Elemental analysis at the microscale: that was the challenge that LIBS met fifty years ago. Since then, the development of the laser technology (from femtosecond pulses to high repetition rates), spectrometers (from ultrafast detection to ultra-compact detectors) and analysis tools (with the growing introduction of chemometrics) have evolved and the applications of LIBS became numerous: from biological analysis to stand-off detection of CBRNE threats to trace detection in soil and optimization of industrial processes. After 50 years of proof of application, where is the golden field for LIBS to be used as the only solution instead of any other technique? This talk will analyze the main fields where LIBS has shown a tremendous advantage and will provide the basis for a discussion about where LIBS is asked to be an analytical solution. The commercial availability and readiness of LIBS systems will be discussed as well and an outlook of some of the next challenges for LIBS will be given.

(280) **Microwave-Assisted Laser-Induced Breakdown Spectroscopy: Signal Enhancement and Beyond**; Yuan Liu[1], Matthieu Baudelet[1], Martin Richardson[1]; [1]the College of Optics and Photonics, University of Central Florida

Laser-induced breakdown spectroscopy (LIBS) is always seeking for lower limits of detection while keeping its character of multi-elemental detection. To this purpose, Microwave-assisted laser-induced breakdown spectroscopy (MA-LIBS) was developed utilizing microwave heating effect on laser plasma to increase the

analytical signal. The initial laser plasma can be coupled to microwave radiation, and plasma emission is sustained up to tens of milliseconds, which is approximately three orders of magnitude longer than the typical LIBS plasma lifetime. As a result, the intensity of the emission lines is increased due to longer accumulation time. Microwave can be generated by a 2.45 GHz magnetron, which makes the microwave system potentially a low cost addition to the LIBS system. Besides the enhancement of the emission lines, some special characteristics that differ from conventional LIBS spectra were observed, such as enhanced molecular emission and selective atomic emission improvement. Such characteristics may bring additional benefits to specific fields of analysis. This work is funded by the ARO Contract W911NF0610446 on "Ultrafast Laser Interaction Processes for Libs and other Sensing Technologies" and the State of Florida.

(281) **Application of Laser-Based Spectrochemical Analysis (LA-ICP-MS and LIBS) for the Assessment of Authenticity of Questioned Documents**; Tatiana Trejos[1], Linet Kamandulis[1], Jose R. Almirall[1]; [1]Florida International University

Forged entries in bank checks, fraudulent contracts and counterfeit currency are examples of common criminal investigations. In these cases, the physical and chemical composition of the ink entries and the paper substrate can provide important information for the assessment of the authenticity of the document. Current methods used for the examination of paper and inks may not provide enough discrimination to differentiate between manufacture brands and/or batches. The aim of this study was to develop and optimize practical laser-based methods for the analysis of inks and paper. Laser Induced Breakdown Spectroscopy (LIBS) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) are determined fit for this purpose providing high sensitivity, rapid analysis and minimal sample destruction. In this study, LIBS and LA-ICP-MS methods were optimized for the forensic analysis of paper, printing inks and writing inks. The analytical performance of the methods was evaluated in terms of limits of detection, precision, bias, and linear dynamic range. Moreover, in order to investigate the evidential value of these materials several collection sets were used to evaluate their homogeneity at a micro-scale and the variation of their elemental composition within a single source, between batches and between brands/manufacturers. A total of 450 ink specimens were examined including black and blue gel inks, ballpoint inks, inkjets and toners originating from several manufacturing sources and/or batches. The paper collection was composed of 20 different types of paper, from 7 different brands, manufactured at 10 different plants at different time intervals, all in the US. The studies show smaller variation of elemental compositions within a single source (i.e, paper sheet, pen or cartridge) than the observed variation between different sources (i.e brands, types, batches). Discrimination ranging from 87% to 100% was observed between samples originating from different sources, depending on the sample set under investigation and the method applied. Overall these results confirmed the high value of the examination of documents by laser-based microspechtrochemical methods. Both LA-ICP-MS and LIBS, can be applied in forensic laboratories to conduct a quick screening of the authenticity of a document and/or to complement the information obtained by conventional methods and enhance their evidential value.

(282) **Laser Ablation Molecular Isotopic Spectrometry for Rapid Analysis of Solid Materials**; Alexander Bol'shakov[1], Xianglei Mao[2], Inhee Choi[2], Dale Perry[2], Richard Russo[1, 2]; [1]Applied Spectra Inc., [2]Lawrence Berkeley National Laboratory

A compact instrument is being developed for analyzing key isotopic composition of solid materials in atmospheric air without sample preparation. The design is based on an advanced modification of LIBS. Our method, Laser Ablation Molecular Isotopic Spectrometry (LAMIS) involves measuring isotope-resolved molecular emission, which exhibits significantly larger isotopic spectral shifts than atomic transitions. Detection of several key isotopes (hydrogen, carbon, nitrogen, boron and strontium) in laser ablation plumes was demonstrated. Carbon, strontium and boron isotopes were quantified. Isotope-resolved molecular spectra of many other species were simulated. Future applications of LAMIS are emphasized for carbon sequestration, ecological and agricultural studies. The biological enhancement of ^{12}C over ^{13}C can be up to 5%. Stable isotope ^{15}N is often used as a marker, particularly to track the efficiency of fertilizers in agronomy. Boron isotope 10B is essential in radio-chemotherapy, nuclear technology and neutron detection. Measurement of ^{86}Sr, ^{87}Sr, and ^{88}Sr isotopes in rocks can be used for geological age determination, particularly on Mars. In principle, LAMIS can operate remotely if a laser beam is focused on a target several meters away while optical emission is collected by a telescope. Alternatively, diode laser absorption can be measured in a close proximity to the sample for detection of spectra providing significantly higher spectral resolution without a need for any dispersive optical spectrograph.

(283) **Application of Laser-Induced Breakdown Spectroscopy to Remote and *in situ* Analysis of Algal Biomass Utilisation for Industrial Biotechnology**; Jozef Kaiser[1], Ota Samek[2], Karel Novotný[3], Martin Trtílek, Pavel Pořízka[1, 4], David Prochazka[1], Radomír Malina[1], Klára Procházková[1]; [1]Institute of Physical Engineering, Faculty of Mechanical Engineering, Brno University of Technology, [2]Institute of Scientific Instruments of the ASCR v.v.i., Academy of Sciences of the Czech Republic, [3]Department of Chemistry, Faculty of Sciences, Masaryk University Kotlářská 2, [4]Photon Systems Instruments

We report on the utilization of Laser-Induced Breakdown Spectroscopy (LIBS) to the determination of biologically important elements (such as potassium, magnesium, calcium, and sodium) and to the monitoring of accumulation of potentially toxic heavy metal ions in living microorganisms (algae), in order to trace e.g. the influence of environmental exposure and other cultivation and biological factors. In this feasibility study we used different experimental arrangements employing double-pulse LIBS technique in order to improve on analytical selectivity and sensitivity for potential industrial biotechnology applications, e.g. for monitoring of mass production of commercial biofuels, utilization in the food industry and control of the removal of heavy metals ions from industrial waste waters.

(284) **Portable Linear Quadrupole Membrane Inlet Mass Spectrometer for Environmental Monitoring**; William Hoffmann[1], Jianing He[2], Dr. Guido Verbeck[1]; [1]University of North Texas, Department of Chemistry, [2]Texas Academy of Math and Science

In the state of Texas as well as around the country, increased energy demand has necessitated the development of novel tools for environmental and process monitoring. With the increased prevalence of urban and suburban oil and gas exploration, BTEX components continue to be at the forefront of monitoring technologies. Polydimethylsiloxane membranes are unique in their ability to selectively pass organic compounds and effectively eliminate matrix interferences. Mass spectrometric based monitoring techniques offer many advantages over sensor-based technologies, including increased sensitivity and the ability to unambiguously identify isobaric interferences. Further, portable instrumentation allows the ability to locate and identify threats and take immediate action. To this end, we have implemented a MIMS system on a commercial mass spectrometer and made the system suitable for portable measurements. Increased utility is realized by mounting this system on mobile platform that allows multiple sampling positions and the potential for room imaging. Room imaging experiments are

unique in that they allow for the direct determination of a contamination source position. Initial performance testing was carried out using an open container of acetonitrile placed in close proximity to the inlet tube. Interestingly, it was found that response time was essentially independent of analyte concentration, and similar trends were observed during analyte pump-out. The analyte introduction pump is capable of moving a volume of air ~576 X greater than the internal volume of the sample inlet, suggesting that the lag in both maximum analyte signal and pump-out phases is dominated by transport phenomena across the membrane. Further it was found that spectra were consistent across the time interval investigated, ensuring reproducible instrumental response. After the initial performance was investigated, the instrument was paired with a controlled flow system to generate known concentrations of toluene in nitrogen gas. Using this system, we realized limits of detection that were 2 orders of magnitude lower than OSHA PEL for a Faraday cup detector, and 3 orders of magnitude lower when using an electron multiplier. Because of the mobility of the instrument, we are now able to conduct in situ experiments to gain insights into mass spectrometric-based air quality monitoring

(285) **Zoom-TOF: A new Mass Spectrometer that Combines Constant-Momentum Acceleration Time-of-Flight Mass Spectrometry (TOFMS) with Classical TOFMS for Improved Resolution**; Elise A. Dennis[1], Steven J. Ray[1], Alexander W. G. Graham[1], Christie G. Enke[,2], David W. Koppenhaal[,3], Charles J. Barinaga[,3], Gary M. Hieftje[1]; [1]Department of Chemistry, Indiana University, [2]Department of Chemistry and Chemical Biology, University of New Mexico , [3]Pacific Northwest National Laboratory

Constant-momentum acceleration time-of-flight mass spectrometry (CMA-TOFMS) was first described in the early 1950s, but has not been implemented in commercial TOFMS instruments. Instead, conventional TOFMS instruments employ a constant-energy acceleration (CEA) scheme. In this presentation, we explore the advantages of incorporating CMA-TOFMS into conventional CEA-TOFMS instrumentation. In particular, we demonstrate that CMA-TOFMS can provide superior mass resolution and spectral-generation rates compared to CEA-TOFMS; however, these advantages apply only to a limited mass range. Our new technique is called Zoom-TOF because it employs CEA-TOFMS to record the full mass spectrum and a new CMA-TOFMS approach to zoom-in on a desired spectral region with enhanced resolution. Advantages of the Zoom-TOF technique stem from a new energy-focusing CMA scheme whose merit is best illustrated by a comparison of CEA- and CMA-TOFMS. In traditional CEA-TOFMS with a reflectron, ion flight times are proportional to (m/z)1/2 and ions are spatially focused at the detector. In CMA-TOFMS with a linear-field reflectron, the time-of-flight axis is expanded because flight time is linearly proportional to m/z and ions can be brought into energy focus at m/z-specific detection times, known as the energy focus time (EFT). At the EFT, initial velocities of ions of a specific m/z in the ion source region are all focused, thus mitigating turnaround time errors that are uncorrectable with CEA-TOFMS. Further, the ability to focus velocity, rather than spatial spread, across the ion source region, can be exploited to produce resolution superior to that of conventional TOFMS. In this presentation, theoretical calculations and experimental evidence will be used to demonstrate several fundamental differences between CEA- and CMA-TOFMS in Zoom-TOF. An existing orthogonal-acceleration TOFMS system has been retrofitted to perform Zoom-TOF with minimal instrument modifications. The current system allows atomic species to be studied by glow-discharge ionization and the Zoom-TOF technique to be characterized over a 35-cm field-free flight path. To date, mass-spectral resolving power (FWHM) of at least 4500 has been demonstrated for lead isotopes with constant-momentum Zoom-TOF, an improvement of 2.75 times over CEA-TOFMS in the same system. Zoom-TOF instrument design and operating characteristics will be discussed.

(286) **Hyphenation of a Microfluidic Platform with MALDI-TOF Mass Spectrometry for Single Cell Analysis**; Mian Yang[1], Tzu-Chiao Chao[1], Randall Nelson[2], Alexandra Ros[1]; [1]Department of Chemistry and Biochemistry, [2]The Biodesign Institute

Resolving the protein heterogeneity within small ensembles of cells, even down to single cells allows the investigation of a variety of biological processes and phenomena, which can not be resolved with traditional cell biology methods. Here, we report our progress towards the development of a combined microfluidic and mass spectrometric approach with the ultimate goal of protein analysis on the single-cell level. Our general approach is based on the integration of all necessary cell manipulation steps prior to MALDI-TOF such as cell trapping and lysis, affinity capture of proteins of interest, as well as enzymatic digestion and mixing with MALDI matrix on a microfluidic platform. The key step in this process involves the removal of the microfluidic manifold from the MALDI-MS substrate. MALDI-TOF analysis is then performed directly with the cocrystallized sample originating from a single cell. For proof of principle, we investigated the sensitivity of this approach for peptides and proteins cocrystallized with matrix within microfluidic channels, the detection of proteins captured on an affinity surface integrated in a microfluidic device as well as enzymatic digestion coupled to MALDI-MS detection in a microfluidic device. We detected ~ 300 molecules of peptide angiotensin I and a tryptic digest of bovine serum albumin (BSA) originating from ~10^6 molecules of BSA. We concluded that high abundant protein and low abundant peptides can be detected with single cell sensitivity with the proposed approach. Next, we investigated whether insulin captured by a specific antibody immobilized on a microfluidic platform could be detected by MALDI-TOF. Our results show clearly, that insulin is captured specifically on the anti-insulin antibody coated surface and moreover that MALDI-TOF is capable to detect proteins captured on a monolayer with surface area of only 5000 μm^2. Moreover, we digested BSA immobilized on microchannel walls, followed by MALDI-TOF analysis with similar strategy. We could demonstrate that BSA can be identified through peptide mass fingerprinting. Our future work is dedicated to improve the quantification of proteins captured on affinity surfaces in a microfluidic platform using isobaric tags and apply our new methodology to the detection of QSOX1 from single cancer cells.

(287) **Assigning N-linked Glycopeptide Compositions in Automated Analysis of Their ETD Tandem Mass Spectra**; Zhikai Zhu[1], Daniel Clark[1], Eden Go[1], David Hua[1], Heather Desaire[1]; [1]Dept. of Chemistry, Univ. of Kansas

ETD data has shown significant promise in the analysis of glycopeptides, particularly for determining the glycan location and peptide sequence, and it is increasingly applied to complement glycopeptide analyses done using CID. Nevertheless, no bioinformatics tool is available yet to match ETD-MS2 spectra with their corresponding glycopeptide compositions. By studying the fragmentation pattern of model glycopeptides undergoing ETD, we developed a novel algorithm that scores different ion types of a glycopeptide candidate independently and weighs individual scores based on the intensity of matched ion series. The implementation of the program will greatly facilitate data analysis in glycoproteomics. Trypsinized fetuin, transferrin and avidin were subjected to LC-ETD-MS/MS and multiple spectra collected from various types of N-linked glycopeptides of 8 to 32 amino acid residues and of +3 to +6 charge states were selected for algorithm testing. During initial testing, it was found that glycopeptides at high charge states have better backbone fragmentation efficiency, yet their spectra have numerous noise peaks in the high m/z end. Hence raw spectra were

processed stepwise to remove interfering peaks and to finally retain one-eighth of original peaks (on average), which represent the most abundant peaks in each unit interval across the spectral mass range. It was also observed that some glycopeptides have relatively high amino acid sequence coverage for c ions with few z ions present, while others have the opposite fragmentation pattern. The algorithm was thus designed to give more weighting to ion series that matched the experimental data better. In this way the total score of the candidate would not be hampered due to a lack of one specific type of ion series, since the contribution from the individual score of this ion type would be minimal. For validation, ETD spectra of glycopeptides were used to test the designed algorithm. For each spectrum, the correct glycopeptide composition along with multiple decoy candidates was scored against the processed data. For every spectrum tested, the correct composition received the highest score, and it was at least two times higher than the best score among the corresponding decoys.

(288) **Prospects for Information-Rich Gas-Phase Analysis of Protein Subunits Directly from their Non-Covalent Complexes**; Deepali Rathore, Eric Dodds; [1]University of Nebraska- Lincoln

In recent years, mass spectrometry (MS) has become a valuable tool for measuring masses and subunit stoichiometries of non-covalent protein complexes. Nanoelectrospray ionization (nESI) of these complexes from aqueous solution enables us to observe and analyze them in a native–like state. The gas-phase dissociation of protein assemblies via tandem mass spectrometry (MS/MS) can yield information on the stoichiometry and, in some cases, the arrangement of subunits within the complex; however, subunit sequence information must usually be determined in a separate experiment. Here, we describe a method which allows subunit sequence information to be directly obtained from the protein aggregate in a single gas-phase experiment. All proteins studied as model analytes were purchased from Sigma. Glucagon (3.5 kDa) and Ubiquitin (8.6 kDa) were prepared under denaturing conditions. Cytochrome C (12.4 kDa) was prepared in native-like solution (at pH 7.4 and buffer-exchanged with NH4OAc using BioRad spin columns). The protein solutions (100 μM) were nanosprayed using a static nESI source fabricated in house. MS, MS/MS, and IM analysis was carried out using a Waters Synapt G2 HDMS instrument. For each protein studied, a single gas phase experiment was conducted that involved stepwise stages of collision-induced dissociation (CID) in combination with ion mobility (IM) separation. Quadrupole selection of dimer followed by CID-IM-CID-TOF analysis, gave information on the masses of constituent subunits and sequence information for the subunits. Subunit fragments obtained from second stage of CID (assigned as b and y ions) matched the theoretical fragment ion masses (when compared using Protein Prospector) to within a few ppm, and resulted in a sequence coverage of about 70%, which confirmed that the observed dissociation spectra were consistent with the known subunit sequences. This approach shows promise for measuring a protein complex mass, complex collisional cross section, subunit mass, subunit collisional cross section, and subunit sequence information in a single experiment. Our ongoing efforts are aimed at analysis of more biologically relevant protein assemblies, and at determining whether the subunit CID spectra are of sufficient quality to allow top-down protein identification.

(289) **Nanoscale Chemical Imaging Using Tip-Enhanced Raman Spectroscopy**; Thomas Schmid[1], Lothar Opilik[1], Carolin Blum[1], Johannes Stadler[1], Renato Zenobi[1]; [1]ETH Zurich, Department of Chemistry and Applied Biosciences

Tip-enhanced Raman spectroscopy (TERS) is an analytical technique that combines the chemical information provided by Raman spectroscopy with the signal enhancement known from surface-enhanced Raman scattering (SERS) and the nanoscale spatial resolution of atomic force (AFM) or scanning tunneling microscopy (STM). Recent technological developments by our team include the optimization of tip fabrication, the demonstration of AFM-TERS in a liquid environment, and the development of a novel top illumination scheme for investigation of opaque samples on metal substrates by STM-TERS. The latter has demonstrated the capability of full-spectroscopic imaging of molecular thin films with high pixel numbers (e.g. 128 × 128 pixels) in reasonable measurement times (down to 50 ms per pixel) with a lateral resolution of < 12 nm. Imaging with chemical contrast by TERS is a fascinating but still challenging way to look at the nanoscale. Technical issues to be considered for TERS imaging, such as spectra interpretation and correction of artifacts will be discussed in the presentation. The application of this technique to the characterization of graphene gained from the selective enhancement of vibrational modes that are oriented parallel to the tip axis and thus, reflect structural elements that are oriented perpendicularly to the graphene sheet or deviations from the 2D structure of graphene. In this way, folds and defects were visualized with high selectivity and spatial resolution, and hydrocarbon-contaminated / hydrogen-terminated areas of graphene were found that are not detectable by normal confocal Raman microscopy. Furthermore, TERS imaging revealed the distribution of two isomeric thiols in a mixed patterned self-assembled monolayer and of two lipids in a mixed supported lipid layer, that is a simple model for lipid raft formation in cell membranes.

(290) **Tip-enhanced Raman Spectroscopy for Nano-Scale Monitoring of Catalytic Processes**; Evelien van Schrojenstein Lantman[1], Tanja Deckert-Gaudig[2], Arjan Mank[1, 3], Volker Deckert[2], Bert Wekchuysen[1]; [1]Utrecht University, [2]Institute of Photonic Technology, [3]Philips Inovation Services

Heterogeneous catalysis plays an important role in industry. One of the major scientific challenges for catalysis is the direct link between the identity of a catalytic particle and its reactivity. The identification of single catalytic particles has been possible for a while, with techniques like electron microscopy and X-ray microspectroscopy. The problem lies with the time-resolved chemical identification of molecules on the nanometer scale, which is only possible with vibrational spectroscopy. As vibrational microscopy mostly uses visible or infrared light, it is therefore limited by the diffraction limit. As this makes the highest possible resolution in the order of 300 nm or larger, there is a large mismatch with the single-nanometer scale of catalytic particles. Tip-enhanced Raman spectroscopy (TERS) allows the application of molecular spectroscopy with a resolution below 30 nm.[1] The inherent combination with atomic force microscopy makes TERS an exceptional technique for in-situ studies of a single catalytic particle. The first step towards this goal has been taken in the form of a TERS study of a photo-catalytic reduction. It is shown that TERS methodology in a dual-wavelength approach permits a 'react-analysis' approach. With one wavelength the photoreaction induced, whereas the second wavelength excitation probes the transformation process during the reduction. By exploiting this multi-probe TERS procedure, it is now possible to follow a single Ag particle catalyzing the photo-reduction of p-nitrothiophenol.

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(291) **Structure and Composition of Insulin Fibril Surfaces Probed by TERS**; Igor Lednev[1], Dmitry Kurouski[1], Tanja Deckert-Gaudig[2], Volker Deckert[2, 3]; [1]University at Albany, State University of New York, [2]Institute of Photonic Technology, [3]Institute for Physical Chemistry, University of Jena

Amyloid fibrils associated with many neurodegenerative diseases are the most intriguing targets of modern structural biology. Significant knowledge has been accumulated about the morphology and fibril-core structure recently. However, no conventional methods could

probe the fibril surface despite its significant role in the biological activity. Tip-enhanced Raman spectroscopy (TERS) offers a unique opportunity to characterize the surface structure of an individual fibril due to a high depth and lateral spatial resolution of the method in the nanometer range. Here, TERS is utilized for characterizing the secondary structure and amino acid residue composition of the surface of insulin fibrils. It was found that the surface is strongly heterogeneous and consists of clusters with various protein conformations. More than 30% of the fibril surface is dominated by β-sheet secondary structure, further developing Dobson's model of amyloid fibrils (Jimenez et al. Proc. Natl. Acad. Sci. USA 2002). The β-sheet fibril core, which is not covered with unordered proteins, may serve as a template for new proto-filament and proto-fibril growth and intertwining as proposed by Winter et al. (Jansen et al. Biophys. J. 2005). The propensity of various amino acids on the fibril surface and specific surface secondary structure elements were evaluated. β-sheet areas are rich in cysteine and aromatic amino acids, such as phenylalanine and tyrosine, whereas proline was found only in α-helical and unordered protein clusters. In addition, we showed that carboxyl, amino and imino groups are nearly equally distributed over β-sheet and α-helix/unordered regions. Overall, this study provides valuable new information about the structure and composition of the insulin fibril surface and demonstrates the power of TERS for fibril characterization.

(292) **Analysis of Hemoglobin and Hemozoin using Tip Enhanced Raman Scattering (TERS)**; Bayden Wood[1], Elena Bailo[2], Mehdi Asghari-Khiavi[1], Leann Tilley[3], Don McNaughton, Tanja Decekrt-Guadig[4], Volker Deckert[2, 4]; [1]Monash University, School of Chemistry, [2]ISAS − Institute for Analytical Sciences, [3]Department of Biochemistry and Centre of Excellence for Coherent X-ray Science, La Trobe University, [4]Friedrich-Schiller-Universität Jena, eInstitute of Photonic Technology, IPHT

Near-field techniques including Tip enhanced Raman Scattering (TERS) and Surface enhanced resonance Raman spectroscopy (SERRS) offer new ways to explore hemes at nanometer resolution. We have been applying these technologies to investigate the surface structure of haemoglobin and malaria pigment (hemozoin) for diagnostic and monitoring purposes. Hemoglobin nanocrystals were analysed with Tip Enhanced Raman Scattering protein (TERS), Surface Enhanced Resonance Raman Scattering (SERRS) and conventional resonance Raman scattering (RRS) using 532 nm excitation. The extremely high spatial resolution of TERS enables selective enhancement of heme, protein and amino acid bands from the crystal surface not observed in the SERRS or RRS spectra. Two bands appearing at 1378 cm^{-1} and 1355 cm^{-1} assigned to the ferric and ferrous oxidation state marker bands, respectively were obsverved in TERS and SERRS spectra but not in the RRS spectrum of the bulk sample (Figure 1). The results indicate that nanoscale oxidation changes are occurring at the haemoglobin crystal surface. These changes could be explained by oxygen exchange at the crystal surface and demonstrate the potential of the TERS technique to obtain structural information not possible with conventional Raman microscopy.[1] We have also applied TERS to probe hemozoin crystals at less than 10 nm spatial resolution in the digestive vacuole of a sectioned malaria parasite-infected cell. The TERS spectra clearly show characteristic bands of haemozoin that can be correlated to a precise position on the crystal by comparison with the corresponding Atomic Force Microscopy (AFM) image. These are the first recorded AFM images of hemozoin crystals inside malaria infected cells and clearly show the hemozoin crystals protruding from the embedding medium. TERS spectra recorded of these crystals show spectral features consistent with a 5-coordinate high-spin ferric heme complex, which include the electron density marker band ν4 at 1373 cm^{-1} and other porphyrin skeletal and ring breathing modes at approximately 1636, 1557, 1412, 1314, 1123, and 1066 cm^{-1}. These results demonstrate the potential of the AFM/TERS technique to obtain nanoscale molecular information within a sectioned single cell. We foresee this approach paving the way to a new independent drug screening modality for detection of drugs binding to the hemozoin surface within the digestive vacuole of the malaria trophozoite.[2]

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2. B. R. Wood, E. Bailo, M. Asghari-Khiavi, L. Tilley, S. Deed, T. Deckert-Gaudig, D. McNaughton and V. Deckert, Tip-Enhanced Raman Scattering (TERS) from Hemozoin Crystals within a Sectioned Erythrocyte. Nano Lett. 11, 1868-1873 (2011).

(293) **A Novel Approach to Near-field Stimulated Raman Microscopy**; Derek Nowak[1, 2], Kam Leang[1, 3], Kumar Wickramashinge[1,4]; [1]Molecular Vista Inc, [2]Department of Physics, Portland State University, [3]Department of Mechanical Engineering, University of Nevada, [4]Department of Electrical Engineering and Computer Science, University of California

The discovery of the Raman effect almost a century ago has given scientists a practical method of spectroscopy that measures the vibrational and rotational modes of molecules. Using Raman spectroscopy one can directly analyze an unknown sample without the use of other spectroscopic markers, such as fluorescent tags. A limitation with the Raman effect is that the scattered light of interest is a very weak signal, typically one part per 10^7. While improved optical components and signal amplification techniques make it easier to extract these signals, the signal quality still suffers from long integration times and signal background levels, especially from small target volumes. We present an instrument based on a recent invention [1] that circumvents these typical problems associated with Raman spectroscopic imaging while extending the spatial resolution down to nanometer range. Using a stimulated Raman method we monitor the force gradient between the excited molecule and the end of metallic imaging probe in the near-field. The dipole-dipole interaction between the stimulated molecule and its image charge in the metallic probe is monitored via the cantilever dynamics of an atomic force microscope (AFM). The instrument has high-speed AFM capabilities combined with the ability to stimulate the Raman signal over a range of 30 - 2400 cm_{-1} in the near-IR with a resolution of +/- 0.2 cm^{-1} at 706 nm. The high-resolution imaging capability of this Near-Field Stimulated Raman Microscope (NSRM) and its many advantages over another technique - tip enhanced Raman spectroscopy (TERS) will be highlighted.

(294) **MARS – Microbial Biomarker Analysis with Raman Spectroscopy**; Jan-Hein Hooijschuur[1, 2, 3, 4], Cees Gooijer[1, 2, 4], Gareth Davies[3, 4], Freek Ariese[1, 2, 4]; [1]Department of Biomolecular Spectroscopy, [2]LaserLaB Amsterdam, [3]Department of Petrology, [4]Vrije University

Was there ever life on Mars? Maybe there still is? This study will not reveal the answer but it is designed to establish the range of Raman spectroscopic techniques pertinent for the detection of microbial life in extreme environments, for example on Mars [1] and Jupiter's icy moons. The challenge is to validate *in situ* methodologies for the detection of microorganism biomarkers that unambiguously prove evidence of (past) life. Detecting low levels of biomarkers on a strong mineral background is expected to be difficult. By applying different Raman spectroscopic methods as: 2D Raman imaging and Time Resolved (TRRS), Resonance (RRS) and Spatially Offset (SORS) Raman Spectroscopy or a combination of these techniques, a higher selectivity and/or sensitivity for biomarker detection is obtained. Microorganisms from extreme environments on Earth, which mimic

the environmental conditions of the first billion years of Mars [2], are used for method development. Single cells of the bacterium (*Deinocuccus Radiodurans*) have been detected on a calcite and amphibole matrix with 2D Raman imaging. Both supervised; data compared with known spectra and unsupervised; principle component analysis, data-analysis elucidated the spectral features of this bacterium from its matrix. The cyanobacterium (*Synechocystis* sp. PCC6803) has also been successfully studied in this project. Eventually these methods will be applied under Martian conditions, low temperature and low CO_2 pressure.

[1] C.P. McKay, **Phil. Trans. R. Soc. A**, vol. 369, pp. 594-606, 2011
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(295) **A Compact, Dual Excitation Raman Probe and Instrument for the Identification of Mineralogical Samples**; Job Bello[1], Christina Gasbarro[1], Anton Smirnov[1]; [1]EIC Laboratories, Inc

Raman spectroscopy has been actively investigated as a robotic investigative tool for lunar as well as Mars surface minerals. Current Raman instruments for planetary exploration utilize a single excitation wavelength, typically with a laser in the near-infrared (IR), typically 785nm, to minimize the fluorescence background. However, even with near-IR Raman excitation, background emissions such as fluorescence, F-center luminescence, and blackbody emission can still be a problem. For mineralogical samples, our previous work in compiling a Raman spectral library indicates that a near-IR laser excitation is not always the best wavelength to use in some cases due to interfering emission backgrounds. In several minerals, the near-IR excitation resulted in a broad fluorescence emission that significantly overwhelms the Raman signal. Another interfering emission at 785 nm is blackbody radiation. For dark minerals that strongly absorb the 785 nm laser beam, significant heating results in blackbody emission that also obscures the Raman bands. F-center luminescence emission is also a problem with several of the minerals excited at 785 nm. The F-center luminescence comprises sharp emission bands that can be mistaken for Raman emission. With many of the minerals exhibiting background emission with a 785 nm excitation, a green excitation (532 nm) works out better as an excitation wavelength, where the minerals do not show any interfering background emissions. Thus, we have developed a dual excitation (532 nm and 785 nm) Raman fiber optic probe microprobe and instrument that allows the acquisition of Raman spectra on the same sample spot at the two-excitation wavelengths. The Raman probe head also incorporates a video camera that allows the acquisition of a live video image of the interrogated sample area.

(296) **Advancements in Raman Spectroscopy for the Deep Ocean**; William Kirkwood[1], Peter Walz[1], Edward Peltzer[1], Peter Brewer[1]; [1]MBARI[4]

The second generation Deep Ocean Raman In Situ Spectrometer (DORISS) has been in operation for eight years at the Monterey Bay Aquarium Research Institute (MBARI). During this period of operation a number of novel advancements have been made to expand the usefulness of the DORISS instrument. These advancements have contributed to a more accurate geochemical understanding of seafloor sediment chemistry, hydrocarbons, and gas hydrates, and have allowed true in situ measurement of both the composition and gradients of pore water fluids. We discuss the basic DORISS instrument and the various elements and modifications that have provided a robust, reliable, and capable instrument for use with ROV platforms at depths up to 4000 meters. Specifically, we compare pore water chemical analysis using traditional laboratory methods with our in situ Raman techniques. We also present preliminary concepts for the next generation of oceanographic Raman systems and the potential capabilities for use with deep sea CO2 storage and sequestration scenarios.

(297) **Geochemical Characterization of Layered Outcrops on Mars using LIBS (Laser-Induced Breakdown Spectroscopy)**; Pablo Sobron[1], Catherine Lefebvre[1], Richard Leveille[1], Alexander Koujelev[1], Timothy Haltigin[1], Hongwei Du[2], Alian Wang[2], Nathalie Cabrol[3], Kris Zacny[4], Jack Craft[4]; [1]Canadian Space Agency, [2]Washington University in St. Louis, [3]NASA Ames Research Center, [4]Honeybee Robotics

The chemistry and the stratigraphy of sedimentary, evaporative, and other deposits are indicators of their depositional environment and climate, and their evolution over time. Compared to its predecessors, the capabilities of NASA's Curiosity (scheduled to land on Mars on August 5th) to investigate outcrops and other deposits are enhanced because the rover incorporates a stand-off laser-induced breakdown spectroscopy (LIBS) instrument within the ChemCam suite. ChemCam's LIBS instrument has the capability to obtain chemical information from a large variety of targets at various distances, up to 7 m, including targets at a distance within stratigraphic layers non-accessible to other payload elements. In this work we demonstrate that accurate chemical stratigraphy can be obtained by performing LIBS measurements on visually distinct layers within an outcrop at a terrestrial Mars analog. We derived the chemical stratigraphy of a layered outcrop in the Atacama Desert, Chile, from laboratory LIBS analysis of samples collected from different layers within the outcrop. This outcrop represent a good analog for sub-meter layered outcrops identified at Gale grater by HiRISE. The samples were also analyzed by LSR (laser Raman spectroscopy) and NIR (near-infrared reflectance spectroscopy) for mineralogy. Our results allows evaluating layer-to-layer variations in the relative concentration of each element within the outcrop, thus providing a semi-quantitative chemical profile of the layered outcrop. When combined with mineralogical information of the layer obtained through LSR and NIR, our results demonstrate that the combination of chemical measurements with mineralogical information enables detailed geochemical and mineralogical description of layered outcrops. The advantages of combining these techniques for the analysis of a given sample are evident: LIBS can reveal the relative concentration of major (and often trace) elements present in a bulk sample, whereas LRS and NIR yield information on the individual mineral species and their chemical and structural nature. In the context of a planetary surface exploration, integrated investigations will provide a rapid mineralogical/chemical evaluation of targets that will be very useful for selecting samples to be collected for sample return purposes or sample sites to be drilled in the search for other species (e.g., organics).

(298) **Laser-Induced Breakdown Spectroscopy in the Deep Ocean Environment**; Mike Angel[1]; [1]University of South Carolina

In recent years we have carried out a wide range of laboratory measurements to validate the use of LIBS in high pressure aqueous solutions under realistic oceanic pressures. The results indicate a consistent ability to measure alkali and alkaline metals at ppm levels using single pulse (SP) LIBS at pressures up to 300 bar (~2800 m water depth equivalent). Recent multi-factorial central composite design experiments indicate that matrix effects produced by interactions between elements in mixtures (such as seawater) are virtually nonexistent and calibration studies in seawater seem to indicate that there are no ionic strength effects for Na, Ca, K, Li and Mn using SP LIBS. High pressure studies also indicate no significant pressure effects on SP LIBS calibration curves. The potential use of H and O as internal standards will be discussed.

(299) **DC Magnetron Sputtered Polyaniline-HCl Thin Films for Chemical Sensing Applications**; Karl Booksh, Devon Boyn, Nicola Menegazzo, Holt Bui, Thomas Beebe; [1]University of Delaware

Thin films of conducting polymers exhibit unique chemical and physical properties that render them integral parts in

microelectronics, energy storage devices, and chemical sensors. Overall, polyaniline (PAni) doped in acidic media has shown metal-like electronic conductivity, though exact physical and chemical properties are dependent on the polymer structure and dopant type. Difficulties arising from poor processability render production of doped PAni thin films particularly challenging. In this contribution, DC magnetron sputtering, a physical vapor deposition technique, is applied to the preparation of conductive thin films of PAni doped with hydrochloric acid (PAni-HCl) in an effort to circumvent issues associated with conventional thin fil m preparation methods. Samples manufactured by the sputtering method are analyzed along with samples prepared by conventional drop-casting. Physical characterization (AFM) confirm the presence of PAni-HCl and show that films exhibit a reduced roughness and potentially pinhole-free coverage of the substrate. Spectroscopic evidence (UV-Vis, FT-IR and XPS) suggests that structural changes and loss of conductivity, not uncommon during PAni processing, does occur during the preparation process. Finally, the applicability of sputtered films to gas-phase sensing of NH3 was investigated with surface plasmon resonance (SPR) spectroscopy and compared to previous contributions. In summary, sputtered PAni-HCl films exhibit quantifiable, reversible behavior upon exposure to NH3 with a calculated LOD (by method) approaching 0.4 ppm NH3 in dry air.

(300) **Mid-infrared Plasmons of Conducting Metal Oxides**; Stefan Franzen[1], Josh Guske[1], Misun Kang[1], Edward Sachet[1], Mark Losego[1], Jon-Paul Maria[1]; [1]North Carolina State University

The generality of plasmonic phenomena has only recently been demonstrated in conducting metal oxides. To date the observations of plasmons has been limited by instrumental detection to the near-infrared range i.e. to wavelengths shorter than 2 μ (5000 cm^{-1}). We have recently shown using an infrared ellipsometer and in parallel experiments using a θ-2θ stage attached to a mid-IR FT-interferometer, that mid-IR plasmons in the range from 2-6 microns can be detected. A large number of conducting metal oxides have plasma frequencies in this range, as we have already demonstrated using CdO, Al-doped ZnO, and F-doped SnO2, we have opened an entire new range of materials for investigation of plasmonic phenomena. Examples of the same types of phenomena observed in Au and Ag abound, including formation of self-assembled monolayers and controlled deposition leading to textured or structured surfaces with possibilities for surface enhancement and specific binding sites for analyte detection. The advantages of various detection geometries and is considered in the context of work to develop mid-IR plasmons for practical detection. Since materials properties can be controlled, work has commenced on the optimization of surface plasmons in these new materials.

(301) **Aptamer Functionalized SPR Surfaces for Selective Blood Protein Monitoring**; Nathan Reaver[1], Rui Zheng[1], Dong-Shik Kim[1], Brent Cameron[1]; [1]University of Toledo

It has been shown that significant diagnostic information can be gained through the monitoring of specific blood proteins and biomarkers. Such monitoring can facilitate early disease diagnosis, in addition to, tracking the therapeutic progress during the treatment of certain diseases such as diabetes. More recently, a shift from biomarker discovery toward research and development of diagnostic platforms has started to occur. Although established clinical methods for biomarker detection are available, such as enzyme linked immunosorbent assay (ELISA), mass spectrometry (MS), and liquid chromatography (LC), a need still exists to further develop robust, rapid, and more cost-effective alternative diagnostic platforms that have similar, if not better, sensitivity and selectivity to these more established methods. Such platforms will play an important role in transitioning toward more personalized medicine, as well as, further facilitating biomarker validation studies. In this presentation, we will report on the use of surface plasmon resonance (SPR) spectroscopy coupled to novel aptamer based functionalization methods to achieve ultrasensitive and selective blood protein monitoring. The specific aptamers used to target various blood proteins have been identified through an adapted version of an in vitro selection process known as Systematic Evolution of Ligands by Exponential Amplification (SELEX). The aptamers are then immobilized onto the SPR sensing surfaces using a variety of coupling methods. These methods are specifically adapted based on the target characteristics to achieve optimal performance. Results, to date, demonstrate that SPR can provide both highly sensitive and specific blood/plasma protein measurements that are comparable to existing clinical analysis techniques.

(302) **Diazonium Derived Aryl Films on Gold for Surface Plasmon Resonance Imaging of Metabolytes**; Mark McDermott[1], John Toman[1], Shereen Elbayomy[1], Lars Laurentius[1]; [1]University of Alberta

A critical step in bioassay development is the construction of a stable film to which biomolecules can be immobilized. Our group is exploring diazonium derived aryl films for use in bioassay development. Diazonium salts can be electrochemically reduced or spontaneously adsorbed at the surface of a conductor (carbon, silver, gold, etc.) through a radical intermediate to produce aryl films. These diazonium derived films can form multilayers and potentially provide more binding sites for biomolecule immobilization. Furthermore, the properties of these films can be tailored to a specific need by changing the functional groups present on the diazonium salt precursor or by further modification of the diazonium derived layer. In this work we will look at a variety of diazonium derived films on gold for their use in biorecognition immunoassays, particularly as ultralow fouling films. The films effectiveness for use in bioassays as well as their ultralow fouling properties will be examined using surface plasmon resonance (SPR). These films are being used to construct arrays for parallel metabolite sensing with SPR imaging. Our preliminary results on the detection of thyroxine in blood will be presented.

(303) **On-chip Multiplexed Label Free Bio-Affinity Analysis and MALDI-MS Characterization of Bound Analyte**; Jeremy Pronchik[1], Sophie Bellon[1], Wilfrid Boireau[2], Patrick Ducoroy[3], Chiraz Frydman[1]; [1]Horiba Scientific, [2]Institut FEMTO, [3]CLIPP

The coupling of Surface Plasmon Resonance imaging (SPRi) and Matrix-Assisted Laser Desorption Ionization Mass Spectrometry (MALDI-MS) is an innovative approach for biomarker discovery in biological fluids. Multiplexed SPRi analysis allows the direct visualization and thermodynamic analysis of molecular avidity and is advantageously used for ligand fishing of captured biomolecules on multiple immobilized receptors on a SPRi-Biochip surface. MALDI-MS is a powerful tool for the identification and characterization of molecules by their molecular weight and peptide sequence. Therefore, the combination of SPRi and MS into one concerted procedure, using a unique dedicated surface, is of great interest for functional and structural analysis of bound molecules. Results will be shown using the Lymphocyte Activation Gene 3 (LAG3) protein, a potential biomarker of breast cancer and tuberculosis. LAG3 was captured in human plasma by SPRi down to several femtomoles/mm^2. After MS pre-processing, LAG3 was successfully identified by MALDI-MS directly on the SPRi biochip.

(304) **Determination of Arsenic-Containing Phospholipids in Marine Samples**; Kevin Francesconi[1], Sara García-Salgado[2], Georg Raber[1]; [1]Institute of Chemistry-Analytical Chemistry, Karl-Franzens University Graz, [2]Civil Engineering: Hydraulic and Energy Technology Department, University College for the Technical Engineering of Public Works, Polytechnic University of Madrid

We use speciation analysis with HPLC/mass spectrometry and GC/mass spectrometry, and high resolution mass spectrometry to investigate the arsenolipid content of ten species of macroalgae and other marine samples. Eleven arsenosugar-phospholipids, including 10 new compounds, and three arsenic-hydrocarbons were identified. Gradient elution reversed-phase HPLC coupled to ICPMS provided quantitative measurements for many of the compounds. Clear interspecies differences in the types and amounts of arsenolipids were found for the various classes of algae. The analytical methods based on HPLC/mass spectrometry enable further investigations into the origin and possible role of arsenolipids in algae and other marine organisms.

(305) **New Dimensions in Speciation Analysis : Implementing Isotopic Signatures at The Molecular Level**; Olivier F.X. Donard[1], Emmanuel Tessier[1], Vladimir Epov[1], Sylvain Berail[1], Christophe Pecheyran[1], David Amouroux[1]; [1]Lab. de Chimie Analytique Bioinorganique et Environnement, CNRS-UPPA, Hélioparc, Pau (France)

Speciation analysis is using the information of the occurrence of different species of an element within the same matrix to improve our understanding of the impact and translocation of the different elemental species in the sample of interest. The development of new instrumentation such as multicollector ICP/MS allows now to add new and essential information. Indeed, after the hyphenation of chromatography separation techniques to MC – ICP/MS, it will also be now possible to assign the exact isotopic signature of the different species of the same element within the same sample. This will bring news dimensions in terms of origin of the elements and also allow to unravel chemical and biological processes involved in the final isotopic signature of the species of interest. We will review the development f this new dimension of elemental speciation and will highlight the potential and current limitations of these new analytical directions.

(306) **Advances in Higher Accuracy Elemental and Molecular Speciated Analyses using Updated EPA Method 6800**; H M Skip Kingston[1], Mizan Rahman[2], Matt Pamuku[2], Greg Zinn[1], Timothy Fahrenholz[2]; [1]Duquesne University, [2]Applied Isotope Technologies

Although the history of isotope dilution dates back to the post-World War II era and the availability of enriched stable isotopes, systematic development and proliferation of speciated isotope dilution mass spectrometry (SIDMS) implemented by modern mass spectrometers for inorganic and molecular compounds has taken place during the past several decades. Today, SIDMS is applied across the globe to solve measurement problems for a long list of difficult- or impossible-to-measure compounds where sensitivity, accuracy and precision are required at the highest levels. One of the recent advances is the development of calibration-curve-free SIDMS where the concentrations of multiple compounds are mathematically derived without serial dilutions or external calibrations. This invention overcomes or eliminates 20 sources of errors inherent in spectrometric analysis. The method has been standardized with the publication, in 2008, of EPA[1] Method 6800 included under the SW-846 chapter of the RCRA and has been updated in 2012. A large number of inorganic and biological samples were analyzed with Method 6800 in various matrices that include blood, hair, urine, cells, soils, solids, water, food, fish, electronic components, crude oil, dietary supplements, fugitive agents (homeland security), and quantitative biomarkers and biochemimarkers. Disease diagnosis, medical assessment and selection of treatment regimens for many medical conditions require accuracy and precision in order to provide health care professionals actionable information. After decades of work, searching such clinically-actionable answers primarily at the genetic level is now re-examined. It is now widely accepted that more than half of the causal factors for many debilitating diseases, including autism, that trigger early onset or negatively impact progression of disease are environmental. In a 3-year double-blind study with 70 autistic children and controls, we have developed SIDMS-enabled measurement tools and measured over 65 priority-toxicants and quantitative protein-biomarker tests. Examples, preliminary conclusions, and multiple inorganic and organic biomarkers are discussed in the over 250,000 high accuracy data by research team are discussed. Examples that demonstrate versatility and analytical capability of Method 6800 SIDMS are its application for the analyses of several different difficult samples, such as dynamic species in drinking water, dietary supplements and crude oil where significantly complex speciation data are provided 1. RCRA SW-846 Methods, Update V, Method 6800, "Elemental and Molecular Speciated Isotope Dilution Mass Spectrometry", Government Printing Office, Office of Solid Waste, 2012.

(307) **The Speciation of Gold in Groundwaters with HPLC-ICP-MS**; Christine Ta[1], Frank Reith[2, 3], Joel Brugger[2, 4], Allan Pring[4], Claire E. Lenehan[1]; [1]School of Chemical and Physical Sciences, Flinders University., [2]Centre for Tectonics, Resources and Mineral Exploration (TRaX), School of Earth and Environmental Sciences, The University of Adelaide., [3]CSIRO Land and Water, Environmental Biogeochemistry, PMB2, Glen Osmond., [4]Department of Mineralogy, South Australian Museum

The determination of gold in groundwaters is an emerging technique in the field of mineral exploration. The time consuming process of analysing a narrow cylinder of rock (core) that represents a small area, is replaced with the analysis of series of groundwater samples that provide information about a larger geological area, thus reducing the reliance on costly drilling programs to identify ores. In general, these methods characterise the total gold concentration in solution, and do not give information about the speciation. The ability to speciate gold will provide additional information about the geological conditions under which gold is mobilised. HPLC-ICP-MS was used to develop an analytical method capable of the differentiation of gold species. A reversed-phase ion-pairing chromatography method was developed for the separation of gold(III) and gold(I) species; particularly gold(III) chloride, gold(III) bromide, gold(I) thiosulfate and gold(I) cyanide complexes. The optimised HPLC conditions comprised of a buffer of 1 mM tetrabutylammonium chloride and 5 mM sodium dihydrogen phosphate/disodium hydrogen orthophosphate prepared in 6: 17.5: 76.5 v/v/v isopropanol: acetonitrile: water. Geochemical modelling indicates that the mobile phase composition will not influence the overall speciation of environmental samples. Application of the developed methodology to environmental waters and mine tailings shows that, for the sites studied, gold is present as the Au(I) cyanide complex.

(308) **Speciation Analysis for Studying the Interaction of Metallodrugs with Blood Components**; Michael Sperling[1], Christine Brauckmann[1], Lena Telgmann[1], Christoph Wehe[1], Olga Reifschneider[1], Uwe Karst[1]; [1]University of Muenster, Institute of Inorganic and Analytical Chemistry

The study of the biochemical activity of pharmaceuticals benefits from the analysis of the active compounds and their metabolites within the blood stream under real conditions. In the case of metallodrugs, where the active center is related to a metal, this metal can also be used as a kind of tag to recognize the compounds formed by the interaction of the drug with blood components. In this way highly sensitive and selective hyphenated techniques for speciation analysis, such as LC-ICP-MS and LC-ESI-MS can be used to study such interactions both in in-vitro but also in in-vivo situations. The combined use of the latter two techniques allows for the highly sensitive detection of the metal-containing species (LC-ICP-MS), their quantification (LC-ICP-MS) and their structure elucidation (LC-ESI-MS). Using examples such as thiomersal (an adjuvant used in

vaccines), mercurochrome or platinum-based chemotherapeutics, the type of information that can be gained from speciation analytical studies will be discussed.

(309) **Liquid Sampling-Atmospheric Pressure Glow Discharge Ion Source: A Practical Microplasma**; R. Kenneth Marcus[1], Lynn X. Zhang[1], Benjamin T. Manard[1], Carolyn Q. Burdette[1]; [1]Clemson University

Of all of the areas of analytical chemistry, atomic spectrometry is surely the least evolved with regards to miniaturization. While there have been developments in terms of introducing small sample volumes into flames and plasmas, they have almost solely approached from the point of view of sample introduction and not an integrated look at matching the above instrumentation aspects. The liquid sampling-atmospheric pressure glow discharge (LS-APGD) was initially introduced by Marcus and Davis as a low power, small footprint optical emission source. The source is configured such that an electrolytic liquid (e.g., 1 M HNO3) flows out a small (~100 μm) glass capillary housed within a slightly larger metal capillary, between which a cooling gas is passed. The metallic counter electrode is placed ~2 mm from the liquid surface, with the plasma discharge potential applied to either electrodes while holding the other at ground potential. The i-V characteristics (10 – 50 mA, 200 – 500 V dc) of the device where shown to exist in the abnormal glow discharge regime of plasma operation. In this configuration, solution flows of up to 0.4 mL min^{-1} could be totally vaporized by the plasma struck to the liquid surface. Advantages of this geometry are the much lower flow rates (down to 0.1 mL min^{-1}), lack of liquid waste generation, and ready coupling to flow injection/chromatography sample introduction without compromise of temporal integrity. Limits of detection on the order of 10 ng for 5 μL injections have been obtained on fairly simple optical detection platforms, while also showing appreciable robustness with regards to addition of easily-ionized matrix species. We describe here the implementation of the LS-APGD ion source on a commercial ion trap-based mass analyzer; the ThermoScientific LCQ. A compete parametric evaluation has been undertaken to elucidate not only optimum operation conditions, but also t gain insights into the operating mechanisms of this unique discharge. It is believed that this source represents a true, practical microplasma device.

(310) **Further Work on the Use of Advanced Computational Statistics ("Expert Systems") for Automatic Evaluation of GD-OES Compositional Depth Profiles**; Arne Bengtson[1], Jonas Gurell[1]; [1]Swerea KIMAB

Glow Discharge Optical Emission Spectroscopy (GD-OES) is a well established technique for Compositional Depth Profile (CDP) analysis of technical surface layers, e.g. metallic, PVD and polymer coatings. It is fast and multi-elemental with high sensitivity and excellent depth resolution. The technique is increasingly used in industry as a routine analytical tool for quality control of surface coated materials. A CDP analysis often contains a very large amount of information from up to 30 elements and their variations in depth. It can be very difficult even for a trained operator to evaluate all this information. For quality control and trouble shooting, the objective of a CDP analysis is normally to assess if the coating/surface properties meet certain technical performance requirements, rather than a detailed analysis of the coating composition. In order to facilitate the interpretation of complex CDP data, work has been performed since several years to develop "expert systems" based on advanced computational statistics. In previous work, it has been shown that e.g. corrosion resistance can be predicted based on GD-OES CDP analysis of Zn – based metallic coatings on steel. Recent work has focussed on developing data pre-processing methods; and evaluation of a variety of classification algorithms. The classification is analogous to conventional calibration in the sense that it is used to find correlations between the analytical data and technical properties of the samples. Examples of algorithms tested include "decision trees", "neural networks" and "rule indiction". All of these algorithms are designed to establish a set of rules that link the data set to defined technical properties. While it is possible to simply use complete sets of CDP data for this purpose, the work has shown that it is advantageous to initiate the evaluation process by extracting characteristic "features" of the CDP data sets. This pre-processing also includes filtering and elimination of sections of the data set considered irrelevant for the application. Such sections can be the first few seconds (when surface contamination is not of interest), or profiles of trace elements which essentially contain just background noise. Examples of results from specific applications will be presented and discussed.

(311) **Development and Application of a Large Glow Discharge Source Suitable for Spatial Imaging**; Volker Hoffmann[1], Maxim Voronov[1], Wolfgang Buscher[2], Carsten Engelhard[2], Steven J. Ray[3], Andrew P. Storey[3], Gary M. Hieftje[3]; [1]Leibniz Institute for Solid State and Materials Research Dresden, IFW Dresden e.V., [2]University of Münster, Department of Inorganic and Analytical Chemistry, [3]Department of Chemistry, Indiana University

Imaging of large samples by glow discharge optical emission spectroscopy requires the development of sputtering sources with a large diameter. We report the first results of a new glow discharge source having 4-cm diameter and a tilted window. This construction suppresses the generation of standing acoustic waves and corresponding effects on the discharge impedance and the optical emission, when pulsed discharges are employed. The source can work with continuous and pulsed, DC and RF discharges, and has a modular structure to simplify the installation of samples of different form and size. Probes for the measurement of voltage and current are integrated.

(312) **Atomic Spectrometry with Glow Discharges at Atmospheric Pressure for the Determination of Analytes in the Gaseous Phase**; José A.C. Broekaert[1]; [1]University of Hamburg, Institute for Inorganic and Applied Chemistry

Since some years glow discharges at atmospheric pressure have been recognized as powerful sources for atomic spectrometry. They proved to have high excitation capabilities, especially when operated in helium but lower gas temperatures as compared to other atmospheric pressure sources like the inductively coupled plasma. For the introduction of analytes in the gaseous phase, many geometries can be used. In the case of an end-on observation of a discharge with hollow anode and cathode where the analytes enter through the cathode [1] and the cold vapor technique, detection limits for Hg were found to be down to 0.2 ng/mL when using the device as radiation source for atomic emission spectrometry. When applying hydride generation the excess of hydrogen produced did decrease the analyte line intensities considerably and asked for isolating the hydrides by trapping and releasing the excess of hydrogen. When using a glow discharge with an alternative geometry as source for mass spectrometry, however, the excess of hydrogen was not found to deteriorate the power of detection and detection limits for As, Sb, Ge were found to be down to the pg/mL level [2]. In the case the cathode plume was used for ionization source, as in the case of the FAPA source, both with molecular species and with atomic species calibration in the case of hydride generation could be performed [3]. In the case of a glow discharge ignited between a tungsten filament and a tungsten rod, dry solution residues could be volatilized very smoothly at a power of 10 W and detection limits for volatile species such as Ag, Cd and Sb in the case of array detector ICP-MS were found to be in the 0.3-3 ng range [4].

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Broekaert and G.M. Hieftje, J. Anal. Atom. Spectrom. 21: 750-756 (2006) (3) G.D. Schilling, J.T. Shelley, J.A.C. Broekaert, R.P. Sperline, M.B. Denton, C.J. Barinaga, D.W. Koppenaal and G.M. Hieftje, J. Anal. Atom. Spectrom. 24: 34-40 (2009), (4) J. Felton, J.A.C. Broekaert and G.M. Hieftje, unpublished work.

(313) **Spatial Mapping with Glow Discharge Optical Emission Spectrometry: The Role of Reflectivity in Heterogeneous Matrices.**; Gerardo Gamez[1], Juan Limon-Petersen[1], Johann Michler[1]; [1]Swiss Federal Laboratories for Materials Science and Technology (EMPA)

Glow discharge optical emission spectrometry (GDOES) has gained popularity because it allows fast, direct elemental analysis on solids and high-resolution depth profiling. Nevertheless, the lateral spatial resolution has been historically limited to the size of the sputtered crater which is in the order of several millimeters. Recently, it was shown that lateral resolution within the sputtered area can be achieved by operating the glow discharge in pulsed mode. The new mode of operation brings the possibility of performing elemental tomography of large area samples very fast. Current efforts are being focused on characterizing and improving the lateral resolution of this technique which is still within hundreds of microns. The purpose of this study is to characterize the lateral resolution in heterogeneous matrix samples. Results showing for the first time the effects of changes in reflectivity of the different components in the perceived spatial resolution will be presented.

(314) **2p or not 2p: Tuppence-based SERS for the Detection of Illicit Materials**; Roy Goodacre[1], Samuel Mabbott[1], David Cowcher[1], Clare Levene[1], Omar Alharbi[1], Elon Correa[1], Ewan Blanch[1]; [1]University of Manchester

There is an ongoing need to detect trace levels of illicit materials that will allow appropriate action to be taken. This may be with respect to responding to biological warfare agents, finding associative evidence in drug trafficking, or for screening individuals who may have taken drugs (both illicit and legal). Due to the molecular specificity of Raman spectroscopy, along with portability of instrumentation, this analytical approach offers great potential. However, due to the rather low Raman scattering probability event signal augmentation methods such as surface enhanced Raman scattering (SERS) are needed. We shall report: our recent developments of a fast and cost-effective approach for the synthesis of thin films used in SERS using galvanic displacement (Mabbott et al., 2012), a method that is appropriate for the detection of illegal drugs and legal highs; quantification of spore biomarkers including dipicolinic acid isolated from Bacillus spores; and quantification of drugs and their metabolites, including the suitable design of experiments needed for the judicious optimization of SERS substrates.

Mabbott, S., Larmour, I., Vishnyakov, V., Xu, Y., Graham, D. & Goodacre, R. (2012) The optimisation of facile substrates for surface enhanced Raman scattering through galvanic replacement of silver onto copper. Analyst, in press.

(315) **Multiplexed and Sensitive Molecular Diagnostics using SERRS**; Karen Faulds[1], Jennifer Dougan[1], Kirsten Gracie[1], Mhairi Harper[1], Kristy McKeating[1], Duncan Graham[11]; [1]University of Strathclyde

Surface enhanced resonance Raman scattering (SERRS) is an analytical technique with several advantages over competitive techniques in terms of improved sensitivity and multiplexing. We have made great progress in the development of SERRS as a quantitative analytical method, in particular for the detection of DNA. However, the lack of quantitative data relating to real examples has prevented more widespread adoption of the technique. Detection of specific DNA sequences is central to modern molecular biology and also to molecular diagnostics where identification of a particular disease is based on nucleic acid identification. Many methods exist and fluorescence spectroscopy dominates the detection technologies employed with different assay formats. Another advantage of SERRS over existing detection techniques is that of the ability to multiplex which is limited when using techniques such as fluorescence. We have clearly demonstrated the ability to identify the presence of a mixture of 6 analytes in solution using data analysis techniques. Here we demonstrate the development of new molecular diagnostic assays based upon SERRS which have been used successfully for the detection of bacterial infections using modified SERRS active probes. The probes have been designed to give a specific SERRS response resulting in discernable differences in the SERRS which can be correlated to a specific DNA hybridisation event.

(316) **Single Molecule Studies of Transport and Reactivity under Conditions of Confinement and Crowding**; Paul W. Bohn[1], Jing Zhao[1], Dane A. Grismer[1], Sean P. Branagan[1]; [1]University of Notre Dame

The localization of optical fields is a powerful method to reduce spectroscopic background signals and enable studies of single fluorescent molecules. Zero-mode waveguides (ZMWs) strongly confine optical fields to zeptoliter volumes and can be coupled with fluorescence microscopy to study the dynamics of single enzyme molecules, due to their excellent optical confinement, precise positioning, and massive parallelism. The redox enzyme, monomeric sarcosine oxidase (MSOX) contains a covalently bound flavin adenine dinucleotide (FAD) cofactor which is highly fluorescent in the oxidized state and dark in the reduced state, thus producing a characteristic on-off fluorescence signal synchronous with transitions between oxidation states. For MSOX reactions involving both the nominal substrate (sarcosine) and an analogous substrate (proline), statistical analysis of single-molecule temporal trajectories reveal the static heterogeneity of single enzyme reaction rates, but no dynamic disorder. In addition, the single molecule data confirm the independence of reductive and oxidative reactions. These structures open the way for systematic studies of the effect of molecular crowding on enzyme dynamics.

(317) **Spatially Offset Raman Spectroscopy: From Aviation Security to Medical Diagnosis**; Pavel Matousek[1]; [1]Rutherford Appleton Laboratory

This presentation will review recent advances in the area of Spatially Offset Raman spectroscopy (SORS), a recently developed analytical tool for noninvasive chemically specific probing of turbid media. The concept has permitted accessing depths an order or two higher than those available with conventional backscattering Raman spectroscopy. The talk will outline the concept and emerging applications focusing specifically on recent developments in noninvasive cancer diagnosis and scanning of bottles for liquid explosives in aviation security. A combination of SORS and SERS to extend usable depth with SERS in biological tissues will also be discussed.

(318) **Practical Understanding of yhe Sers/Serrs Process Using Chemistry, Plasmon Resonance And Eels**; Ewen Smith[1, 2]; [1]University of Strathclyde, [2]Renishaw Diagnostics Ltd

Renishaw Diagnostics Ltd has launched a molecular diagnostics product for the detection of bacterial and viral infections which uses SERRS for detection due to the high sensitivity and the ability to detect several targets in the one sample. The system requires SERRS methodology which is reliable, repeatable and effective. It uses dyes as labels and the additional molecular resonance enhancement means that the signals detected are solely from the dye labels with little to no interference from other materials. A study of excitation frequency, plasmon resonance frequency and dye absorption maximum indicates that the maximum enhancement from the dye label is not always at

the plasmon resonance maximum. Efficient coupling of the dye to the surface is essential to quench the fluorescence signal and remove background. This requires consideration of the surface chemistry of the silver nanoparticles used as substrate making it easier to combine the detection with standard solution based molecular biology procedures. A crucial feature is the use of controlled aggregation to increase signal. By titrating dyes into colloid which adhere strongly to the surface but create different surface charges, the effect of controlled aggregation on cluster size, stability and signal strength was characterised. Along with the wavelength study this permits a consideration of what is practical in a simple and reliable assay. The formation of aggregates prompts the question of the relative efficiencies of scattering from different dye labelled clusters. A comparison of thousands of particles by TEM, surface plasmon resonance and EELS shows wide variations in scattering efficiency with 1% or so of single particles giving detectable signals and, in small clusters, an almost linear increase in signal with cluster size. The EELS data helps characterise the plasmon excitation but there is evidence of more subtle effects which require a physics and surface chemistry explanation. In the practical assay used, accumulation times are of the order of 1 second and many aggregates are present in the interrogation volume at any one time. Thus, during the accumulation time, many single Raman events occur and it is the averaging of these events which gives the quantitative response.

(319) **Fine-Tuning the Flow Profile, Direction, and Speed of Fluids on a Chip with Redox-Magnetohydrodynamics**; Ingrid Fritsch[1], Vishal Sahore[1], Christena Nash[1], Preston Scrape[1], Adam Kreidermacher[1]; [1]University of Arkansas

Controlling localized motion of small volumes of fluid on a small scale is of interest for performing multiple steps of chemical analysis processes on a chip and in separations. Redox-magnetohydrodynamics (MHD) has the unique capability to do such fine-tuning of fluid flow through the use of strategically located and programmable electrodes where redox species undergo oxidation and reduction in the presence of a magnetic field and without the need for traditional channel walls that physically confine and direct fluid flow. The MHD body force, $\mathbf{F_B}$, which determines the direction and magnitude of the fluid flow, can be described through the right-hand rule as the cross product of the charge or ionic current density, **j**, with the magnetic flux density, **B**: $\mathbf{F_B} = \mathbf{j} \times \mathbf{B}$. The addition of a chemical (redox) species to an electrolyte solution that can be easily oxidized and reduced through electron transfer processes at electrodes allows ionic current to pass through the solution without electrode corrosion or bubble formation. Redox-MHD microfluidics have been investigated with chips containing individually-addressable microelectrodes in the presence of a permanent magnet placed beneath them. The fluid speed for a given cell-electrode geometry is proportional to the applied current, allowing fine-tuning of flow simply by controlling the electrode current. Localized flow can be started, stopped, and reversed simply by turning on, off, and reversing the polarity of the electrodes, respectively. The fluid can be pumped in different patterns, depending on distance between, size of, and current at the electrodes. In addition, and of great interest to the separations community, a flat flow profile is achievable. Discussion will focus on factors affecting extremely flat flow profiles between microband electrodes over a distance of 25 mm, and across a 5.6-mm width and >0.8-mm height, exceeding typical cross sectional channel dimensions of capillary electrophoresis chips. Greater expanses for flat flow profiles with redox-MHD are possible. Fluid manipulation using other electrode and magnet geometries, including magnets smaller than the gaps between electrodes will also be addressed.

(320) **Low Low Cost Paper-PDMS Electrophoretic Separation Devices**; Christopher R. Harrison[1], Dylan C. Mitchell[1]; [1]San Diego State University

Paper based analysis devices have gained popularity in recent years due to their ease of fabrication, low cost and effectiveness for simple analyses. Though very capable as analytical tools, these devices have significant limitations due to their inability to perform complex separations of samples. The vast majority of these devices utilize specific, deposited, reagents to act as indicators or to selectively capture the analytes of interest as the sample is wicked over the paper. Consequently, the quantitative information available from such a device is significantly limited by the design of the device. Our desire is to improve upon these paper based devices and, through the use of appropriate (e.g. simple, low cost, low power...) materials, gain greater potential from these low cost, disposable, devices. Consequently, we have moved to a system where the paper substrate is fully enclosed within the PDMS substrate rather than being an exposed paper surface. This design allows for the use of electrophoresis as a means of separating analytes in a wetted paper channel. Furthermore, the paper substrate which forms the channel can act as a chromatographic surface, effectively allowing for electrochromatographic separations without the associated difficulties of traditional packing materials and frits. This work will present our efforts to modify native PDMS and the incorporated paper substrate to control the electroosmotic flow in addition to our modifications of the paper aimed at altering the chromatographic behavior of the channels. Finally, we will present our work to incorporate simple, inexpensive, electronic detection systems into the PDMS device.

(321) **Electrodeionization for Selective Separations**; Alex Lopez[1]; [1]University of Arkansas

Electrodeionzation is a mature technology in ultrapure water production. It works by using ion exchange moieties to take low concentration ions from solution in between ion exchange membranes. Recently, the J. Hestekin group at the University of Arkansas has used highly selective wafers to introduce electrodeionzation to continuous fermentation. Using selective separations, electrodeionization in fermentation has a lot of potential advantages. This talk will discuss the applications as well as the fundamental limitations of the technology in terms of concentration, purity, and power conversion.

(322) **A On-animal Separation Based Sensor with Amperometric Detection**; David Scott[1, 2], Ryan Grigsby[1, 2], Susan Lunte[1, 2]; [1]University of Kansas, [2]Ralph N. Adams Institute for Bioanalytical Chemistry and Departments of Chemistry

The online-coupling of microdialysis to microchip electrophoresis provides an attractive technology for near real time monitoring of drugs and neurotransmitters in pharmacokinetic and behavioral studies. In this paper, a microdialysis-microchip electrophoresis (MD-ME) system for continuous in vivo monitoring of nitric oxide metabolites using amperometric detection will be described. The system incorporates telemetry for remote control, data acquisition, and has been optimized for the continuous on-line analysis of microdialysis samples obtained using a linear probe following nitroglycerin or histamine administration. The on-line microdialysis-microchip electrophoresis system was fabricated using an all glass substrate that includes an electrophoresis separation channel, integrated platinum working and reference electrodes, as well as an interface for direct coupling of the chip to the microdialysis probe. This presentation will describe the development of the integrated system including optimization of the electrophoresis conditions, injection of samples into the chip using the on-line microdialysis-microchip electrophoresis interface, and evaluation of the overall ruggedness of the system. The ultimate goal is to use the separation based sensor for on-animal in vivo analysis of drugs and

neurotransmitters in order to correlate neurochemistry and/or metabolism with behavior in freely roaming animals.

(323) **Evaluation of Amyloid Protein Oligomer Formation Using Microchannel Electrophoresis**; Christa Hestekin[1], Elizabeth Pryor[1], Melissa Moss[2]; [1]University of Arkansas, [2]University of South Carolina

The assembly of monomeric proteins into amyloid fibrils has deleterious implications in amyloid diseases. An understanding of the amyloid assembly process is fundamental to the development of strategies to inhibit or manipulate amyloid assembly. Increasing efforts have been directed toward understanding the growth of late stage aggregates, including fibrils and protofibrils. However, early stages of amyloid protein assembly, including nucleation and oligomerization, remain elusive as a result of difficulties presented in the measurement of early oligomeric aggregates, which are transiently present at very low concentrations relative to other reaction species. The efficient separation capabilities and low detection limits of microchannel (capillary and microchip) electrophoresis offers an effective means of selectively and sensitively detecting the appearance of oligomeric structures. This talk will focus on the detection of aggregate formation by two amyloidogenic proteins, insulin and the amyloid-β protein (Aβ). The ability of microchannel electrophoresis to detect physiological concentrations (pM), small oliomgeric species (<20 mers), and perform rapid separations (minutes) will be presented.

(324) **Resolution Enhancement in 2D Correlation Spectroscopy**; Isao Noda[1]; [1]The Procter & Gamble Company

One of the well-recognized utilities of two-dimensional (2D) correlation spectroscopy is the apparent enhancement of spectral resolution by spreading overlapped bands along the second dimension. Features not so obvious in a conventional 1D spectrum often become more easily observable. This benefit is especially prominent in the asynchronous 2D correlation spectrum, where the subtle difference in the pattern of intensity variations is selectively accentuated. Thus, 2D correlation spectroscopy has been utilized extensively in the analysis of various complex systems, like biomolecules, solution mixtures and composite materials, to sort out the overlapped spectral contributions of individual system constituents. Techniques other than 2D correlation, such as Fourier self deconvolution and the second derivative method, are also well known for the enhancement of spectral resolution. It is possible, in principle, to combine these resolution enhancement techniques with 2D correlation spectroscopy to further discriminate the overlapped fine spectral features. Although such a combination seems attractive, certain care must be taken to avoid producing artifacts or phantom peaks from the side lobes often generated by conventional resolution enhancement technique. A useful procedure for spectral resolution enhancement without producing side lobes will be presented, which can be safely combined with 2D correlation spectroscopy.

(325) **Analysis of the Molten Globule State of Bovine α-Lactalbumin by Using Vibrational Circular Dichroism**; Laurence A Nafie[1, 4], Soo Ryeon Ryu[2], Young Mee Jung[2], Bogusława Czarnik-Matusewiczb[3], Rina K Dukor[4]; [1]Syracuse University, [2]Kangwon National University, [3]University of Wrocław, [4]BioTools, Inc.

The molten globule state of α-lactalbumin was investigated by using vibrational circular dichroism (VCD) and two-dimensional (2D) correlation spectroscopy. To investigate details on the denaturation mechanism of α-lactalbumin, 2D correlation spectroscopy was applied to the pH-dependent VCD spectra of α-lactalbumin aqueous solutions. The denaturation transition point of α-lactalbumin was determined by the 2D gradient mapping method. Large spectral changes of VCD spectra were observed at pH 4.75 and 2.75 in the 2D gradient map, which correspond to transition points. Based on the analysis of 2D VCD correlation spectra, we suggest the following sequence changes from the pre-molten globule state to the molten globule state. Intermolecular β-sheet changes first, and then lower-frequency β-sheet structure changes before α-helices with continued lowering of the pH.

(326) **2D-Correlation Spectroscopy in Polymer Chemistry**; Heinz Siesler[1], Miriam Unger[2]; [1]University of Duisburg-Essen, Department of Physical Chemistry, [2]Synchrotron Radiation Center

To illustrate the potential of generalized two-dimensional correlation spectroscopy (2DCOS) and the perturbation-correlation moving window two-dimensional (PCMW2D) correlation analysis these techniques have been applied to the FT-IR/ ATR spectra recorded during a polyurethane solution polymerization by in-line measurements with a light-fiber coupled ATR probe. In this experiment the polymerization reaction of 4,4´-diphenylmethan-diisocyanate (MDI) and 1,4-butane diol (1,4-BDO) in a 50/50 % (v/v) chloroform/diglyme solution was monitored at temperatures between 40°C and 70°C. The original background of the variable-temperature measurements was the determination of the reaction kinetics and the calculation of the activation energy of the reaction. In the present communication it will be demonstrated that by the application of the 2D-correlation techniques to representative spectra series in the wavenumber region 1800 – 1200 cm-1 a better understanding of the observed spectral changes as a function of reaction progress can be achieved.

(327) **Concepts on Information Theory in Two-Dimensional Correlation Spectroscopy**; Nicolas Spegazzini[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University

Information theory is a shared field between mathematics and engineering and is involving in the quantification of the information. The intention of information theory is to find limits on signal processing operations such as compressing data and on reliably storing and communication data and is applied to broad range forms of data analysis. On the other hand the fundamental concept governing 2D correlation spectroscopy is a quantitative comparison of the patterns of spectral variables, ν^1 and ν_2, over some finite observation interval. The intensity of 2D correlation spectrum $X(\nu^1, \nu_2)$ represents quantitative measure of a comparative similarity o dissimilarity of spectral intensity variations y (ν, t) measured at two different spectral variables, ν^1 and ν_2, during a fixed interval. This is possible through a cross-correlation function designed to compare the dependence patterns of two chosen quantities on time, based on in the time series analysis. This direct relation with the signal processing field make possible introduce the concepts of entropy of the information, with the objective to understand and explain the indetermination of the origin of the spectral change due to the frequency and intensity shift, and propose a limit of application to the sequential order of events.

(328) **2D Correlation Spectroscopy as a Tool for Spectral Interpretation**; James de Haseth[1], Franklin Barton, II[1]; [1]Light Light Solutions, LLC

Near Infrared Spectroscopy has always been hampered by a lack of "classical" spectral interpretation. In the mid-infrared the fundamental vibrations of organic and inorganic molecules have been well studied and numerous texts have been written for the student of spectroscopy. In the near IR it is difficult to interpret dynamic processes or to ascertain with certainty the exact interaction of spectral lines with sample functionality. However, the near infrared does not contain any of the fundamental vibrations, only combination bands and overtones of the fundamentals. Twenty years ago two-dimensional (2D) spectroscopy techniques were developed that allowed the comparison of different spectral regions and correlated the responses. The technique was needed to help with the interpretation of NIR spectra and chemometric models. Classical

spectroscopists were skeptical of wavelengths chosen which did not appear at the top of a band and the inclusion of wavelengths which did not appear to relate to the analyte. The technique has been used to describe the process of digestion, the de-lignification of cell walls by white rot fungi and the effect on carbohydrates and the difference between hard red winter and hard red spring wheat which removed instrument differences. Calibration transfer and instrument differences and similarity have been topics of great interest throughout the past forty years of the use of Near Infrared Spectrometry (NIRS) to determine the properties of agricultural and food products. This paper describes the general 2DCOS work used for interpretation and newer studies which show the differences and similarities of instruments and a graphical representation of calibration transfer potential. In all these studies there are useful points for teaching the use of vibrational spectroscopy and how to structure experiments.

(329) **Frontiers of Biomedical Application of SERS：New Strategies for**; Yukihiro Ozaki[1]; [1]Kwansei Gakuin University

Raman scattering, an inelastic scattering of a photon, can be dramatically enhanced (102-1014) by adsorption of molecules on a surface of noble metal, transition metal or semiconductor substrates, which is called surface-enhanced Raman scattering (SERS). With more than 30 years of development, SERS has been attracting more and more attention in the fields of physics, chemistry, surface science, nanoscience and biomedical science. It is very useful in detecting conformational changes and structural differences regarding preferred orientations of molecules on a metal surface. SERS technique has proved to be a very effective analytical tool due to its high sensitivity, high selectivity and fluorescence quenching properties.Recently, SERS and surface-enhanced resonance Raman scattering (SERRS) have widely been used as a powerful tool for ultrasensitive chemical analysis down to single molecule level under favorable circumstances. Rapid development of SERS-based biosensors leads to its realm of applications from chemical-biochemical analysis to nanostructure characterization and biomedical applications(1,2). Acquiring intrinsic SERS spectra of target bimolecules is a preferred way when detecting biomolecules by SERS technique, which is so-called label-free detection, and in this case, SERS spectra of biomolecules or molecular bridges are used as fingerprints for biomolecule identification. However, it is difficult for some bimolecules with high molecular weight (e. g., simple proteins and DNA) to be detected by the same way as the label-free protocol. An indirect way using extrinsic SERS labeling thus emerged to fulfill highly sensitive detection of biomolecules. These extrinsic Raman labels are usually covalently attached to bimolecular ligands and used to detect target analytes via biomolecule─ligand recognition. SERS spectra of these labels are used as representatives of masked target biomolecules, and their intensities indirectly correspond to the analyte concentration.

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(330) **High Speed Single Cell Spectroscopy: Integrating Fluorescence and Raman Scattering in Cytometry**; John Nolan[1]; [1]La Jolla Bioengineering Institute

Cytometry, the quantitative analysis of cells and cell systems, relies heavily on optical methods, especially fluorescence and elastic light scatter. Most often, spectral resolution is low, with dichroic mirrors and bandpass filters used to select different "colors" of light for detection with photomultiplier tubes or cameras. However, interest in performing high speed spectral analysis of individual cells can be traced back to the earliest days of cytometry. Recently, with the availability of improved light sources, optics, and detectors, high speed spectral cytometry has become a practicality. We have developed instruments and software that can acquire and analyze high resolution single particle optical spectra from individual cells in flow at rates of hundreds per second. These new tools open new possibilities for fluorescence-based analyses, but also for new optical approaches including Raman spectroscopy. We have also developed nanoparticle surface enhanced Raman scattering (SERS) tags that exhibit distinctive spectra and can serve as labels for antibodies or other targeting molecules. The sensitivity and performance of nanoparticle SERS tags is comparable to fluorescence for immunostaining and the narrow spectral features of Raman scattering compared to fluorescence offer new possibilities for highly multiplexed measurements of cells and molecules. By altering the composition of the SERS tag, more than a dozen spectrally distinct labels can be detected with a single laser excitation and spectral detection. Moreover, the SERS measurement is compatible with simultaneous fluorescence measurements in a multilaser configuration, enabling a significant increase in the number of parameters that can be measured in individual cells. In addition, the combination of nanoparticle SERS tags with spectral detection can also be applied in an automated imaging format, enabling this approach to be applied to adherent cells and tissue sections.

(331) **Deep-UV Resonance Raman Spectroscopy of Biomolecules**; Renee D. JiJi[1], Michael K. Eagleburger[1], Jian Xiong[1], Jason W. Cooley[1]; [1]University of Missouri-Columbia

Deep-UV resonance Raman spectroscopy is an emerging technique for the study of biological processes such as protein folding. Bands arising from the peptide backbone are enhanced with respect to the rest of the spectrum enabling determination of protein structure during folding or ligand binding. Resonance enhancement of select vibrational modes, such as the backbone amide modes, occurs when the excitation wavelength corresponds to or overlaps the absorption band of the chromophore of interest. In addition to proteins, various small molecules can also be studied by deep-UV resonance Raman spectroscopy including flavonoids, cholesterol and fatty acids.

(332) **Polarized Raman Spectroscopic Analysis of Polymeric Products**; Mark Henson[1]; [1]ExxonMobil Chemical Co

Raman spectroscopy is an extremely versatile analytical technique, having evolved over the past several decades from a bulk laboratory technique into a range of diverse incarnations spanning confocal microscopes, fiber optic process analyzers, and in-field hand-held or stand-off detection systems for hazardous material identification. In addition to this myriad of sampling options, Raman provides detailed information about molecular structure and morphology. Further, polarized Raman experiments may be performed to assess phase-specific material orientation. This combination of aspects makes Raman a powerful tool for the characterization of semi-crystalline polymeric materials. This talk will detail the application of polarized Raman toward the increased understanding of the characteristics of polymers, via both laboratory-based analyses as well as online process monitoring during production.

(333) **Monitoring the API Form in Drug Product Using Spectroscopy**; Shawn Mehrens[1], Heather Frericks[1], Slobodan Sasic[2]; [1]Pfizer Worldwide Research and Development, [2]Vertex Pharmaceuticals

In drug discovery and development, the active pharmaceutical ingredient (API) is characterized thoroughly during pre-formulation activities to understand the polymorphic landscape of the molecule. Milling, blending, and other formulation unit operations can frequently cause process induced transformation. Depending on the stability of the physical form of the ingoing API, i.e., propensity to

hydrate, solvate or dissociate in the case of a cocrystal, the physical stability of the API in the unit dosage form may need to be assessed to assure the integrity of the physical form. This presentation will demonstrate the importance of monitoring the physical form of an API during stability, processing and in the final drug product using several different types of spectroscopy. The application areas include: 1) API detection in a low dose tablet, 2) detection of a hydrate form of an API during wet granulation, and 3) the physical stability of a cocrystal as API and in drug product. A Raman mapping method was highly effective and sensitive at detecting low levels of undesired forms in a low dose drug product. During wet granulation studies of a clinical candidate, DOE samples were assayed by Raman spectroscopy and no hydrate was identified during the process. When the ingoing API was spiked with hydrate, the concentration of hydrate increased during wet granulation, but none was detected if the starting API was purely anhydrous. The physical stability of a cocrystal API alone and as a low dose drug product was assessed using multiple solid state methods (Raman, SSNMR and PXRD) and the results are compared. These methods demonstrate that PXRD with standard methods may flag dissociation of the cocrystal, but more sensitive techniques such as Raman spectroscopy and SSNMR show significant improvements in monitoring the dissociation of the cocrystal at varying stability conditions.

(334) **High Resolution Laser-induced Breakdown Spectroscopy for Complex Spectra**; Jill Scott[1], Jeremy Hatch[1], Andrew J. Effenberger[2], Cynthia Hanson[1], Timothy McJunkin[1]; [1]Idaho National Laboratory, [2]University of California San Diego

Because of its relatively low cost, robust nature of the equipment, and the ability to rapidly collect data without sample preparation, laser-induced breakdown spectroscopy (LIBS) is an attractive technique for elemental analysis. However, broad application of LIBS to scientific and industrial analysis is limited by the complexity of the spectra produced that may have >1000 emission lines that overlap. For example, distinguishing between various alloys of stainless steel can be challenging because they are composed of mostly the same elements with small variations in concentrations and many of the elemental lines are superimposed on each other. Analysis of rare earth elements is difficult because of the number of emission lines. Standard spectrometers used for LIBS typically have a resolution of ~4500 ($\lambda/\Delta\lambda$) or 100 pm FWHM, which is insufficient for many materials. If application requires isotopic data for nuclear forensics, providence, or isoscapes, then the resolution challenge can be even greater. Thus, LIBS could benefit from higher resolution.While higher resolution spectrometers are available, they tend to be large and expensive, which negates some of the attractive features of LIBS. Recently, we have adapted a typical 0.5 m Czerny-Turner spectrograph with a Fabry-Perot etalon to achieve improved resolution in a cost effective manner. The resolution is predicated on the finesse and free spectral range of the Fabry-Perot with the Czerny-Turner spectrograph providing nominal separation of wavelength to help simplify the data interpretation. Initial results were obtained with a narrow band Fabry-Perot for the Hg hyperfine doublet from LIBS of the mineral cinnabar, which demonstrated a resolution of ~45,000 or 11 pm FWHM. Recently, a broadband etalon has been used to resolve lines in stainless steel and lanthanide samples. The results demonstrate that this is an economical method for acquiring high resolution for LIBS.

(335) **Effects of Local Plasma Cooling in LIBS Analysis**; M. Asgill[1], D.W. Hahn[1], S. Groh[2], K. Niemax[3]; [1]University of Florida, [2]ISAS at Technische Universität Dortmund, [3]Federal Institute for Materials Research and Testing (BAM)

A fundamental problem with real-time quantitative chemical analysis under the current state of LIBS technology is the non-linear analyte response that may at times occur when the composition of a sample's background matrix is altered. The inconsistencies that occur when investigating an analyte in different material matrices are generally referred to as matrix effects. For true quantitative analysis, calibration of the LIBS system must often be made with matrix matched samples, presenting limitations in performing in situ and real-time analysis. Careful analysis of laser-induced plasmas and the resulting emission processes can play a vital role in solving the current problems associated with the plasma-analyte interface and related matrix effects, thereby providing an essential step forward in quantitative plasma-based and plasma-assisted analysis. This talk will emphasize the effect of local plasma cooling during vaporization and ionization on atomic emission in LIBS plasmas. Recent research, including temporal analysis of plasma species derived from multi-element analyte particles, will be presented and discussed in the context of relevant physical processes that lead to the observed matrix effects.

(336) **Detection of Organic Particles in the Organic Gas Background using LIBS and LIF**; Seok Hwan Lee[1], Jack Yoh[1]; [1]Seoul National University, School of Mechanical and Aerospace Engineering Department

Organic particles such as soot and glucose can be detected in the organic gas (CO2) background using LIBS combined with LIF. LIBS alone cannot distinguish whether the signal comes from the solid particle or the gas, whereas LIF provides just the particle fluorescence signal from the excited surface of the particle at the laser focused spot. Here we propose a novel configuration to distinguish different phases having the same chemical composition by making use of LIBS together with LIF. The organic particle quantity is obtained from LIF signal, while both solid and gas phase quantities are attained from LIBS signal. Soot and glucose particles are injected into the test channel with CO2 as a carrier gas. The particles are excited by the UV beams (266 and 355 nm) with low laser energy at 1 mJ for the fluorescence signal. The higher energy at 100 mJ enables breakdown of both the particle and the CO2 gas for the LIBS signal. The broadband spectrum is obtained from the solid phase particles using LIF, and the spectral line of carbon (C 247.86 nm, CN 388.3 nm) is detected from the organic particles and gas using LIBS. From the combined LIF and LIBS spectra, the quantity of sample having different phases (solid and gas) with the same chemical composition can be distinguished.

(337) **LIBS Analysis of Coal Samples: Comparison of the Ablation Behavior between UV (266nm) and IR (1064nm) Laser Wavelengths**; Meirong Dong[1, 3], Jhanis Gonzalez[1, 2], Chunyi Liu[2], Jidong Lu[3], Richard Russo[1, 2]; [1]Lawrence Berkeley National Laboratory, [2]Applied Spectra, Inc, [3]South China University of Technology

This study is focus of on the effect of laser wavelength (1064nm and 266nm) and laser energy on coal samples ablation behavior. Seven coal standards were used in this study and the broadband LIBS spectra were compared. A comparison based on the emission line integrated intensity, shot-to-shot stability, and repeatability between locations for all elements of interest in coal (C, H, O, N, Si, Al, Ca, Mg, K, Na, Fe and Ti) was made and differences were explained based on the plasma properties. Calibration curves for some of the elements were established and are discussed in this study. The results revealed that both setups produced good calibration curves, however significant differences between their slopes were found. Also significant differences were notice between ionic emission lines of some metal elements and atomic emission of some elements like hydrogen, oxygen and nitrogen from the air surrounding of the samples.

(338) **Measurement of Silica in Coal Dust by Laser-Induced Breakdown Spectroscopy**; Art Miller[1], Chris Stipe[2], Jonathan Brown[3], Edward Guevara[3], Emanuele Cauda[1]; [1]CDC/NIOSH, [2]Photon Machines, Inc, [3]Seattle University

Laser-induced breakdown spectroscopy (LIBS) was used to quantify free silica in coal dust samples collected on filter media, with an eye toward developing a new technique for monitoring airborne silica in coal dust in near real-time. Silica is common in coal mines and represents a respiratory hazard that can lead to silicosis, a potentially fatal lung disease. Pure silica (Minusil-5), Georgia kaolin, and Pittsburgh-4 and Illinois-6 coal dusts were deposited separately and at multiple mass loadings onto 37-mm PVC filters. LIBS-generated silicon emission was monitored at 288.16 nm, and non-silica contributions to that signal from kaolinite were removed by simultaneously detecting aluminum. Measurements of Minusil-5 and Georgia kaolin were used to calculate limits of detection (LOD) for silicon and aluminum of approximately 0.08 µg/cm2 and 0.05 µg/cm2, respectively (corresponding to 0.16 µg/cm2 and 0.20 µg/cm2 for silica and kaolinite, respectively). Relative errors of prediction are around 10%. Results demonstrate that LIBS can dependably quantify silica on filter samples of coal dust and confirm that accurate quantification can be achieved for very lightly loaded samples, which supports the potential application of LIBS to near real-time monitoring.

(339) **Structural Identification of Fragment Ions Using Guided Ion Beam Tandem Mass Spectrometry**; Peter Armentrout[1]; [1]University of Utah

High energy collision-induced dissociation (CID) has long been used as a means of structural identification, although this application primarily involves simple bond cleavages such that CID establishes connectivity only. Structures involving rearrangements of complex molecules at lower excitation energies are not easily assigned using only mass-to-charge information. In this talk, we illustrate an in-source fragmentation technique that forms thermalized fragment ions, which can then be probed by threshold collision-induced dissociation. Threshold energies for subsequent dissociation of the fragment ion of interest can be compared with those calculated theoretically for various possible fragments, generally allowing unambiguous structural identifications, as well as providing valuable experimental thermodynamic information that permits predictions of subsequent reactions. Several case studies will be provided.

(340) **Inorganic and Organometallic Actinide Chemistry Studied by Tandem Mass Spectrometry**; John Gibson[1], Daniel Rios[1], Yu Gong[1], Ana Lucena[2], Joaquim Marçalo[2], Maria Michelini[3]; [1]Chemical Sciences Division, Lawrence Berkeley National Laboratory, [2]Instituto Tecnológico e Nuclear, Instituto Superior Técnico, Portugal, [3]Dipartimento di Chimica, Università della Calabria, Italy

Excitation of gas-phase actinide (An) coordination complex ions can impart sufficient energy to surmount kinetic and/or thermodynamic barriers to ligand fragmentation. If one or more product fragments effectively bind to the metal center as a ligand, new coordination complexes can be prepared; this approach is considered as "*in situ* ligand synthesis." We produce gas-phase actinide complexes by electrospray ionization, and then employ energetic collisions with helium gas in a quadrupole ion trap mass spectrometer (QIT/MS) to excite the complexes and induce *in situ* ligand synthesis. A variety of synthetic targets are being pursued by this approach, examples of which are organometallic actinyl complexes by decarboxylation as given by the following decomposition reaction of an actinyl ion, $U^{VI}O_2^{2+}$, $Np^{VI}O_2^{2+}$ or $Pu^{VI}O_2^{2+}$, coordinated by carboxylate anion ligands, $OOCR^-$: $[An^{VI}O_2\ (OOCR)_3]^- = [R\text{-}An^{VI}O_2\ (OOCR)_2]^- + CO_2$. This example illustrates guiding principles for *in situ* ligand synthesis, which here include creation of strong actinide-ligand bonds such as An-C, liberation of stable molecules such CO_2, and retention or creation of stable actinide oxidation states such as An^{VI}. The efficacy of decarboxylation for different carboxylates (i.e., varying R in $OOCR^-$) reveals electronic and steric effects in these processes; differences among the actinyls reveal variations across the series. Gas-phase reactions of produced ion complexes are studied in the QIT/MS to explore fundamental chemistry and intrinsic stabilities; an example is the comparative susceptibilities of organoactinyls towards hydrolysis according to the following reaction: $[R\text{-}An^{VI}O_2\ (OOCR)_2]^- + H_2O = [An^{VI}O_2\ (OH)(OOCR)_2]^- + HR$. Density functional theory is employed to elucidate observed transformations, as well as the structures and bonding in the actinide coordination complexes. This realm of gas-phase synthetic actinide chemistry accesses new types of bonding not yet achieved in condensed phase actinide chemistry. The gas-phase syntheses and reactivity results can provide insights and guidance for the preparation of related condensed phase materials. [This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences; by Fundação para a Ciência e a Tecnologia, Portugal; and by Università della Calabria, Italy.]

(341) **Using Tandem-MS to Obtain Isomer-Specific Vibrational Spectra of D2-tagged ions Cooled in a Cryogenic Ion Trap**; Christopher Leavitt[1], Arron Wolk[1], Michael Kamrath[1], Etienne Garand[2], Joseph Fournier[1], Peter Jordan[1], Michael Van Stipdonk[3], Scott Miller[1], Mark Johnson[1]; [1]Yale University, [2]University of Wisconsin-Madison, [3]Lawrence University

The infrared spectra of several gas-phase peptide ions are collected using vibrational predissociation spectroscopy. The ions are generated by electrospray ionization and tagged with weakly bound D_2 molecules in a cryogenically cooled ion trap maintained at a temperature of ~10 K. The infrared spectra are constructed by monitoring the photoinduced dissociation of the D_2 tags as a function of laser wavelength. This technique is demonstrated on the four model dipeptides $GlyGlyH^+$, $GlySarH^+$, $SarGlyH^+$, and $SarSarH^+$ [Gly=glycine; Sar=sarcosine] and the infrared action spectra are shown to result from single photon absorption events which make the spectra directly comparable to harmonic frequency calculations. In the case of $GlySarH^+$ and $SarSarH^+$, the spectra are complicated by extra bands that cannot be assigned to a single isomeric species. In order to explore the possibility of contributions from multiple conformers, a pump-probe photochemical hole-burning scheme involving two tunable infrared lasers and two stages of mass selection is utilized to isolate the isomer-specific spectra for these species. Both systems are shown to occur in two conformations based on *cis*- and *trans*-configurations with respect to the amide bond. The technique was also applied to a tripeptide bromination catalyst engineered to bind substrate molecules through specific hydrogen bonding interactions. The large number of low lying isomers indicated by theoretical calculations required the use of site specific isotope substitution to unambiguously assign spectral features to particular oscillators in the molecule. These additional constraints effectively guide the computational search and facilitate rapid convergence to a plausible conformation. The catalyst binding interactions to various substrates was explored by labeling potential hydrogen bond donors (^{15}N-H) and acceptors (^{13}C=O) to identify their contributions to the infrared spectra. The locations of these vibrational transitions reveal their local chemical environment and effectively identify the point contacts that tether the various catalyst substrate complexes.

(342) **Electron Capture Dissociation: An Introduction and Recent Developments**; Benjamin J. Bythell[1], Christopher L. Hendrickson[1, 2], Alan G. Marshall[1, 2]; [1]Ion Cyclotron Resonance Program, National High Magnetic Field Laboratory, Florida State University, [2]Department of Chemistry and Biochemistry

This presentation will provide an introduction to electron capture dissociation [1] and related techniques [2]. We shall briefly description the discovery of the technique, its applications and current implementation in Fourier transform ion cyclotron resonance [3] mass spectrometers as well as the current state of theoretical description(s). Recent examples will be provided to illustrate several of the many current approaches and potential future applications will be discussed too.

Acknowledgment

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(343) **Structures and Activation Energies for Glycosidic Bond Cleavage of Protonated Nucleosides from Energy-Resolved Collision-Induced Dissociation and Theoretical Studies**; Mary T. Rodgers[1], Ranran Wu[1]; [1]Wayne State University

The stability of the glycosidic bond in the protonated forms of the DNA and RNA nucleosides is investigated by examining the cross sections for collision-induced dissociation (CID) of these species as a function of kinetic energy. The primary and lowest energy dissociation pathway observed upon CID of all of the protonated nucleosides involves cleavage of the glycosidic bond resulting in elimination of the protonated nucleobase. Glycosidic bond cleavage resulting in elimination of the neutral nucleobase is also observed in competition with elimination of the protonated nucleobase at elevated energies. The branching ratios and energy dependence of these two primary dissociation pathways vary depending upon the identity of the nucleobase and the presence or absence of the 2′-hydroxyl group. Absolute 0 and 298 K activation energies (AEs) for nucleobase elimination are extracted via thermochemical analysis of the threshold regions of the CID product cross sections. Theoretical calculations suggest that hydrogen bonding interactions between the sugar and nucleobase moieties provide stabilization of the excess charge and result in relatively compact structures. The presence of multiple favorable proton binding sites, the flexibility in the hydrogen bonding interactions, the orientation of the nucleobase, and puckering of the sugar ring result in multiple low-energy conformers for many of these systems being populated at room temperature. The calculations also find that in some cases protonation stabilizes minor tautomers of the nucleobase. The energetics of glycosidic bond cleavage for the primary dissociation pathways observed are modeled theoretically and compared to the measured AEs. The effects of the identity of the nucleobase and the presence or absence of the 2′-hydroxyl group on the structures and stabilities of the protonated nucleosides are examined in detail.

(344) **Determining the Distribution of Magneisum Stearate in Tablets and Blends via Raman Chemical Mapping**; Slobodan Sasic[1], Martin Warman[1], Peter Ojakovo[1]; [1]Vertex Pharmaceuticals

Magnesium stearate is used as a lubricant in pharmaceutical manufacturing in order to prevent binding of tablets to the die during compression. Determining its distribution matters in the manufacturing campaigns experiencing issues with tabletting and in particular in cases it is added in a way alternative to the usual blending with other components (e.g. self lubricating presses). In this study, Raman and to a much smaller extent NIR chemical imaging are used to map distribution of Magnesium stearate in several tablets and blends produced in various manners with the concentrations varying but not exceeding 1.5% w/w. Several computational approaches are tested (univariate and multivariate) for producing images with the particular attention paid to the principal component analysis (PCA). Magnesium stearate Raman bands are clearly recognized in the higher PC loadings that account for minuscule variance in the data and that would not have been retained by any criterion for analyzing the eigenvalues. Mg Stearate distribution is hence reflected in the corresponding score maps that have to be carefully considered in some cases due to the contamination of the loadings of interest with some other bands (predominantly from the API). The maps are thresholded when possible and the distributions compared with regards to the concentration / manufacturing process utilized. NIR global illumination imaging proves much less efficient in comparison to Raman mapping mainly due to insufficient sensitivity.

(345) **Revisiting Analytical Approaches with Fast Confocal Raman Microscopy**; Don Clark[1], Jordan Cheyne[1]; [1]Pfizer Global Supply

The speed and spatial resolution obtainable from the new generation of confocal Raman microscopes has changed the use of this technology in the analysis of pharmaceutical products. This presentation will give examples of where the improved spatial resolution of these instruments have provided better understanding of pharmaceutical products and how this links to their manufacture and performance. The significantly faster spectral acquisition rates now approach those that have been enjoyed for many years with FT-NIR microscope mapping systems. This has made the use of chemical image fusion (CIF) to more fully describe the whole composition of a pharmaceutical tablet a much more realistic posibility rather than being just a technical curiosity. Our progress in delivering this revisited analytical approach and its impact on drug product understanding will be presented.

(346) **Quantitative Descriptions of Pharmaceutical Architecture using Ripley's K-function with Raman Chemical Images**; Gary McGeorge[1]; [1]Bristol-Myers Squibb

Compositional uniformity of unit dosages is recognized as a critical attribute of pharmaceutical finished products. Chemical imaging techniques, including Raman Imaging, are capable of discretely sub-sampling an intact dosage, and afford the opportunity to understand compositional variations within a single dosage (intra-dose uniformity). This presentation applies Ripley's K-function to describe the arrangement of ingredients in a series of component-specific images of pharmaceutical products. Besides providing an intuitive way to reduce the spatial information of hyperspectral imaging datasets, Ripley's K-function will be shown as an effective tool for assessing the size of agglomerates, the regional compositional variations around agglomerates, and the approximate length-scale of homogeneity in pharmaceutical products. This work demonstrates the role of Raman Imaging as a guide for development of both analytical methods and pharmaceutical manufacturing processes.

(347) **Analysis of API distribution and Migration through the Intravaginal Ring using Raman Imaging**; Eunah Lee[1], Philo Morse[2], Robert Lee[2], Andrew Whitley[1]; [1]HORIBA Scientific, [2]Particle Sciences

An intravaginal ring is composed of a physiologically inert polymer into that is incorporated with an active pharmaceutical ingredient (API) or APIs. The final formulation in the ring is typically developed in an iterative procedure of designing the candidate formulation, producing pilot samples, and determining the drug release profile. The results from drug release tests are used to design the next cycle until the formulation is optimized. Spatial distribution (at a given time) and the migration (over time) of API(s) throughout the sample are important aspects of the formulation characterization, and can help understanding the correlation between the performance and the formation. When assessed across the sample, and treated statistically, a Raman image offers the mean to analyze the spatial distribution of API(s), and comparing Raman images over time to characterize the formulation behavior over time. The samples in this paper are intravaginal rings formulated with an antiretroviral compound for AIDS treatment. A test formulation was produced by melt mixing ethyl vinyl acetate (EVA) with API and cryogrinding after cooling. Raman images of samples containing varying amounts of API were obtained to establish the relationship between the Raman spectra and the composition. Vaginal rings were formed with a lab scale injection molding equipment. A Raman image of a cross-section of a ring was obtained as it is. Four rings were placed in separate in-vivo elution buffer reservoirs and held for a maximum of 1 month. A ring was removed at 1 week increments, and a Raman image of a cross-section was obtained. Reference spectra of known samples (pure API, placebo, samples containing known amount of API) were used to analyze the data. The results demonstrate that Raman imaging provides valuable insight into the API distribution and migration in the polymer matrix.

(348) **3D Confocal Raman Imaging of Transparent and Opaque Samples**; Ute Schmidt[1, 2], Jianyong Yang[2], Thomas Dieing[1], Wei Liu[1, 2], Klaus Weishaupt[1]; [1]WITec GmbH, [2]WITec Instruments

Recently after its invention, confocal microscopy has been used to reconstruct three-dimensional images from micro-objects by using a spatial pinhole to eliminate out-of focus light in specimens that are thicker than the focal plane. Raman imaging benefits from the confocal setup, since it reduces the volume from which the Raman spectrum is collected, leading to a diffraction limited resolution in chemical imaging of samples. The latest spectroscopic detector technology combined with a high-throughput confocal microscope allowed significant improvements in sensitivity allowing acquisition times for a single Raman spectrum to be reduced to 0.7 milliseconds. Using such a sensitive setup can also be an advantage when performing measurements on delicate and precious samples requiring the lowest possible levels of excitation power. Time resolved investigations of fast dynamic processes can also benefit from such ultrafast spectral acquisition times. Confocal Raman imaging of rough opaque samples was thus far very challenging and time consuming, due to the inability to keep the samples in focus. The topographic Raman imaging method allows confocal Raman imaging guided by the surface topography obtained by an integrated profilometer. Large area topographic coordinates from the profilometer measurements can be precisely correlated with the large area confocal Raman imaging data. This allows true surface Raman imaging on heavily inclined or rough surfaces, with the true surface held in constant focus, while maintaining highest confocality. The aim of this contribution is to show how 3D Raman imaging can be applied in various fields of applications such as pharmaceutics, biology, and material sciences and lead to a better understanding of microscopic samples.

(349) **Impurity Profiling in Chemical Forensics: Recent Developments and Path Forward**; Carlos Fraga; [1]Pacific Northwest National Laboratory

Chemical threat agents (CTAs) such as highly toxic industrial chemicals and chemical warfare agents pose a serious threat to national security. In the event that a CTA is used in a crime or act of terrorism, there will be a need to provide evidence for attribution. Pacific Northwest National Laboratory and other labs are developing collection, preservation, and forensic analysis methods in order to provide chemical evidence for attribution following a CTA attack. Our presentation will cover recent developments in the discovery, collection, and exploitation of trace impurities in representative CTAs and precursors for source attribution. We will report on the use of head-space analysis, hyphenated chromatography, and chemometrics to discover and exploit CTA impurities for sample matching and synthetic-route determination and discuss our path forward in developing a forensic attribution capability.

(350) **Ultra Performance Liquid Chromatography and Mass Spectrometry for Forensic Characterization of Dyes Extracted from Millimeter-length Textile Fibers**; Stephen L. Morgan[1], Scott J. Hoy[1], Molly R. Burnip[1], Oscar G. Cabrices[1]; [1]University of South Carolina

Forensic examinations involve comparison of trace evidence fibers with one or more known fibers to determine possible associations between victims, suspects, and crime scenes. Fiber evidence is class evidence: discovery of a fiber at a crime scene and its identification as a particular fiber type (e.g., acrylic, cotton, nylon, polyester) may not provide much support for a forensic investigation. What is required is information that makes the trace evidence more specific and discriminating. While fast nondestructive methods such as microscopy, and UV/visible microspectrophotometry or IR spectroscopy are preferred for forensic fiber examinations, these techniques do not always provide enough discriminative information to establish a common origin between fibers. The premise of our ongoing research is that if dye formulations on trace fibers can be reliably profiled at trace levels, match exclusions be made with higher reliability, and "results consistent with" will have increased significance. Population studies report that fibers at crime scenes can be as small as 2 mm in length. Because extraction of dyes from a fiber is destructive to the evidence, we desire to analyze fibers in the mm or sub-mm range. Microextraction coupled with ultra performance liquid chromatography (UPLC) and UV/visible or mass spectrometric detection typically results in the detection of low ng amounts of extracted dyes from mm-length fibers. Fibers that are similar in visual appearance can often be discriminated just by retention time matching and UV/visible profile comparison without the need for mass spectrometry. The use of tandem mass spectrometry with multiple reaction monitoring further provides exquisite sensitivity for dye detection with limits of detection as low as 0.15 ng/μL of extract. Separation and detection of individual dye components provides a qualitative and semi-quantitative fiber dye 'fingerprint.' Determining the number and relative amounts of dyes present, and characterizing those dyes at the molecular level by MS, offers an entirely new level of discrimination. Such information may also open the possibility of tracing specific dye formulations to the textile manufacturer. Additionally, the separation and identification of dyestuffs, such as fluorescent brighteners or other finishing agents, demonstrates discrimination is possible among otherwise colorless fibers.

(351) **Direct Injection Mass Spectrometry for Nondestructive Forensic Chemical Analysis and Tracking of Chemistry Networks from Source to User**; Guido Verbeck[1]; [1]University of North Texas

Tracking illicit drugs and chemistries from an illicit source can be accomplished, even if there are no added markers and the chemistry has been cut and processed multiple times. This is accomplished by using the absolute presence and relative quantification based on impurities and side chemistries produced during the manufacturing process. A more difficult issue in tracking and showing dependency is the use of differing forms of mass spectrometry (MS) and standard operating procedures (SOP) to compare results, though all the instruments produce relative quantification for direct inject, or added chromatographies to MS. Here we present a method of extracting illicit chemistry residues from field samples via Direct Analyte-Probed Nanoextraction-coupled to nanospray ionization-mass spectrometry (DAPNe-NSI-MS). This instrumental technique allows for direct probing of trace analytes, provides higher selectivity, and lower limits of detection than current methods, and does not compromise the integrity of the field sample. Other techniques capable of this level of sensitivity lack selectivity, require extensive sample preparation, or destroy a sample beyond further use. DAPNe will be compared to these other direct techniques, and comparison of samples after multiple processing will be shown for tracking purposes.

(352) **Direct Analysis of Forensic Samples by Laser Ablation Electrospray Tandem Mass Spectrometry (LAESI-MS/MS)**; Robert Deimler[1], Trust Razunguzwa[2], Brent Reschke[2], Matthew Powell[2], Glen Jackson[1]; [1]Ohio University, [2]Protea Biosciences, Inc.

Forensic applications of LAESI–MS/MS are demonstrated using three distinct matrices: 1) aqueous solutions—to confirm the identity of scheduled drugs directly from the well plates of presumptive color tests, 2) human hair fibers—for direct confirmation of drugs of abuse and metabolites at biologically relevant levels, and 3) Plant matter—for direct confirmation of cannabinoids in Cannabis botanical matter. In all three applications, the liquid, hair or plant matter samples are directly ablated with a mid-IR laser beam to generate a plume that is directed into a mass spectrometer using an electrospray stream. Benefits of LAESI sampling over other ambient techniques like DESI or DART are the micrometer sampling tolerances and the ability to probe samples sub-surface. The identities of the drugs and mixtures of drugs were confirmed by measured m/z values as well as fragment ions from MS/MS fragmentation patterns. Common cutting agents like caffeine and quinine were also added to the scheduled drugs and could also be confirmed through MS/MS analysis. A NIST standard reference material consisting of drugs of abuse in human hair provided MS/MS spectra consistent with reference spectra of drugs in the NIST MS/MS database. Example hits include cocaine and codeine at approximately 7.0 and 2.9 mg/kg, respectively. THC was also identified from Cannabis leaves in positive mode MS/MS. These applications demonstrate that drug confirmations are possible from different matrices with almost no sample preparation necessary before analysis. A well plate containing 96 samples can be analyzed in a matter of minutes, in contrast to the standard GC-MS protocols used in crime labs that would take several days to confirm this number of samples.

(353) **Detection and Preliminary Characterization of Inorganic Nanomaterials in Food by Asymmetric Flow Field Flow Fractionation Coupled to ICP-MS**; Julien Heroult[1], Volker Nischwitz[1], Heidi Goenaga-Infante[1]; [1]LGC Limited

The presence of nanomaterials (with size range from approximately 1 nm to 100 nm) in food is not new [1]. The addition of nanomaterials to food has increased over the last decade since they may offer benefits to both industry and consumers. For instance, inorganic nanoparticles have been used as food additives for enhancing colours, flavours, for preservation and to facilitate manufacturing processes. However, nanotechnologies may also present new risks as a result of their novel properties. In view of this potential hazard, regulatory and scientific assessment requires an understanding of exposure to both humans and the environment. To date, metrology has focused on the development of methods to characterise nanomaterials for their physical properties in their powder forms or in simple matrices. Therefore, there is an increasing need for traceable methods and reference materials for quality assurance of nanoparticle characterisation in complex matrices including food. Such methods will help support upcoming regulation and enable quality control of existing products. In particular, the extraction of nanomaterials from the solid food sample without altering their properties is an important challenge. In this work, a systematic approach to the characterization of silicon dioxide nanoparticles in coffee creamers by asymmetric flow field flow fractionation (FFF) coupled on-line to ICP-MS has been developed. Optimisation of sample preparation conditions such as sample to extractant ratio, defatting with organic solvents, temperature and sonication time, that may affect nanoparticle size and size distribution in suspensions were considered. The use of sample preparation procedures that mimic real coffee creamer preparation were also investigated to obtain meaningful results regarding size and size distribution of SiO2 nanomaterials in the studied food matrix. FFF-ICP-MS analysis of extracts of both non spiked coffee creamer and coffee creamer spiked with food-grade silicon dioxide, using different approaches for size estimation enabled determination of SiO2 size-based speciation. Finally, performance characteristics of the developed methodology (e.g. repeatability, Si limits of detection) for the quantification of silicon dioxide particles in coffee creamers and quantitative recovery data will be presented. [1] CEN ISO/TS 27687:2009.

(354) **Analysis of Single Nanoparticles by ICP-MS: Where is the Limit?**; Carsten Engelhard[1], Bastian Franze[1], Ingo Strenge[1], Christoph Wehe[1], Michael Sperling[1], Uwe Karst[1]; [1]University of Muenster

Engineered nanomaterials are used increasingly around the world in consumer and industrial products. In recent years, environmental concerns are being raised that call for risk assessment, toxicity studies, and nano safety policies. It is therefore important to provide analytical tools that are able to characterize and quantitate various types of nanomaterials. In this presentation, it will be discussed how inductively coupled plasma mass spectrometry (ICP-MS) can provide such information when operated in a unique fashion termed single-particle mode. In contrast to conventional ICP-MS operation, single particle detection is accomplished by transient analysis of very dilute nanoparticle (NP) solutions. Atomization and ionization of single particles in the ICP produce discrete ion clouds which in turn create detector signals that correspond to the particle size. Size characterization and quantification of commercially available nanoparticles was performed. The influence of different parameters such as sample introduction systems on the ICP-MS performance will be presented. Furthermore, the influence of the type of detector and signal acquisition on the analysis will be critically reviewed. Current challenges in single particle detection will be discussed as well as potential solutions to these challenges.

(355) **Measurement and Calibration Strategy for ICP-MS Single-Particle Analysis**; Wing-Tat Chan[1], Thomas K.O. Lui[1], Jeff K.H. Lee[1]; [1]University of Hong Kong

Calibration of ICP-MS single-particle analysis using standard particles of known particle mass is required for accurate measurement. Calibration using the average particle mass of a batch of standard particles is effectively a single-point calibration. In this study, the feasibility of constructing a calibration curve by correlating the distribution of ICP-MS spike intensity and the distribution of the

mass of standard particles is investigated. Gold nanoparticles are used as the test particles. The particle size is determined using TEM. The particle mass is calculated from the volume and density of the particle. The mass range of monodisperse gold nanoparticles is relatively small, spanning over approximately a factor of 2. Linear calibration curves for Au nanoparticles of nominal diameter of 80, 100, 150, and 200 nm are obtained. The slope of the calibration curves, however, reduces as the diameter increases. The combined calibration curve of all 4 batches of standard particles is non-linear although the mass range spans over a factor of 30 only. The limited linear dynamic range is probably combined effect of incomplete vaporization of the large particles and relatively significant diffusion loss of analyte atoms for the small particles. A computer program that accounts for the rate of particle vaporization and analyte atom diffusion is used to estimate the relative ICP-MS intensity of standard particles at different ICP sampling depth. Simulated calibration curves of 4 kinds of hypothetical nanoparticles representing 4 combinations of boiling point and analyte diffusion rate will be presented. The relative contribution of the rate of particle vaporization and analyte diffusion on the linearity and slope of the calibration curve will be discussed. The conditions for satisfactory calibration using continuous flow of aerosols of standard solutions will also be discussed.

(356) **Posttranslational Modifications as an Insight into Silver Nanoparticle Ecotoxicity**; Traci Hanley[1], Cheolho Yoon[,2], Ryan Saadaiw[1], Julio Landero[1], Joseph Caruso[1]; [1]University of Cincinnati, Department of Chemistry, [2]Korea Basic Science Institute, Seoul Center

The use of silver nanoparticles (AgNP) are rapidly increasing, introducing a noteworthy opportunity for inevitable release into the environment, where few studies have been performed to characterize their ecotoxicity[1,2]. Although there are many benefits associated with AgNP applications, in vitro studies show AgNPs and their products can induce liver and nervous system toxicity and affect cellular phosphorylation in rats, proliferating nitric oxide (NO). Increased NO in turn negatively affects the coronary system.[3,4] Cellular phosphorylation is by far the most common posttranslational modification, where protein activity is either induced or inhibited directly resulting from exposure to toxins. It is widely noted that free Ag+ ions may be the product of AgNP, inducing toxicity as seen with the Daphnia magna, a water flea commonly used for laboratory ecotoxicity studies. [5] Posttranslational modification studies are imperative to ascertain the toxicity of AgNP in nature, where future studies will need to be performed to evaluate whether it's the nanoparticle or ion responsible for AgNP's toxicity. [6] The objective of this study is to evaluate the degree of phosphorylation changes resulting from AgNP exposure in Skeletonema costatum grown in simulated salt water; an aquatic phytoplankton test species utilized by the U.S. E.P.A in water quality/toxicity studies. Phytoplankton will provide an excellent bio-monitoring source in salt water environments to elucidate the degree of AgNP contamination, and silver species inducing toxicity. [6] Two dimensions of chromatographic separation are proposed to decrease the complexity of the cell lysates, size exclusion and anion exchange chromatography, coupled to the ICP-MS are a very effective tools to separate the S. costatum proteome into simpler fractions to be analyzed by LC-ESI-MS in a shot gun proteomics aproach. The nanoflow/phosphochip-ESI-MS will specifically reveal phosphorylation related changes induced by AgNP, indicating possible secondary toxic effects. In addition, ionic silver-protein interactions will be screened as we try to answer the question, is it the silver ion or nanoparticle responsible for cellular toxicity.

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(357) **Strategies about the Biodistribution of Nano Gold and Nano Silver by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)**; Petra Krystek[1]; [1]VU University Amsterdam, Institute for Environmental Studies (IVM)

The analysis of engineered nanoparticles (NPs) in biological materials is of growing interest because the knowledge on exposure and possible toxicity of nanotechnological products is still limited. Therefore biodistribution studies have been designed to investigate the (time-depending) distribution of nanoparticles in selected organs and body fluids. Special focus is given to the strategies as well as to the use of the ICP-MS technique for the determination of the NPs containing metals. Examples of the recent research applications on gold and silver NPs will be presented. While for gold NPs a large variety of very different size, shape and coating are known, they also provide many opportunities in imaging, diagnostics, and therapies of nano medicine. Hence, their bio kinetics in the body are prerequisites for specific tailoring of nano medicinal applications and for a comprehensive risk assessment. Silver NPs are applied in many consumer products; therefore it is useful to get a better understanding of their in vivo distribution. Next to the chemical composition of the nanoparticles, attention is also paid to different sizes and to different shapes (nanodots vs. nanorods) as well as to possible coatings. Different procedures of sample pre-treatment and quantification by ICP-MS, especially on ultra-trace levels, will be shown. The results and interpretations of several distribution studies as well as quality control aspects will be presented.

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(358) **Multivariate Optical Computing Applied to Phytoplankton Fluorescence Excitation Spectroscopy**; Michael Myrick[1], Tammi Richardson[1], Timothy Shaw[1], Heidi Sosik[2], Robert Olsen[2], Joseph Swanstrom[1], Megan Baranowski[1], Larua Bruckman[1], Shawna Tazik[1], Elizabeth Abernathy[1]; [1]University of South Carolina, [2]Woods Hole Oceanographic Institution, [3]Sandia National Laboratory

Phytoplankton account for most of the carbon sequestration on our planet, but there are many species of phytoplankton. Some are light so they're more likely to be eaten by predators when they die. Others have dense inorganic shells, so they're more likely to sink and take their carbon with them. Our lack of knowledge of the relative populations of these organisms leaves a big unknown in climate modeling. We've been working on classification of phytoplankton based on their single-cell fluorescence excitation spectra, using a method called multivariate optical computing. In this form of modeling, linear spectroscopic patterns are expressed as the spectra of interference filters. This enables wide-band spectral information to be used, providing benefits in speed, simplicity, power consumption, and sensitivity. The presentation will cover aspects of the spectroscopy of individual phytoplankters, linear discriminants analysis, multivariate optical element modeling, design of instruments for barcoding phytoplankton, software for interpreting

plankton fluorescence tracks and extracting organism size from blurred streaks, plus laboratory results. In conclusion, we'll describe field trial data obtained from Martha's Vineyard.

(359) **Novel High Throughput EEM Detection for Flowing Samples—Obviation of Mie and Raman Scattering**; Timothy Corcoran, Charles Schreyer[1], Ivonne de la Torre[1], Jacob Balthazor[1], Phillip Allen[1], Alisha Lewis[1]; [1]California State Polytechnic University Pomona

Excitation-emission matrix (EEM) fluorescence detection has normally been performed on a series of static samples or under slowly flowing conditions due to experimental constraints. By redesigning the experimental approach, we have extended the technique to allow real-time capillary flow detection with millisecond time resolution, to develop a method suited for sheath-flow capillary electrophoresis. The tiny capillary diameter requires that the excitation light be very tightly focused and the rapid acquisition time requires that it be intense—conditions not suited to conventional arc lamp sources, but satisfied by use of supercontinuum laser excitation. As usual, parallel factor analysis (PARAFAC) may be used for analysis, but the fact that the camera frame rate is faster than the rate at which the sample transits the excitation region required the development of a velocity compensation algorithm for the data cube, since the EEM data of each sample is spread over many camera frames. Two major contributors to noise in EEM data may be discerned: Raman scatter from the solvent and Mie scattering from particles. These have distinct signatures in the flowing samples since the motion of the latter is clearly apparent in the data, and may be redressed both by particular care in the optics along with weighted PARAFAC methods.

(360) **Traps and Pitfalls when Applying Chemometrics to Biomedical Problems**; Jerome Workman[1, 2, 3]; [1]Unity Scientific, [2]National University, [3]Liberty University

Are chemometric approaches, rather than improved signal quality, the primary answer to most analytical applications as we repeat the refrain, "Math is Cheaper than Physics?" Or do robust modeling solutions for challenging spectroscopic applications require a more comprehensive strategy to provide the highest quality signal combined with appropriate preprocessing and calibration steps. A dual approach including hardware modifications combined with chemometric approaches involves altering instrument design characteristics specific to the analytical application requirements. In addition, one must ask if automated expert algorithms must be included for quality and performance monitoring in near real time. Comprehensive strategies for applying chemometric methods include: experimental design optimization relative to calibration, data selection and preprocessing, outlier or 'non-analysis' sample detection, upset condition monitoring or mitigation, improved modeling approaches, calibration transfer strategies, and continuous monitoring and quality control metrics. This paper discusses the potential traps and pitfalls when applying 'standard' approaches for accurate prediction and monitoring of challenging spectroscopic biomedical applications.

(361) **Scrutinizing Attributes of Data of Very High Dimension**; Robert Lodder; [1]University of Kentucky

Optical and acoustic spectra are analyzed using a new feature screening procedure employing a unified model framework that covers a range of commonly used parametric and semiparametric models. The method is flexible and does not require forcing a specific model structure on regression functions, and so it is particularly attractive for ultrahigh-dimensional regressions, where there are a huge number of candidate predictors but little information about the actual model forms. With the number of predictors growing at an exponential rate of the sample size, the procedure possesses consistency in ranking, which is both useful in its own right and can lead to consistency in selection. The new procedure is computationally efficient and simple, and exhibits a useful empirical performance in simulations and real data analysis.

(362) **Raman, Infrared and NMR Spectroscopies on the Same Samples and the Etiology and Cure for Dry Eyes**; Douglas Borchman[1], Marta Yappert[1], Gary Foulks[1]; [1]University of Louisville

Meibomian gland dysfunction (MGD) is a common clinical problem that is often associated with evaporative dry eye disease. Alterations of the lipids of the meibomian glands have been identified in several studies of MGD. Raman, Infrared and NMR spectroscopies and mass spectrometry were all performed on the same human meibum samples as a prospective, observational, open label clinical trial to document the improvement in both clinical signs and symptoms of disease as well as spectroscopic characteristics of the meibomian gland lipids after therapy with topical azithromycin ophthalmic solution and oral doxycycline treatment. Subjects with symptomatic MGD were recruited. Signs of MGD were evaluated with a slit lamp. Symptoms of MGD were measured by the response of subjects to a questionnaire. Meibum lipid-lipid interaction strength, conformation and phase transition parameters, meibum protein were measured using Fourier transform infrared spectroscopy (FTIR), Raman and principal component analysis (PCA). Terpenoids, short chain CH3 moieties, lipid oxidation, wax, cholesterylesters and glycerides were measured with a nuclear magnetic resonance (NMR) spectrometer. Topical therapy with azithromycin and doxycycline relieved signs and symptoms and restored the lipid properties of the meibomian gland secretion towards normal. In subjects with clinical evidence of MGD changes in ordering of the lipids and phase transition temperature, were brought closer to normal with azithromycin treatment but not doxycycline treatment. Treatment with doxycycline but not azithromycin restored the FTIR PCA scores and relative area of the 1H-NMR resonance at 1.26 ppm. Both doxycycline and azithromycin treatment restored the levels of the relative areas of the 1H-NMR resonances at 5.2 and 7.9 ppm to normal levels. The level of meibum protein and meibum lipid oxidation were not influenced by azithromycin or doxycycline treatment. The mechanism of action of doxycycline may be different than that of azithromycin. It is exciting that when carotenoids in meibum are low as in MGD, the tear film is unstable and patients have the signs and symptoms of dry eye. When terpenoids are restored with azithromycin and doxycycline treatment, tear film stability is restored and patients no longer have the signs and symptoms of dry eye.

(363) **Dielectric and Dielectrophoretic Measurements and Manipulations of Cells for Human Health and Energy Applications**; Brian Kirby[1]; [1]Cornell University

We present work focused on three projects: (1) we are using dielectrophoresis to screen Mycobacterium species to find membrane-relevant mutations. Here, a dielectrophoretic spectrometer is used that transduces DEP mobility to spatial location in microdevices, identifying mutated cells with potential to inform study of antibiotic resistance in M. tuberculosis. (2) we are using dielectrophoresis in conjuction with GEDI rare cell immunocapture microdevices to capture rare cells at high purity and efficiency; here, dielectrophoresis is used in the vicinity of an immunospecific surface to help prevent nonspecific adhesion. (3) We are using dielectric characterization of algal cells to monitor lipid concentration in lipid-accumulating algae for biodiesel applications.

(364) **Interfacial Microfluidics for Biochemical and Cellular Analysis**; Jachary Gagnon[1]; [1]Dept of Chemical and Biomoleuclar Engineering Johns Hopkins Univ

To date, AC electric fields have been exploited to manipulate liquid

(electro-osmosis) bubbles, particles, biomolecules and cells (dielectrophoresis) in microfluidic devices. Research and application in this area, however, has been limited to the interfaces formed between two immiscible metal-liquid, particle-liquid, or gas-liquid surfaces. The influence of AC electric fields across aqueous liquid-liquid interfaces remains unexplored. As the majority of microfluidic applications involve aqueous liquid flows at low Reynolds number, fluid interfaces formed between co-flowing fluid streams are a natural occurrence in microfluidic devices. Fundamentally, many electrokinetic phenomena arise from discontinuities in ionic flux and charge accumulation at electrical interfaces. These regions of net charge interact with an external electric field and a body force is exerted on the interface. Using a microfluidic channel with embedded electrodes, two fluid streams - one with a greater electrical conductivity, the other a greater dielectric constant - were made to flow side-by-side. An AC field was applied across the flow channel and fluid was observed to displace across the interface. The displacement direction is frequency dependent, and is attributed to the Maxwell-Wagner interfacial polarization at the liquid-liquid electrical interface. At low AC frequency (< 1 MHz), below the interfacial charge relaxation time, the high conductive stream is observed to displace into the high dielectric stream. Above this frequency, the direction of liquid injection reverses, and the high dielectric stream injects into the high conductivity stream. Hence, a liquid crossover frequency is observed and is well described by Maxwell-Wagner polarization mechanics. Utilizing this mechanism, we explore the use interfacial polarization at liquid-liquid and polymer-electrode electrical interfaces for fluidic sensing and processing. Here, we demonstrate how these small microfluidic force fields, generated at polarized electrical interfaces, can be used to produce a portable and robust microfludic platform capable of precision fluid manipulation, electrolyte ion-sensing, particle and cell separation and solute concentration control.

(365) **Dielectrophoresis of Polyelectrolytes in Nanofluidic Landscapes**; Robert Riehn[1], Chunda Zhou[1], Zubair Azad[1]; [1]North Carolina State University

Electrodeless a.c. dielectrophoresis is a relatively well-explored tool for the manipulation of DNA. In this talk we discuss phenomena that arise if the dimensions of the the fluid system become smaller than the polymer coil. In this case interesting transport phenomena can arise. We demonstrate a nanofluidic metamaterial with a d.c. mobility tensor that can be directed by application of an a.c. electric field. We will also explore the phase transition that DNA can undergo in strong electric fields with a frequency of a few hundred Hz. We argue that the strong collapse of single molecules with and without nanoconfinement are a manifestation of long-range counter- and co-ion correlations, which point to a breakdown of the free-draining assumption of polyelectrolyte electrophoresis.

(366) **Single-cell Electrofusion: Three DEP Elements in one Process Chain**; Magnus S. Jaeger[1]; [1]Fraunhofer Institute for Biomedical Engineering (IBMT)

Microfluidic chips for performing electrofusion in small sample volumes have been around for several years now. However, small volumes are not the same as small cell numbers. While conventional chips feature an excellent through-put and a fair pairing efficiency, they still rely on auxotrophy selection of fused cells, e. g. employing classical HAT medium. This is prohibitive when only few cells are available, such as in identifying T cell sub-species in mice. In contrast, dielectrophoretic (DEP) systems can fuse two individual cells and subsequently provide the single hybrid product for downstream cell culture. This unmatched precision comes at the small price of having to integrate and manage more microelectrodes. Through-put is also much lower in set-ups that handle cell pairs sequentially instead of in parallel, making the latter more economically feasible. However, the former's single-cell resolution may help to elucidate basics of post-fusion re-organisation - a prerequisite to understanding virus-related tumorigenesis. DEP also adds two further tools accessory to the fusion unit: firstly, it serves to identify cells that enter the chip. To this end, they are individually deformed in the electric field. The differences in their response to this stress were found to be a marker that depends strongly on cell type and malignancy, thus providing a label-free and on-chip method. Secondly, DEP helps to accumulate cells in a reduced fluid volume, e. g. before they are flushed from the chip. For this, they may be trapped in electro-hydrodynamic flow eddies occurring above microelectrode arrays. These eddies provide a tunable filter element which can be switched at will. In contrast to mechanical filters, they therefore do not clog.

(367) **A Dielectrophoretic Sorter for Nanoparticle and Nanocrystal Separation**; Bahige Abdallah[1], Tzu-Chiao Chao[1], Petra Fromme[1], Alexandra Ros[1]; [1]Arizona State University

We propose a method to sort photosystem I crystals based on size using a combination of dielectrophoresis (DEP) and electrokinesis within a microfluidic structure. Due to heterogeneous crystal size distribution inherent to macroscale protein crystallization, a method to sort and isolate protein crystals into various size fractions is important for nanocrystallographic analysis. Our work improves upon previous designs with the objective to sort nanoparticles on the order of 100 nm by a combination of dielectrophoretic focusing and electrokinetic migration. DEP is size dependent which makes it ideal for sized based separations. However, DEP with nanoparticles suffers from the fact that high electric field gradients are necessary to achieve considerable DEP effects. To accommodate a nanoparticle sorter in a microfluidic device, we couple electrokinesis and DEP to further affect the selectivity between nanoparticles in the presence of an electric field. We utilize an elastomer microdevice consisting of an inlet leading to a restrictive insulator that continues on to a series of outlet channels. Upon potential application, a heterogeneous electric field develops in the insulator region inducing DEP on the nanoparticles. The potential in each outlet channel is differentially controlled allowing for a variation in the electrokinetic force experienced by the nanoparticles. With this method, we could show experimentally that larger 1 μm polystyrene beads focus into the center outlet whereas smaller 100 nm beads disperse into other outlets for collection. Further numerical simulations have confirmed this behavior. In the case of the larger particles, electrokinesis contributes to particle directionality in tandem with dielectrophoresis to enhance the focusing effect. DEP affects the smaller beads marginally allowing them to deflect into collection outlets. These results indicate that a balance between DEP and electrokinesis is necessary for adequate sorting of various sized nanoparticles. Our ongoing work is dedicated to the application of this sorting mechanism for nanocrystal fractionation.

(368) **Sequential Identification of Model Parameters by Derivative Double Two-Dimensional Correlation Spectroscopy and Calibration-Free Approach in Chemical Reaction Systems**; Yukihiro Ozaki[1], Nicolas Spegazzini[1], Heinz W. Siesler[2]; [1]Kwansei Gakuin University, [2]University of Duisburg-Essen

A sequential identification approach by two-dimensional (2D) correlation analysis for the identification of chemical reaction model, activation and thermodynamics parameter is presented in this study. The identification task is decomposed into a sequence of subproblems. The first step is the construction of reaction model through the suggested information by model-free 2D correlation analysis using a novel technique called Derivative Double 2D correlation spectroscopy (DD2DCOS), which enables one to analyze intensities with nonlinear behavior and overlapped bands. The second step is a model-based 2D correlation analysis where the activation

and thermodynamic parameters are estimated by indirect implicit calibration or calibration-free approach, in this way a minimization process between the spectral information by sample-sample 2D correlation spectroscopy and kinetic hard modeling (using ordinary differential equation) of the chemical reaction model are carried out. The sequential identification by 2D correlation analysis is illustrated in the isomeric structure of diphenylurethane synthesized from phenylisocyanate and phenol. The reaction was investigated by FT-IR spectroscopy. The activation and thermodynamic parameters of the isomeric structures of diphenylurethane linked through a hydrogen bonding equilibrium were studied by means of an integration of model-free and model-based 2D correlation analysis called sequential identification approach. The study determined the enthalpy (ΔH = 15.2 kJ/mol) and entropy ($T\Delta S$ = 14.6 kJ/mol), of C=O•••H hydrogen bonding of isomeric structure of diphenylurethane through direct calculation from the differences in the kinetic parameters ($\delta\Delta^{\ddagger}H$, $-T\delta\Delta^{\ddagger}S$) at equilibrium in the chemical reaction system.

(369) **2D Correlation Raman Spectroscopy for Probing the Mechanism of Folding and Aggregation**; Igor Lednev[1], Vitali Sikirzhytski[1]; [1]University at Albany, State University of New York

Protein and RNA/DNA folding and aggregation involve typically many consecutive steps and often demonstrate a cooperative behavior. Raman spectroscopy allows for probing various parts of a biological system, which could be considered as intrinsic markers. Specific examples will be discussed to demonstrate the power of 2D correlation Raman spectroscopy for elucidating the folding/aggregation mechanism.

(370) **Two-Dimensional Correlation Spectroscopy of Polymer in Terahertz Frequency Region**; Hiromichi Hoshina[1], Shinya Ishii[1, 2], Yusuke Morisawa[3], Harumi Sato[3], Shigeki Yamamoto[3], Isao Noda[4], Yukihiro Ozaki[3], Chiko Otani[1]; [1]RIKEN, [2]Miyagi University of Education, [3]Kwansei Gakuin University, [4]The Procter & Gamble Company

The recent development of time domain spectroscopy in the terahertz (THz) frequency region has enabled the facile and rapid acquisition of absorption spectra in the frequency range of 0.1~3 THz. A plethora of information about intermolecular structure and interactions (rather than intramolecular structure) can be garnered from terahertz spectroscopy, which is a powerful tool for monitoring higher order conformations of large molecules. For example, our prior studies of the THz spectra of poly(3-hydroxybutylate) (PHB) have highlighted clear differences between the spectrum of amorphous PHB and that of crystalline PHB. Furthermore, on the basis of these studies, using polarization spectroscopy, the vibrational peaks of crystalline PHB corresponding to the skeletal vibration of the helical structure and the vibration between helical structures could be assigned. In this study, the isothermal crystallization of PHB was studied by monitoring the temporal evolution of terahertz absorption spectra in conjunction with spectral analysis using two-dimensional correlation spectroscopy. Correlation between the absorption peaks and the sequential order of the changes in spectral intensity extracted from synchronous and asynchronous plots indicated that crystallization of PHB at 90 °C is a two step process, in which C-H...O=C hydrogen bonds are initially formed before well-defined crystal structures are established.

(371) **2D Correlation Analysis in Tracing the Absorbance Changes Caused by the Transitions of Polymer and Protein**; Young Mee Jung[1], Min Kyung Kim[1], Soo Ryeon Ryu[1], Bogusława Czarnik-Matusewicz[2], Isao Noda[3]; [1]Kangwon National University, [2]University of Wrocław, [3]The Procter & Gamble Company

Thermal behavior of spin-coated films of P(HB-*co*-HHx)/PEG (HHx = 3.8, 7.2 and 10.0 mol%) blends and transition of α-lactalbumin (α-LA) from the native to the molten globule state were investigated by 2D correlation spectroscopy. From the analysis of 2D IRRAS correlation spectra of spin-coated films of P(HB-*co*-HHx)/PEG blends, we could determine the sequence of spectral intensity changes with increasing temperature. The changes attributed to the PEG band are ahead of any other, next a band for crystalline component of P(HB-*co*-HHx) changes before a band for amorphous component. Their transition temperatures were successfully determined by 2D gradient mapping method. Null-space 2D projection correlation spectra clearly showed the contribution of PEG in spin-coated films of P(HB-co-HHx)/PEG blends during heating process, which is barely observable in conventional 2D correlation spectra. The pH-induced structural alternations of Ca^{2+}-bond (holo) α-LA were monitored on the base of IR spectra of aqueous solutions of this protein measured both in the transmission (TR) and the attenuated total reflectance (ATR) mode. To examine the water influence on absorbance distribution of the amide bands due to hydration of the two domains of α-LA, we have also done the FTIR-ATR measurements for two kinds of samples, measured as a solution and as a low level hydrated film on the ATR element. The 2D correlation procedure was applied to the analysis of the three sets of data. Because the pH values were unevenly distributed this fact was taken into account during the 2D calculations. Moreover, the spectra were composed from strong absorbance variations assigned to the $\nu_{as,s}COO^-$ and νC=O bands and the weak ones attributed to the amide I absorbance. For enhancement of the weak component the Pareto scaling method was selected. 2D correlation analysis shows that both state of sample (solution or solid film) and the mode of measurement (TR or ATR) have strong influence on the relative correlation between the absorbance changes due to vibrations developed in the side chains and in the main backbone of α-LA. Employing the 2D correlation procedure to the analysis detailed description of the hydration induced changes accompanying the N-to-MG transition in α-LA was obtained.

(372) **Raman Optical Activity Studies of Pharmaceutical Compounds**; Ewan Blanch[1], Clare Levene[1], Saeideh Ostovar pour[1], Belen Nieto-Ortega[2], Katarzyna Chruszcz-Lipska[3], Javier Ramirez[2], Babur Chodhry[4], Trevor Dines; [1]University of Manchester, [2]University of Malaga, [3]Jagiellonian University, [4]University of Greenwich

Raman optical activity, which measures the small difference in Raman scattering from chiral molecules in right- and left-circularly polarized light [1,2], is making a significant impact as a tool for characterizing the structures and conformational dynamics of proteins and other biomolecules. Due to its sensitivity to stereochemistry, ROA is also highly suitable for characterizing chiral pharmaceuticals, and so complement existing techniques in the pharmaceutical industry. As an illustration of this potential, this talk presents results from recent conformational studies of three chiral pharmaceuticals; i) aeroplysinin-1, an antiangiogenic [3], ii) detection of (-) bornyl acetate in pichtae essential oil (Siberian fir needle oil, Abies sibirica oil) [4], and iii) acetylation and cyclization of dipeptides with neurotransmitter function. The integration of computational modelling of spectra with experimental results is a rapidly developing methodology in ROA spectroscopy, and is an important aspect of the work presented here. Results from these studies illustrate the role that ROA spectroscopy can play as an analytical tool for the pharmaceutical sciences.

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(373) **Detection of Polymorphism and Quantitative Determination of Active Ingredients in Pharmaceutical Formulations by Raman Spectroscopy**; Heinz Siesler[1]; [1]University of Duisburg-Essen

Polymorphism in active ingredients is usually investigated by x-ray diffraction. This technique provides distinctive diffraction peaks that allow the identification of different polymorphs as pure or mixed forms. As an alternative to this complex and time-consuming technique the present communication will demonstrate and compare the application of Raman, mid-infrared and near-infrared spectroscopy in combination with chemometric evaluation routines for this purpose. Specifically, the discrimination of the two relevant polymorphs A/C of mebendazole – a broad spectrum anthelminthic drug – will be discussed. Furthermore, the use of these analytical techniques for the quantitative determination of A/C polymorph mixtures will be outlined. Finally, the performance of hand-held Raman and NIR spectrometers will be compared with ref-erence to the quantitative determination of the active ingredients in a solid five-component pharmaceutical drug formulation.

(374) **Use of Raman Spectroscopy to Investigate the Physical Stability of Compacted Solid Dispersions**; Ryanne N. Palermo[1], Benoit Igne[2], Carl A. Anderson[1, 2], James K. Drennen, III[1, 2]; [1]Duquesne University, Graduate School of Pharmacy, [2]Duquesne Center for Pharmaceutical Technology

Various strategies have been employed to compensate for low solubility drug candidates, including the use of the high energy, non-crystalline amorphous state formulated in a single-phase dispersion with polymer (i.e., solid dispersions). While these dispersions have been shown to inhibit crystallization of the drug compound (and hence, the loss of enhanced solubility), the mechanisms and kinetics of this stabilization are not well understood. Because physical instability can manifest in phase separation and/or recrystallization of the drug substance, quantification of crystallinity requires a method that can adequately differentiate between both crystalline and non-crystalline forms in a polymer matrix. Moreover, phase separations or transformations are generally accompanied by a combination of changes in the number or extent of intermolecular chemical interactions (i.e., a change in the ratio of hetero- to homo-molecular interactions) and spatial heterogeneity of a sample, both of which may be a challenge to observe empirically. In this study, multivariate figures of merit was used to compare the performance of reflectance Raman vibrational spectroscopy against the gold standard powder X-ray diffraction. Moreover, Raman methods were employed in combination with designed experiments to evaluate the effect of various formulation factors (polymer type and concentration and compaction force) and storage conditions on crystallization tendency, and to visualize molecular interactions with precede or occur simultaneously with physical instability.

(375) **Raman Spectroscopy for Monitoring the Production of Pharmaceutically Active Compounds in a Bioreactor**; Johannes Kiefer[1, 2], Kristina Noack[2], Christina Dilk[2], Matthias Schirmer[2], Rainer Buchholz[2], Alfred Leipertz[2]; [1]University of Aberdeen, [2]University of Erlangen-Nuremberg

Biotechnology represents a very important area concerning the production of pharmaceuticals. However, monitoring and controlling the output of cultivations in bioreactors is a difficult task and typically done offline viz. a sampling step is followed by a series of downstream processes to obtain samples suitable for conventional analytics, for example high performance liquid chromatography or mass spectrometry. These downstream processes are time consuming and expensive. In this work, we demonstrate and examine the applicability of polarization-resolved shifted-excitation Raman difference spectroscopy (pol-SERDS) as a new in situ and fast measurement tool for monitoring phototrophic microorganisms producing complex molecules of pharmaceutical relevance in a bioreactor. Proof-of-concept experiments are carried out in dye solutions of dimethyl sulfoxide and imidazolium ionic liquids. Thereafter, the red unicellular micro alga Porphyridium purpureum is used as model system segregating sulfated exopolysaccharides possessing antiviral activity. The spectroscopic results evaluated by principal component analysis and partial least square regression are discussed against the corresponding results of the conventional offline analytics used in the downstream process. The Raman method is found to deliver comparable results without the requirement of downstream processing the samples. The presented pol-SERDS monitoring approach turns out to be a green alternative to conventional technologies and has even the potential for inline applications in the future.

(376) **Near-Infrared Spectroscopy for In-Line Monitoring of Protein Unfolding and its Interactions with Lyoprotectants during Freeze-Drying**; Thomas De Beer[1]; [1]Ghent University

This work presents near-infrared spectroscopy (NIRS) as an inline process analyzer for monitoring protein unfolding and protein-lyoprotectant hydrogen bond interactions during freeze-drying. By implementing a noncontact NIR probe in the freeze-drying chamber, spectra of formulations containing a model protein immunoglobulin G (IgG) were collected each process minute. When sublimation was completed in the cake region illuminated by the NIR probe, the frequency of the amide A/II band (near 4850 cm−1) was monitored as a function of water elimination. These two features were well correlated during protein dehydration in the absence of protein unfolding (desired process course), whereas consistent deviations from this trend to higher amide A/II frequencies were shown to be related to protein unfolding. In formulations with increased sucrose concentrations, the markedly decreased amide A/II frequencies seen immediately after sublimation indicated an increased extent of hydrogen bond interaction between the protein's backbone and surrounding molecules. At the end of drying, there was evidence of nearly complete water substitution for formulations with 1%, 5%, and 10% sucrose. The presented approach shows promising perspectives for early fault detection of protein unfolding and for obtaining mechanistic process information on actions of lyoprotectants.

(377) **UV-SERS for Electrochemical Interfaces**; Bin Ren[1], Li Cui, Zhi-Lin Yang[1], Zhong-Qun Tian; [1]State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, [2]Department of Physics, Xiamen University

Different from surface-enhanced Raman scattering(SERS) excited in the visible to infrared region, the use of UV excitation laser, can not only make use of the resonance effect of some molecules, especially biological molecules, but also provide new insights and experimental data to elucidate the complicated SERS mechanisms. For this purpose, we developed the UV-SERS by the use of the unique optical properties of transition metals other than Au, Ag and Cu. We developed several methods for fabricating substrates with UV-SERS activity, including electrochemical roughening, template assisted electrochemical deposition, and core-shell nanoparticles via chemical synthesis. We have been able to successfully obtain UV-SERS signal from Pt, Rh, Pd, Co and Ni, which are very important to catalysis and electrochemistry by using 325 nm laser for excitation. The traditional SERS metals, like Ag and Au do not show obvious SERS effect in the UV region. We found that the size, shape and crystallinity of Pt and Pd nanoparticles critically affect the UV-SERS enhancements and that the nanocrystals with good crystallinity show better UV-SERS activity. For Rh and Pd substrates, we could use lasers from UV to the near-infrared for excitation, which significantly expands the wavelength region that can be studied compared with the Au and

Ag substrates. This feature can be fully employed to study the enhancement mechanism. We found an obvious shift of Emax (potential at which intensity reach the maximum) with the excitation energy, and a linear relationship between photon energy and Emax. These results convincingly demonstrate the presence of CT enhancement and that the charge transfer direction is from the metal to adenine molecules. With further improvement in the performance of Raman spectrometer, the detector, and the optical elements in UV region, together with the rational fabrication of nanostructures with a higher UV-SERS activity, UV-SERS will find important applications in biological as well as surface sciences.

This work was supported by NSFC and MOST.

(378) **Quantitative UV Resonance Raman Studies of Explosive Materials: Raman Cross Sections**; Sanford Asher[1], Luling Wang[1], Manash Ghogh[1]; [1]University of Pittsburgh

Standoff Raman detection of explosives and other threat chemical and biological species requires maximizing the spectral signal-to-noise ratios (S/N). This requires maximizing the intensity of the analyte signals while minimizing that of interferents and that of backgrounds. This optimization can be accomplished by deep UV resonance Raman excitation that simultaneously increases the Raman cross sections, increases the spectral selectivity and avoids relaxed fluorescence interference. Unfortunately, the intensity is attenuated by self absorption. We will discuss the dependence of the observed intensities and spectral S/N in standoff detection of resonance Raman spectra of energetic molecules on these phenomena and the trade-offs required to maximize spectral S/N.

(379) **Structure and Formation Mechanism of Amyloid Fibrils: the Role of Disulfide Bonds**; Igor Lednev[1], Dmitry Kurouski[1], Jacqueline Washington[1], Mehmet Ozbil[2], Rajeev Prabhakar[2], Alexander Shekhtman[1]; [1]University at Albany, State University of New York, [2]University of Miami

Amyloid fibrils are β-sheet-rich protein aggregates commonly found in the organs and tissues of patients with various amyloid-associated diseases. Understanding the structural organization of amyloid fibrils can be beneficial for the search of drugs to successfully treat diseases associated with protein misfolding. The structure of insulin fibrils was characterized by deep ultraviolet resonance Raman (DUVRR) and Nuclear Magnetic Resonance (NMR) spectroscopy combined with hydrogen-deuterium exchange. The compositions of the fibril core and unordered parts were determined at single amino acid residue resolution. All three disulfide bonds of native insulin remained intact during the aggregation process, withstanding scrambling. Three out of four tyrosine residues were packed into the fibril core, and another aromatic amino acid, phenylalanine, was located in the unordered parts of insulin fibrils. In addition, using all-atom MD simulations, the disulfide bonds were confirmed to remain intact in the insulin dimer, which mimics the fibrillar form of insulin.

(380) **Trace Detection of Organics and Microbes Using Fused Deep UV Raman & Native Fluorescence Spectroscopy**; Rohit Bhartia[1], William Hug[2], Everett Salas[2], Kripa Sijapati[2], Ray Reid[2]; [1]Jet Propulsion Laboratory, [2]Photon Systems, Inc

We present a label free detection and classification methodology for trace dissolved or particulate organics material and microbes in aqueous solutions and on natural surfaces. The in-situ method employs simultaneous detection of deep UV (<250 nm) resonance Raman scattering and native fluorescence emissions either immersed in the water column, on a surface, or in a flow cell. Unless excitation occurs at wavelength less than about 250 nm, there is significant overlap between Raman and native fluorescence spectral regions from a wide array of common background materials. This overlap obscures weak Raman emissions and alters the emission spectra of fluorescence emissions due to strong CH and OH Raman bands, both of which reduce the fidelity of spectral classification. Simultaneous acquisition of both forms of emissions coupled with chemometric analysis enables detection and characterization of organics, microbes and a variety of chemical precipitates with both exquisite sensitivity and a high degree of specificity. Detection of bacterial cells and spores is associated to the unique combinatorial signature of aromatic and non-aromatic compounds and for organics it is related to the aromaticity and specific functional groups. In addition this methodology enables detection of mineral by-products as indicators of microbial activity such as nitrates, carbonates, sulfates, and phosphates. The applications presented will range from water and surface contamination studies, to biological hazard assessment, and to in-situ planetary exploration.

(381) **Deep UV Raman Spectroscopy of Biological and Mineralogical Samples**; Michael Schmitt[1], Petra Rösch[1], Ralph Heinke[1], Sandra Kloß[1], Ute Neugebauer[1, 2], Nicolae Tarcea[1], Thomas Dörfer[1], Hans Thiele[1, 3], Jürgen Popp[1, 2]; [1]Institut für Physikalische Chemie and Abbe Center of Photonics, Friedrich-Schiller-Universität Jena, [2]Institut für Photonische Technologien, [3]Kayser-Threde GmbH

We report about the great capabilities of deep UV Raman experiments to investigate biological samples (e.g. microorganisms) and meteorites. The application of Raman excitation wavelengths in the deep UV marks a promising approach exhibiting several advantages: (I) higher scattering efficiency compared to VIS-IR Raman excitation wavelengths, (II) electronic resonance effects increasing the intrinsically weak Raman signal thus improving the S/N ratio of the detected Raman signals, (III) spectral separation of Raman and fluorescence signals. First we will show that UV-resonance Raman spectroscopy allows for a genotaxonomic classification of bacteria since Raman signals from macromolecules like DNA/RNA or proteins can be selectively enhanced. Staphylococcus aureus, a highly human-adapted organism, is the most common pathogen causing nosocomial infections. Among S. aureus, especially the methicillin-resistant S. aureus (MRSA) causes problems in therapy and infection control. Here we will show that UV Raman spectroscopy can be applied to even subtype the different S. aureus strains. Furthermore Raman spectroscopy has been recognized in the last few years also as a possible and extremely promising method for in situ planetary analysis like e.g. the search for signs of extinct and/or extant life on Mars. Here we report on deep UV micro Raman experiments to investigate extraterrestrial material (meteroites) without disturbing fluorescence and with very convincing S/N ratios. Finally we will present a breadboard deep UV Raman spectrometer designed for space applications.

(382) **Discriminant Analysis in the Presence of Interferences: Combined Application of Target Factor Analysis and a Bayesian Soft-Class**; Michael Sigman[1], Caitlin Rinke[1]; [1]University of Central Florida, Department of Chemistry

A method is described for performing discriminant analysis for LIBS data of metal transfer in the presence of an interfering background signal. The method is based on performing target factor analysis (TFA) on a data set comprised of contributions from an analyte and interfering components and a spectral library comprised of representative analyte classes. A Bayesian soft-classier utilizes correlations, r, obtained from TFA in the calculation of posterior probabilities to assist in identifying the presence of one or more analytes. Bullet jacketing transfers to porcelain and steel, and bullet holes in steel were analyzed to identify the jacketing materials. Of 36 single transfer lines, copper (CJ) and non-jacket (NJ) had calculated posterior probabilities of 1; the metal jacketed (MJ) transfers were not detected. NJ and CJ bullet hole transfers were successfully identified by posterior probabilities greater than 0.8, despite 50% of the bullet holes resulting in insufficient transfers.

(383) **A General Method for Predicting the Precision of Isotope Ratios Measured by Resonance Ionization Mass Spectrometry**; David Willingham[1], Michael R. Savina[1], Kim B. Knight[2], Michael J. Pellin[1], Ian D. Hutcheon[2]; [1]Argonne National Laboratory, [2]Lawrence Livermore National Laboratory

The high sensitivity and elemental selectivity of Resonance Ionization Mass Spectrometry (RIMS) has proved to be useful for the analysis of atom-limited samples with minimal sample preparation even in the presence of significant isobaric interferences. There is great potential to employ RIMS as a routine way to measure isotope ratios with high precision; however, the intricacies of the resonance ionization process have limited RIMS analyses to applications where precision requirements are less stringent. We describe the development of a methodology for correlating the spectral resolution of a given resonance transition to the maximum achievable precision of the isotope ratio measurements for the associated RIMS scheme. The precision of isotope ratio measurements depends heavily on the sensitivity of the isotope ratio to variations in the laser wavelength; measured as the percent change in the isotope ratio per GHz deviation in the laser frequency. We show that wavelength sensitivity is a function of the intrinsic isotope shifts, the spectral linewidth induced by the excitation/ionizing lasers and the laser bandwidth. We demonstrate that the measured spectral linewidth distributions can be fit using a Voigt approximation profile specifically derived to characterize the spectral response of atoms excited/ionized by high bandwidth, high power lasers. The spectral resolution calculated from the center wavelengths and spectral linewidths obtained from the Voigt approximation fits of the experimental data can be correlated to the wavelength sensitivity of the associated isotope measurements. We show that sensitivity to variations in the laser wavelength decreases as the spectral linewidth distributions of each isotope become less resolved. This behavior is observed generally over a diverse set analyses and represents an empirically-based method for predicting the precision of isotope ratios measured by RIMS.

(384) **SF-ICPMS Determination of Plutonium Activities and Atom Ratios in Environmental and Biological Samples Collected from Amchitka Island, Alaska**; Kaixuan Bu[1], James Cizdziel[1]; [1]Department of Chemistry and Biochemistry, University of Mississippi

Three underground nuclear tests were conducted by the United States on Amchitka Island (Alaska), including the nation's largest nuclear test at 5 megatons. The radionuclides are believed to be vitrified and trapped in the glass-like matrix which formed instantly from the melting of rocks by the extreme heat generated by explosion. However, the active geological activities on Amchitka Island may increase the likelihood of radionuclides leakage into the surrounding environment. Monitoring the radiological environment on Amchitka and in the surrounding marine environment continues to be of interest. In this study, lichen (Cladonia rangiferina), aquatic moss (Fontinalis neomexican), dragon kelp (Eualaria fistulosa) collected from Amchitka and from a background site (Adak Island) were analyzed for plutonium activities (239+240Pu) and atomic ratios (240Pu/239Pu) using Sector Field-Inductively Coupled Plasma Mass Spectrometry (SF-ICPMS). Plutonium was pre-concentrated by co-precipitation with calcium oxalate or calcium fluoride, and extracted by lab-made TEVA colomns. Plutonium-242 was spiked as a yield tracer and for isotope dilution quantitation. The detection limit of SF-ICPMS for Pu was 0.0005 Bq/kg. Plutonium (239+240Pu) activities ranged from ~0.022 Bq/kg for lichen to ~0.445 Bq/kg for moss, with algae in between. The 240Pu/239Pu ratio ranged from 0.179 to 0.221 suggests global fallout is the source for Pu in the samples, not leakage from the Amchitka test site.

(385) **Total Metal Analysis in Hookah Tobacco Pre- and Post Consumption**; Ryan Saadawi[1], Traci Hanley[1], Julio Landero[1], Joseph Caruso[1]; [1]University of Cincinnati

Various trace metal studies have been performed on cigarette, cigar, and pipe tobacco while virtually no studies have been performed on hookah tobacco. It is well documented that other tobaccos are known to contain toxic metals such as As, Cd, Cr, and Pb. However, little is known about the metal content in hookah tobacco. Hookah has been popular in the Middle East and surrounding regions for ages and its use is emerging rapidly in Western cultures making it imperative to study trace metal profiles and their species. Relative to cigarettes, our hookah study is appreciably more complicated because of 3x lower burn temperature, glycerin/molasses/or honey making up ~ 50% of the hookah mix, the water filtration and the addition of flavorings and colorants. The actual tobacco in the hookah mix was separated from the water soluble portions by extraction and both resulting portions were analyzed. Microwave assisted digestion in combination with ICP-MS was utilized to elucidate the toxic metal content in an array of different brands/flavors, extract and tobacco and the geographic region of preparation of hookah tobacco. The process used to burn the tobacco simulated the typical manner in which hookah is consumed. The tobacco was analyzed pre/post consumption for trace elements as well as other components involved in pre- and post-consumption. Interestingly, higher amounts of the most toxic metals in this study were found for Middle Eastern preparations vs. USA preparations. Statistical analyses were done for the 12 samples utilized to verifying groupings and overlaps for various hookah mixtures. Overall for the samples we utilized, by estimating one hookah smoking session equal to smoking one cigarette (if such an estimate is possible), the data suggest that the hookah smoker will inhale less of the toxic elements than the cigarette smoker.

(386) **Multivariate Analysis of Emission-Line Rich Spectra for Metal Alloy Identification**; Ryan Carn[1], Gary Rayson[1]; [1]New Mexico State University

Identification of trace metal signatures of metal alloy is required for determination of the source of materials. Conventional approaches typically use intensities of specific emission wavelengths for quantitative and qualitative determinations of selected trace metals within an alloy material. This becomes problematic when the emission source results in line-rich spectra. Application of multivariate data analysis tools provides a means of overcoming spectral interferences, provided the data are sufficiently over determined. The present study involves evaluation of statistical tools as applied to total emission spectra from metal alloys using an ICP emission spectrometer equipped with a panoramic charge injection device detector. The results of these studies will be presented and their implications for the analysis of forensic samples will be discussed.

(387) **Experimental and Computational Investigation of SERS Signal Variations**; Siyam Ansar[1], Dongmao Zhang[1, 2], Shengli Zou[2]; [1]Mississippi State University, [2]University of Central Florida

One of the most challenging issues in Surface enhanced Raman spectroscopic (SERS) study is reliably determination of the SERS enhancement factors afforded by various molecules or SERS substrates. To date SERS enhancement factors ranging from 1 (water, which has apparently has no detected SERS activity) to 1014 have been reported. Theoretically the SERS enhancement factors can be calculated by dividing the SERS activity of the analyte by its normal Raman activities. In practice However many instrumental-, chemical-, and SERS substrate- related issues can affect the SERS spectral acquisitions, thus compromising the reliability of the reported SERS EF factors. Presented in this talk are a series of computational and experimental studies, aiming to enhancing a fundamental understanding of the SERS signal variation and to

identify way to enhance the reliability of the SERS EF determination. In addition to the experimental methodologies, we will discuss present several key new findings that will help clarify a series of perplexing issues associated with the SERS that include chemical enhancement, effect of nanoparticle aggregation on the analyte SERS activity, and SERS activities of the nanoparticle junction areas, etc.

(388) **Parallel Raman and Surface-Enhanced Raman Microspectroscopy**; Wei-chuan Shih[1], Ji Qi[1]; [1]University of Houston

Raman spectroscopy can provide molecular information via inelastic light scattering without physical contact. Coupled with microscopic imaging, Raman microspectroscopy is a powerful technique for material analysis, for example, stress and temperature measurement in silicon and compositional analysis of polymer microparticles. However, due to the small Raman cross-section, the single-point spectrum acquisition time is significantly longer than other optical modalities. The traditional design of conventional charge coupled detector (CCD) readout electronics introduces additional latency, resulting in slow Raman imaging throughput. In this paper, we present a novel parallel Raman microspectroscopy scheme for simultaneously collecting Raman spectra from multiple points. This scheme is realized by projecting a multiple-point laser illumination pattern using a spatial light modulator (SLM) coupled with wide-field Raman imaging collection. We demonstrate the performance of this scheme using uniform samples, trapped polymer microparticles and fixed polymer microparticle with mixed molecular composition within a ~ 100 x 100 μm^2 field of view. This scheme enables the acquisition of Raman spectra from as many as 80 points simultaneously using a single illumination pattern and detector recording frame without scanning. Multiple SLM-generated patterns can be rapidly projected sequentially without mechanical scanning. We show that the throughput of this scheme can be orders of magnitude faster than a single-point scan-and-readout scheme, is significantly more flexible than the line-scan approach, and maintains smaller power fluctuation compared to time-sharing of a single-point illumination.

(389) **Label-Free Method to Detect Glycan-Lectin Interactions with Surface Enhanced Raman Spectroscopy**; Sharon Martin[1], Xiuru Li[1, 2], Richard Dluhy[1], Gert Jan Boons[1, 2]; [1]Department of Chemistry, University of Georgia, [2]Complex Carbohydrate Research Center, University of Georgia

Glycans are oligosaccharides and polysaccharides which may be found inside or on the surface of cells. They are involved in many important cellular processes such as protein folding, cell signaling fertilization, embryogenesis, pathogen recognition, and protein binding. Understanding the structure and role glycans play in regulating these processes is of great importance. This can be done by the development of glycan array detection methods. Surface Enhanced Raman Spectroscopy (SERS) is a biosensing technique which yields a chemically sensitive signature of the analyte molecule and its use as a glycan array detection method has not been fully established in research. Using this method, glycan-lectin interactions can be monitored by Copper (Cu) free click chemistry reactions. To investigate glycan-lectin systems, lactose is attached to gold nanoparticles by Cu-free azide-alkyne cycloaddition reactions. Spectral band characteristic of lactose indicates the presence of this glycan on the nanoparticle. After attachment of lactose is verified, nanoparticles were reacted with galectin proteins where spectral bands characteristic of the protein are present in the spectra. The use of Cu-free azide alkyne cycloaddition and SERS create a label free method for examining gylcan-lectin systems.

(390) **Detection of SERS Active Labelled DNA Based on Surface Affinity to Silver Nanoparticles**; Mhairi Harper, Jennifer Dougan, Karen Faulds, Duncan Graham; [1]University of Starthclyde

Surface enhanced Raman scattering (SERS) spectroscopy has been an invaluable tool for enhancing the knowledge and understanding of DNA surface chemistry properties. Currently, the detection of specific DNA sequences through SERS has been widely exploited and proven highly effective, with many diagnostic assays utilising SERS to detect specific DNA sequences through varying propensities of DNA structures to adsorb onto silver and gold nanoparticle surfaces. This study utilises SERS to demonstrate an understanding of the differences in affinity of dye labelled DNA through differences in electrostatic interactions with silver nanoparticles. The varying strength of electrostatic interactions between dye labelled single stranded DNA (ssDNA), double stranded DNA (dsDNA) and an unattached dye label onto a silver nanoparticle surface were investigated. Results demonstrated discrimination between TAMRA labelled ssDNA, dsDNA and a dye molecule, through significant differences in the resultant SERS signal, with higher SERS intensities obtained for ssDNA compared to dsDNA. It was further demonstrated that surface attraction is driven through the constituent bases of the DNA sequence with the dye contributing minimally to surface adsorption, as a result of negligible SERS signals obtained for the unattached TAMRA dye. Thus, more sensitive SERS detection is obtained for detecting dye labelled DNA. Finally, we have shown with optimisation of experimental conditions and careful consideration of sequence composition, a DNA detection method with increased sample discrimination at lower DNA concentrations can be achieved. A DNA detection method has been demonstrated which, through careful consideration of SERS conditions and target sequences, can provide a simple and selective biological assay method with vast potential applications.

(391) **Lab-on-a-Bubble: Direct and Indirect SERS Assays**; Keith Carron[1, 2], Aaron Strickland[1, 4], Richard Martoglio[1, 3], Virginia Schmit[1], Brandon Scott[1]; [1]University of Wyoming, [2]Snowy Range Instruments, [3]Depauw University, [4]iFyber

Lab-on-a-Bubble (LoB)is a new method for SERS assays that combines separation and concentration of the assay results. In addition, direct LoB techniques create much more stable SERS assay due to pre-aggregation of the nanoparticles on the ~30 micron silica bubbles. Indirect assays couple a LoB and a SERS reporter together through the analyte. In this case, the method is similar to a paramagnetic pull-down assay, except the separation between the buoyant bubbles and the sinking SERS reporters is significantly improved. Paramagnetic methods can produce large blanks due to inclusion of the SERS reporters during the pull-down process. In addition to LoB methods we will discuss spectroscopic methods to explore the SERS spectra from aggregated nanoparticles. Time dependent Raman spectroscopy can be used to distinguish between aggregate sizes and will produce site selective spectroscopy.

(392) **Backpack Mass Spectrometer Combined with Ambient Ionization for Automated, In Situ Analyses**; Jacob Shelley[1], Paul Hendricks[1], Jon Dalgleish[1], Tsung-Chi Chen[1, 2], Jason Duncan[1, 3], Matt McNicholas[1, 4], Linfan Li[1, 2], John Denton[1, 4], Zheng Ouyang[2], Graham Cooks[1]; [1]Department of Chemistry, Purdue University, [2]Weldon School of Biomedical Engineering, Purdue University, [3]Center for Analytical Instrumentation Development, Purdue University, [4]Department of Electrical & Computer Engineering Technology, Purdue University

Miniaturized and portable analytical instrumentation has proven very useful over the past couple of decades for various applications that require an analytical measurement to be made on-site. While many analytical methodologies, including X-ray fluorescence, Raman scattering, and UV-visible absorption spectroscopy, have been made

portable, there is a need for more selective and sensitive techniques. Mass spectrometry is one such technique that can provide a wealth of information about a sample. However, wide-spread development and commercialization of miniature, portable mass spectrometers has been precluded by the need for complex electronics and bulky vacuum pumps as well as an inability to directly analyze samples of any given phase (solid, liquid, or gas). The latter of these problems has been solved through the advent of ambient ionization methods which directly desorb/ionize molecules from samples without the need for sample pretreatment. Here we describe a portable, backpack mass spectrometer combined with a plasma-based ambient ionization source that is ideal for direct, in situ MS analyses. This instrument houses the compact pumping system and control electronics in a backpack, while the mass analyzer and integrated coaxial LTP/MS-inlet, for geometry independent sampling, are contained in a hand-held unit connected to the backpack via flexible vacuum tubing. Ions are introduced into the rectilinear-ion-trap mass analyzer with a discontinuous atmospheric-pressure interface (DAPI) valve. The system electronics allow execution of complex functionalities including stored inverse Fourier transform (SWIFT) isolation, fast sampling speeds, and improved data management/storage and library matching. This instrument is also capable of detecting both positively and negatively charged ions with mass resolutions of 1 - 2 Th across the entire mass range (75 – 600 Th) and allows tandem MS functionality to improve the selectivity and S/N of the analytical measurement. Furthermore, the in-house designed software autonomously controls the system and is capable of performing MS/MS on detected ions and matching the results with a user-defined library for automated analyte identification. The design and performance characteristics of the instrument will be presented. One example will be the detection of illicit drugs and chemical warfare simulants at nanogram levels from non-standard surfaces, such as human skin.

(393) **Toward Advanced Breath Diagnostics: Combining Mid-Infrared Sensors with Differential Ion Mobility Spectrometry**; Felicia Seichter[1], William Cheung[2], Michael Schivo[3], Frank Vogt[4], Cristina E. Davis[2], Boris Mizaikoff[1]; [1]Institute of Analytical and Bioanalytical Chemistry, University of Ulm, [2]Department of Mechanical and Aerospace Engineering, University of California, Davis, [3]Department of Internal Medicine, Division Pulmonary, Critical Care, & Sleep, School of Medicine, University of California, Davis, [4]Department of Chemistry, University of Tennessee, Knoxville

Breath analysis is an emerging area in clinical research and health diagnostics with substantial potential for non-invasively detecting a variety of medical conditions and diseases including therapeutic progress and metabolic processes. Commonly applied analytical methods detecting biomarkers in exhaled human breath include gas chromatography – mass spectrometry (GC-MS), ion mobility spectrometry (IMS), differential ion mobility spectrometry (DMS), and infrared (IR) spectroscopy. Especially DMS and IR spectroscopy/sensing - the latter based on compact hollow wave guides serving both as light pipe and miniaturized gas cell - show promise as compact, sensitive, and robust clinical tools. The combination of DMS with IR sensors combines the sensitivity of DMS with the inherent molecular selectivity of IR spectroscopy, thereby facilitating innovative and compact sensing platforms. The complexity of breath samples and the challenge of combining or fusing data sets of both techniques require advanced multivariate data analysis strategies. In this study, the potential of combining of DMS and IR-HWG sensors toward breath analysis was investigated and supplemented by suitable multivariate data analysis techniques for exploiting the potential of combined IR and DMS data sets.

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(394) **Standoff Detection of Chemical Warfare Agents with UV Raman Chemical Imaging**; Ryan Priore[1], Stephen Styk[1], Charles Gardner[1], Doug Green[2], David Schiering[2]; [1]ChemImage Corp., [2]Smiths Detection

Molecular chemical (i.e. hyperspectral) imaging technology developed by ChemImage Corporation has shown potential to detect chemical, biological and explosive (CBE) threats. These technologies include short-wave infrared (SWIR) and Raman hyperspectral imaging sensors for both laboratory and standoff applications. A UV Raman-based surface agent detector has been developed for the detection of chemical warfare agents (CWA) in a standoff configuration. High quality Raman Chemical Images were acquired using Fiber Array Spectral Translation (FAST) technology for a series of CWA stimulant materials on a variety of surface materials. An overview of the UV Raman Chemical Imaging prototype and representative standoff measurement results will be presented.

(395) **Self-normalizing SERS-based Trace Detection of TNT**; Benoit Lauly[1], Marc Wadsworth[1], Paul Repasky[1], Jonathan Scaffidi[1]; [1]Miami University

In addition to the hazards associated with its use as an explosive, the intrinsic toxicity of 2,4,6-trinitrotoluene (TNT) poses a threat to both the environment and human health. Most frequently, SERS-based TNT quantitation is performed via either direct detection or formation of a "Meisenheimer complex" in which TNT interacts with an amine-containing, particle-anchored molecule such as para-amino thiophenol to form a colored charge-transfer complex. Unfortunately, direct detection of TNT via SERS can be challenging because in-plane vibrations are not significantly enhanced if TNT lies flat on the surface of a nanoparticle. Likewise, Meisenheimer-type complexation typically increases the intensity of pre-existing Raman bands, so it can be difficult to determine whether SERS intensity has increased due to the presence of TNT as opposed to changes in nanoparticle aggregation. To improve upon existing approaches to TNT detection via SERS, we have developed highly SERS-active nanoparticles combining high sensitivity to TNT and a built-in internal standard. In the absence of TNT, non-TNT-related SERS bands associated with the internal standard are visible. In the presence of TNT under basic conditions, new TNT-related bands appear in the SERS spectrum. Normalization versus the internal standard is straightforward, allowing accurate quantitation of TNT at concentrations ranging from 0.5 – 200 ppb while avoiding false positives associated with changes in particle aggregation. Preliminary experiments examining the utility of these highly TNT-sensitive SERS-active nanoparticles for stand-off detection of TNT at 15 meters have been promising, with limits of detection in the low ppb.

(396) **MEMS Chemicapacitive Chemical Sensor Systems**; Todd Mlsna[1], Sanjay Patel[2]; [1]Mississippi State University, [2]Seacoast Science Inc

Seacoast Science has developed chemical sensors that use polymer filled micromachined capacitors to measure the dielectric constant of

an array of selectively absorbing materials. These microfabricated sensor chips measure 5 x 2 mm and can contain 3 to 16 capacitors, which can each receive a different analyte-sensitive coating. These interdigital transducers (IDT) are approximately 400 µm long and 3.5µm wide, and have 25 alternating sense and drive electrode pairs (each beam separated by 3.5µm) in parallel supported by 2µm tall insulating posts above the lower substrate. The electrode fingers are coated with a polymer using an ink-jet. The interaction between target analyte and polymer modifies the dielectric properties of the polymer resulting in a change in capacitance. The differently coated sensor array can be used to improve selectivity for detection of vapors of organic compounds and inorganic gases and for redundancy and interferent rejection. We have developed MEMS sensors for gas-phase analytes including volatile organic compounds (VOCs), chemical warfare agents (CWA), toxic industrial chemicals and materials (TICS & TIMS), emission gases and hydrogen. The compact size, low power consumption, and low cost of these sensors make them ideal for integration into varied packages for numerous applications. Portable sensor and chemical separation systems are needed for defense and civilian monitoring applications. With recent advances in microfabrication, these systems have achieved capabilities comparable to analytical equipment in laboratories for some applications. We have developed and tested several prototypes that utilize our MEMS sensors with varied configurations. Our most advanced is a miniature gas chromatograph that is compatible with the restrictive size, power and weight limits needed for use in the field or in many industrial monitoring situations. This system can operate with multiple detectors including our polymer-filled, micromachined capacitors. In front of the detector we have built a device containing an air or liquid injection sampling mechanism, a chemical preconcetrator and a chromatographic capillary column. This small system is capable of separating and detecting many target analytes such as common volatile organic compounds, solvents and chemical warfare agents. Technical specifications and performance data will be presented.

(397) **Service and Research: Symbiosis or Conflict?**; Gary Hieftje[1]; [1]Indiana University

There are many ways in which each of us can provide service, and that service can be to our employer, our scientific discipline, our society, our community, or to other individuals. Naturally, such service requires time, energy, and sometimes money. It therefore comes at a cost. In this presentation, the focus will be on service to science and on the question of whether such service comes at a cost to the very science it is intended to benefit. It is often believed, for example, that some scientists are too productive, too brilliant, too driven to waste time on service. Wouldn't it be better for someone less capable in science to perform the "grunt work"? The thesis here is that the answer to this question is a resounding NO. Evidence can be found in the other speakers in this session, all of whom have served science long, well, and in many capacities, yet have contributed deeply and importantly to scientific discovery. Personal evidence will be offered in this lecture, by correlating past and present periods of service with scientific activities that were contemporary with them.

(398) **The Impact of Chemometrics on Open-Path FT-IR Atmospheric Monitoring**; Peter Griffiths; [1]University of Idaho

Open-path Fourier transform infrared spectroscopy (OP/FT-IR) is an effective and convenient technique for atmospheric measurements, with the main advantages being the capability for measurements in the field with no sample handing and the high temporal resolution (seconds). Since the measurements are made in open air, the OP/FT-IR spectrum is not only a multi-component system, but usually complicated with unpredictable interferences. Several methods of data analysis have been applied to OP/FT-IR measurements, including CLS, which is recommended by US-EPA and the European Committee for Standardization; the multiple atmospheric layer transmission (MALT) forward model with nonlinear least squares fitting and PLS. It should be stressed that in the analysis of OP/FT-IR measurements, however advanced is the analytical technique, it cannot yield better results than what the experimental data could provide. Therefore, the credibility of the absorbance spectrum is a necessary condition for the quality of the result of data analysis. The most difficult aspect of OP/FT-IR spectroscopy is the acquisition of a suitable reference spectrum. Most methods involve the estimation of the background in the complete absence of the analyte and all are fraught with difficulty. I will describe an approach whereby a short-path background spectrum is measured with the retroreflector less than a meter from the telescope. The long-path absorbance spectrum is calculated from the ratio of the long-path to the short path background spectra and concentrations are calculated by PLS. The advantages of this approach will be demonstrated, the long-term viability of the reference spectrum and the transferability of the short-path background spectrum to a different instrument will be demonstrated in this talk.

(399) **Utilizing Spectral Information to Adaptively Mitigate Spectral Interferents**; Bryon Herbert[1], Karl Booksh[1]; [1]University of Delaware

The transfer of a calibration model from the laboratory applied within a process or an environmental setting can fall victim to the presence of unanticipated chemical or spectral components. With the cost and time committed towards the generation of these models, it is necessary to identify a method which may improve the reliability and lifetime of a regression model when encountering new components. This method was developed to account for the unmodeled aspects through the adaptation of spectral features, the extraction of analyte specific freatures and the reduction of external sources of variance. The information present within the calibration set can establish the descriptive characteristics necessary to identify possible interferents, isolate the contaminated features to be removed, and generate a more accurate prediction value though the removal of inconsistent variables. This Adaptive Regression by Subspace Elimination algorithm is capable of prediction values closer to the true value and targeting the removal of spectral bias.

(400) **Assessment of Sample Selection Methods for Local Modeling**; Kevin Higgins[1], John Kalivas[1]; [1]Idaho State University

Local modeling can be a useful tool for improving prediction errors when compared to a global model. The goal of global modeling is to build a robust model that can predict a large number of samples with small prediction errors. However, with local modeling, a smaller set of calibration samples are generally chosen to build a more accurate model for each sample. When a large library set of samples are available to select local samples from for the corresponding prediction sample, different approaches can be used. This poster describes the use of traditional methods (such as Euclidean distance, and cos(θ)) as well as some newly developed approaches to choose local calibration samples. Selected calibration samples are used with ridge regression (RR) to form local calibration models. The sample selection methods are studied using near-infrared spectra of pharmaceutical tablets and corn samples measured over four prediction properties. Prediction results from local modeling are compared to the global RR model based on the full library set.

(401) **Localized Model Selection for Multivariate Calibration Using Tikhonov Regularization with Net Analyte Signal**; Jonathan Palmer[1], John Kalivas[1]; [1]Idaho State University

A typical approach to multivariate calibration is to predict new samples using a model constructed from a large calibration set. Presented in this poster is a targeted approach that improves the model formed from the calibration set by localizing it for each new

sample. The process under development uses Tikhonov Regularization (TR) of the calibration set enhanced with net analyte signal (NAS) processing of the new sample. This new method, abbreviated TR-NAS, begins by projecting a new sample spectrum into the space orthogonal to non-analyte spectral information. Non-analyte information is effectively filtered out by this projection, revealing the NAS as a vector consisting of residual analyte information. Uniquely customized for each sample, this NAS vector is a dual purpose tool for model construction and selection. To construct the model, TR regression is augmented with the projected NAS vector as a weighted target. The result is a series of candidate models, specific to the new sample, each with its own NAS vector prediction. Selection then proceeds by geometric comparison of the projected NAS vector against model-predicted NAS vectors. For example, accurate models can be selected by minimizing the euclidean distance between the two NAS vectors. Also presented are additional NAS-derived metrics which further guide the selection process toward improved accuracy. Results are compiled from TR-NAS analysis of a three component NIR spectral data set consisting of water, ethanol and isopropanol.

(402) **Forensic Applications of Pattern Recognition Assisted Infrared Library Searching Techniques**; Ayuba Fasasi[1], Nikhil Mirjankar[1], Barry Lavine[1], Mark Sandercock[2]; [1]Oklahoma State University, [2]National Centre for Forensic Services (RCMP)

Search prefilters utilizing the wavelet packet transform to denoise and deconvolute infrared spectral bands of clear coat paint smears by decomposing each spectrum into wavelet coefficients identified by a genetic algorithm for pattern recognition analysis are coupled to a library searching algorithm based on the cross correlation function to identify the make and manufacturer of an automobile from a spectral library of clear coats. The advantages of pattern recognition assisted approaches to perform both identity and similarity searching are demonstrated by way of a study recently completed in our laboratory on assessing the information content of clear coats.

(403) **FTIR Spectral Searching - How to Assess a the Quality of a Match**; Michael Boruta[1]; [1]ACD/Labs, Inc.

The algorithms used in spectral searching always produce a number one match and always compute a Hit Quality Index (HQI). Due to various factors which will be discussed, neither number gives us a reliable indication of the quality of the match. Rather than using the just the reported match value or the position of a hit in the result, the difference, or gap in the HQI between successive hits can be used as an indicator of the quality of a match. This work will look at progress made on using an assessment of the gap between hits to determine the quality of a match, what represents a significant gap and when this assessment can fail.

(404) **Multivariate Calibration and Maintenance Using Principle Component Selection**; Trevor O[1], John Kalivas[2], Parviz Shahbazikhah[2]; [1]Texas Tech Univeristy, [2]Idaho State University

Calibration maintenance confronts the problem of updating a model developed in primary condition to accurately predict the calibrated analyte in samples measured in new secondary conditions. Previously, the L2 norm (TR2) variant of Tikhonov regularization (TR) have been used with spectroscopic data where a few samples measured in the secondary conditions are augmented to the primary calibration data to update the model. In this poster, the augmented data is solved by principle component regression (PCR) to determine whether selection of principle components may improve prediction errors. The measures are evaluated with a benchmark near infrared spectroscopic pharmaceutical tablet data set. It is found that principle component selection does not offer any improvements over TR.

(405) **Calibration Maintenance without Laboratory Prepared or Determined Reference Analyte Values**; John Kalivas[1], Jeremy Farrell[1], Josh Ottaway[1]; [1]Idaho State University

A majority of the work that goes into multivariate calibration comes in the collection and analysis of reference samples and/or preparing reference samples. Analysis of and/or preparation of reference samples typically involves meticulous laboratory methods that are often time consuming and costly. A purpose of this presentation is to report on a new variant of Tikhonov regularization that forms a calibration model without the need to collect or form reference samples. In the approach presented, a pure component analyte spectrum is used in conjunction with non-analyte spectra base on pure component interferent spectra, blanks, and/or constant analyte samples. For constant analyte samples, actual concentrations of the analyte are not needed; samples must just be constant within a certain tolerance. Using near infrared and fluorescence spectral datasets it is shown that the pure component analyte spectrum can be measured in one set of conditions and the non-analyte spectra can be measured in completely different conditions and hence, calibration maintenance is possible. Validation prediction errors from the new approach are comparable to those from a model built with reference samples.

(406) **A Bayesian Approach to Bridge Partial Least Squares**; Kenneth Morton[1], Leslie Collins[1], Peter Torrione[1]; [1]Duke University

Partial least squares (PLS) has become one of the most widely used algorithms for regression and classification tasks throughout chemometrics and genomics. PLS and the closely related principal component regression (PCR) both model a set of observed data and response variables using two factor models that share common scores. The primary difference between the two approaches is that in PLS the factors that model the data are influenced by the underlying prediction problem whereas in PCR they are influenced only by the data. In practice, the two approaches offer similar performance with each algorithm being better suited to different datasets. The similarity of the two approaches has led several researchers to develop algorithms, such as bridge-PLS and elastic component regression, that blend the two approaches using an additional parameter to smoothly vary the behavior between that of PLS and PCR. By selecting this parameter through cross-validation, improved performance has been demonstrated. However, each of the algorithms that offer this capability requires formation and storage of a large covariance matrix with size equal to the number of data dimensions. In chemometrics and genomics the number of data dimensions can be quite large making these techniques difficult to use in practice. In this work, the dual factor model underlying both PCR and PLS is analyzed in a Bayesian context and it is shown that utilizing a specific model structure yields an algorithm with similar characteristics to elastic component regression and bridge-PLS but does not require formation of a large covariance matrix. Furthermore, because the algorithm makes use of Variational Bayesian (VB) inference, stochastic VB methods can be employed to further reduce memory requirements. Therefore, the proposed algorithm can be used for very large datasets that feature both a very large number of data dimensions and more observations than can be stored in computer memory. The algorithm is evaluated using both simulated data and several standard chemometric datasets and comparable or superior performance to Bridge-PLS, PLS and PCR is demonstrated.

(407) **Classification and Quantification of Edible Oils and Adulterants via Adaptive Regression by Subspace Elimination**; Joshua Ottaway[1], Bryon Herbert[1], Karl Booksh[1]; [1]University of Delaware

Recently the authentication of edible oils has become an important issue for distributors and regulatory agencies for various economic and dietary reasons. Various high priced edible oils, including extra

virgin olive oil, have been shown to be adulterated with lower quality oils as a way to increase profits. Chemometrics paired spectroscopic techniques have proven to be a vital tool in determining the quality of edible oils. Presented is a study of edible oils, including olive oil, coconut oil, corn oil, and several others, in both pure and blended forms examined via Raman spectroscopy. The Raman spectra were analyzed via adaptive regression subspace elimination algorithm yielding classification of the oils as well as identification and quantification of any adulterant present.

(408) **Taxonomic Classification of Natural Phytoplankton Populations**; Shawna Tazik[1], Joseph Swanstrom[1], Elizabeth Abernathy[1], Tammi Richardson[1], Timothy Shaw[1], Michael Myrick[1]; [1]University of South Carolina

Phytoplankton contribute significantly to the global carbon cycle through photosynthesis, but their overall effect is species- and class-dependent. We are developing a method for phytoplankton classification based on fluorescence excitation spectroscopy. Chlorophyll a fluorescence from single cells in a flowing stream is imaged onto a CCD array in a variation on flow cytometry. Specially designed optical filters are used to filter the excitation light so that the images collected contain a series of streaks produced from the cell's fluorescence. Integrated streak intensities are used to generate models using cluster analysis methods such as principal component analysis, hierarchal cluster analysis and SIMCA. The application of these methods to natural populations of phytoplankton from the Marta's Vineyard area in different seasons will be presented.

(409) **Conformational Stability Determination of Cyclohexylisocyanate by Infrared, Raman and Microwave Spectroscopy**; Xiaohua (Sarah) Zhou[1], Michael J. Tubergen[2], Ranil M. Gurusinghe[2], James R. Durig[1]; [1]University of Missouri-Kansas City, [2]Kent State University

The microwave spectrum of cyclohexylisocyanate, *c*-$C_6H_{11}NCO$, has been investigated from 10,000 to 21,000 MHz and forty-four transitions for the more stable equatorial-trans conformer were assigned. The rotational constants of the ground vibrational state have been determined A = 3546.87(28), B = 936.12(1) and C = 839.06(1) MHz. By utilizing these rotational constants along with ab initio MP2(full)/6-311+G(d,p) predicted structural values, adjusted r_0 parameters have been obtained for the *equatorial-trans* conformer. Variable temperature (−55 to −100°C) studies of the infrared spectra (400 to 3500 cm^{-1}) of cyclohexylisocyanate, dissolved in liquid xenon have been recorded as well as the infrared spectra of the gas and solid. Additionally, the Raman spectrum (100 to 3600 cm^{-1}) of the liquid has also been investigated. These spectral data indicated the present of two conformers in the fluid states which are the *equatorial-trans* and *axial-trans* forms. The second part of the conformational name refers to the relative position of the NCO moiety relative to the alpha hydrogen. By utilizing seven conformer pairs, an enthalpy difference of 442 ± 7 cm^{-1} (5.28 ± 0.83 kJ/mol) was obtained with the equatorial-trans conformer the more stable form. To aid in the vibrational assignment, ab initio calculations have been carried out by the perturbation method (MP2) to second order with full electron correlation by using a variety of basis sets up to 6-311+G(2df,2pd).

(410) **Crystal Structure and Thermal Behavior of Polyglycolide Studied by Vibrational Spectroscopy, Wide Angle X-ray Diffraction, and Quantum Chemical Calculation**; Mai Miyada[1], Harumi Sato[1], Shigeki Yamamoto[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University

Recently, biodegradable polymers attract much attention as environment-friendly materials. In our previous studies, we reported that there is a particular inter- or intermolecular interaction between the C=O group and the CH3 group in poly(3-hydroxybutyrate) (PHB) along the a axis. It seems that the C-H…O=C hydrogen bonding stabilizes the chain folding in the lamella structure of PHB and that the high crystallinity partly comes from the C-H…O=C hydrogen bonding. Polyglycolide (PGA) is also a biodegradable polyester. It is not only biodegradable polymer but also has the high mechanical strength and the unique gas barrier. In this study, crystal structure and thermal behavior of PGA were investigated by vibrational spectroscopy, wide angle x-ray diffraction (WAXD), and quantum chemical calculation. Temperature dependent IR spectral variations of PGA were analyzed for CH2 stretching and C=O stretching vibration regions. We carried out the quantum chemical calculations of the model compounds of PGA. Comparison of the results between the CH2 stretching band region of IR spectra and quantum chemical calculations revealed that PGA has intermolecular interaction along the a-b axis direction. We calculated temperature dependence of lattice parameters from the WAXD profile of PGA. The b lattice parameter increases with temperature more than the lattice parameters a and c. This result shows intermolecular interaction exists along the b axis. We calculated the distance between H and O atom by reported crystal structure of PGA. We found that the distance (2.53Å) is shorter than the sum of van der Waals separation (2.72Å) in the a-b axis direction. It is in a good agreement with the results of IR and quantum chemical calculations. Therefore, it seems that PGA has intermolecular interaction along the a-b axis direction.

(411) **Optical Constants and Vibrational Intensities of Tribromomethane and Trichloromethane**; Dale Keefe[1], Erica Campbell[1], Karanbir Pahil[1]; [1]Cape Breton University

Many important physical properties can be explained in terms of intermolecular forces. Although the importance of intermolecular interactions is widely recognized, a detailed understanding of their origins, strength, and orientational dependence is not yet known particularly in the liquid phase – arguably the most important chemical phase. Vibrational intensities have long been pursued as a means to glean information about molecular structure and intermolecular interactions in the liquid phase. Continuing the experimental and computational work on the vibrational intensities of substituted benzenes in the liquid phase that have been carried out in this laboratory over the last number of years, we have started to look at substituted methanes in the liquid phase. In this paper, the vibrational intensities of neat liquid tribromo- and trichloromethane are presented for the first time. Infrared and Raman spectra have been measured and the infrared optical constants have been determined across the infrared for the title compounds and their deuterated analogues. From the optical constants the imaginary molar polarizabity spectra were calculated and curvefit to separate integrated intensity for individual fundamentals. Using the force constants calculated at the MP2/aug-cc-pVTZ level of theory as a starting point, the experimental force constants were determined using a nonlinear regression on the experimental vibrational frequencies. The resulting normal coordinates were used to determine the dipole moment derivatives with respect to internal coordinates enabling a comparison between the two substituted methane compounds. The results will be discussed in terms of the effect of halogen substitution on the vibrational intensities, particularly for the CH stretch coordinate.

(412) **Conformational and Structural Studies of Four and Five Membered Rings from Temperature Dependent Infrared and/or Raman Spectra of Xenon Solutions and ab initio Calculations**; Joshua Klaassen[1], James Durig[1]; [1]Department of Chemistry, University of Missouri-Kansas City

In the years before the genome project it was thought that the sequence of DNA and RNA would reveal all their inner workings. This has been found to be wrong, the structure and conformation has increasingly been found to be of importance. A portion of what determines the conformation of DNA and RNA is the substituted

five-membered rings (the backbone sugar groups). The importance of conformational stability is reinforced in enzyme binding where the geometry of the protein will change its function and/or deactivate it. Variable temperature infrared spectra of xenon solutions have allowed for precise determinations of conformational stabilities in the last decade and recently Raman spectra is used. Considering the importance of the ring motif in biology we began to study substituted four and five membered rings. Initially it was shown that bromocyclobutane had two conformers present at ambient temperature but from later microwave studies the second conformer was not found. At that time it was generally concluded that only one conformer was present for monohalocyclobutanes. More recently we observed the second conformer in variable temperature infrared spectra of xenon solutions and determined the enthalpy difference. The first of these studies were the chloro-, bromo-, cyano- and fluoro- cyclobutane molecules which were followed by the silylcyclobutane molecule and the monosubstituted five-membered rings of which examples are ethynylcyclopentane and isocyanocyclopentane. Recently we have also begun to explore the structural changes of the enzyme substrates due to allosteric regulation of the protein by utilizing difference spectra in the mid-infrared region.

(413) **Wavelength Dependence of the Production of No From Photdissociated C6H5NO2**; Christopher Lue[1, 2], Chakree Tanjaroon[1, 2], Scott Reeve[1, 2], Bruce Johnson[1, 2], Susan Allen[1, 2]; [1]Arkansas Center for Laser Applications and Science, [2]Department of Chemistry and Physics, Arkansas State University-Jonesboro

Upon absorption of a UV photon, nitrobenzene readily dissociates into C_6H_5, NO_2 , C_6H_5NO, O, C_6H_5O, and NO through three different channels. [a] We have looked at the NO producing channel as a means of detecting nitro-aromatic compounds. When UV light (λ <320 nm) is used to dissociate nitrobenzene to form NO, some of the NO produced will be vibrationally hot ($v = 1$ or $v = 2$). We can then probe the hot NO using laser induced fluorescence (LIF). Specifically, the a tunable picosecond OPO laser system probed the $A^2\Sigma^+ \rightarrow X^2\Pi(1/2,3/2)$ NO band system between 225-260 nm. If the A←X (0,1) or (0,2) band of NO at 236 and 246 nm respectively is excited,the LIF spectrum of hot NO will contain fluorescence blue-shifted relative to the excitation wavelength (A→X (0,0); 226 nm), which is of interest because it is the background-free region of the spectrum. In order to examine the production of hot NO, we have recorded high resolution excitation spectra of the NO resulting from photo-fragmented nitrobenzene using a two color process. In a two color process, photons of a particular energy are used to dissociate the nitrobenzene while photons of a different energy are used to probe the resultant NO. By varying the wavelength of the dissociation laser pulse, we can monitor the production of hot NO as a function of wavelength. Such monitoring is performed by comparing the relative intensity of NO emission from exciting the (0,1) versus the (0,0) bands. For all cases, we have determined the rotational and vibrational temperatures of the nascent NO .DISTRIBUTION STATEMENT A. Approved for public release; distribution is unlimited.

[a]Lin, M.-F.; Lee, Y. T.; Ni, C.-K.; Xu, S. and Lin, M. C. J. Chem. Phys., AIP, 2007, 126.

(414) **Application of a Multistage Algorithm to a Floppy Molecule: Normal Mode Assignments for 2-ethyl-1-hexanol**; Trocia Clasp[1], Tiffani Johnson[1], Michael Sullivan[1], Hideya Koizumi[2], Scott Reeve[1, 2]; [1]Arkansas Center for Laser Applications and Science (ArCLAS), Arkansas State University, [2]Arkansas State University

A multistage algorithm was developed to randomly fit the computational vibrational spectra for 150 low lying conformers of 2-ethyl-1-hexanol to observed FTIR and Raman spectra. Vibrational line centers and intensities for each of the 150 conformers were divided into small clusters as a means to evaluate the precision and accuracy of the fit to the observed spectra, as well as to reduce the computational cost. Once the small cluster analysis was completed, vibrational frequency assignments were obtained by correlating the output from the Gaussian 03 and the Vibrational Energy Distribution Analysis (VEDA 4) programs together with symmetry considerations.

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(415) **Raman and Infrared Spectra, r0 Structural Parameters, and Vibrational Assignments of (CH3)2PX where X= H, CN, and Cl**; Bhushan Deodhar[1], Savitha Panikar[1], Dattatray Sawant[1], Joshua Klaassen[1], June Deng[1], James Durig[1]; [1]University of Missouri - Kansas City

The infrared (3500 to 80 cm) $^{-1}$ and Raman spectra (3500 to 40 cm^{-1}) of gas/or liquid and solid $(CH_3)_2PX$ with X = H (DMH), CN (DMCN) and Cl (DMCl) as well as $(CD_3)_2PH$ have been recorded and complete vibrational assignments are given for all three molecules. To support the spectroscopic study, ab initio calculations by the Møller-Plesset perturbation method to second order MP2 (full) and density functional theory calculations by the B3LYP method have been carried out. The infrared intensities, Raman activities, vibrational frequencies and band contours have been predicted from MP2 (full)/6-31G(d) calculations and these theoretical quantities are compared to experimental ones when available. By utilizing the previously reported microwave rotational constants for DMH and DMCN along with the MP2 (full)/6-311+G(d,p) predicted values, adjusted r_0 structural parameters for DMH and DMCN have been determined. The heavy atom parameters for DMH are: r_0 (P-$C_{3,4}$) = 1.8477(30)Å, angle CPC = 99.88 (50)° and for DMCN: r_0 (N-C) = 1.159(3), r_0 (C-P) = 1.790(3), r_0 (P-$C_{4,5}$) = 1.841(3)Å, angle NCP = 175.7(5), angle $CPC_{4,5}$ = 97.9(5) and angle CPC = 100.7(5)°. Barriers to internal rotation are reported. The experimental values are compared to the corresponding values of some similar molecules whenever possible.

(416) **Are Molecular Interactions in Ionic Liquid-Cosolvent Mixtures Predictable?**; Kristina Noack[1, 2], Florian M. Zehentbauer[3], Marta Martinez Molina[3, 4], Johannes Kiefer[3]; [1]Institute of Engineering Thermodynamics, Friedrich-Alexander-University Erlangen-Nuremberg,, [2]Erlangen Graduate School in Advanced Optical Technologies (SAOT), Friedrich-Alexander-University Erlangen-Nuremberg, [3]School of Engineering, University of Aberdeen, [4]Department of Chemical Engineering, University of Bayreuth

There is an ever increasing interest for applications of room-temperature ionic liquids (RTILs) in chemistry and chemical engineering. The interionic interactions as well as intermolecular interactions with other solvents are a hot topic in this context. Basically, these interactions represent a key factor in the determination of the molecular and macroscopic properties of a pure liquid or a solution. Hence, developing a fundamental understanding at the molecular level and its relationships with the macroscopic scale is the key to allow a task-specific design of solvents in the future. In imidazolium based RTILs the interactions are believed to predominantly take place in the form of hydrogen bonds at the C2-H position of the cation owing to its slightly acidic nature. In the present work, we compare a series of different polar solvents in their binary mixtures with 1-ethyl-3-methylimidazolium ethyl sulfate, [EMIm][$EtSO_4$]. The molecular interactions in the mixtures are studied using IR and Raman spectroscopy. In order to extract as much information as possible, several evaluation methods are applied to the experimental spectra including deconvolution and frequency shift analysis, excess spectroscopy, and chemometrics. The results

show that solvents containing hydroxyl groups form distinct interactions with the aromatic C-H groups of the cation. Whereas, for acetone for example it is found, that an on-top configuration, where the carbonyl oxygen interacts with the π-electrons of the imidazolium ring, is preferred. The experimental data indicate that with the successive addition of acetone molecular clusters consisting of an ion pair plus one or two acetone molecules form before ion pair dissociation occurs. A third case is represented by mixtures of the RTIL and dimethyl sulfoxide. In these solutions the spectroscopic data suggest the formation of sandwich-like complexes. To answer the question asked in the title, we can claim that we understand the molecular interactions in selected RTIL/cosolvent systems. However, a full understanding and thus the possibility for reliable predictions is yet to be developed.

(417) **Comparison of Solvent Models for Quantum-Chemical Predictions of Peptide Conformation and Spectral Properties**; Václav Parchaňský[1, 2], Jakub Kaminský[1], Josef Kapitán[3], Petr Bouř[1]; [1]Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic,, [2]Department of Analytical Chemistry, Institute of Chemical Technology, Prague, [3]Department of Optics, Palacký University

Density functional theory (DFT) computations are an indispensible tool for interpretation of Raman optical activity (ROA) and other vibrational spectra. For flexible systems strongly interacting with the solvent, however, realistic solvent models must be included. Many available implicit solvent models account for hydrogen bonds only partially; also the dipersion (van der Waals) solvent-solute interactions are rather neglected. The dispersion often plays, however, leading role in peptide conformations.[1] Therefore, we tried to assess performance of various solvent models for description of model molecules. The DFT results were compared with molecular dynamics (MD) simulations. For the Ac-Ala-NMe diamide system, the simulated results were confronted with experimental ROA spectrum.

[1] Hudecová, J.; Horníček, J.; Buděšínský, M.; Šebestík, J.; Šafařík, M.; Zhang, G.; Keiderling, T. A.; Bouř, P. ChemPhysChem 2012, 13(11), 2748–2760.

(418) **Target Detection Applied to Detection of Adulterants in Powdered Raw Material using Near Infrared Hyperspectral Imaging**; Robert Roginski[1], Neal Gallagher[1], Gregory Israelson[2]; [1]Eigenvector Research, Inc., [2]Nestle Purina

A significant challenge to any detection algorithm is that the background and background variability (clutter) changes sample-to-sample and impacts detection sensitivity. Hyperspectral imaging (HI) is fast, non-invasive and provides a large sampling without additional sample preparation. This sampling is used to characterize the background and background variability (termed clutter) that is specific to each individual sample. The clutter is then used to optimize a generalized least squares target detection algorithm. HI also benefits because, although the overall adulterant quantities may be low on a mass basis, signal in individual pixels can be dominated by the adulterant. Therefore, detection of low quantities of adulterants via HI is less hampered by dilution effects expected from wet chemistry methods. However, sampling must consider that the target of interest must be at or near the sample surface if it is to be detected. Results are shown for HI detection of melamine in wheat gluten.

(419) **Parallel Factor Analysis of Multi- Excitation UV Resonance Raman Spectra for Protein Secondary Structure Determination;** Olayinka Oshokoya[1], Renee JiJi[1]; [1]University of Missouri- Columbia

Studies pertaining to protein or peptide structure, dynamics or function fundamentally require a method for secondary structure measurement. The structurally sensitive protein vibrational modes (amide I, II, III and S) in deep-ultraviolet resonance Raman (DUVRR) spectra resulting from the backbone C-O and N-H vibrations make DUVRR a potentially powerful tool for studying secondary structure changes. Experimental studies reveal that the position and intensity of the four amide modes in DUVRR spectra of proteins are largely correlated with the varying fractions of α-helix, β-sheet and disordered structural content of proteins. Employing multivariate calibration methods and DUVRR spectra of globular proteins with varying structural compositions, the secondary structure of a protein with unknown structure can be predicted. A disadvantage of multivariate calibration methods is the requirement of known concentration or spectral profiles. Second-order calibration methods, such as parallel factor analysis (PARAFAC), do not have such a requirement due to the "second-order advantage." An exceptional feature of DUVRR spectroscopy is that DUVRR spectra are dependent on excitation wavelength. Thus, higher-order data can be created by combining protein DUVRR spectra of several proteins collected at multiple excitation wavelengths. Recently, PARAFAC has been used to analyze DUVRR data collected at multiple excitation wavelengths on several proteins to determine secondary structure content. Comparison of the known secondary structure content of each protein versus that recovered from PARAFAC analysis showed strong correlation, suggesting that higher order data may be used for quantification of protein secondary structure without prior knowledge of underlying spectral or concentration profiles.

(420) **Direct Analysis in Real Time (DART) Analysis with a Modified GC/MS System**; Joseph LaPointe[1], Elizabeth Crawford[1], Michael Festa[1], Brian Musselman[1]; [1]IonSense, Inc

DART is an open air desorption ionization method that enable rapid determination of sample composition with little sample preparation. The DART source requires an atmospheric pressure inlet (API) to introduce ions into the mass spectrometer for analysis and, thus, it is typically interfaced to LC/MS systems. We have integrated an API into an Agilent-Mass Selective Detector (MSD) in order to facilitate DART analysis with this low cost mass analyzer. Agilent GC/MSD is used extensively in food laboratories for routine analysis such as fatty acid distribution and essential oil characterization. Application of this modified DART-MSD for characterization of foodstuffs, edible oils, supplements as well as detection of contaminant in these samples will be described. The use of this system to complete rapid inspection of either simple or complex samples for similarity to samples of the same type previously analyzed using a database search approach will be described also.

(421) **The Effects of Hydrogen on a Helium Based Dielectric-Barrier Discharge Ambient Desorption/Ionization Source**; Jonathan Wright[1], Matthew Heywood[1], Glen Thurston[1], Paul Farnsworth[1]; [1]Brigham Young University

Plasma sources have been shown to be fast and effective ionization sources in the quickly developing field of ambient desorption/ionization mass spectrometry (ADI-MS). Of these sources, the low temperature plasma (LTP), direct analysis in real time (DART), and the dielectric-barrier discharge (DBD) have received considerable attention. In our lab, we have developed a helium based DBD with which we have carried out our experiments. It is proposed that the ionization mechanism for many helium based plasma desorption-ionization sources is initiated by the Penning ionization of atmospheric nitrogen by helium metastable atoms. This initial step in the ionization mechanism is supported by the correlation of helium metastable fluorescence and excited nitrogen ion emission. Helium metastable fluorescence imaging of a helium plasma with 1% hydrogen mix shows an almost complete depletion of the helium metastable population. Initial spectral images of the plasma emission show a decrease in excited helium and excited nitrogen ion emission as well. Despite the apparent depletion in the helium metastable population caused by the addition of hydrogen, an

improvement of a factor of up to 33 can be seen in the ambient desorption-ionization mass spectrometric signal of a variety of target analytes. The magnitude of the enhancement is strongly dependent on the percentage of hydrogen added to the support gas and on the operating conditions of the plasma. The differences between the pure helium and the helium/hydrogen plasmas and the influence of hydrogen on ion source performance will be discussed.

(422) **Development and Characterization of a New Concentric-Geometry Flowing Atmospheric Pressure Afterglow**; Kevin P. Pfeuffer[1], J. Niklas Schaper[2], Jacob T. Shelley[3], Steven J. Ray[1], George C.Y. Chan[1], Nicolas H. Bings[2], Gary M. Hieftje[1]; [1]Department of Chemistry, Indiana University, [2]Institute for Inorganic and Analytical Chemistry, Johannes Gutenberg University Mainz, [3]Department of Chemistry, Purdue University

The field of ambient mass spectrometry has shown great potential for providing rapid chemical analysis. Because sample preparation is not required, sample throughput can be increased over traditional ionization methods, while the selectivity and sensitivity inherent to mass spectrometry are preserved. Two main types of ambient desorption/ionization mass spectrometry (ADI-MS) sources are: 1) spray-based, which include desorption electrospray ionization (DESI), and 2) plasma-based, such as direct analysis in real time (DART). An alternative plasma-based source, the flowing atmospheric pressure afterglow (FAPA) has been developed within the Hieftje group. The FAPA operates in a manner similar to that of most plasma-based ADI-MS sources; excited species are formed in a discharge, which are used to desorb and/or ionize analytes of interest. In the previously described geometries, difficulty arises in balancing two competing goals: close interaction of the plasma and analyte for efficient ionization, and isolation of the plasma from the sample to prevent contamination of the discharge. To reconcile these seemingly contrasting aims a concentric-geometry flowing atmospheric-pressure afterglow (termed halo-FAPA) has been developed. The halo-FAPA accomplishes these goals by means of a toroidal plasma formed between two concentric tube electrodes separated by an insulating layer either (polyimide tubing or a ceramic spacer). The inner capillary serves as the discharge cathode with the outer tube as the anode. A short length (1 - 2 mm) of the inner capillary (cathode) is exposed by removing some of the polyimide tubing to restrict the area the discharge covers. Two helium flows are utilized, one through the inner capillary (0.2-1.0 L/min) that can be used also for gaseous sample introduction and cooling; and one through the outer capillary (0.4-1.0 L/min) to sustain the discharge. The halo-FAPA can be utilized in a similar manner to established ADI-MS methods by introducing samples in front of the discharge, or by introducing a gaseous sample or liquid aerosol into the center channel. This presentation will describe the development of the halo-FAPA source and its characterization through optical and mass spectrometric means. An application utilizing droplets introduced into the central channel of the halo-FAPA will also be described.

(423) **Analysis of Cosmetic–Related Chemicals Using Desorption Electrospray Ionization Mass Spectrometry**; Jamie Nizzia[1], Adam O[2], Christopher Mulligan[3]; [1]Illinois State University, [2]Illinois State University, [3]Illinois State University

Over the last few years, several problems related to cosmetic chemicals have become a matter of public concern. Rapid and accurate monitoring of these analytes is critical for quality control, regulatory matters, toxicology, and environmental monitoring. Study of these compounds can require analysis of surface-bound traces, authentic cosmetic formulations, and aqueous samples. In this study, the rapid detection of cosmetic compounds is investigated via ambient mass spectrometry. Desorption electrospray ionization mass spectrometry (DESI-MS) is used to rapidly screen these compounds at ambient conditions, allowing samples to be analyzed directly from surfaces and as minor components in commercial products. The rapidity of the technique coupled with little to no sample preparation requirements leads to very low total analysis times. DESI-MS utilizes a pneumatically-assisted electrospray to desorb/ionize analytes from a surface of interest, allowing subsequent detection by mass spectrometers capable of sampling externally-generated ions. For trace residue studies, known amounts of cosmetic compounds were deposited onto printed teflon slides by spotting volumes of analytical standards and allowing the solvent to completely evaporate before analysis. Multi-component chemical mixtures were analyzed, utilizing both positive and negative ion modes. Authentic cosmetic formulations were also directly analyzed after spotting onto porous teflon. Overall, DESI-MS was shown to be an effective analysis alternative for the target chemicals. Low nanogram limits of detection were attained when screening surface-bound cosmetic traces, with confirmatory MS^2 analysis that was comparable to other analytical techniques. Quantitative ability was also shown by construction of calibration curves, demonstrating decent linearity over several orders of magnitude. Analysis of a complex chemical mixture was shown when implementing both positive and negative ion scan modes, and direct screening of active ingredients in cosmetic formulations (*i.e.* hair dye and acne cream) was observed and confirmed by literature.

(424) **Forensic Applications of a Portable Mass Spectrometer Capable of Ambient Ionization**; Kyle Vircks[1], Adam O[1], Christopher Mulligan[1]; [1]Illinois State University

One of the greatest problems with today's crime laboratories is low sample throughput and increasing backlogs. One method of combatting this issue is the development of reliable analytical techniques that are much more rapid than currently accepted protocols that typically involve lengthy, difficult processes. A more immediate solution involves the ability to screen physical evidence on-scene and send only pertinent samples to off-site laboratories for confirmatory analysis, dramatically reducing the potential for backlogged casework. Presumptive color tests for illicit drugs are readily available for screening physical evidence, but the nature of these tests result in numerous false-positives, leading to vast amounts of non-essential physical evidence being sent to crime laboratories for time-consuming analyses. In an effort to provide more reliable presumptive testing procedures, a portable ion trap mass spectrometer capable of ambient ionization techniques is being investigated for rapid screening of physical evidence on-scene. Recently, this portable instrument equipped with various ambient mass spectrometry ionization (MS) sources has been employed to rapidly detect and identify various forensically-relevant chemicals. Such examples include detection of illicit drugs and abused pharmaceuticals with desorption electrospray ionization (DESI) and accelerant detection utilizing atmospheric pressure chemical ionization (APCI). Instrument characterization was mainly conducted using purchased analytical standards; however, confiscated drugs were provided through collaboration with a local law enforcement agency and successfully analyzed. The results of these studies, including initial instrument characterization and analytical performance, will be shown. Being equipped with an ion trap mass analyzer, confirmatory tandem MS analysis is also possible. This allows for rapid screening as well as accurate identification of unknown chemical species before evidence collection. When screening of evidence with irregular geometry is necessary, positioning such objects near the ionization source of the instrument becomes difficult. In such cases, swabs are directly analyzed after being used to sample chemical residues from evidentiary surfaces. Swabbing techniques are especially useful when screening large surface areas is needed. Transfer efficiencies of various swabbing methods, including dry vs. wet, will be presented.

(425) **Characterization of Thermally-Assisted Desorption Electrospray Ionization Mass Spectrometry for Water Contaminant Analysis**; Alain Ton[1], Christopher Mulligan[1]; [1]Illinois State University

Government regulatory agencies like the U.S. Environmental Protection Agency (EPA) have set legal limits on specific chemical concentrations, such as agricultural chemicals and industrial chemicals, which may be present in drinking water supplies. Low level concentrations of these compounds may not have an immediate effect on human health, but there could long-term effects on the general population, warranting further research in this area. The ability to continuously detect these low level contaminants is of importance to ongoing toxicology studies and the general safety of the population. Established techniques such as liquid chromatography-mass spectrometry (LC-MS) have been used for years in such detection, and while known for their analytical performance, these techniques can require lengthy sample preparation, multiple methods for broad coverage of analyte classes, and long analysis times. In our studies, we utilize desorption electrospray ionization mass spectrometry (DESI-MS), which has been shown to be a very sensitive technique that requires little or no sample preparation for the analysis of condensed phases. To allow trace analysis of contaminants directly from water samples with DESI, we incorporate thermal assistance into the ionization/desorption step via a heated sample stage, which expedites solvent evaporation and enhances the ionization efficiency of target analytes. Contaminated water samples are continuously infused onto the heated stage, serving as an analysis point to which the DESI sprayer impinges. The constructed ionization source allows continuous monitoring of infused sample with minimal carryover. Broad characterization of this technique is important to show general applicability to the variety of chemical classes that can exist as contaminants and the water supplies in which they can be present. Towards this need, the effect of various water properties upon detection limits of target compounds was investigated, and low part-per-trillion detection limits were readily achieved.

(426) **Direct Analyte-Probed Nanoextraction coupled to Nanospray Ionization-Mass Spectrometry for Analysis of Illicit Drugs**; Kristina Clemons[1], Guido Verbeck[1]; [1]University of North Texas

Trace analysis is a rapidly growing field of forensic research. Many new, innovative methods have been developed in recent years displaying advantages such as reduced sample preparation, lower limits of detection, or minimum evidentiary destruction. All of these traits are desirable in forensic analysis methodology due to the need to maintain evidence integrity while still making the necessary definitive characterizations. Direct analyte-probed nanoextraction coupled to nanospray ionization-mass spectrometry (DAPNe-NSI-MS) has proven to be an effective tool to attain all of these qualities when applied to illicit drug analysis. DAPNe uses a nanomanipulator mounted to a microscope stage and controlled by a three-axis joystick. A capillary tip, backfilled with 10 µL of solvent [typically 1:1 (v/v) methanol:water, 1% acetic acid], is placed in a nanopositioner. The surface to be analyzed is placed under the microscope. Upon location of a particle of interest, the capillary tip is then maneuvered within 1 µm of the particle or sample of interest. Using a pressure injector, the solvent is injected onto the surface where it dissolves the analyte. The analyte solution is then extracted back into the capillary tip and directly analyzed via NSI-MS. In this work, trace amounts of illicit substances were placed on glass slides for extraction (other surfaces have also been tested, i.e., plastic, metal, and computer board). Cocaine, black tar heroin, crystal methamphetamine, and ecstasy have all been successfully extracted and identified. Additionally, fingerprints on glass slides were doped with each drug to examine the destructiveness of this method. Extractions from within the print area were successfully performed, leaving ridge detail intact. The viability of the prints was confirmed by the Denton County Sherriff's Office in a comparison with latent prints on which no extraction had been performed. DAPNe-NSI-MS makes single particle analysis possible which greatly reduces the sample size necessary for positive identification and preserves the integrity of sensitive evidence.

(427) **A Study of the Ionization Behavior of Several Compound Families in Low Temperature Plasma Ambient Desorption/Ionization High Resolution Mass Spectrometry**; Carsten Engelhard, Anastasia Albert; [1]University of Muenster

Low temperature plasma (LTP) probe high resolution mass spectrometry (HR-MS) is an attractive method for the direct analysis of complex samples. Desorption and ionization of analytes is performed at the sample surface in the ambient environment. Benefits of the method include high sensitivity and mass accuracy and little to no sample pretreatment. In the present study, the ionization behavior of selected compound families was investigated in LTP-HR-MS and directly compared to electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI). The home-built LTP probe is based on a dielectric barrier discharge that is formed in helium by applying a high-voltage, alternating current waveform between two electrodes separated by a glass tube. The LTP was coupled to a high resolution Orbitrap mass spectrometer. Several model analytes of different compound families were studies. Ionization efficiencies for amides, amines, aldehydes, imides, polycyclic aromatic hydrocarbons (PAHs), ionic species, a nucleoside, and a pharmaceutical were determined and directly compared to ESI and APCI. In general, LTP can be considered to be a relatively soft ionization method because little fragmentation of model compounds was observed. Further, it was found that LTP shows comparable ionization characteristics to APCI for amides, amines, and aldehydes. A benefit of LTP over conventional methods is the possibility to successfully ionize PAHs and imides. Here, the studied model compounds could be detected by neither APCI nor ESI. From the results reported above, LTP can be classified to be an attractive method for the ionization of low molecular weight compounds over a relatively wide polarity range.

(428) **Fingerprinting Network Architectures in Model Siloxane Networks through Multivariate Statistical Analysis of Pyrolytic Degradation Profiles**; James Lewicki[1], Rebecca Albo[1], Jasmine Finnie[1], Cynthia Alviso[1], Robert Maxwell[1]; [1]Lawrence Livermore National Laboratory

Crosslinked Poly(dimethylsiloxane) elastomeric networks (silicones) are an academically and technologically relevant sub-group of polysiloxane based materials, having wide-spread application in a large number of diverse technological, commercial and research areas . In order to achieve the desired properties for an application, commercial silicones are formulated as complex multi-component and often propriety systems. These materials incorporate multi-modal distributions of chain lengths, varied crosslink topologies/densities, chemically modified free chain ends, non-stoichiometric excesses of reactive moieties and often large volume fractions of a variety of reactive and/or passive filler materials. To date, there exists no reliable, rapid and experimentally robust method for the forensic identification and discrimination of complex, chemically similar silicone elastomers. In this study Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC/MS) in tandem with multivariate statistical analysis has been employed to study in-depth the degradation chemistry of a well defined series of model end-linked silicone systems. These model materials have been formulated to incorporate individually and in combination, key structural elements: Mono- and bimodality, ranges of crosslink density, inter-chain molar mass, conventional silica and nano-scale filler materials. Multivariate statistical analysis has been utilized in order to provide a direct link

between the degradation 'fingerprint' and the starting network structure. In doing so, the influence of differing architectural elements on the degradation profile of a silicone network can defined. This work represents an important step towards building a rapid and predictive method of indentifying silicone elastomer structure and formulation from a pyrolytic degradation profile

(429) **Forensic Profiling of Dye Extracts from Millimeter-Length Cotton Fibers using Ultra Performance Liquid Chromatography and Mass Spectrometry**; Scott Hoy[1], Molly Burnip[1], Stephen Morgan[1]; [1]University of South Carolina

Forensic fiber examinations involve the comparison of trace evidence fibers with one or more known fibers to determine possible associations between victims, suspects, and crime scenes. Microscopic examinations, including simple and comparison microscopy (for morphology) and polarized light microscopy (for birefringence, sign of elongation, and refractive index), are usually the initial steps in polymer identification and fiber comparison. Fluorescence microscopy, UV/visible microspectrophotometry, and infrared spectroscopy are valuable follow-up techniques that may assist in revealing differences or confirming similarities among questioned and known fibers. While fast nondestructive methods such as these are preferred, these techniques do not identify dye mixtures. The premise of our ongoing research is that if dye formulations on trace fibers can be reliably profiled at trace levels, match exclusions can be made with higher reliability, and "results consistent with" will have increased significance. Microextraction, followed by ultra-performance liquid chromatography (UPLC) can often distinguish similar fibers containing different, but similar, dyes with the combination of retention time matching, UV/visible spectrum comparison, and structural analysis by mass spectrometry. Separation and detection of individual dye components provides a qualitative and semi-quantitative fiber dye 'fingerprint.' The analysis of cotton fibers is challenging because they can be dyed with three different classes of dye, each requiring a different method for extraction and analysis. This work focuses on the chemistries of direct and reactive dyes, their optimum extraction conditions and chromatographic methods, as well as structural analysis of reactive dyes before and after extraction. We have successfully extracted and characterized cotton fibers as small as 1 mm in length, and have identified multiple dye components by mass spectrometry. Analytical figures of merit and validation statistics, including extraction reproducibility, linearity, limits of detection and quantitation, and UPLC precision, will also be reported. Determining the number and relative amounts of dye components present on fibers, and characterizing those dyes at the molecular level, offers an entirely new level of discrimination. Examples will also be shown of 'pure dyes' containing multiple smaller trace components that suggest potential for tracing specific dye formulations to a textile manufacturer.

(430) **Copper Material Source Discrimination using Trace Element Concentrations**; Joshua Dettman[1], Alyssa Cassabaum[1], JoAnn Buscaglia[2]; [1]Oak Ridge Institute for Science and Education, Federal Bureau of Investigation Laboratory, [2]Federal Bureau of Investigation Laboratory

Copper can be involved in criminal cases such as theft (as raw material from mines and as wiring or piping from construction sites and homes) and bombings (wiring in explosive devices). The goal of this research is to assess the potential of using trace element concentrations of a copper item from a crime scene to provide a link to a copper item associated with a suspect. Concentrations of trace elements in copper were initially determined in standard reference materials using solution ICP-MS for method validation. Standard reference materials were also used to construct a matrix matched calibration curve, which was compared to non matrix-matched calibration. To increase the number of elements available for source discrimination, noncertified elements present in the standard reference materials were determined using solution ICP-MS and confirmed with laser ablation ICP-MS. To discriminate between copper items, the variation in trace element concentrations within a "source" (e.g., from different parts of the copper item and/or from the same production batch) must be small compared to the variability in trace element concentrations between production batches from the same manufacturer, items produced by different manufacturers, and geographic location of raw material mining. Statistical techniques are used to identify elements that contribute significantly to the variation within and between samples, and to group samples based on their trace element concentration profiles. Statistical analysis of the trace element concentration profiles could potentially provide a link between the copper item recovered from the crime scene and an item associated with a suspect, or exclude a suspect from further investigation.

(431) **Detection Limits for Blood on Fabrics using Diffuse Reflection Infrared Spectroscopy**; Stephanie DeJong[1], Wayne O[1], Brianna Cassidy[1], Zhenyu Lu[1], Stephen Morgan[1], Michael Myrick[1]; [1]University of South Carolina

Infrared spectroscopy provides a non-destructive method for detecting biological fluids on substrates of forensic interest. In our laboratory, we have studied one typical forensic sample of interest: blood deposited on fabric samples. A dip coating based method of doping samples enables the creation of reproducible samples suitable for calculating detection limits. Measurements can be made in a range of different optical frequencies in the mid- and near-infrared spectral regions that may provide differential sensitivity, penetration depth, and interference from thermal radiation. In this report, we provide diffuse reflection spectra over three energy ranges: mid-infrared (600-5000 cm-1), near-infrared (5000-8000 cm-1), and short-wave near infrared (8000-12000 cm-1). Samples were prepared by depositing rat blood onto acrylic, cotton, nylon, and polyester fabrics by dip coating from solutions of 25, 50, 100, and 200 times dilute rat blood. We discuss some characteristic molecular vibrational features observed for blood and the fabrics in the optical spectra and also discuss the advantages and disadvantages of the various spectral ranges, such as overlap with room temperature thermal radiation spectrum, presence of dispersion artifacts, and availability and cost of light sources and detectors with appropriate characteristics. Detection limits for blood on the four fabrics were estimated in several bands of the infrared and near-infrared spectrum by the application of partial least squares (PLS) with various data pretreatments. These detection limits are presented.

(432) **Analysis of Blue Gel Inks by Micro FT-IR Spectroscopy**; Liling Cho[1], Hung-Yi Huang[2], Chia-Ching Kuo[3], Yi-Jyun Chang[4]; [1]Central Police University, [2]Taoyuan County Police Department, [3]Central Police University, [4]Kaohsiung City Police Department

Micro FT-IR spectroscopy is a useful tool for blue gel pen analysis and is capable in distinguishing different pens especially in forensic laboratory. Because of lack of infrared database in this area, forensic scientists in Taiwan can not use infrared as an analytical tool in questioned document examination. In this research, 60 blue gel pen inks, of different brands, models were collected on Taiwan's market. The results of this study showed that Micro FT-IR spectroscopy classified all 60 ink samples into 38 groups with a high discriminating power of 0.97. In addition to pigments C.I. PB 15:1, C.I. PB15:3 and C.I. PV 23, three other dyes of contents in blue gel pen inks including Brilliant Blue G, Patent Blue Violet, and Erioglaucine has been detected by infrared microspectroscopy. We hope that this blue gel pen inks database can be a useful resource in rapidly identifying the blue gel ink in Taiwan forensic laboratory.

(433) **Analysis of Stamped Seal Ink by ATR Microspectroscopy**; Kai-Bin Huang[1], Liling Cho[1], Chia-Ching Kuo[1]; [1]Central Police University

Seal inks have been used to represent one's signatures in Taiwan for a long time. The forensic cases involving seal inks in questioned documents were increasing in recent year. FTIR microspectroscopy is a powerful analysis tool for the non-destructive analysis of seal ink on paper. In this study, 68 seal inks were analyzed by reflectance FTIR microspectroscopy to create infrared database. ATR microspectroscopy were used to determine the sequence of intersecting lines from ballpoint pen ink, laser toner and seal ink in withdrawal form or check from different banks. The determination of the sequence of intersecting lines is an important aspect in examining forensic questioned documents. From different ATR spectra, we can determine the sequence of intersecting lines between stamped seal ink and signature with ballpoint pen. The results shown here can provide a good way and non-destructive analysis to solve the fraud cases in the forensic laboratory.

(434) **Forensic Classification of Blue Gel Inks using Raman Microspectroscopy**; Liling Cho[1], Shie-Ru Wang[2], Chia-Ching Kuo[1], Kai-Bin Huang[1]; [1]Central Police University, [2]Taipei City Police Departmet Forensic Science Center

In forensic science, there are two techniques in analyzing the gel inks, the classical thin layer chromatography and Raman microspectroscopy. However, since the complicated procedures and unable to analyze gel ink by thin layer chromatography, Raman microspectroscopy becomes a major analytical tool. Its characteristics in non-invasive and non-destructive allow samples to be examined without any pre-treatment. This study proposed that Raman microspectroscopy can be a general tool for blue gel pen inks analysis and is capable in distinguishing different pens. To test it, 61 blue gel pen inks from different models and brands, available in Taiwan market, were collected and then analyzed using Raman microspectroscopy. The samples were written on the papers and then emitted by two wavelength laser sources, 633nm and 780nm. We found that 37 of 61 samples can be analyzed by Raman microspectroscopy, furthermore, two main pigments were identified, C.I. Pigment Blue 15 and C.I. Pigment Violet 23. The discriminating power was 0.95 from the 37 samples under 633nm wavelength laser source, 0.87 under 780nm wavelength laser source, and 0.98 when using both of them. The results have been shown that Raman microspectroscopy can be an ideal technique for rapidly analyzing pigment-based gel pen inks instead of using classical thin layer chromatography. The database also can be a useful resource in rapidly identifying the blue-pigmented gel pen in Taiwan.

(435) **Differentiation of Bacterial Spores Grown under Different Culture Conditions using Raman Microspectroscopy**; Joshua Dettman[1], Kristina Scott[1], Leslie McCurdy[2], Jason Bannan[3], James M Robertson[4]; [1]Oak Ridge Institute for Science and Education, Federal Bureau of Investigation Laboratory, [2]Chemical, Biological, Radiological, and Nuclear Sciences Unit, Federal Bureau of Investigation Laboratory, [3]Biological Sciences Program Advisor, Federal Bureau of Investigation Laboratory, [4]Counterterrorism and Forensic Science Research Unit, Federal Bureau of Investigation Laboratory

Association of a production laboratory to bacterial spores recovered from a crime scene may be based on the differences in spore molecular makeup. Production sourcing of bacterial spores has previously been based on analysis of stable isotope ratios, fatty acid methyl esters, carbohydrates and proteins, and residual agar. Culture conditions and growth media formulation may influence the molecular characteristics and phenotype of the cultured organisms. Studies of the effect of the production process on microorganism threat agents could provide important investigative leads in criminal investigations and intelligence applications. The purpose of our research is to adapt Raman spectroscopy for rapid analysis of bacteria. We test whether spores can be matched to the source of production by comparing specific Raman markers of spores grown in a particular growth medium with those in a database of Raman signatures obtained for growth in more than thirty culture media formulations. Raman microspectroscopy is an attractive orthogonal method to other analytical approaches usedin microbiology such as fatty acid methyl ester (FAME) analysis and mass spectrometric analysis of proteins, carbohydrates,isotope ratios, and residual chemicals of the processing regimes. It is rapid and non-destructive, requires very little sample, and has sufficiently low detection limits for single cells. Raman spectra were collected from well characterized, washed Bacillus cereus spores that were grown under a variety of media conditions. Variation in growth media formulations was obtained through the manipulation of protein and carbohydrate sources, component concentrations, micro-nutrients, and sporulation salt concentrations. The growth media formulations and culture conditions were taken from the literature and from information obtained during investigations. Principle components analysis was used to identify the Raman peaks that account for the most variability between growth conditions. The statistical significance of the variations in Raman spectra between spores is assessed.

(436) **Analysis of Color Printer Inks by Raman Microspectroscopy**; Liling Cho[1], Hung-Chieh Lin[2], Yun-Seng Giang[1], Kai-Bin Huang[1]; [1]Central Police University, [2]New Taipei City Police Department Forensic Science Center

Document examiners are frequently asked to determine whether a color printout has originated from a particular inkjet printer or not. Indeed, this is a real problem to most forensic scientists. While many publications describe the inkjet printing process, few forensic science pspers refer to the analysis of inkjet printing inks. Being non-destructive and non-invasive and needing little sample pretreatment, Raman microspectroscopy plays an important role in forensic science. This study aims analyze color inkjet inks in Taiwan by Raman microspectroscopy with a hope to compile a database of inkjet printer inks, including original equipment manufacturer(OEM) inks and non-OEM inks. Color inkjet inks of 20 different brands and models were collected from Taiwan market. Generally, results obtained upon analyzing color inkjet inks using Raman microspectroscopy are reproducible. Magenta inks are more easily discriminated than other colors, with a discriminating power of 0.925 under 780 nm wavelength laser source.

(437) **Determination of Colloidal Gold Nanoparticle Surface Areas, Concentrations, and Sizes through Quantitative Ligand Adsorption**; Manuel Gadogbe[1], Siyam Ansar[1], Dongmao Zhang[1]; [1]Mississippi State

Determination of the true surface areas, concentrations, and particle sizes of gold nanoparticle (AuNP) is a challenging issue due to the nanoparticle morphological irregularity, surface roughness, and size distributions. A ligand adsorption-based technique for determining AuNP surface areas in solution is reported. Using a water soluble, stable, and highly UV-vis active organothiol, 2-mercaptobenzimidazole (MBI), as the probe ligand, we demonstrated that the amount of ligand adsorbed is proportional to the AuNP surface area. The equivalent spherical AuNP sizes and concentrations were determined by combining the MBI adsorption measurement with Au^{3+} quantification of the aqua regia digested AuNPs. The experimental results from the MBI adsorption method for a series of commercial colloidal AuNPs with nominal sizes of 10, 30, 50, and 90 nm in diameter were compared with those determined using the dynamic light scattering, transmission electron microscope, and localized surface plasmonic resonance methods. Atomic force microscopy (AFM) revealed that the AuNP surfaces are rough,

causing the surface area measured by MBI adsorption to be consistently larger than that obtained with other methods. The ligand adsorption-based technique is highly reproducible and simple to implement. It only requires a UV-Vis spectrophotometer for characterization of in-house prepared AuNPs.

(438) **Optimization of Self-Normalizing SERS-Based Trace Detection of TNT**; Marc Wadsworth[1], Benoit Lauly[1], Paul Repasky[1], Jonathan Scaffidi[1]; [1]Miami University

At high concentrations, 2,4,6-trinitrotoluene (TNT) presents hazards as an explosive. At lower levels, concerns remain due to its impacts on human health. Typical SERS-based approaches to trace TNT detection rely on formation of charge-transfer "Meisenheimer complexes" which enhance the intensity of already-present Raman bands through resonance Raman effects. Unfortunately, a wide variety of factors can increase SERS intensities through aggregation effects independent of the presence or absence of TNT. This is particularly true when dealing with real-world samples. Our laboratory has developed TNT-sensitive, SERS-active nanoparticles incorporating a built-in internal standard. This internal standard allows us to correct for aggregation-induced changes in SERS intensities, thereby circumventing one of the primary stumbling blocks encountered by typical SERS-based TNT assays. We have additionally examined and optimized the reaction chemistry to enable rapid detection of TNT at ppb concentrations, with no visible interference from other nitro-toluenes.

(439) **SERS imaging of fungi via in vivo synthesis of gold nanoparticles**; Fatemeh Farazkhorasani[1], Martin Prusinkiewicz[2], Susan Kaminskyj[2], Kathleen Gough[1]; [1]Department of Chemistry, University of Manitoba, [2]Department of Biology, University of Saskatchewan

Surface Enhanced Raman Scattering (SERS) can provide chemical information on materials that are in close contact with appropriate metal substrates, such as nanopatterned gold surfaces and gold nanoparticles (AuNPs). Since nanoparticles can be generated by living cells, we have created conditions for AuNP formation within and on the surface of fungal hyphae of *Aspergillus nidulans*, in order to explore the potential for SERS analysis. AuNP distribution and composition have been examined by UV-Vis spectroscopy, fluorescence light microscopy, transmission electron microscopy, and scanning transmission x-ray microscopy. Our NPs have characteristic shapes comparable to those generated by other microorganisms or by chemical reduction. These AuNPs exhibit surface plasmon resonance and can be used as substrates for SERS spectra, enhancing the scattering intensity by several orders of magnitude. Both 1 mM and 5 mM $HAuCl_4$ treatments produced SERS-active particles. AuNPs were often associated with hyphal walls, both in the peripheral cytoplasm and on the outer wall surface. We are continuing to develop methods for better control of NP formation (size, shape and location). In addition to variables such as initial concentration of $HAuCl_4$, pH, temperature and duration of exposure, we are evaluating different growth media in an effort to generate AuNPs selectively on or in the hyphal walls.

(440) **Surface-enhanced Raman Spectroscopy (SERS) of Ricin B Chain in Whole Human Blood**; Antonio Campos[1], Marty Blaber[2], Christy Haynes[1], Richard van Duyne[2]; [1]University of Minnesota, [2]Northwestern University

Soldiers in the battlefield are susceptible to many risks including bloodborne infection and exposure to bioterror agents. Current diagnosis of bioterror agent exposure or sepsis biomarkers is done after the onset of symptoms and, in some cases, are too late for any effective treatment to be performed. Thus, there is a need for a rapid, real-time detection of toxins in the bloodstream of soldiers. Recently developed detection methods using aptamers for the detection of ricin via surface-enhanced Raman spectroscopy (SERS) can be applied to this end. Ricin is a naturally occurring toxic protein composed of two chains (A and B) derived from the castor bean. Herein, aptamer-modified silver film-over-nanosphere substrates (AgFONs), a commonly used SERS substrate with an enhancement factor on the order of 10^6, were used within a microfluidic device for real-time detection of bioterror agents in whole human blood. This platform enabled ricin b chain detection within whole human blood even after a 3 day incubation in whole blood. Principle component analysis (PCA) of the SERS spectra shows distinct clustering of spectra recorded from AgFONs modified with an aptamer, aptamer-modified substrates in blood, and aptamer-modified substrates in blood after ricin b chain incubation. The achieved SERS signals are dependent on ricin b chain concentration spiked into whole blood, and SERS detection is reversible with mild heating of the substrate. This platform holds great promise for multiplex detection of bloodborne analytes based on the affinity of aptamers for specific targets and the vibrational fingerprints provided by Raman scattering.

(441) **Determination of the SERS Enhancement Factors using Solvent as an Internal Reference**; Fathima Ameer[1], Dongmao Zhang[1]; [1]Mississippi State University

Accurate determination of the SERS enhancement factor (EF) is critical important for fundamental understanding of the SERS phenenomena. While mathematical expression of the SERS EF is deceitfully simple(EF=(I_SERS⁄N_SERS)/(I_NR⁄N_NR)), experimental quantification of the SERS EF is challenging because of a series of instrument, analyte, and SERS substrate related issues. Presented in this work is a solvent internal reference method for determination of the absolute SERS EF factors. Using the thiobarbituric acid-malondialdehyde and mercaptobenzimidazole as the model analytes, we found that the absolute SERS EFs for these two analytes are very similar despite of their significant difference in their normal Raman and SERS activities. In addition to mathematic validation of this solvent internal reference method, we will also discuss the implications of our findings in our understanding of chemical enhancement and single molecule detection.

(443) **Facile Route to the Purification and Separation of High Aspect Ratio Single-Walled Carbon Nanotubes**; Nidh Bhatt[1], Pornnipa Vichchulada[1], Marcus Lay[1]; [1]University of Georgia

This poster presents a new batch processing method for the purification of arc discharge soot, and the concurrent enrichment in unbundled single-walled carbon nanotubes (SWNTs) having average lengths in excess of 2 μm. Since the SWNT growth process results in high percentages of amorphous C impurities and large bundles of SWNTs, such processing methods are essential to the use of SWNTs in a wide variety of electronic, structural, and mechanical materials. In order to determine the effect of centrifugation at low relative centrifugal force on suspension purity, SWNT soot was dispersed in aqueous sodium dodecyl sulfate via probe sonication. Then, several aliquots of each suspension were carefully collected to assess the effect on the purity and/or SWNT length gradients formed under these conditions. Shorter processing periods left longer SWNTs in suspension. However, longer processing times resulted in greater levels of purity. This sedimentation method of centrifugation differs from the density gradient ultracentrifugation in that separation occurs without the addition of reagents designed to change the density of the suspensions. Such agents may also change the electrical properties of the SWNTs, as they are difficult to remove. To achieve greater levels of purity, an iterative method that involved shorter processing times was used to not only removed amorphous C and catalyst nanoparticles, but also isolate surfactant encapsulated, unbundled, high aspect ratio SWNTs in the supernatant. UV-Vis-NIR and Raman spectroscopy were used to verify the simultaneous removal of residual impurities from suspensions of as-produced soot and enrichment in unbundled, undamaged, high aspect ratio SWNTs. The

laminar flow deposition process used to form 2-D networks of SWNTs prevented bundle formation during network growth. Therefore, this deposition method allowed the observation of the purity of suspensions by using atomic force microscopy to examine deposits. Comparison of the change in Raman spectra for suspensions vs deposits indicated that the deposition process further enhanced purity by preferentially depositing high aspect ratio SWNTs over globular impurities. This is due to the inverse relationship between the translational diffusion coefficient and length for suspended nanoparticles resulting in the preferential deposition of high aspect ratio SWNTs over any residual impurities.

(444) **Reduction of Electrical Resistance in Carbon Nanotube Networks through Electrochemical Nanowelding**; Darya Asheghali[1], Pornnipa Vichchulada[1], Marcus Lay[1]; [1]University of Georgia

The ability to form low resistance interfacial electrical contacts between conductive nanomaterials and metal electrodes is a fundamental challenge for the formation of a wide variety of electronic materials. Single-walled carbon nanotubes (SWNTs), in particular have drawn great interest since they are low resistance conductors that are not susceptible to electron migration, like metals. The conductivity of individual SWNTs varies with their diameter. Therefore, 2D networks provide a route to harnessing the enhanced properties of individual SWNTs, while increasing their reproducibility to levels required for manufacturable electronic materials. Depending on the density of SWNTs in the network, they can act as conductors or semiconductors and maintain their electrical properties upon bending. This allows their implementation in systems like flexible displays, lightweight photovoltaics, and sensors. However, due to the non-Ohmic junctions that form between sp2 hybridized C and metals, interfacial resistance is problematic. Additionally, within a network, the inter-SWNT contacts act as high resistance tunnel junctions that degrade electrical conductance. In this work, an electrochemical nanosoldering approach was used to reduce the resistance at metal/SWNT network interfaces and inter-SWNT tunnel junctions by the electrodeposition of metal nanoparticles. SWNT networks were deposited with bidirectional crossbar and unidirectional aligned patterns onto lithographically patterned Ti electrodes. This enabled control over the number of SWNT/SWNT junctions and thus the overall conductivity of the network. The reduction in resistance observed was 51% and 31% for the crossbar and aligned patterns, respectively. This is due to the greater number of junctions in the crossbar pattern allowing greater opportunity for the reduction of resistance. The increased electrical performance of these networks is attributed to the metal nanoparticles' ability to lower the Schottky barrier height between semiconductive and metallic SWNTs in the network. This is due in part to the compatibility between the work functions of SWNTs and Cu. Additional improvement in resistance is derived from the formation of enhanced tunnel junctions at the Ti/SWNT interface. The effect of electrochemical nanowelding on the on/off ratio for field-effect transistors will also be presented.

(445) **Trace Detection of Hazardous Materials with Commercial Surface Enhanced Raman Scattering (SERS) Substrates**; Mikella Farrell[1]; [1]US Army Research Labs

Sensitive, accurate and reliable methods are needed for the detection and identification of hazardous materials (chemical, biological, and energetic) in the field. Utilizing such a sensing capability incorporated into a portable detection system would have wide spread beneficial impact to the U.S. military and first responder communities. Surface enhanced Raman scattering (SERS) is increasingly becoming a reputable technique for the real-time, dynamic detection and identification of hazard materials. SERS is particularly advantageous as it does not suffer from interferences from water, requires little to no sample preparation, is robust and can be used in numerous environments, is relatively insensitive to the wavelength of excitation employed, and produces a narrow-band spectral signature unique to the molecular vibrations of the analyte. We will report on the characterization and sensing capabilities of these next generation SERS substrates for the detection of energetic materials (ammonium nitrate, TNT, PETN, and RDX). Additionally, new efforts producing highly uniform samples, with known concentrations of energetic materials inkjet printed onto the SERS sensing surface using a precisely calibrated MicroJet system will be shown.

(446) **Optimization and Comparison of DC Magnetron and Thermally Evaporated Polyaniline Thin Films for Chemical Sensing Platforms**; Devon Boyne, Nicola Menegazzo[1], Karl Booksh[1]; [1]University of Delaware

Since conducting polymers were discovered in the late 70s their electrochemical and physical properties have attracted much attention. Near metal like conductivity as well as chemical and environmental stability make intrinsically conducting polymers (ICPs) attractive substitutes for several applications. Molecular sensing, gas sensing and microelectronics are just a few of these applications. Polyaniline, when doped in an acidic medium, has been shown to exhibit exceedingly high conductivity, heavily dependent on the chemical structure and dopant type. Difficulties arising from poor processability, loss of structural integrity and poor topography make the deposition of polyaniline into thin films particularly challenging. Recently a method of DC magnetron sputtering has been reported in our lab in an attempt to resolve some of these issues. Though loss of conjugation is evident, the use of this method produces thin films with controllable morphology that have been successfully applied to ammonia gas sensing with SPR detection. In order to optimize these deposition conditions and decrease structural deformation, the use of longer chain lengths, vapor chopped deposition and different dopants is investigated. Comparison of sputter deposited polyaniline with thermal evaporation, a method of producing polyaniline films with similar characteristics is also considered. These methods are evaluated in an effort to improve and explore the use of polyaniline for various chemical sensing platforms.

(447) **Evaluating Plasmonic Substrates by Improved Surface Plasmon Penetration Depth Calculations and Extended vis-NIR Wavelength Range**; Laurel Kegel[1], Nicola Menegazzo[1], Karl Booksh[1]; [1]University of Delaware

The properties of plasmonic nanostructures may be selected to improve surface plasmon resonance (SPR) spectroscopy sensitivity and Raman scattering enhancement. Specifically, SP penetration depth and wavelength may be chosen to maximize SPR spectroscopy sensing capability and facilitate coupling of plasmonic materials for gap mode enhancement. The characterization of plasmonic materials with tunable penetration depth and extension into the near-infrared (NIR) region with a novel variable angle NIR-SPR accessory is demonstrated allowing for vast tailoring of SPR attributes. A more accurate method for evaluating penetration depth is presented utilizing the generally used calculation from SPR response to given adsorbate thickness with an additional factor for SPR response to adsorbate bonding. This effect is amplified for thin layers of adsorbate and materials with small penetration depth such as nanostructures. The presented techniques enable accurate selection of penetration depth and vis-NIR wavelength for optimal sensitivity of SPR and surface enhanced Raman spectroscopies.

(448) **Hookah Smoking - from an Analytical Point of View!**; Joseph Caruso[1], Ryan Saadawi[1], Julio Landero[1], Traci Hanley[1], Matthew Winfough; [1]University of Cincinnati

Many trace metal studies have been performed on cigarette, cigar, and pipe tobacco, while virtually no studies have been performed on

hookah tobacco. It is well documented that other tobaccos are known to contain toxic metals such as As, Cd, Cr, and Pb. [1] However, little is known about the metal content in hookah tobacco. Hookah has been popular in the Middle East and surrounding regions for ages. The first documentation of the hookah was written in a poem by Shirazi in 1535 A.D. [2] The rapidly spreading use of the hookah is emerging world-wide making it imperative to determine trace metal profiles, species and lung cell cytotoxicity. Microwave assisted digestion in combination with ICP-MS was utilized to elucidate the toxic metal content in an array of different brands/flavors of hookah tobacco from Middle-Eastern and American formulations. The process used to burn the tobacco simulated the typical manner in which hookah is consumed. In this presentation we also discuss trace element in the hookah smoke as well as the presence of various toxic organic species and cell signaling changes for a well studied lung cell line.

(1) Bernhard, et al. "Metals in Cigarette Smoke". Life, 57(12): 805 – 809, 2005

(2) Chaouachi K. Tout savoir sur le narguilé. Société, culture, histoire et santé. Paris

(449) **The Long and Winding Road of Laser Ablation Inductively Coupled Plasma Mass Spectrometry**; Detlef Günther[1], Joachim Koch[1], Bodo Hattendorf[1]; [1]ETH Zurich, D-CHAB, Laboratory of Inorganic Chemistry

Simple sample preparation, easy spectra, few interferences and low limits of detection were the early promises of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Instead, drawbacks and limitations were discovered and the technique became famous for being "only qualitative" or "elemental fractionation", keywords still seen today in combination with this technique. The complexity of a wide variety of interactive parameters made it very challenging to unravel individual sources of error, hampering wider application of this direct solid sampling approach. However, progress in both laser technology and ICP-MS instrumentation, together with stepwise understanding of individual processes, allowed LA-ICP-MS to achieve rapidly-growing success in geology, biology, medicine, archeology and materials science. Age, or trace element, determinations in geology would not be as efficient without laser ablation. Provenance studies, forensic applications, and imaging of tissues, bones and other materials, have benefited significantly since bulk ICP-MS was complemented by LA-ICP-MS. This presentation will highlight the contribution of LA-ICP-MS in a selection of key applications, as well as outlining the most recent fundamental studies to determine the quantification limits in terms of precision and accuracy.

(450) **Time and Distance: Exploring New Instrumentation Strategies in Mass Spectrometry**; Steven Ray[1], Elise Dennis[1], Alex Graham[1], Christie Enke[3], Charles Barinaga[2], Anthony Carado[2], David Koppenaal[2], Gary Hieftje[1]; [1]Indiana University, [2]Pacific Northwest National Laboratory, [3]University of New Mexico

This presentation will describe a new set of instrumental strategies that are being developed around distance-of-flight mass spectrometry (DOFMS). The DOFMS concept is best explained by comparison with traditional time-of-flight mass spectrometry (TOFMS). Time-of-flight mass analyzers measure the m/z of an ion by imparting the same energy to all ions and then measuring the time required for each m/z to traverse a known distance and arrive at a single detector. In contrast, DOFMS measures the m/z of an ion by measuring the distance each ion travels during a set time period. More specifically, ions accelerated to a constant momentum separate in space according to their various m/z-dependent velocities, with ions of lower m/z traveling longer distances than ions of greater m/z. At a specific instant after acceleration, all m/z achieve a sharp spatial focus and can then be directed onto the surface of a position-sensitive ion detector where their m/z is determined based upon location. Like TOFMS, DOFMS is architecturally simple, rapid, and has an unlimited m/z range. However, DOFMS is able to employ new solid-state array ion detectors to tremendous advantage, providing greater detection efficiency and dynamic range than typical TOFMS, and obviating the need for fast electronics and timing circuits. As important, the DOFMS strategy permits new experiments to be performed not possible with typical TOFMS. Because TOFMS and DOFMS share a very similar architecture but possess very different strengths and capabilities, we have recently incorporated both strategies into a single physical instrument. Interestingly, we have also found that the different ion-focusing strategies used in both TOFMS and DOFMS can also be retrofit into extant, commercial TOFMS systems to realize new analytical benefits. The theory of operation and experimental performance of these systems using both atomic and molecular ionization sources will be described.

(451) **Pioneering Contributions and Advances in Atomic Mass Spectrometry**; David Koppenaal[1, 2], Charles Barinaga[2], Anthony Carado[1, 2], M Lizabeth Aelxander[1, 2], R Kenneth Marcus[3]; [1]Environmental Molecular Sciences Laboratory (EMSL), [2]Pacific Northwest National Laboratory, [3]Clemson University

This talk will discuss new approaches and directions in atomic mass spectrometry, a field in which the symposium honoree (Gary M. Hieftje) has been a pioneer for nearly 3 decades. Atomic or elemental mass spectrometry has seen a complete renaissance or rebirth during this time, largely due to the development of atmospheric pressure plasma ionization sources and ready incorporation into mass spectrometric analyzers. Work at our laboratories (much of it in conjunction with the GMH Indiana University group) has been directed at improving the performance and utility of plasma source mass spectrometry. In recent years we have developed a new type of array detector for MS (enabling simultaneous mass detection), explored new ultra-high resolution approaches (using orbital trapping techniques, building on our early ion trap MS efforts), and have developed a new type of glow discharge ion source (that is easily and effectively interchangeable with conventional ESI sources, thereby extending the utility of plasma ionization to many other mass spectrometers and applications). Our recent technical endeavors and successes will be described and related to influences and efforts undertaken by the Hieftje/Indiana group. Opportunities for future advances in the next 50 years will also be forecast, in the spirit of the nominee's distinguished career.

(452) **Basic and Applied Research: The two Sides of Spectrochemical Analysis**; Nicolo Omenetto[1]; [1]University of Florida

This lecture will attempt to reiterate the well-know axiom that the creation of new research ideas, analytical methodologies and associated instrumentation in the field of spectrochemical analysis is not possible without improving our understanding of the basic underlying physical principles of the various approaches. In particular, the complex route leading to the analytical signal, and involving the product of several efficiencies like sample introduction, desolvation, vaporization, excitation, ionization and photon detection, needs to be critically and thoroughly investigated. In recent years, classical atomic spectroscopic techniques have been forced to combine with molecular techniques in order to fulfill the challenging task of providing simultaneous elemental and molecular information about the sample. Such challenges in chemical analysis, rather than being detrimental, have triggered the development of new, sensitive methodologies, detectors and detection schemes: all this, in agreement with the above considerations, having being accompanied by the gaining of deeper fundamental insights, better calibration approaches or even ways to avoid them (standard-less analysis). The lecture will focus mainly on the use of lasers in analytical atomic and molecular spectroscopy, with examples taken from the literature as well as from our own research. Laser ablation and Laser Induced

Breakdown Spectroscopy (LIBS) offer most of the pertinent material. In particular, the number of LIBS applications to widely different fields, e.g., biomedicine and geochemistry, necessitates the parallel design of robust instrumentation and user-friendly methodologies. Finally, we stress the fact that, after all these years of activity in the field of micro-sampling of solids by arc, spark and laser ablation, the accuracy has not improved at the same pace as precision, again indicating a lack of complete understanding of the physical processes of sampling, vaporization and excitation.

(453) **Using Multimodal Imaging Techniques to Monitor Limb Ischemia: A Rapid, Non-Invasive Method for Assessing Extremity Wounds**; Rajiv Luthra[1], Nicole J. Crane[1, 2], Jonathan Forsberg[1, 2, 3], Eric A. Elster[1, 2, 4]; [1]Department of Regenerative Medicine, Naval Medical Research Center, Silver Spring, MD, [2]Department of Surgery, Uniformed Services University of Health Sciences, Bethesda, MD, [3]Department of Orthopedics and Rehabilitation, Walter Reed National Military Medical Center, Bethesda, MD, [4]Department of General Surgery, Walter Reed National Military Medical Center, Bethesda, MD

Almost 70% of military casualties resulting from Operation Iraqi Freedom (OIF) and Operation Enduring Freedom (OEF) were recorded as involving major limb injury. Of these, 90% were caused by blast injuries from improvised explosive devices (IEDs). Soldiers face traumatic amputations, open fractures, crush injuries, and acute vascular disruption. Ischemia is a major concern, as lack of blood flow to tissues leads to tissue deoxygenation and necrosis. If left unaddressed, a potentially salvageable limb may require amputation. Often, due to complications, the wound healing process is protracted, involving a series of debridements. During a debridement, surgeons visually inspect tissue and subjectively determine whether it is necrotic and requires removal. To minimize the number of debridements necessary, the need for an accurate and objective method for determining wound healing is evident. In this study, our goal is to integrate two non-invasive, rapid, and low-cost techniques to develop an objective and quantitative model of wound perfusion and tissue viability. Integrating thermal and 3-charge coupled device (3-CCD) imaging techniques allows us to visually and quantitatively identify and track regions of tissue oxygenation and perfusion as they change in real time. To simulate the different types of injuries sustained by soldiers, two methods are used in a swine limb ischemia model: direct occlusion of the iliac vessels and pneumatic tourniqueting of the hind limb. Data collected from this study gives both a surface indication of tissue oxygenation as well as overall limb perfusion. The combined data analysis provides a more complete indication of tissue health. This study aims to not only increase fundamental understanding of the processes involved with limb ischemia and reperfusion, but also develop tools to monitor overall limb perfusion and tissue oxygenation in a clinical setting. A rapid, objective diagnostic for extent of ischemic damage and overall limb viability could provide surgeons with a more accurate indication of optimized timing for wound closure. Reducing the number of surgical interventions required has the obvious benefits of reducing patient distress and decreasing both the overall recovery time and cost of rehabilitation.

(454) **Raman Molecular Imaging in the Digital Pathology Laboratory: Distinguishing Chromophobe Renal Cell Carcinoma from Renal Oncocytoma**; Shona Stewart[1], Ryan Priore[1], Heather Kirschner[1], Maria Tretiakova[2], Pat Treado[1]; [1]ChemImage Corporation, [2]University of Chicago Medical Center

The introduction of digital methods to the field of biomedicine, and in particular pathology, has paved the way for new analytical technologies to make considerable impact on disease diagnoses, treatments and prognoses. As a digital pathology tool, Raman molecular imaging could benefit both clinicians and patients due to its inherently high molecular specificity. Chromophobe renal cell carcinoma and renal oncocytoma are two kidney tumors that frequently possess overlapping histological features, making the differential diagnosis challenging, especially on limited needle biopsy material. There is no reliable alternative method to routine histological examination for differentiating these neoplasms, except for comprehensive genetic analysis. However, a conclusive diagnosis is important, as chromophobe renal cell carcinoma can metastasize, requiring different treatment options to renal oncocytoma, which is benign. We have demonstrated that Raman molecular imaging is able to distinguish renal oncocytoma from chromophobe renal cell carcinoma in an 88 case study of conventional formalin-fixed paraffin-embedded tissues. Statistical models generated from Raman molecular images of histologically definitive renal oncocytoma and chromophobe renal cell carcinoma yielded 86% sensitivity and 81% specificity for both tumors. These initial observations suggest that Raman molecular imaging may be applied not only to the differentiation of these tumors, but also to other pathological applications for which traditional histological studies are not sufficient for a conclusive diagnosis.

(455) **Surface Enhanced Raman Spectroscopy Analysis of the Mycolic Acid Profiles of Clinical Isolates of Mycobacterial Species**; Omar Rivera[1], Russ Karls[1], Frederick Quinn[1], Richard Dluhy[1]; [1]University of Georgia

A rapid and sensitive diagnostic method is a critical component for the identification and detection of tuberculous and non-tuberculous mycobacteria. In particular, new diagnostic methods that are able to evaluate the drug resistance of mycobacterial isolates are necessary, in order to evaluate the efficacy of drug therapy, and to ensure that the most appropriate treatment is prescribed. Mycolic acids represent major envelope components of mycobacteria . Along with other lipids in the cell wall, they form a permeability layer in mycobacteria that contributes to their intrinsic resistance to antibiotics. We have employed Ag nanorod-based surface enhanced Raman scattering (SERS) to detect the mycolic acid profiles found in the bacterial cell envelope of tuberculous (MTB) and non-tuberculous (NTM) mycobaterial species. Spectral differences were observed for the mycolic acids isolated from the NTM and MTB species. Multivariate statistical analysis methods, including principal component analysis (PCA) and hierarchical cluster analysis (HCA), were employed to identify and classify the mycolic acids profiles. We have found that chemometric analysis of the SERS spectra of mycolic acids was able to rapidly differentiate NTM and MTB mycobacterial strains/groups from one another. The work to date suggests that Raman analysis of cell wall components is a fast and accurate method for bacterial discrimination. Future efforts will determine whether this method is applicable to clinical specimens without extensive sample preparation.

(456) **Unexpected Complications: the Effect of Trace Contaminants on Bone Raman Spectra**; Karen Esmonde-White[1], Francis Esmonde-White[2], Michael Morris[2], Blake Roessler[1]; [1]University of Michigan Medical School, [2]University of Michigan

In the course of an on-going clinical study using Raman spectroscopy to identify compositional changes in bone infections, Raman spectra from a bone biopsy specimen (Specimen DOM004) contained unusual bands. These unusual bands were initially interpreted as the bacterial pigment xanthomonadin from the bacteria Stenotrophomonas maltophilia, which was found in the wound culture. However, another bone biopsy specimen (Specimen VA002) from another patient contained these same bands but was contaminated by a tissue marking dye prior to Raman examination. Comparison of spectra from these two samples revealed that our original interpretation was incorrect. The purpose of this study was to obtain Raman spectra of commonly-used tissue marking dyes and

assess whether they are compatible with bone Raman spectroscopy. The clinical study was approved by the Ann Arbor Veterans Affairs (AAVA) and University of Michigan IRB. 13 tissue marking dyes commonly used for pathology were provided by the AAVA pathology laboratory and examined as-is. Approximately 10 µl of the dye was deposited onto a gold-coated glass slide and allowed to dry in ambient conditions. Raman spectra (λ=785 nm) were collected across the surface of the dried drops. Raman spectra of tissue marking dyes contained strong, narrow bands in the region of most interest to tissue Raman spectroscopy, 1000-1700 cm^{-1}. Although there was no visual evidence of pathology dye on the surface of specimen DOM004, Raman spectra contained strong bands from what is now attributed to blue tissue marking dye. We suspect that cross-contamination occurred while the specimen was prepared in the pathology laboratory, but such a small level of cross-contamination would be inconsequential for most standard pathology tests. Our data suggest that even vanishingly small amounts of pathology dye generate a strong Raman signal that may interfere with data interpretation.

(457) **Cell-type Discrimination in Breast Tissue with Raman Imaging**; Matthew Schulmerich[1], Michael Walsh[1], Matthew Kole[1], Krishna Tangella[2], Andre Kajdacsy-Balla[3], Rohit Bhargava[3]; [1]University of Illinois at Urbana-Champaign, [2]Provena Covinent Medical Center, [3]University of Illinois at Chicago

Myoepithelial cells makeup the basal layer of normal mammary epithelial tissue. Their identification has particular diagnostic value as they are lost in malignancy but retained in most benign lesions. Raman images were acquired from regions containing epithelial cells, myoepithelial cells, and stroma on normal tissue and tissue with invasive carcinomas. Serial sections were stained with Hematoxylin and Eosin (H&E) as well as the immunohistochemical (IHC) stain P63 to verify the presence of myoepithelial cells in the regions of interest. Several Raman bands can be used to achieve chemical contrast in distinguishing epithelial cells, myoepithelial cells, and stroma. For example, spectra collected over stromal tissue have larger amide III contribution (1244 cm^{-1} and 1274 cm^{-1} correlated with C-N and N-H vibrational modes) than spectra collected over epithelia or myoepithelial cells. Additionally, the Raman signal at 1045 cm^{-1} (C-C stretch) also has a larger relative contribution in the stroma and myoepithelium than the epithelium. We show that Raman imaging could be used to identify the presence or absence of myoepithelial cells and discuss the prospects of clinical utility.

(458) **Selecting Multivariate Calibration Basis Set Vectors to Optimize Spectroscopic Performance**; John Kalivas[1], Parviz Shahbazikhah[1], Erik Andries[2, 3]; [1]Idaho State University, [2]Central New Mexico Community College, [3]Univeristy of New Mexico

To form a multivariate calibration model, several algorithms can be used. The methods of partial least squares (PLS) and principal component regression (PCR) are projection based. In these approaches, the calibration space is spanned by respective basis vectors (factors, latent vectors, etc., for PLS and principal components (PCs) for PCR, albeit PCs are sometimes used to denote PLS basis vectors as well). Up to rank k basis vectors can be formed to span the complete calibration space including the noise. The magnitude of k is set by the number of calibration samples (m) or the number of measured variables (n), wavelengths for spectral data, with $k \leq \min(m,n)$. Once the k respective basis vectors have been formed, the user needs to decide how many and which ones to form the final model. To avoid the second issue, basis vectors are selected in a top-down manner starting with first one formed and continuing to add another one until model merit criteria are satisfied. An alternative approach is to select a subset from the total available, similar to wavelength selection. Basis set selection is not new and several studies have been performed in the past with PCR and a few with PLS. Presented in this talk are approaches using sparse modeling methods developed for variable selection. Because PCR, PLS, ridge regression (RR), and others can be expressed as linear combination of the singular vectors from the singular value decomposition of the calibration set, the focus is on selecting singular vectors. The algorithms are variations of Tikhonov regularization (TR), as are many sparse modeling methods, and will be referred to as TRb. The approach is applied to several spectroscopic data sets. Weights applied to the basis vectors for TRb, PCR, PLS, and RR are compared.

(459) **Search Prefilters for Spectral Library Matching**; Barry Lavine[1], Ayuba Fasasi[1], Jerome Workman[2]; [1]Oklahoma State University, [2]Unity Scientific LLC

Pattern recognition methods have been used to develop search prefilters for infrared (IR) library searching. A two step procedure was employed to develop the search prefilters. First, the wavelet packet tree was used to decompose each spectrum into wavelet coefficients that represent both the high and low frequency components of the signal. Second, a genetic algorithm for pattern recognition analysis was used to identify wavelet coefficients characteristic of the functional group. Even in challenging trials involving carboxylic acids, compounds that possessed both carbonyl and hydroxyl functionalities could be readily differentiated from carboxylic acids. The proposed search prefilters which are rotted on structural information increase the selectivity of the search as the size of the library is culled down for a specific match diminishing the likelihood of obtaining a match due to chance while permitting the use of more sophisticated and correspondingly more time-consuming algorithms for IR spectral library matching.

(460) **Fast Chemical Classification, Quantitation, and Imaging using Digital Compressive Detection**; Dor Ben-Amotz[1], David S Wilcox[1], Brad Lucier[1], Greg Buzzard[1], Nathan Gardner[1]; [1]Purdue University

A key bottleneck to high-speed chemical imaging and monitoring of dynamic chemical processes is the time required to collect and analyze hyperspectral data. Here we demonstrate, both theoretically and experimentally, a means of greatly speeding up the collection of such data using a new digital compressive detection strategy. Our preliminary theoretical and experimental results demonstrate photon level chemical identification, as we show that fewer than 100 Raman scattered photons can be sufficient to positively identify and locate chemical species as well as quantify the compositions of liquid or solid mixtures..

(461) **Adaptive Regression by Subspace Elimination: Refined Algorithm, Various Applications**; Karl Booksh[1], Bryon Herbert[1]; [1]University of Delaware

In many cases Adaptive Regression by Subspace Elimination (ARSE) enables accurate prediction in the presence of uncalibrated interferents with multivariate data. Wavelet transformations are exploited to generate multiple pseudo-variables, each describing a facet of information contained within the spectra. An improved algorithm has been developed to identify which variables in 'wavelet space' are contaminated by uncalibrated interferents. These variables are removed and the calibration model is rebuilt with the remaining variables. Thus the regression model adapts to the presence of the interferent and the contaminated subspace is eliminated. A more accurate prediction is realized at the expense of increased variance. ARSE is applied to quantitative determination of hydrocarbon mixtures with IR spectroscopy and classification of cooking oils with Raman spectroscopy.

(462) **Pitfalls and Practical Issues in Chemometric Applications**; Susan Rose-Pehrsson[1], Kevin Johnson[1], Robert Morris[1], Jeffrey Cramer[1], Christian Minor[2]; [1]Naval Research Laboratory, [2]NOVA Research Inc.

Chemometrics has become an essential part of most analytical methods, elucidating critical information in very complex spectra. However, any application of chemometric methods has pitfalls and practical issues that must be considered to achieve the full potential of the methods. At the Naval Research Laboratory, we have used chemometrics in many detection problems that are important to the Navy. This presentation will use our work as illustrative examples of the pitfall and practical issues that may arise. In one example, the development of the Navy Fuel Property Monitor (NFPM) will be discussed. The NFPM uses near infrared analysis with quantitative chemometric modeling to determine the suitability of fuels for shipboard use. In another example, multisensor data fusion is being investigated to improve the detection of chemicals. Data fusion metrics and performance descriptors are being assessed by examining test scenarios combining multivariate analytical techniques such as mass spectrometry and infrared spectroscopy for a large database of chemicals, as well as through simulation of univariate sensor array responses. This work is aimed at guiding the development of future multisensor systems for specific applications and towards rationalizing fused multisensor system capabilities within the framework of current chemometric multivariate figures of merit. For example, as normally implemented, an array of univariate sensors is essentially a first-order instrument, like an FTIR or and GC-FID. This implies that sensor arrays are limited to calibration against the presence of known interferents. Potential approaches towards overcoming this limitation and constructing sensor arrays that provide the second-order advantage will be discussed.

(463) **Single Molecule Tracking Studies of Flow-Aligned Mesoporous Silica Monoliths: Aging-Time Dependence of Pore Order**; Seok Chan Park[1], Takashi Ito[1], Daniel Higgins[1]; [1]Department of Chemistry, Kansas State University

Single molecule diffusion in surfactant-templated mesoporous silica monoliths prepared within glass microfluidic channels was probed by total internal reflection fluorescence microscopy, and in-plane mesopore alignment and order in the flow-aligned silica monoliths have been characterized. A fluorescent perylene diimide dye (OPDI) was employed as the probe molecule. Wide-field fluorescence videos depicting dye motions at the single-molecule/single-pore level revealed the majority of dye molecules in these samples exhibit one-dimensional (1D) diffusive motions parallel to the flow direction. Orthogonal regression analysis of these motions provides a measure of the mesopore orientation distribution function, which is in turn used to quantify mesopore order via a 2D orientational order parameter, . Mesoporous silica sols were aged for a period of 0 to 20 hours prior to loading into the microfluidic channels and mesopore organization was explored as a function of aging time between sol preparation and filling of the microfluidic channels. Channels filled prior to gelation of the sol are shown to incorporate large monodomains having average pore alignment within a few degrees of the flow direction. These monodomains extend over several millimeters and yield aging-time-independent values larger than ~ 0.80. In contrast, channels filled close to or after gelation of the sol yield monoliths with misaligned pores that are also more disordered, having ~ 0.35. SMT results are compared to those from small angle X-ray scattering (SAXS) anisotropy experiments to confirm materials alignment and order. The SAXS and SMT results are consistent across the range of samples investigated. A simple model describing the aging-time dependence of sol organization has been developed. These studies demonstrate that well-aligned mesoporous silica monoliths can be obtained by simple flow alignment procedures, but that short sol aging times are required to achieve optimum pore organization.

(464) **Investigation of the Mobile Phase-Stationary Phase Interface with Vibrationally Resonant Sum-Frequency Generation: Challenges and Successes**; James Patterson[1]; [1]Brigham Young University

At its roots, chromatographic retention is an interfacial phenomenon. Changes in operational parameters, such as mobile phase composition, pH, ionic strength, etc. likely cause changes in the structure of the mobile phase-stationary phase interface that affect analyte retention. Vibrationally resonant sum-frequency generation (VR-SFG) spectroscopy is a nonlinear optical technique that is particularly sensitive to the molecular structure of surfaces and interfaces. An improved understanding of the links between the structure of the chromatographic interface and retention would enable better prediction of optimal separation routines. However, certain aspects of VR-SFG complicate this type of study. The most significant factor is the nonresonant contribution to the measured VR-SFG spectrum. Nonresonant signal invariably distorts the resonant features of the spectrum, possibly leading to an incorrect determination of frequencies, amplitudes, and even the number of peaks in the spectrum. In fact, the magnitude of the nonresonant response can change in response to the experimental conditions and these changes can affect the resonant signal in such a way as to suggest a structural change at the interface. Only when the nonresonant response is properly accounted for is it possible to determine how the stationary phase-mobile phase interface is affected by operational parameters.

(465) **Characterization of Microparticles Utilizing Optical Chromatographic Methods**; Soo Kim[1], Joseph Taylor[1,2], Alex Terray[1,2], Sean Hart[2]; [1]National Research Council postdoctoral fellow, [2]Naval Research Laboratory

The sensitivity of optical chromatography is demonstrated through analysis of similar microparticles to categorize them based upon subtle differences of intrinsic properties. Mildly focusing a laser beam into a microfluidic channel of opposing fluid flow creates a counterbalance of fluid drag force and optical pressure that results in a stable trapping of particles in the beam. The magnitude of the optical force exhibited from the laser depends heavily on the size, composition and/or refractive index of the particle. Previous researchers have demonstrated partial optical separation of a fraction of particles based on size as well as size-independent separation of polymeric particles based on slight variations in the bulk refractive index. Current studies extend the application towards the effects of a minor shift in the refractive index of a particle due to a coating of another material on the surface. The suitability of optical chromatography for investigation of biofunctionalized or surface-coated microparticles presents an ideal platform to interrogate anticipated surface related paradigms, as changes in refractive index between various polymeric microbead coatings have been attributed to the relatively large differences in optical force. The potential benefits of specifically characterizing particles with small, although significant, variations may aid in providing a straightforward avenue to study more elaborate systems, such as biological pathogens on cells.

(466) **Molecular Diffusion in Nanopores Studied with Super Resolution Optical Microscopy**; Gufeng Wang[1], Bhanu Neupane[1], Fang Chen[1]; [1]North Carolina State University

Fluorescence correlation spectroscopy (FCS) contributed greatly to the understanding of molecular diffusion and transportation. The probe volume of FCS in conventional fluorescence microscopy, however, is limited by diffraction and may cover an ensemble of heterogeneous environments. This limits its usefulness in complex systems like nano- to mesoporous materials and biological cell

samples. To reduce probe volume, stimulated emission depletion (STED) microscopy is implemented and a lateral resolution of ~75 nm is achieved. We demonstrate the 3D mapping of nanopore profiles in alumina membranes (anodiscs). Measurement of single molecule and single nanoparticles diffusion reveals anomalous diffusion coefficient in the nanopores. Such study will provide important insight into the microenvironment in nanoporous materials.

(467) **Probing Chemical Interactions and Transport Kinetics within Single Chromatographic Silica Particles**; Joel Harris[1], Justin Cooper[1], Jay Kitt[1], Jennifer Ramirez[1]; [1]University of Utah

The understanding of chromatographic retention mechanisms can be facilitated by spectroscopic studies to examine the interfacial interactions that are responsible for solute selectivity and separation efficiency. Most spectroscopic investigations of chromatographic retention phenomena have relied on model systems that are compatible with spectroscopic probing; typically these are planar structures where the solid-liquid interface is accessible with reflection or internal reflection excitation. Unfortunately, the organization of C18 or other ligands bound to planar surfaces may differ significantly from their structure within highly curved surfaces within nanoporous chromatographic particles. In addition, the pore structure of silica gel stationary phase supports contributes to the dynamics of molecular transport into and out of the particles, the dynamics of which cannot be duplicated in a planar model system. In this talk, two spectroscopic microscopy methods will be used to probe the chemical interior of individual, C18-modified chromatographic silica particles. Confocal Raman microscopy is used to investigate the mechanism of ion-pair interactions that contribute to the retention of ionic solutes on C18 stationary phases. The benefit of using this method is that it can report the absolute surface coverages of ion-pairing amphiphiles and ionic solutes versus their solution concentrations, yielding unique insight into the mechanism of ion-pair retention. Probing a single particle allows the absolute surface coverage of hydrophobic solutes such as PAH compounds to be easily determined at retention levels that cannot be assessed by chromatographic measurements because the source-phase volume, needed to supply the needed solute to reach equilibrium, is too great. The dynamics of molecular transport within a chromatographic particle can be probed by single-molecule fluorescence imaging. The characteristic residence times of molecules can be measured, and their diffusion rates within the porous network of the particle can be observed and quantified, providing insight into molecular transport contributions to chromatographic band broadening.

(468) **The Impact of Microspectroscopy on Forensic Investigations**; John Reffner[1]; [1]John Jay College, CUNY

Applying the scientific method and advanced technologies to analyze evidence in legal matters is the foundation of forensic science. Because of advances in infrared, Raman, ultraviolet and visible light micro-spectroscopy, molecular spectroscopy now plays a major role in forensic investigations. When microscopes became available accessories to Fourier transform spectrometer benches, the forensic community quickly recognized their advantages for microanalysis of trace evidence. In 1986, California equipped each of their 12 regional state forensic laboratories with FT-IR microscopes. Today, every major crime lab around the world has infrared microspectroscopy instrumentation. When the internal reflection objective was introduced in 1989, it was quickly put to work analyzing evidence. An advantage internal reflection is its ability to produce ATR spectra from the surface of thick samples. Paint transferred onto paint in a hit-run case could be analyzed directly without removing the transferred paint. More recently, diamond ATR objectives became available for analyzing glass and minerals which would damage earlier internal reflection elements. Using diamond extended the range of samples the forensic scientist could analyze by ATR. The acceptance of molecular spectroscopy by forensic scientists increased with the availability of spectral data bases. Spectra of unknowns can be compared with standard reference materials in spectral libraries. This is of special interest in the analysis of powders related to homeland security issues. Field portable infrared or Raman spectrometers are used by first responders to identify "white powders". These units contain spectral libraries of hazardous chemical agents and are used for on-site, real-time analysis. The library searching software quickly suggests leads to assist the analyst in the identification of an unknown and its potential hazard. The advances in spectrometer design, solid-state lasers, low noise /high sensitive detectors, and improved notch filters have led to the development of new Raman spectrometers and micro-probes. These systems are being used in numerous forensic laboratories and show much promise for forensic applications. The future for molecular spectroscopy in forensic investigations is very exciting. Molecular spectroscopy provides rapid, reliable and reviewable record to aid the court in their decisions.

(469) **Investigating Product Complaints and Contaminations by Spectroscopy**; Ming Zhou[1]; [1]MVA Scientific Consultants

Product contaminations, complaints and failures are major issues that many manufacture factories face every day. Manufacturers often have to recall their products or pay a large sum of money to consumers to settle any contamination, complaint and failure issues. To solve the issues, manufacturers have to first identify what the contamination is or what caused the products to fail. Mid infrared spectroscopy is a robust technique for identifying the common organic and inorganic compounds. Scanning electron microscopy coupled with x-ray analysis can give elemental information that would help in the identification of inorganic and in the interpretation of IR spectra. In this presentation, I will share four different case studies to illustrate the effectiveness of FTIR and SEM in helping companies identify their problems and give leads for them to address their issues. The first case involves the suspected failure of an endotracheal tube during patient use. The second case describes the identification a brown stain on a consumer product. The third case illustrates determining the source of contamination in a drug solution. The last case shows the identification of corrosion materials on an alcohol interlocking device used in automobiles.

(470) **Advances in Microanalytical Characterization of Forensic Paint Samples: Addressing New Developments in Paint Technology**; Jennifer Herb[1], Christopher Palenik; [1]Microtrace LLC

As automotive paint formulations undergo constant evolution, so must the characterization techniques used by the forensic community. In recent years, a variety of new technologies have been pushing the analytical limits of commonly applied methods. For example, layer thicknesses have continually decreased and are commonly measured at less than 10 micrometers in many samples, paint and pigment chemistries are constantly changing, and new application methods such as tinted clear coats and wet-on-wet layers are requiring new approaches to the analytical evaluation of forensic paint evidence. Here we present the implications arising from our characterization of over three hundred automotive paint samples from various colors, makes, models, and years. While the techniques of cross section characterization have been known and taught for many years, they are still rarely or only crudely applied in many forensic laboratories examining paint evidence. The surprising complexity and significance of examining and describing layer thickness will be illustrated through numerous examples. While FTIR analysis is commonly applied to paint samples, the characterization of colorants, one of the most variable components of paint, is almost entirely ignored in forensic casework. Through the results of over 5 years of research, our laboratory has developed a pigment identification scheme based on over 300 organic and inorganic pigments. The

application of this scheme to the identification of colorants in paints and the impact of this analysis on the forensic approach will be addressed.

(471) **Advances in Handheld Spectrometers and their Applications**; Michael Hargreaves, Lin Zhang, Wayne Jalenak, Robert Green, Craig Gardner[1]; [1]Thermo Scientific Portable Analytical Instruments

Advances in handheld instrumentation are providing significant additional capabilities for unknown chemical identification in the field. Rather than removing a sample from the hazard zone, whether from a specific area/location or container, responders may now rely on handheld instruments for rapid identification directly in the hot-zone, saving time and increasing responder safety. The rapid, non-destructive identification of chemicals, including items of interest to the military and law enforcement by, rugged, portable Raman and FTIR spectroscopy is discussed. The techniques have been widely deployed and are now used frequently by the military, homeland security personnel, police and forensic personnel, mostly due to the high chemical specificity which allows robust identification of bulk contraband materials. The presentation will discuss the application of the latest generation handheld Raman device, for the application of narcotics identification/screening in field. Several examples will be discussed highlighting the power of Raman spectroscopy, over the more conventional colorimetric field narcotic tests.

(472) **COTS Technology and the Future of Chemical Analysis**; Alexander Scheeline[1]; [1]University of Illinois at Urbana-Champaign

A toy spectrophotometer, designed to have poor resolution, high stray light, and mechanical instability specifically to make it easy for students to understand the engineering considerations that go into optical design, led to an approach to optical spectrometry that shows promise for development of small, inexpensive spectrophotometers at least good enough for classroom use and perhaps for use by the general population. The story of the device's invention, the pedagogical successes it has already catalyzed, and progress towards developing an instrument that may be marketable, make for an enjoyable story and perhaps the specter of enlightenment. The talk is a condensed version of a presentation used on the SAS Tour Speaker circuit in spring, 2012.

(473) **Screening "The Good, The Bad and The Ugly" Pharmaceutical Counterfeits Using Raman and NIR Spectroscopy**; Ravi Kalyanaraman[1]; [1]Bristol-Myers Squibb

Pharmaceutical counterfeiting has become a major issue in the recent decade in developing countries. It has also placed a significant pressure on the assurance of supply chain integrity in developed countries due to increasing international trade due to globalization and sales via the internet. The recent incident of counterfeit Avastin in the United States shows the vulnerability of the supply chain even in developed countries. Pharmaceutical industry and federal agencies are finding ways globally to counteract the increasing threats caused by pharmaceutical counterfeiting. Recent estimates are that perhaps 15% of pharmaceutical drugs world-wide are counterfeited. Several technologies are currently available to detect counterfeit drugs rapidly and efficiently. These include covert and overt features added to the packaging material and to the drug product itself, and authenticating the suspect drug for these features. Also, Infrared (mid and NIR) and Raman spectral techniques, which are complimentary in nature, have been used widely to detect counterfeit drugs. Both techniques are rapid, nonintrusive and nondestructive that can be used for the analysis of many classes of pharmaceutical dosage forms. The nonintrusive nature of both techniques makes it feasible to analyze a drug product directly through the packaging, such as bottles or blisters, and through capsule shells for encapsulated products. Portable versions of Infrared (mid and NIR) and Raman spectrometers have paved the way to take the 'lab' closer to where the counterfeit activities are taking place, such as deceitful manufacturing facilities and pharmacies. An effective analytical technique that can be applied in the field is by developing unique spectral signatures for the drug product using these portable spectrometers and to test the suspect product against these signatures in order to spot counterfeits and also to authenticate legitimate products. This talk will feature the various portable and bench-top spectral analytical techniques (Raman, NIR and mid-IR) that are currently being used to detect pharmaceutical counterfeits which include both, small and big (biologics) molecular entity.

(474) **Deep UV Resonance Raman Spectroscopy of Formulated Proteins**; Sergey Arzhantsev[1]; [1]US Food and Drug Administration

With an increasing number of therapeutic proteins and biosimilars expected to reach the pharmaceutical market, it is important to develop orthogonal analytical methods for the assessment of safety and quality of protein drug products. Deep UV resonance Raman (DUVRR) spectroscopy has the potential to be a good alternative technique to UV and vibrational circular dichroism for determination of secondary structure. The resonance excitation provides increase in Raman signal, specifically enhancing intensity of peptide vibration bands, and completely removes fluorescence background. DUVRR spectroscopy does not usually require any sample preparation and is as sensitive as circular dichroism. The analysis of formulated protein products involves a mathenmatical algorithm for mixture decomposition. This presentation will evaluate the use of DUVRR spectroscopy as a rapid analytical method for the quality assessment of therapeutic proteins.

(475) **Raman Identification through the Pharmaceutical Supply Chain**; Jeffry Denault[1]; [1]Jeffry W Denault

The use of Raman spectroscopy for identification of pharmaceutical materials, e.g., raw materials, starting materials, and drug product, has become more prevalent with the commercialization of portable/handheld analyzers. The deployment of this technology provides unique implementation opportunities with respect to streamlining identification testing. This talk will address the opportunities and challenges encountered when implementing a handheld Raman device for testing across the pharmaceutical supply chain.

(476) **Particle Identification and Material Analysis in the Biopharmaceutical Industry with Raman Microspectroscopic Technique**; Xiaolin Cao[1]; [1]Amgen Inc

Particle identification and material characterization are critical elements to ensure the successful delivery of protein therapeutics during process and product development, manufacturing, and supply chains management. Raman microscopy is a proven microspectroscopic technique that has unique advantages in solving challenging problems encountered in the particle identification and material characterization (1-4). Contrast to other microspectroscopic techniques, Raman microscopy has the unique capability to perform in situ and noninvasive detection that are required in a variety of biomanufacturing processes. These include, but not limited to, the preparation of raw materials, cell culture and fermentation, protein separation and purification, preparation of proteins in buffer or the formulated solutions, and fill and finish. Here we present several case studies to demonstrate the advancement of Raman microscopic applications in the biomanufacturing industry. These applications include (i) the identification of oil-like microparticles in the formulated solutions and inside pre-filled containers, (ii) the confirmation of small glass chips observed during sample stability studies, and (iii) the unexpected precipitates during the preparation of cell culture media.

Keywords: Raman Microscopy; Biopharmaceutical Manufacturing; Microspectroscopy; Material Characterization; Particle Identification

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(477) **A Comparative Study of In-Line Measurements for the Real-Time Determination of Particle Size during Organic Bead Milling**; Peter Hamilton[1, 2], Ha Pham-Vu[1], Thomas Bentley[1], Darryl Ertl[1], David Littlejohn[2]; [1]GlaxoSmithKline, Research Triangle Park, Durham, NC, USA, [2]CPACT/ WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK

In recent years, the pharmaceutical industry has been forced to adapt to increasing pressure to become more efficient in its practices. This includes striving to become more energy efficient and environmentally friendly, as well as implementing initiatives such as Quality-by-Design which are encouraged by regulatory authorities. As a result, scientists are being challenged to find new and innovative ways to improve the pathways for drug manufacturing and delivery to patients. One such method that many companies are exploring is the development of API nanoparticles to enable more effective medicines. Particle size reduction caused by media milling has been identified as a possible approach to achieve drug material in the desired size ranges. Current understanding of the critical quality parameters of the process indicate that proper control of the particle size and distribution are desired in order to prevent over milling of the particles where they may re-agglomerate or become unstable in suspension. Thus, the ability to monitor particle size reduction in situ allows the end-point to be identified in real-time without the requirement of off-line testing. Furthermore, it also facilitates the development of closed loop feed-back control as greater understanding of the critical factors such the generation of amorphous material is established. In this study, in-line NIR and turbidity measurements were recorded during the completion of a design of experiments study that was performed to enhance process understanding during the operation. The position of the probes in the recirculation loop of the mill was considered first, before factors such as flow rate, rpm of the agitator, grinding media size and concentration of the slurry were evaluated to determine their effect on outputs such as particle size, amorphous content, suspension quality and viscosity. In doing so, a comprehensive evaluation of the spectral data could be performed so that correlations with the respective outputs could be established. Regression models developed at the small scale were then tested at pilot plant scale. Lastly, the relative advantages of implementation at the full manufacturing scale were compared with respect to both of the in-line techniques assessed.

(478) **Extracting Data from a Dirty Bioprocess!**; David Lovett[1]; [1]Perceptive Engineering

Traditionally, the objective of anaerobic digestion (AD) in wastewater treatment (WWT) has been that of sludge stabilisation and odour reduction. Biogas production, solids destruction and pathogen reduction are now key focus areas for the process. Additionally, digestate quality is inevitably becoming more important as the industry changes from disposal-based solutions to the exploitation of digestate as a valuable end-product. Research has revealed a strong necessity for increased robust instrumentation on, and better control of, AD processes. Lack of instrumentation is the main bottleneck in the process, as sensors and analysers are necessary to reduce uncertainty related to the initial conditions, kinetics and in the input concentrations of the process. Volatile Solids provide an indication of the stability of the digestate and of the process. Online instrumentation for VS is not available and, although offline analysis can be conducted, this often has low and irregular rates of sampling. VS may provide a better indication of the sludge quality (biochemistry) than other measurements such as %DS (Dry Solids). Measurement test procedures for VS are also simpler than those conducted offline for Volatile Fatty Acids. For these reasons, VS is an important digestate quality attribute and the use of online monitoring and control of VS will result in a better quality digestate. The work discussed in this presentation involves the analysis and hybrid modelling using six months of online and laboratory process data from an industrial wastewater AD plant, augmented by simulated data from a recognised first principle model. In order to develop a robust soft sensor model of the VS process variable, the use of data cleaning, pre-processing and multivariate correlation techniques have been explored.

(479) **Hierarchical Models: Adding Logic to Data-Driven Results**; Katherine Bakeev[1], Frank Westad[2]; [1]CAMO Software Inc, [2]CAMO Software AS

Hierarchical Modeling (HM) is the joining of a number of multivariate models using logic statements in order to arrive at a single, unique result. In some applications the application of a single global model may not be sufficient to fully or precisely describe a system. A user could manually set standard operating procedures in place such that based on the result of one model, another model is specified and applied based on this result. But for process control, real-time analysis of data as it is generated is required, without any user intervention. The hierarchical modeling tool combines projection, classification and prediction and multiple conditions may be set based on any sample-related model output such as class membership, residuals, Hotelling's T2 statistics and predicted values. Hierarchical modeling provides a means of automatically using the outcome of one model to choose the next model to allow one to drive down to a model and result that is specific to a given condition or sample.

(480) **Characterisation of Pigment/Polymer Processing Using *in-situ* Molecular Spectroscopy**; Alison Nordon[1], David Wilsdon[1], Suresh Thennadil[1], Jill Johnston[2], Rupert McIntyre[2], Ewan Polwart[2]; [1]University of Strathclyde, [2]FujiFILM Imaging Colorants Ltd

A number of physical factors determine the properties of polymer-stabilised pigment dispersions such as the concentration, size and size distribution of the pigment particles, and the distribution of the stabilising polymer. Therefore, it is important to be able to measure such properties during the development of new pigment-based ink products. Existing approaches to analysis of the dispersions involve time consuming and often difficult off-line centralised laboratory testing. Moreover, they often require manipulation before analysis such that they no longer exhibit the same properties as the original process sample taken. Therefore, the aim of this project is to assess the use of optical spectroscopy for in-situ characterisation of mixed polymer/pigment dispersions during product development and manufacturing. Focussing on near infrared (NIR) measurments, the fundamental optical properties of pigment dispersions were investigated. The methodology for extracting the bulk optical parameters consisted of measuring the diffuse reflectance and transmittance spectra of the samples using a CARY 5000 spectrophotometer fitted with an integrating sphere accessory and

inverting these measurements by solving the radiative transfer theory using the adding-doubling method. The change in the absorption and scattering coefficients was then used to rationalise NIR spectra collected from lab scale experimentation and plant scale production. It was possible to correlate changes from the in-situ near infrared measurements with off-line particle size data collected using dynamic light scattering (DLS). The benefits of using NIR measurments for real-time process monitoring and control in plant scale manufacturing will be discussed, along with some of the challenges of implemetation.

(481) **Some Recent Applications of Calibration Transfer for Handheld Near-infrared (NIR) Spectrometer**; Lin Zhang[1], Suzanne Schreyer[1], Dan Klevisha[1]; [1]Thermo Fisher Scientific

Recent advance in semi-conductor industry (e.g., Micro Electro-Mechanical Systems, MEMS) has enabled the commercial availability of handheld NIR spectrometers. Comparing with their desktop peers, these handheld NIR newcomers provide additional benefits such as the capability of bringing test to the point of need, lower cost, fast measurement etc. There is a growing trend of handheld NIR applications due to these benefits. NIR models are often built upon large database. It will be time-consuming and resource-demanding to build the database on handheld unit again. This study will illustrate various methods which could be used to transfer existing quantitative or qualitative methods into a handheld ThermoFisher Scientific microPHAZIR™ spectrometer for different applications. Examples will be given from food and agricultural applications as well as pharmaceutical applications.

(482) **Challenges to Fulfill on the Deployment of Handheld Raman For a More Comprehensive Raw Materials Identification.**; Travis Thompson[1], Enrique Lozano Diz[1]; [1]B&W Tek

The deployment in recent years of handheld and portable Raman across the pharmaceutical industry, and more recently across other chemical industries, has promoted an impressive improvement on the analytical capabilities of the identification and control of materials. This has helped to create a higher quality assurance of the traceability of the product and a more comprehensive, faster, and economically-viable analysis for raw materials verification. Nevertheless, the notable speed of implementation of portable Raman instrumentation and its success has not been without debate, especially across the community of users in some demanding areas like polymorphic identification and source traceability. We will describe here the challenges that the recent deployment of handheld and portable Raman analyzers have met in the field of raw materials identification and how the latest development on the technology is addressing those deficiencies. The combination of field case studies with technical data will provide a broad picture of what this technology can – realistically – offer in the areas of raw material identification and trends for future developments.

(483) **Computer Modeling of the Raman Optical Activity**; Petr Bour[1]; [1]Academy of Sciences

From the experimental Raman optical activity information about molecular structure and conformation can be deciphered with the aid of computer simulations. For example, previous comparison of the theoretical spectra with experiment provided conformer ratios comparable(1) or superior(2,3) to those obtained by NMR. To facilitate such modeling for larger, flexible, or strongly hydrated systems, such as peptides, we explored the potential of implicit and explicit solvent models,(4) and other computational tools (5,6,7).

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(484) **Raman Optical Activity in Deep UV Spectral Region**; Josef Kapitan[1, 2], Laurence D. Barron[2], Lutz Hecht[2]; [1]Department of Optics, Palacky University in Olomouc, [2]School of Chemistry, University of Glasgow

Raman optical activity (ROA) has proved to be very sensitive probe into biomolecular structure and it often provides information not available by other analytical techniques [1,2]. Until now, it has been used in visible or near infrared spectral region [3]. We have experimentally realized ROA spectrometer in deep ultraviolet (DUV) spectral region for the first time, with excitation wavelength 244 nm. Motivation for undertaking such work was large: fourth power of frequency dependence of Raman and fifth power of frequency dependence of ROA scattering intensity for the same incident power, absence of fluorescence background and further intensity advantage of near resonance Raman scattering represented together attractive promise for significant extension of capabilities of ROA technique. The novel UV ROA instrument is based on backscattering geometry and incident circularity polarization (ICP) modulation scheme that proved to be very successful in spectrometers operating in visible spectral region [4]. The UV ROA spectrometer is equipped with specially designed UV grade polarization optics and fast DUV imaging lens-based spectrograph [5]. Performance of the spectrometer was tested by comparison of UV ROA spectra of both enantiomers of nonabsorbing samples (menthol, borneol and glucose) with spectra recorded in visible spectral region. Finally, spectra of both enantiomers of model peptides with different number of peptide groups were measured and analyzed. Experimental results represent very good benchmark for resonance and near resonance ROA theory [6].

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(485) **Expanding ROA Beyond Structural Biology: Studying Non-Local Chirality and Resonance Effects**; Christian Johannessen; [1]University of Manchester

As the 40th anniversary of the first reproducible experimental study of Raman optical activity (ROA) draws near [1,2], the method has developed from its humble origins into a powerful tool for solution-phase structural analysis, especially of biological molecules. While ROA is a proven tool in the detailed structural analysis of biomacromolecules, little attention has been given to non-biological or inorganic compounds over the last forty years, in part due to the difficulties encountered when studying these compounds, such as low solubility, fluorescence impurities and molecular resonance effects from the samples. Combining modern ROA spectrometry techniques with state-of-the-art computational approaches, it is now possible to

employ ROA in the studies of compounds previously deemed "too difficult" to analyse. Here, we will present results on studies of compounds exhibiting non-local chirality, ranging from small metallo-complexes to helically chiral polymers, as well as studies of compounds showing molecular resonances at the chosen excitation wavelength. These studies highlight how ROA can be employed as a chiral detector in a host of non-biological cases, achieving remarkably strong and clear conformational distinguishing of enantiomeric pairs, hence showcasing how ROA is applicable in a range of research fields, including (bio)inorganic chemistry and polymer science, as well as in the pharmaceutical industry.

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(486) **Structures of Native Insulin and its Amyloid Fibril Explored by Raman Optical Activity**; Shigeki Yamamoto[1]; [1]School of Science and Technology, Kwansei Gakuin University

To clarify the detailed molecular structures of proteins in solutions is crucial to the understanding of their functions and properties. Especially the mechanisms of the denaturing of proteins are currently subjects to explore, relating to the diseases which occur with the denatured proteins. Raman optical activity (ROA) spectroscopy can be a sensitive analytical tool of the protein structures, especially for the flexible, denatured, or unfolded ones which are still difficult to analyze by the other measurement techniques. The secondary-structural changes of the amyloid fibril form of insulin and its re-naturing intermediates were explored based on the experimental ROA spectra with the empirical assignments of the ROA bands.[1,2] Alternatively, the quantum mechanical calculations of ROA with the aid of the Cartesian-coordinate tensor transfer (CCT)[3,4] method were successfully applied for the native insulin in order to verify the assignments of the ROA bands and to know the details of the signal generation of ROA.[5] The results confirmed a high sensitivity of ROA to the protein conformation.

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(487) **Vibrational Optical Activity of Cysteine in Aqueous Solution: A Comparison of Theoretical and Experimental Spectra**; Maciej Kaminski[1], Magdalena Pecul[1], Andrzej Kudelski[1]; [1]University of Warsaw, Chemistry Department

Raman optical activity (ROA) and vibrational circular dichroism (VCD) are chiral counterparts of Raman and infra red (IR) spectroscopies. ROA is inelastic scattering of left and right circularly polarized light by a chiral sample, while VCD is differential absorption of left and right circularly polarized IR radiation. Both ROA and VCD are very sensitive probes of molecular structure, providing information not only on the absolute configuration of a molecule, but also about its conformational space, dynamics and interactions with the environment. However, the very sensitivity of VCD and ROA spectra to conformational changes and influence of the environment which makes them good indicators of molecular structure causes quantum chemical calculations of them to be a challenging task, especially in the case of flexible molecules with polar group in an aqueous environment. The main purpose of the research carried out in our group has been to check how different hydration models perform for the ROA and the VCD spectra of cysteine - an amino acid which has particularly interesting vibrational spectrum because of the presence of the thiol group. Raman, ROA, IR, and VCD spectra of cysteine in aqueous solutions of different pH have been measured and calculated by means of density functional theory, with the influence of aqueous environment on the spectra simulated by means of implicit (polarizable continuum model) and explicit (molecular dynamics, solute–solvent clusters) methods. The results indicate that, while PCM reproduces some of the features of the spectra, the best description is rendered by the microsolvation model (solute–solvent clusters). The shape of the bands is in some cases more correctly reproduced by MD, but their intensities and positions are not, since these simulations are hampered by the standard force field being parametrized for conformations of peptides rather than isolated amino acids. The calculated ROA spectra have been used to extract conformational ratios from the experimental spectra, and again, the best results (as verified by simulations of other spectra) have been obtained when using the microsolvation model.

(488) **Detecting Cancer Markers using Metallic Nanostructures**; Alexandre Brolo[1], Ting Yu[1], Chiara Valsecchi[1], Koh Yiin Hong[1]; [1]University of Victoria, Department of Chemistry

Nanostructured gold support surface plasmon excitation in the visible range. The effect of adsorbates on the position of their surface plasmon resonance constitutes the basis for the application of these nanostructures in biosensing. In this work, we will demonstrate the application of organized gold nanostructures, mainly arrays of sub-wavelength hole arrays, on the detection of the lung cancer marker EGFR. An integrated system, involving nanohole arrays coupled to microfluidics, was also used for the simultaneous detection of Ig-type of antibodies from blood samples. The analysis of the ratios of the different Ig-types antibodies can be used to monitor leukemia. The concepts that will be presented in this paper show the potential of gold nanostructures as a new generation of biosensors for cancer diagnosis and for monitoring the response of patients to treatments.

(489) **Plasmonic Response at Electrified Metal-Liquid Interfaces during Faradaic and non-Faradaic Reactions by Enhanced Optical Transmission**; Paul W. Bohn[1], Sean P. Branagan[1], Yang Yang[1]; [1]University of Notre Dame

Thin Au films, patterned by focused ion beam (FIB) milling to contain an array of subwavelength nanopores, exhibit enhanced optical transmission (EOT) via front-back resonance coupling. These films can also serve as working electrodes capable of controlling the local potential, allowing electrochemical processes to be monitored using wavevector-resolved spectral mapping. The precise value of the surface plasmon resonance (SPR) wavevector can be extracted from the enhanced optical transmission signal and correlated with several distinct classes of electrochemical processes: double layer reorganization, faradaic adsorption/desorption, heterogeneous electron transfer, and anion adsorption. Specifically, the protonation/deprotonation reaction of an adsorbed monolayer of 4-mercaptobenzoic acid, the adsorption/desorption reaction of dodecanethiol to Au, the solution-phase reaction of ferri-ferrocyanide, and sulfate adsorption/desorption will be described. A simple model will be presented encompassing both the EOT signal and electrochemical processes which produces semi-quantitative agreement with the SPR spectral wavevector mapping observed experimentally.

(490) **Plasmonic Imaging Sensors using 1, 2 and 3 Dimension Structured Substrates**; Michael Canva, Maha Chamtouri, Alexandra Sereda, Mondher Besbes, Anne-Lise Coutrot, Julien Moreau; [1]CNRS Institut

Plasmonic sensing is now a mature field with many demonstrated applications, in particular in the field of label-free and /or real-time characterization of surface interactions. This is especially true in domains such as chemical, biochemical and biomedical, often making

use of biochip reading type instruments. In terms of sensitivities, close to theoretical instrumental limitations have been reached using the classical propagative plasmons on homogenous thin films (1D). Current studies are now focused on the use of localized plasmons on metallic nanostructures, and furthermore in making use of the coupling of localized and propagating plasmons, taking advantage of both micro and/or nano- structured substrates. Depicted from above the biochip surface, such structuration can be mono or bi dimensional, leading to 2D or 3D structured substrates. In order to guide the sample designs, simulations have been extensively performed. In particular, a hybrid code taking advantages of both Finite Element Method (FEM) and Fourier Modal Method (FMM) allowing precise simulations with reasonable computation costs has been developed. Concerning the 2D type structures, exhaustive simulations of nano to micro ribbons, grooves and ridges, will be presented as well as some experimental results based on large range angulo-spectral plasmonic reflectivity characterization. Continuum of states involving propagative plasmons as well as localized plasmons and interrelated coupling will be showed, together with the impact on the sensors sensitivities. Concerning the 3D type, the possibilities are endless, involving different shapes and packing arrangement in the two transverse dimensions and some examples will be given. Prototype samples are realized using e-beam lithography. Experimental plasmonic signals, quantified as reflectivity variation and/or shift of coupling wavelength or angle, are measured using an angulo-spectral SPR imaging system. Multiple nanostructures zones on a chip with different geometrical parameters can be simultaneously characterized and compared to simulations. Sensitivities are measured both as a function of step index (in "% / RIU" (Refractive Index Unit)) and biofilm binding (in "% / nm" (of thickness of given optical index contrast)). Simulations show the further need for precise target localization to really take advantage of the structured localization of the electromagnetic field enhancement.

(491) **Comparative Study of SPR on Nanohole Arrays in Transmission and Kretchmann Configuration**; Jean-Francois Masson[1], Maxime Couture[1], Ludovic Live[1], Anuj Dhawan[2]; [1]Universite de Montreal, [2]IIT-Delhi

The debate is still ongoing on the optimal mode of interrogation for surface plasmon resonance (SPR) sensors. Comparative studies previously demonstrated that nanoparticle exhibiting a localized SPR (LSPR) have similar performances to thin Au films (J. Am. Chem. Soc., 2004, 126, 12669-12676 and NanoLetters, 2009, 9 (12), 4428-4433). To the contrary of these prior studies, it is demonstrated here that nanohole arrays (1000 nm periodicity, 600 nm diameter and 125 nm depth), which support both LSPR and propagating SPR modes, exhibit superior sensitivity to refractive index and improved detection limits for IgG sensing by using the Kretschmann configuration. Gold nanohole arrays in the Kretschmann configuration of SPR was more sensitive to bulk refractive index and to IgG detection than thin Au films and to the enhanced optical transmission (EOT) mode of nanohole arrays. This enhanced sensitivity was obtained despite the shorter penetration depth of nanohole arrays excited in the EOT configuration. The decay length of the electromagnetic field in EOT mode was estimated to approximately 140 nm using a layer-by-layer deposition technique of polyelectrolytes (PAH and PSS), but significantly increases in the Kretschmann configuration. RCWA and FDTD simulations were in good agreement with the experimental results. The angle of incidence of the light influences the analytical properties of nanohole arrays in the enhanced optical transmission mode. For example, the excitation wavelength of the (1,0) mode blueshifts by 16 nm/degrees within the 0 to 16 degrees range investigated. While bulk sensitivity remains invariable with excitation angle, the sensitivity to monolayer formation (polyelectrolyte bilayer) was improved by a factor of three by tuning the excitation angle to 13 degrees. This demonstrates a facile method to improve the sensitivity of nanohole arrays analyzed in transmission mode.

(492) **On-Chip Synthesis of RNA Aptamer and Protein Microarrays for Multiplexed Protein Biosensing with SPR and SPR Phase Imaging Measurements**; Ting Seefeld[1], Yulin Chen[1], Aaron Halpern[1], Wenjuan Zhou[1], Robert Corn[1]; [1]University of California, Irvine

RNA aptamer microarrays and protein microarrays are fabricated from double-stranded DNA (dsDNA) microarrays by a one-step, multiplexed enzymatic synthesis in an on-chip microfluidic format and then employed for antibody biosensing measurements with surface plasmon resonance imaging (SPRI). For the RNA aptamer microarrays, single-stranded RNA oligonucleotides are transcribed on-chip from double-stranded DNA (dsDNA) templates attached to microarray elements (generator elements) by a surface transcription reaction, then diffuse in the microfluidic channel and are quickly captured by hybridization adsorption onto adjacent single-stranded DNA (ssDNA) microarray elements (detector elements) that contain a partially complementary sequence to 5'-end of the ssRNA. For the protein microarrays, a microarray of dsDNA elements (generator elements) that encode either a His-tagged green fluorescent protein (GFP) or a His-tagged luciferase protein is utilized to create multiple copies of messenger RNA (mRNA) in a surface RNA polymerase reaction. The mRNA transcripts are then translated into proteins by cell-free protein synthesis and the synthesized protein diffuse to adjacent Cu(II)-NTA microarray elements (detector elements) where they are specifically adsorbed. The RNA aptamer and protein microarrays can be subsequently used in SPRI measurements for the detection of protein biomarkers and antibodies. The technique of surface plasmon resonance phase imaging (SPR-PI) is used in addition to SPRI for enhanced sensitivity in the multiplexed biosensing of proteins and nucleic acids.

(493) **Computer Modeling for Gaining a Better Insight in Plasma Spectrochemistry**; Annemie Bogaerts[1], Maryam Aghaei[1], Peter Simon[1], Helmut Lindner[1], David Autrique[1], Zhaoyang Chen[1]; [1]University of Antwerp

To improve the analytical applications of plasmas, a good insight in the plasma behavior is desirable. We try to obtain this by computer modeling. In this talk, four case studies will be presented, for four different types of analytical plasmas. The first example is the low pressure glow discharge. We developed a comprehensive modeling network to describe the behavior of the various plasma species (Ar gas atoms and ions, as well as sputtered atoms and ions, both in the ground state and in various excited levels, and the electrons). Typical calculation results include the densities, fluxes and energies of the various species, and information on their collision processes in the plasma, the electric field distribution, as well as results of direct interest for the analytical application, i.e., sputter yields, crater profiles, optical emission intensities, and insight in the origin of relative sensitivity factors for GDMS. In recent years, there is a growing interest in glow discharges operating at atmospheric pressure, for gaseous analysis, such as (among others) the flowing atmospheric pressure afterglow (FAPA), developed by Hieftje and coworkers. We are developing a model for the FAPA, operating in He, including the effect of the gas flow, air impurities, and gas heating. Calculation results that will be presented, include the gas flow pattern, the electric field distribution and the density profiles of the various plasma species. The third case study is the laser induced plasma, as used for LIBS or for LA-ICP-MS. A model, describing laser-solid interaction (including heating, melting and vaporization), plume expansion and plasma formation, as well as laser-plasma interaction, was developed. Moreover, the behavior of laser-produced particles in the ablation cell, and their transport towards the ICP, was described by computational fluid dynamics. Finally, the ICP itself is

being modeled, again by computational fluid dynamics, focusing on the power deposition inside the plasma, the plasma temperature, electron density and gas flow pattern inside the ICP. The effect of the sampling interface on the plasma behavior was also investigated.

(494) **High Rep-Rate Saturation Time Resolved LIF applied to Surfatron Induced Plasmas in Argon and Argon Mixtures**; Joost van der Mullen[1], Emile Carbone[1], Simon Hubner[1], Jose-M Palomares[1], Wouter Graef[1]; [1]Eindhoven University of Technology

By combining high rep-rate YAG-Dye laser systems with well-known and controllable surfacewave induced plasmas we are able to explore the excitation kinetics in the argon atom system ArI and to unravel the excitation transfer between ArI and other atomic and molecular systems. The laser systems offer 8 ns pulses of typically 1 mJ of tunable wavelength with a rep-rate of 1 to 5 kHz. Thus, we get at least 100 times more relevant LIF photons per unit of time than what conventional 10 Hz YAG-Dye systems can provide. The post-pulse decay of the laser-populated level gives the total destruction rate of that level. By changing the plasma in a controlled way we get for that level the destruction rates of electron and atom induced transitions. Assuming that we operate in saturation LIF we can relate the density of the lower level, a (quasi) meta-stable, to the peak value of the upper level. This method of Saturation Time Resolved Laser Induced Fluorescence (SaTiRe LIF) makes it possible to study the density of (quasi) meta-stables as a function of plasma conditions and spatial position. Via the responses of non-directly laser affected levels, the so-called second order responses, we found how the population surplus of the upper level and depletion of the lower level propagates through the Ar I system and how these density waves affect other systems. Second order responses, visible in pure Ar but also in Ar admixtures like Ar-N2, Ar-H2 and Ar-O2 mixtures, can be used to unravel conversion activities between levels and systems. Several experimental results will be presented together with a versatile collisional radiative model. Experimental and theoretical results will be compared with each other and it will be demonstrated that, apart from the electron-induced transitions, heavy particle collisions are also important in plasma sources used for analytical atomic spectroscopy.

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(495) **Effect of Electron-Ion Recombination on Laser-Induced Plasmas Spectra and Consequent Implications to LIBS Elemental Analysis**; Alessandro De Giacomo[1, 2], Marcella Dell[2], Rosalba Gaudiuso[1], Olga De Pascale[2]; [1]Department of Chemistry, University of Bari, [2]IMIP-CNR

Laser-Induced Plasmas (LIPs) are generally investigated assuming that Local Thermal equilibrium (LTE) conditions are completely fulfilled and that equilibrium relations are valid for material particles balances. These relations can be exploited for estimating plasma temperature and ionization degree, as well as for determining the elemental composition of the ablated sample with Calibration-Free methods (CF-LIBS). In this work the effect of the recombination character of LIPs on the emission spectrum is discussed during the entire temporal evolution of the expanding plasma. The appearance of continuum radiation in the initial stage of the expansion can be ascribed to the prevailing of radiative recombination on radiative de-excitation (i.e. spontaneous emission), due to Debye effect limiting the number of accessible electronic levels. It is interesting to observe that, immediately after the ejection of material through the laser ablation process, absorption lines corresponding to transitions involving low energy levels can be detected on the continuum radiation, as a consequence of the initial ionization character of the plasma. On the other hand, after a certain delay from the laser pulse, when atomic and ionic emission lines become clearly distinguishable in the spectrum, the link between ion-electron recombination and emission line intensity is discussed. In this frame, the emission process is interpreted as the preferred decay route corresponding to excitation collisional processes that are not counterbalanced by superelastic collisions. The slight unbalance between excitation/de-excitation collisional processes can be ascribed to the low kinetic energy of recombining electrons, which causes them to be mainly involved in de-excitation impacts. On this basis, electron excitation cross sections are estimated experimentally by acquiring time-resolved emission spectra and then used for analytical purposes. This methodology is applied to the LIBS spectrum in order to propose a different approach to CF methods and is tested for the chemical analysis of several kinds of samples, including iron alloys, soils and rocks.

(496) **New Developments in ICP-MS**; Sam Houk[1], Chris Ebert[1], Stan Bajic[1], Dan Zamzow[1], David Baldwin[1]; [1]Ames Laboratory USDOE

This talk will describe new instrumentation for and applications of ICP-MS. New research from the author's lab will be presented on several topics: a) the fate of droplets and particles in the ICP studied by high-speed movies, b) new ICP torches designed specifically for ICP-MS, and c) laser ablation ICP-MS for analysis small individual particulates or agglomerates.

(497) **Aspects of Buffer-Gas-Assisted High Irradiance Laser Ionization Source**; Wei Hang[1]; [1]Xiamen University [4]

Laser ionization is the primary stage in high irradiance laser ablation & ionization mass spectrometry. When inert gas is introduced into the source, it changes the characteristics of ions in many aspects. At the buffer gas pressure of several hundred Pascal, the plume length becomes short, while the mean-free-path of the ions is several tens of micrometers. The ions experience sufficient collisional cooling and will be sampled efficiently by MS. The electrons escaping from the plasma are also trapped by the ambient gas “wall”, and three-body collisional recombination happens with these electrons as the third body, which will reduce the difference in charge distributions between ions. The interference of multiply charged ions can be greatly reduced. The element RSCs stay close to unity when the irradiance is larger than109 W/cm2. Matrix effects and elemental fractionation, which are associated with differences in the material absorptions, element IPs, melting points, and boiling points, were greatly “minimized” in the high irradiance. High irradiance will induce the dissociation of polyatomic ions. The proportion of polyatomic ions decreases with increasing laser irradiance and is almost eliminated at a laser irradiance of 1011 W/cm2. Collisional dissociation is also effective in reducing the amount of polyatomic ions because the polyatomic ion population decreases with an increase in pressure. When femtosecond laser is applied, the matrix effect is further reduced due to the coulombic explosion. Multiply charged ions are almost eliminated with the disappearance of inverse bremsstrahlung process. All these changes improve the performance of laser ablation & ionization as an ion source for MS.

(498) **Flagging Matrix Effects and System Drift in Organic-solvent Based Analysis in Axial-Viewing ICP-AES**; Yan Cheung[1], George Chan[1], Gary Hieftje[1]; [1]Indiana University

Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP–AES) is one of the most widely used techniques for elemental analysis. For many petroleum and pharmaceutical samples, in particular, ICP-AES analysis of organic-solvent based samples has gained popularity over traditional aqueous analysis, because of the reduced sample-preparation burden. However, matrix interference in the analysis of these samples remains one of the major challenges to

overcome. Furthermore, when better detection limits are needed, axial-viewing ICP-AES is often employed, even though it is known to be even more prone to matrix effects. In the present study, spatial emission profiles across the axially viewed plasma are examined with an aim to flag matrix interferences and system drift for organic-solvent based samples. This method is based on the difference in relative magnitudes of changes in emission signals caused by matrix interferences or system drift along cross-sectional locations in the plasma. Because of the direct proportionality between an emission signal and the concentration of an analyte element, the spatial dependence of matrix-induced or drift-induced changes in the emission signal leads to different determined concentrations of the analyte in the same sample at various cross-sectional positions in the plasma; this dependence allows the matrix interference to be flagged. Here, isopropanol was used as the solvent for the analysis of seven analytes (Cd, Cu, Cr, Fe, Mn, Ni, and Zn). Three types of matrix effects were examined: spectral, plasma-related and sample-introduction-related interferences. Results demonstrate that the cross-sectional profile of an emission line can effectively flag signal changes caused by all three types of matrix interferences and system drift, even for analytical inaccuracy as little as ±5%. In this presentation, the application of this method to various samples and the magnitude of matrix effects under various levels of plasma robustness will be discussed.

(499) **fs-LA-ICP-MS Metal Analysis of Asphaltenes Samples After Separation using Thin Layer Chromatography**; Jose Chirinos[1, 2], Jhanis Gonzalez[1], Dayana Oropeza[1], Rick Russo[1], Maria Ranaudo[2], Francia Marcano[2]; [1]Lawrence Berkeley National Laboratory, [2]Universidad Central de Venezuela

Quantitative information of metal content in crude oils and their derivates is essential for petroleum industry due: i) they exhibited a propensity to accumulate in the human body, causing irreversible damage; ii) affects the oceans and water reservoirs through oil spillage and effluents discharge from industrial companies; iii) allows corrective actions during oil production and refining such as catalyst poisoning, corrosion or pollution control and iv) contribute to the geochemical characterization of crude oil origin. Metals are mainly concentrated in asphaltenes, the heaviest, polar and aromatic portion of the crude oil. As a routine, the asphaltenes are precipitated and separated from the crude oil by addition of n-heptane and analyzed by ICP OES or ICPMS by direct introduction of the sample. This method is labor intensive, time consuming and requires large quantities of sample and solvents. The use of fs-LA as sample introduction presents an exciting alternative to tedious, time consuming traditional wet methods. However, the direct ablation of these crude samples may create messy depositions that could contaminate the ablation cell, transport tubing, sampling cones, etc. Therefore an alternative procedure which includes a method to separate fractions from the crude oil was tested. The method is based on thin layer chromatography (TLC). The TLC method is fast and easy to implement, low sample consumption with a low waste generation since only 1.00 mL of the solvent is necessary. This method was tested on some Venezuelan crude oils samples and the results were compared to those obtained using a classical asphaltene separation method. The combination TLC and fs-LA-ICP-MS proved to be an efficient way to obtain fast and reliable asphaltene results comparable to those obtained with traditional analytical methods.

(500) **Application of Laser Ablation ICP-MS - Imaging of Li, Mg, Ba, Sr, Mn, Zn, Ni, Pb in otoliths of BluefinTuna**; Saijin Zhang[1], Jay Rooker[2], Danielle Creeley[1], Peter Santschi[1]; [1]Marine Science, [2]Marine Biology

Trace element levels in otoliths have the potential to provide excellent natural markers. Variability in these markers can be applied to estimate past environmental or diet history as well as movement patterns of fish. For example, Sr and Mg were found to be related to water temperature and salinity. However, the application has been largely limited to purely freshwater or marine fish. Bulk solution-base analysis can provide accurate trace element levels in otolith but until now has failed to provide monthly and/or annual information. Laser ablation ICP-MS is an emerging technique that allows to determine monthly and/or annual trace metal levels in otoliths, but it had so far been difficult to find matrix-matched and concentration-fitting standards as concentrations of trace elements in otoliths are very low and cover a wide range, ranging from 0.01~1000 µg/g. This study has utilized Nist 616, Nist 614, Nist 610 and Nist 612 to determine trace metals at different ambient concentration levels. Potential inaccuracy caused by using unsuitably high standard reference materials was evaluated. In addition, by determining the distribution of trace elements (Li, Mg, Ba, Sr, Mn, Zn, Ni, Pb) across the whole otolith, estimation on the diet history as well as movement patterns of Bluefin Tuna, which is in high demand and also highly migratory, will be attempted.

(501) **Identifying and Overcoming Spectral Overlaps in ICP-MS Measurements of Complex Samples**; Fang Liu[1], John Olesik[1]; [1]Ohio State University

Complex samples, such as flue gas desulfurization (FGD) waste waters, contain high concentrations of dissolved solids that can produce molecular ions in ICP-mass spectra. However, the analyte elements of interest may be present at ppb or lower concentrations. The molecular ions can occur at the same nominal m/z as analyte ions, producing spectral overlaps that could lead to large errors for analyte elements present at low concentrations. The goals of this research were to: (1) identify molecular ions formed from high concentrations of B, Br, C, Ca, Cl, Mg, Na and S, (2) determine the background equivalent concentration of each molecular ion per ppm of the matrix element and (3) determine the efficacy of approaches to overcome the spectral overlaps using a collision/reaction cell. Molecular ions were identified by exact mass measurements using an ICP-SFMS in high resolution mode ($m/\Delta m$=10,000) and comparison of measured to natural molecular ion isotopic abundances. Spectra from complex samples were compared to those from synthetic samples containing a single element at high concentration. Background equivalent concentrations due to molecular ions were determined on both ICP-SFMS and ICP-DRC-MS instruments. Kinetic reaction rate data are not available for reactions of many of the molecular ions with neutral reaction gases. Therefore, the effectiveness of different neutral reaction gases to reduce molecular ion signals was investigated. Kinetic reaction rates were estimated from these data.

(502) **Elemental Analysis of Single Droplets of Means of a Sector-field Mass Spectrograph Equipped with an Integrating Array Detector**; Jeremy A. Felton[1], Yuki Kaburaki[2], Steven J. Ray[1], Roger P. Sperline[3], M. Bonner Denton[3], Charles J. Barinaga[4], David W. Koppenaal[4], Akitoshi Okino[2], Gary M. Hieftje[1]; [1]Indiana University, [2]Tokyo Institute, [3]University of Arizona, [4]Pacific Northwest National Laboratory

A Mattauch-Herzog geometry mass spectrograph (MHMS) equipped with a novel focal plane camera (FPC) solid-state array detector was used to analyze single droplets by means of inductively coupled plasma mass spectrometry. The FPC detector differs from conventional single-channel detectors in that it is composed of an array of 512 individual detector elements, each of which is able to integrate ion current continuously. When the FPC is installed at the focal plane of the MHMS, the mass spectrum is spatially distributed across the surface of the FPC, and a section of the mass spectrum can be observed simultaneously. Further, because the FPC detector is based on a monolithic semiconductor architecture, each detection

pixel can be individually interrogated at will, and with high speed. In this work, the ion signal resulting from the elements and isotopes within individual droplets was monitored by integrating ion current for a portion of the mass spectrum during each droplet event. In this manner, elemental composition and isotope information could be collected on a droplet-by-droplet basis. The advantages of employing simultaneous multi-elemental analysis in this application will be examined, as will the benefits of using single droplets for analysis. Aspects of the data analysis approach and experimental setup will be discussed, and the current analytical figures of merit including limits of detection and isotope-ratio precision will be presented.

(503) **Will Tunable Lasers Have an Impact On Mid-Infrared Spectrometry in the Next Ten Years?**; Curtis Marcott; [1]Light Light Solutions

Although tunable infrared (IR) lasers have been commercially available for over thirty years, they have mainly been used for specific applications like gas phase analysis in relatively narrow spectral ranges. They have not replaced Fourier transform infrared (FT-IR) spectrometers, which remain the main tool used for general broadband IR spectroscopy in most academic and industrial laboratories. Recently, advances in tunable laser technology leads us to reconsider the role such lasers may play in mid-IR spectroscopy in the next decade. Tunable quantum cascade lasers and optical parametric oscillator (opo) lasers, in particular, have emerged with broader tunability across the mid-IR spectral range. Future specific applications of such lasers, including spectral imaging and sub-diffraction-limited spectroscopy, will be discussed.

(504) **What May be the Next Advances in mid-IR Microspectrometry?**; Carol Hirschmugl; [1]University of Wisconsin-Milwaukee

Infrared telescopes have expanded our knowledge of the Universe. For example, the discovery of stars orbiting a black hole in our galaxy was made using IR telescopes, and IR telescopic data have also determined the existence and composition of exoplanets. Similarly, infrared microscopy has the potential to expand the knowledge of our "micro-verse" when biologically relevant time-scales and length-scales can be achieved. With the recent development of synchrotron-based FTIR wide-field imaging. [1,2,3,4] that will be presented in this talk, the potential for this expanded understanding is greatly enhanced. Examples from our work will be presented and used to highlight what can be achieved presently, and the largest remaining instrumental and analytical challenges and bottlenecks will be assessed. Instrumental challenges include source development and accessibility; speed and availability of, and access to, focal plane array detectors; and implementation of 3D imaging strategies. The sheer volume of data (1000's of independent images, or 100,000's of spectra) that is generated dominates the analytical barriers. Successful demonstration of reconstruction and abstraction of spatially resolved absorption data in the face of confounding scattering effects will be demonstrated. The volume and complexity of the data require novel approaches to extracting relevant information into comprehendible images, mining the data for the unusual information, and/or evaluating the changes in time-dependent data. Some thoughts about future directions will be mentioned as a departure point for open discussion.

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(505) **Medical Diagnostics and via Infrared Spectral Cytopathology and Spectral Histopathology**; Max Diem[1], Benjamin Bird[1], Miloš Miljković[1], Jennifer Schubert[1], Antonella Mazur[1]; [1]Northeastern University, Lab for Spectral Diagnosis

During the past decade, optical methods for the detection, diagnosis and classification of disease, especially cancer, have been refined. Infrared and Raman microspectroscopy are particularly promising since they provide fingerprint sensitivities toward small changes in bio-molecular composition between normal and diseased states. For these experiments, tens of thousands of individual spectra are collected from pixels of tissue, and assembled into pseudo-color pictures via multivariate methods. The resulting images are based on label-free and morphology-independent metrics, and can be correlated with classical histo- and cytopathology for training of machine-learning algorithms for final diagnoses. In spectral cytopathology, infrared spectra of individual, unstained cells are collected and deposited on a suitable substrate. Spectra of individual cells are re-constructed, after noise adjustment, scattering correction and water vapor compensation, from pixel spectra collected from areas of about 40 μm2; typically, 20 to 60 individual pixel spectra are co-added to produce one spectrum of an individual cell. This methodology can readily be adapted for the analysis of biopsy tissue. Tissue sections are imaged by collecting hyperspectral datasets which subsequently are analyzed by multivariate methods to produce pseudo-color images that reproduce the tissue architecture that can be observed by visual microscopy after suitable staining of the tissue. We and others have demonstrated that spectral histopathology (SHP) can distinguish normal tissue types from each other, and can detect and classify cancerous tissues as will be shown by a typical application of this technique. SHP readily distinguishes normal from cancerous tissues, and areas of inflammatory response. Spectra from well-defined pathological states can subsequently used to train ANNs for the automatic diagnosis of unknown tissue sections. Such ANNs have performed extremely well at the LSpD, where data sets comprising millions of spectra were analyzed to classify various cancers; this classification occurred with an average sensitivity and specificity of about 95 %. In addition, it was demonstrated that SHP can determine the primary tumor sites of metastatic lesions in different organs. Thus, the analysis of lymph nodes may hold information on the primary tumor, since the lymphocytes in the germinal centers are activated in response to a nearby primary tumor site.

(506) **Next Advances in Mid-Infrared Spectroscopy: IR-on-a-Chip**; Boris Mizaikoff[1]; [1]University of Ulm, Institute of Analytical and Bioanalytical Chemistry

State-of-the-art biodiagnostic platforms increasingly take advantage of miniaturized and integrated sensing and assay technologies ideally providing direct access to molecule-specific information. With point-of-care and personalized medicine becoming more prevalent, detection schemes that do not require reagents or labeled constituents facilitate on-site analysis providing close to real-time information, or may be used in a continuous monitoring mode e.g., in intensive care scenarios. However, decreasing the analytically probed volume may adversely affect the analytical figures of merit such as the signal-to-noise-ratio, the representativeness of the sample, or the fidelity of the obtained analytical signal. Yet, probing minute samples volumes facilitates rapid analysis, minimally intrusive or even non-invasive sampling, and a rapid diagnostic response. Consequently, the guiding paradigm for the miniaturization of diagnostic devices should be creating analytical platforms that should be as small as still useful, rather than as small as possible by smartly balancing the benefits and disadvantages of small device dimensions. Optical/spectroscopic sensor technology taking advantage of the mid-infrared (MIR) spectral range (3-20 μm) is increasingly adopted in bioanalytics due to the inherent molecular specificity enabling discriminating

constituents at ppm-ppb concentration levels in condensed and vapor phase media. Recently emerging strategies take advantage of innovative waveguide technologies such as planar waveguide structures in combination with compact FT-IR spectrometers or highly efficient broadly tunable quantum cascade lasers, thereby facilitating highly miniaturized yet robust MIR diagnostic platforms [1-6].

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(507) **What May be the Next Advances in Raman spectrometry?**; Ian Lewis[1]; [1]FACSS

Only 30 years ago, Raman spectroscopy was a technique used, in the most part, by specialized academics for the study of pure small molecules and gases and available to researchers in major corporate R&D laboratories only. Today Raman spectroscopy can be found both inside and outside the laboratory used and operated by people with varying backgrounds and skillsets from academicians to analyzer control technicians to first responders in fields from the A's - archeometry to Z's – zoology. In this presentation a whirlwind review of the many developments that have occurred during that timeframe will be given, a selection of applications will be discussed , and will conclude with some personal thoughts from the author on where Raman may be found in the next 30 years.

(508) **Recent Progress and Advances in Biomedical Raman Spectroscopy**; Michael Blades; [1]The University of British Columbia

Raman spectroscopy has become an important research tool in medicine, biology and biotechnology because it has the potential to provide useful information about biological environments. Although not as widely applied as fluorescence spectroscopy, the value of Raman lies in the fact that it can be used in a "label-free" way and, in many cases, is minimally invasive. In addition there are a variety of specialized Raman techniques, each with particular advantages and disadvantages - spontaneous Raman, stimulated Raman, coherent anti-Stokes Raman, SERS, TIRS to name a few of the more popular. Raman spectra reflect a superposition of all the active molecular vibrations within the sampled volume, and as a result, their measurement can be used to characterize the composition and intracellular structural elements within single cells or populations of cells. Additionally the frequencies and relative intensities of specific spectral bands can be used to measure the secondary, tertiary and quaternary structures of specific biomolecules, and composite spectra can be analyzed with an array of multi-variate methods to identify biological motifs, determine the composition of multi-component samples, and to sense biochemical changes in the cell in response to stimuli such as drug administration or external stress. In our group we principally apply Raman micro-spectroscopy and coherent Raman spectroscopy, for the non-invasive characterization of cell status and cell-colony dynamics of stem cells, blood cells, and cancer cells. We seek to identify and characterize the Raman bands most sensitive to cellular changes accompanying processes such as differentiation, stress, and autophagy, and to develop analytical protocols for use by cell biologists, bioengineering cell culturing groups, and blood service groups. This talk will review recent progress in the field and speculate on what the future may hold for Raman in the biomedical sciences.

(509) **Predicting Wound Outcome from Raman Spectroscopic Data: Univariate versus Multivariate Techniques**; Nicole Crane[1, 2], Rajiv Luthra[1], Jonathan Forsberg[1, 2, 3], Eric Elster[1, 2, 4]; [1]Department of Regenerative Medicine, Naval Medical Research Center, [2]Department of Surgery, Uniformed Services University of Health Sciences, [3]Department of Orthopaedics and Rehabilitation, Walter Reed National Military Medical Center, [4]Department of General Surgery, Walter Reed National Military Medical Center

Predicting wound outcome during the management of modern traumatic war wounds remains a significant challenge for inexperienced clinicians. Though the ensuing inflammatory response that follows injury determines the pace of wound healing and tissue regeneration, the timing of wound closure is often subjectively based. Improved objective assessment of combat wounds may ultimately guide surgical decision-making, resulting in faster healing times, decreased infection rates, and decreased local and systemic complications of injury. Vibrational spectroscopic techniques such as Raman spectroscopy offer the potential to evaluate the molecular environment of acute wounds throughout the debridement process while in the surgical arena. We collected Raman spectra from over 200 ex vivo combat wound tissue biopsies, and compared them to eventual wound outcome - wounds that heal normally or wounds that suffer from delayed healing. Interpretation of Raman spectra of biological samples can be complex; Raman spectral bands are often the sum of several components. Here, we compare the ability of univariate and multivariate data analysis techniques to accurately predict whether or not a wound will heal normally.

(510) **Microfluidic Tools Coupled to Numerical Simulations to Study Membrane Protein Crystallization**; Bahige Abdallah[1], Christopher Kupitz[1], Petra Fromme[1], Alexandra Ros[1]; [1]Arizona State University

In this work we propose a salting-out diffusion method as a means to crystallize the large membrane protein complex photosystem I within a microfluidic device. Traditional macroscale crystallization is accomplished by exploring a range of protein and precipitant concentrations in solution until a suitable combination is attained. This methodology is time consuming and resource intensive which hinders efficient structure determination of complex membrane proteins. Microfluidic tools have the potential to explore protein crystallization conditions with small sample amount in high throughput. Here, we demonstrate an unusual protein crystallization experiment in a microfluidic device utilizing an ionic strength gradient in order to obtain phase diagrams for photosystem I crystallization. In the case of photosystem I, crystallization is achieved by reduction of ionic strength. The solubility of the protein complex is decreased as the ionic strength is decreased leading to crystallization. To adapt this process to our microfluidic device, we set up a system in which the salt within a microchannel diffuses out into an outlet reservoir. Over time, a salt concentration gradient develops along the microfluidic channel causing nucleation and growth of crystals which allows us to determine optimal crystallization concentration conditions. This selective diffusion is possible due to the difference in diffusion coefficients between protein and salt ions of one to two orders of magnitude. To prevent convection, an agarose gel is incorporated in the outlet reservoir. Obtaining phase diagrams from the experimental data requires quantifying salt and protein concentrations at each time point in the experiment. We use numerical simulations with Comsol Multiphysics 4.2a to compute the concentration profile along the microchannel coupled to inlet and outlet reservoirs adapted to the corresponding diffusion characteristics of salt and protein ions. Second harmonic generation optical data (SONICC) are used to monitor crystal-

formation along the channel, where SONICC allows detection of nanocrystals as small as 100nm. The experimental data are compared to simulation data for quantitative analysis. We propose that with minor adaptations, this approach could be utilized to crystallize and efficiently study and optimize crystallization conditions for a wide range of complex proteins with the goal to solve their molecular structures.

(511) **Identifying the Differentiation Stages of Individual Hematopoietic Cells from Mice by Multivariate Analysis of Secondary Ion Mass Spectra**; Mary L. Kraft[1, 2], Jessica F. Frisz[2], Ji Sun Choi[1], Robert L. Wilson[2], Brendan A. C. Harley[1]; [1]University of Illinois, Department of Chemical and Biomolecular Engineering, [2]University of Illinois, Department of Chemistry

Identification of the mechanical and biochemical properties that induce hematopoietic stem cells (HSCs) to self-renew or differentiate into various types of blood and immune cells is an important goal in tissue engineering. Combinatorial biomaterial substrates permit screening the effects of multiple microenvironments on stem cell fate while using a minimum number of cells. To utilize these substrates, robust and quantitative methods to identify the differentiation stages of individual cells with location specificity are required. For this purpose, we have used time-of-flight secondary ion mass spectrometry (TOF-SIMS) to collect spectra that encodes for the surface chemistries of individual cells from distinct hematopoietic cell populations. We then used a chemometric technique, partial least-squares-discriminant analysis (PLS-DA) to construct a PLS-DA model that could be used to identify the differentiation stages of individual hematopoietic cells that were isolated from mouse bone marrow according to their mass spectra. This approach may facilitate correlating HSC fates with the properties that control them.

(512) **Transmission Raman Tomography on a Cylindrical Tissue Phantom**; Matthew R Kole[1], Matthew V Schulmerich[1], Matthew K Gelber[1], Rohit Bhargava[1, 2]; [1]University of Illinois at Urbana-Champaign, Department of Bioengineering, [2]Department of Electrical and Computer Engineering, Department of Mechanical Science and Engineering, University of Illinois Cancer Center

The use of Raman spectroscopy to provide label-free chemical contrast of analytes buried below light scattering media has a wide variety of biomedical related applications ranging from disease diagnosis to monitoring drug delivery. Developing and validating methods for obtaining the size, shape, and position of buried targets is a first step towards realizing this potential. In this research, we present experimental results and theoretical considerations from a series of transmission Raman tomography measurements on targets (Teflon spheres) buried inside of Intralipid-based tissue phantoms along with the resulting two-dimensional image reconstructions. Measurements were collected with a fiber-based Raman instrument using varying source-detector collection angles. We compare two forward-modeling methods, radiative transport calculation (Nirfast, an open-source diffuse optical tomography modeling package)[1] and Monte Carlo simulation (written in-house), for the modeling of light fluence throughout the phantom. Reconstruction of the size and position of buried targets can be employed without the use of spatial priors via an iterative modified-Tikhonov minimization algorithm, and these results are validated against computed tomography (CT) images. We present the differences between the two forward algorithms and highlight the important advantages and disadvantages of each approach.

(513) **Determination of Spectroscopic Uncertainty for Non-Linear Regression Models and Its Implications for Biomedical Diagnostics**; Ishan Barman[1], Narahara Chari Dingari[1], Jaqueline S. Soares[1], Gajendra Pratap Singh[1], Ramachandra Rao Dasari[1], Janusz Smulko[2]; [1]G.R. Harrison Spectroscopy Laboratory, MIT, [2]Gdansk University of Technology

Raman spectroscopy has provided promising results for a wide variety of biomedical applications especially for disease diagnostics, due to its excellent chemical specificity and lack of sample preparation requirements. Nevertheless, its translation to the field and clinical settings has been impeded by the lack of accuracy and robustness of existing spectroscopic models. In order to overcome this issue, investigators have recently initiated the application of sophisticated non-linear chemometric models that can appropriately model cured effects in the relationship between the property of interest and the tissue spectra. In this talk, we present an analytical formulation for assessment of the spectroscopic uncertainty in such non-linear regression models with special focus on support vector regression. The modeling precision is computed as a function of measurement noise and model parameters. Subsequently, using clinical data (Raman spectra) acquired from glucose clamping study on an animal model subject, we perform the first systematic characterization of the relative effect of additive interference components (namely, noise in prediction spectra, calibration spectra and calibration concentrations) on the prediction error of non-linear spectroscopic models. We anticipate that the analytical formalism and the corresponding noise-induced instability findings will be valuable for uncertainty estimation in similar biomedical applications where the precision of measurements and its response to noise in the dataset is as important, if not more so, than the accuracy level.

(514) **Discrimination of Live Cell Differentiation Using Confocal Raman Spectroscopy**; Sota Takanezawa[1, 2], Shin-ichi Morita[1], Michio Hiroshima[1], Toshiyuki Mitsui[3], Yukihiro Ozaki[2], Yasushi Sako[1]; [1]RIKEN, [2]Kwansei Gakuin University, [3]Aoyama Gakuin University

The differentiation of biological cells is induced in response to external factors, but it is important to note that the response differs in each cell. Cellular states related to the difference of chemical composition in each cell should cause the variance of cell response. Therefore, the search for state space of cellular chemical compositions is required for regenerative medicine and single cell diagnosis. The specific gene, protein, and metabolic production can be used to define the state space. However, these markers should be pre-determined for each specific case. In addition, conventional methods such as microarray analysis, western blotting, and mass spectroscopy are destructive at present. Raman spectroscopy, non-destructive and non-labeling optical technique, provides the information about compositions, structure, and dynamics of molecules. And now, Raman microscopy allows to measure and image a single living cell. In this study, we confirmed whether the Raman spectroscopy is effective to discriminate cellular states along a cell differentiation process. MCF-7, which is a breast cancer cell line, was used for a model of cell differentiation. MCF-7 differentiated by heregulin (HRG) produces oil droplet in the cytoplasm. As a function of time after HRG stimulation, Raman spectra of MCF-7 expressed multivariable data in channels (Raman shift) and measurement locations (cytoplasm, nucleus, etc.). For comprehensive understanding of Raman spectra of MCF-7, we calculated a state diagram for visualizing cell differentiation dynamics, basing on principal components analysis (PCA) and calculation of Mahalanobis distance. In the state diagram of cell differentiation, non-differentiated and differentiated MCF-7 were discriminated from each other. And we confirmed a non-monotonous dynamics which indicated diversity of chemical components from non-differentiation to differentiation. These results suggested that

Raman microscopy was possible to detect cell differentiation and dynamics.

(515) **High Resolution Imaging of Breast Calcification**; Marleen Kerssens[1, 4], Alina Zoladek[2], Pavel Matousek[3], Sergei Kazarian[2], Keith Rogers[4], Nick Stone[1, 4]; [1]Biophotonics Research Unit GRH NHS FT, [2]Imperial College, [3]Central Laser Facility, Rutherford Appleton Laboratory, [4]Cranfield University

The presence of microcalcifications in breast is one of the key features screened for during routine mammography. Calcifications frequently indicate the location of the most important abnormality within the breast and are associated with positive lymph node status, poorer histologic grade and a decreased survival rate. Although breast calcifications have a high diagnostic value, it is not known how they are formed in mammary tissue and their relation to disease. In this study the disease specific chemical composition of calcifications was investigated in order to elucidate the link between carcinogenesis and calcifications in the tissue. Breast tissue specimens with pathology grades 'benign', 'in situ ductal carcinoma', and 'invasive ductal carcinoma' were collected at Gloucestershire Hospitals NHS Foundation Trust. Ethical approval was obtained from the Gloucestershire Local Research Ethics Committee. The calcifications in these samples were studied by standard benchtop FTIR, synchrotron FTIR (IRENI beamline, synchrotron radiation center, University of Wisconsin, USA and B22 beamline, Diamond Light Source Ltd, United Kingdom), mid-IR ATR-imaging, and Raman imaging. The resulting spectral images from similar locations on the tissue were compared to enable identification of disease specific changes and the spatial distribution of biochemical constituents. Variations in calcification size and grade of surrounding disease were explored in order to observe possible maturation processes of the calcifications. By applying high resolution imaging such as synchrotron FTIR, more insight could be obtained by comparing the core of the calcifications with the calcification/tissue interface.

(516) **An Assessment of Stored Red Blood Cells Using Raman Spectroscopy**; Chad Atkins[1], H. Georg Schulze[2], Michael Blades[1], Robin Turner[1, 2]; [1]University of British Columbia, [2]Michael Smith Laboratories

This research describes the first-ever Raman approach for measuring cellular degradation of stored red blood cells (RBCs). When stored using standard protocols, RBCs are considered to be viable for 42 days. However, this time-frame is based on averages from conventional assays that are costly and time-consuming; in reality, blood from different patients will degrade at significantly different rates. This degradation is called 'storage lesion' and refers to a multitude of chemical, physiological, and morphological changes that occur in the stored units over time. Clinical evidence exists which suggests these variations are responsible for a variety of post-transfusion illnesses. It would therefore be advantageous to assess the state of stored blood rapidly and accurately without needing to destructively sample the contents of the bag. Raman spectroscopy is the ideal technique, as many of the age-related changes associated with RBC storage (e.g., denatured hemoglobin, cell membrane changes, loss of metabolic regulators, etc.) should be reflected in the Raman signatures. The project's objective is to identify specific spectral features that can be designated as indicators of the lesion progression. Preliminary measurements were made with a commercial Renishaw inVia Raman microspectrometer. Samples of RBCs from the same donor at various stages of storage (0-49 days) were obtained, followed by two measurements for each sample: a dry-fixed smear, and bulk liquid analysis on a small aliquot of cells. The majority of Raman features in this initial data were representative of contributions from hemoglobin, but distinct differences existed between different donors and the ageing of different donors. Furthermore, the liquid data provided useful insight into the oxygenation state of the degrading red cells. To address the complexities presented by the cells themselves, the research direction has grown to include measurements of the storage mixture supernatant. As the RBCs degrade and expel their interior components into the bulk matrix, it is expected that valuable biochemical information can be revealed from a detailed Raman analysis.

(517) **Sensitive and Specific Detection of Long-Term Glycemic Markers using Raman Spectroscopy**; Narahara Chari Dingari[1], Ishan Barman[1], Jaqueline Soares[1], Gary Horowitz[2], Ramachandra Dasari[1]; [1]Laser Biomedical Research Center, G. R. Harrison Spectroscopy Laboratory, Massachusetts Institute of Technology, [2]Division of Clinical Pathology, Beth Israel Deaconess Medical Center, Harvard Medical School

Glycemic control refers to the typical levels of blood sugar in a person with diabetes mellitus. Much evidence suggests that many of the long-term complications of diabetes, especially the microvascular complications, result from many years of hyperglycemia. Long-term glycemic control has become an important goal of diabetes care and in the development of therapeutics for diabetes. The essential examination that has usually been performed in a clinical chemistry laboratory is the measurement of blood HbA1c and fructosamine levels as a functional metric of glycemic control over the past two to three months and three weeks, respectively. In my talk, we present the first demonstration of non-enhanced Raman spectroscopy as a novel analytical method for qualitative and quantitative detection of HbA1c and glycated albumin. Using the drop coating deposition Raman (DCDR) technique, we observe that the non-enzymatic glycosylation of these proteins results in subtle, but consistent, changes in vibrational features, which with the help of multivariate classification techniques can be used to distinguish the glycated proteins from their unglycated variants with 100%. The acquired Raman spectra demonstrate excellent reproducibility of spectral characteristics at different locations in the drop and show a linear dependence of the spectral intensity on the analyte concentration. Furthermore, the developed multivariate calibration models show a high degree of prediction accuracy even at substantially lower concentrations than those typically encountered in clinical practice. The excellent accuracy and reproducibility accomplished in this proof-of-concept study opens substantive avenues for basic investigations of glycated proteins as well as in high-throughput glycemic marker sensing in multi-component mixtures and potentially even in serum and whole blood samples. Finally, we also discuss the caveats in determining these two glycemic markers in patients with diabetic complications and how they correlate with the development of diabetic complications. We believe that the proposed approach can provide a uniquely powerful tool for glycemic marker determination in routine clinical diagnostics in the near future.

(518) **Flexible Correction in Spectroscopic Calibration for Noninvasive Glucose Tracking using a Physiological Glucose Dynamics Model**; Nicolas Spegazzini[1], Ishan Barman[2], Narahara Chari Dingari[2], Gajendra Pratap Singh[2], Ramachandra Rao Dasari[2], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]Massachusetts Institute of Technology

The physiological delay between blood and interstitial fluid (ISF) glucose is a major challenge for noninvasive glucose concentration measurements. This is a particular problem for spectroscopic techniques, which predominantly probe ISF glucose, creating inconsistencies in calibration, since blood glucose measurements are typically used as the "gold standard" values. To overcome this problem, we have previously introduced a dynamic concentration correction (DCC) scheme, based on the mass transfer of glucose between blood and ISF, to ensure consistency with the spectral

measurements. The proposed formalism allowed the transformation of glucose in the concentration domain, ensuring consistency with the acquired spectra in the calibration model. However, the existing calibration method does not address two crucial pieces, namely the challenges associated with calibration maintenance and transfer. This can be largely attributed to the rigidity of the classical calibration method. The maintenance issue is a direct consequence of the calibration-based method, arising from fluctuations in instrument and environment. In addition, the calibration transfer necessitates that the calibration model which is developed on a primary instrument is able to predict the sample composition from a spectrum measured on a secondary instrument. In order to address these constraining issues, we propose a novel flexible or adaptive correction (iFlex-Corr) methodology using the idea of indirect implicit calibration as a minimization of spectral information and kinetic (mass transfer) hard modeling of the chemical model. In the proposed indirect implicit calibration, the calculated concentrations are considered as the "measured" variables and the fitting is performed in concentration units. Put differently, this is actually a multivariate calibration with "floating" data. This reduces effects of baseline shifts, spectral overlap, and drift improving the contribution of each component to the data during the fitting. Consequently, we are able to achieve a measure of independence from calibration maintenance problems as the non-orthogonality problems largely reside in the spectral domain. Using clinical datasets obtained from human volunteers undergoing glucose tolerance tests, we demonstrate that the predicted glucose concentrations using the iFlex-Corr calibration model closely match the measured glucose concentrations, while those generated with the conventional calibration methods show larger deviations from the measured values.

(519) **Developing Improved Systems for the Reliable Detection of Analytes using Surface-Enhanced Raman Scattering (SERS) Techniques**; Brandon Scott[1], Keith Carron[1]; [1]University of Wyoming

Surface-enhanced Raman spectroscopy (SERS) is a popular research topic for trace detection problems ranging from environmental to forensic applications. Understanding of the underlying mechanisms is important to develop precise and reproducible tests. There are two accepted mechanisms of enhancement, electromagnetic and chemical theories, each of which are not totally understood. We are using a novel autocorrelation technique to elucidate specific sites on nanoparticles that are "hot" or highly enhancing. Our method has the advantage of examining large populations of nanoparticles in solutions where aggregation can be promoted. It is well known that salts enhance SERS signals, but the mechanism is yet to be proven. We will discuss our results with respect to "hot" sites created by gaps between particle aggregates. Another aspect of the autocorrelation work is the realization that solution based nanoparticle assays have inherently larger noise levels due to Poisson noise created by the particle motion. This noise contributes to decreased sensitivity due to poorer signal to noise values in an assay. To overcome this we have developed a Lab-on-a-Bubble assay that spatially localizes a SERS assay result and overcomes the noise contribution due to Brownian motion in colloidal particles. We will present Lab-on-a-Bubble results for cyanide and Cholera toxin. As a second year graduate student I would be honored to present my findings in the "Young Scientist in SERS" session.

(520) **SERS Nanoparticles for Biological Sensing**; Brent DeVetter[1], Sean Sivapalan[1], Timothy Yang[1], Thomas van Dijk[1], Matthew Schulmerich[1], P. Scott Carney[1], Catherine Murphy[1], Rohit Bhargava[1]; [1]University of Illinois at Urbana-Champaign

Motivated by the development of early cancer diagnostics, we aim to design novel contrast agents for the sensing and imaging of cancerous tissues using surface enhanced Raman spectroscopy (SERS). Here, we discuss the synthesis and design parameters of colloidal suspensions of gold nanoparticles. SERS measurements were performed on nearly aggregate free colloidal suspensions. We find that absorptive effects in solution play a significant role in obtaining intense SERS signals. Electromagnetic theory is combined with experimentally characterized gold nanoparticles to understand and design highly sensitive nanoparticle probes.

(521) **Looking Inside Catalyst Extrudates with Time-Resolved Surface-Enhanced Raman Spectroscopy**; Clare Harvey, Ingeborg Iping Petterson[2], Bert Weckhuysen[1], Cees Gooijer[2], Freek Ariese[2], Arjan Mank[3]; [1]Utrecht University, [2]VU University Amsterdam, [3]Philips Innovation Services

Heterogeneous catalysis is a vital field of research for many industries; it has been estimated that 90% of all chemical processes use heterogeneous catalysis. Porous catalyst support materials such as Al_2O_3, TiO_2 and SiO_2 are often shaped into extrudates, which present a high surface area for catalytic reactivity whilst retaining high mechanical stability under reaction conditions. A range of invasive and non-invasive techniques have been utilised in the past to visualise catalyst preparation methods and in-situ processes. However, non-invasive in-situ measurements for single catalyst extrudates, allowing the monitoring of a reaction below the surface, are rare. Raman spectroscopy has been frequently utilized as a non-destructive technique for the study of heterogeneous catalysts and catalytic reactions as it provides valuable structural information and does not require invasive sampling. It has been used to study chemical reactions on the surface of catalyst bodies, but a major problem in characterizing real extrudates is the large fluorescence background often encountered in catalytic solids. This makes analysis inside extrudates extremely challenging, especially since the pellet material is normally highly scattering. A new approach for characterizing catalyst extrudates has been found in Time-Resolved Raman Spectroscopy (TRRS) by means of an intensified CCD camera. It overcomes one of the major problems in the practical application of Raman spectroscopy in this field, the fluorescence background from side-products and the scattering nature of the extrudate material, and allows for the visualization of analytes at different depths. For extrudates the combination of TRRS with Surface Enhanced Raman Scattering (SERS) has been demonstrated to selectively characterize a region in the material using locally applied SERS nanoparticles. This provides additional spatial selectivity within the catalytic body, creating a basis for more detailed 3D studies of catalytic activity in industrially relevant settings.

(522) **Shell Isolated Nanoparticle Enhance Raman Spectroscopy (SHINERS) Using a Picosecond Excitation Source**; Wenbin Jiang[1], Gary Rayson[1]; [1]Department of Chemistry and Biochemistry. New Mexico State University[4]

Surface Enhancement Raman spectroscopy is a very powerful analytical method. It can provide rich structural information to help characterize or even identify molecules. There are two significant disadvantages to the application of SERS: lack of substrate generality and lack of measurement reproducibility. The deposition of a thin coating of SiO2 (4-10 nm) onto metal nanoparticles (e.g., Au) facilitates generation of enhanced Raman signals [1]. Shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) can well address these challenges. The present study involves excitation of surface plasmons using a novel picoseconds laser source using a fiber amplified telecom diode laser at 1552 nm (and its associated harmonics). Specifically, 2 ps pulses with 5 μJ peak energy have been used for generation of surface enhanced Raman spectra. Capabilities and limitations of this combination of source and substrate will be described. The implications of these results for analysis of environmental samples will be discussed.

[1] Zhong-Qun Tian, Jason R. Anema, et al. Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy: Expanding the

Versatility of Surface-Enhanced Raman Scattering. Annu. Rev. Anal. Chem. 2011. 4:129-150.

(523) **Detection and Identification of Influenza Virulence Factors**; Pierre Negri[1], Cheryl A. Jones[2], Stephen M. Tompkins[2], Richard A. Dluhy[1]; [1]Department of Chemistry, University of Georgia, [2]Department of Infectious Diseases, University of Georgia

We have developed a rapid, sensitive, and specific multiplexed SERS-based assay allowing detection, identification, and assessment of virulence factors associated with pathogenesis in influenza A virus. The assay consists of an oligonucleotide-based array immobilized on the surface of a SERS-active substrate that allows detection of various influenza RNA strains containing a gene mutation coding for the PB1-F2 protein associated with high virulence. Hybridization of the DNA probes to their complementary RNA sequences was probed using surface-enhanced Raman spectroscopy (SERS) and accomplished without amplification or labeling. The spectral signature due to their highly selective interaction was differentiated from that of the immobilized DNA probes alone or the DNA probes incubated with non-specific RNA targets and based on their intrinsic SERS spectra. Multivariate statistical methods were employed to differentiate the spectra of the complementary DNA probe-RNA target hybrid from those of non-complementary sequences. This approach has the potential to provide scientific foundation for the development of new screening methods critically needed for risk assessment in human influenza infections. The results demonstrate that bio-nanotechnology combined with vibrational spectroscopy has the ability to enhance both detection and diagnosis of emerging viral infections while allowing point-of-care testing in clinical applications to rapidly determine disease risk and the appropriate course of action to reduce its spread.

(524) **Improved Spatial Resolution in the Imaging of Biological Tissue using Desorption Electrospray Ionization**; Dahlia I. Campbell[1], Christina R. Ferreira[1], Livia S. Eberlin[1], R. Graham Cooks[1]; [1]Purdue University

Desorption electrospray ionization (DESI) imaging allows biomarker discovery and disease diagnosis through chemical characterization of biological samples in their native environment. Optimization of experimental parameters including emitter capillary size, solvent composition, solvent flow rate, MS scan-rate and step-size is shown here to improve the resolution available in the study of biological tissue from 180 μm to about 35 μm using an unmodified commercial mass spectrometer. Mouse brain tissue was used to optimize and measure resolution based on known morphological features and their known relationships to major phospholipid components. Features of approximately 35 μm were resolved and correlations drawn between features in grey matter (principally PS (18:0/22:6), *m/z* 834) and in white matter (principally ST (24:1), *m/z* 888). The improved spatial resolution allowed characterization of the temporal changes in lipid profiles occurring within mouse ovaries during the ovulatory cycle. An increase in the production of phosphatidylinositol (PI 38:4) *m/z* 885 and associated fatty acids such as arachidonic acid (FA 20:4) *m/z* 303 and adrenic acid (FA 22:4) *m/z* 331was seen with the postovulatory formation of the *corpus luteum*.

(525) **Forensic Analysis of Illicit Drugs and Trace Explosives using Ambient Pressure Ionization Mass Spectrometry**; Tim Brewer[1], Jennifer Verkouteren[1], Greg Gillen[1]; [1]National Institue of Standards and Technology

The detection of illicit drugs and trace explosives represents one of the most significant challenges for law enforcement and forensic communities. Of particular interest to the forensic analyst is the ability to rapidly identify suspected illicit drug materials and explosives residues in their native state (powder, tablet or liquid form), under atmospheric conditions and with a high level of specificity and sensitivity. Ambient pressure ionization techniques such as atmospheric pressure glow discharge (APGD), low temperature plasma (LTP), and desorption electrospray ionization (DESI) can effectively remove and ionize materials from most sample surface, including human skin, liquid and gas matrices under ambient conditions. Here a series of ambient pressure ionization techniques coupled with mass spectrometry are used and compared for the forensic analysis of a series of illicit drugs, over-the-counter pharmaceuticals and trace explosives. Characteristic mass spectra from each ambient pressure ionization technique are used for the comparison. These results highlight the techniques' ability to rapidly detect multiple species at once in ambient pressure without prior sample preparation and chromatographic separation.

(526) **DART-MS in Forensic Science: Synthetic Cannabinoids and Other Applications**; Jason Shepard[1], Rabi Musah[1], Marek Domin[2]; [1]University at Albany, SUNY, [2]Boston College

The emergence of numerous cannabinoid designer drugs have been tied to large spikes in emergency room visits and overdoses. Identifying these substances is difficult due to the myriad of closely related compounds, isomers, or analogs that come on the illegal market regularly as well as the requirement for extensive sample preparation/extraction in testing them. Direct analysis in real time mass spectrometry (DART-MS) employing collision induced dissociation (CID) conditions provided sub-structural information to characterize the various cannabinoid analogs, including instances with mixtures of active components, building off the idea that closely related compounds are likely to fragment in a similar fashion, but their structural differences will result in unique fragments that vary enough between the singular cannabinoids to serve as a means to uniquely identify each substance. Major fragments were predictable and relatable to core chemical sub-structure. Five different cannabinoid analogs/cannabinoid mixtures were identified in six illicit products and differentiated by their CID fragment patterns.

(527) **Schlieren Diagnostics of a Flowing Atmospheric Pressure Afterglow (FAPA) Ambient Desorption/Ionization Source**; Kevin P. Pfeuffer[1], Steven J. Ray[1], Gary M. Hieftje[1]; [1]Department of Chemistry, Indiana University

Ambient desorption/ionization mass spectrometry (ADI-MS) is a rapidly developing area in analytical science that offers numerous advantages over conventional mass spectrometric analysis. Traditional mass spectrometry ion sources, such as electrospray ionization (ESI) and matrix assisted laser desorption ionization (MALDI), require extensive sample preparation, which limits throughput when rapid analysis or screening is necessary. In contrast, ambient mass spectrometry reduces sample preparation time enormously, while maintaining the sensitivity and specificity associated with mass spectrometry. Well known ADI-MS sources include desorption electrospray ionization (DESI) and direct analysis in real time (DART), which are capable of desorbing and ionizing a wide variety of compounds directly from solid samples. Unfortunately, there remain numerous shortfalls associated with these sources, including poorly understood analyte desorption/ionization mechanisms, inconsistent analyte transport, and serious matrix effects. It would be desirable to study these shortcomings fundamentally. In discharge-based ADI-MS sources such as DART and the flowing atmospheric pressure afterglow (FAPA), the plasma support gas is responsible for desorption and ionization of the analyte; however, this gas is optically transparent, so a technique for visualization of the gas is needed. In the present study, schlieren imaging is utilized to render the plasma support gas visible and thereby to gain insight into mass-transfer phenomena from the sample to the mass spectrometer inlet. Schlieren imaging produces a spatial map in which intensity is proportional to the first spatial derivative of refractive index. Helium is often utilized as the support gas for plasma-based ADI-MS sources because of the high energy

(~20 eV) of its excited state. Conveniently, the refractive index difference between helium (1.000035) and air (1.000292) is substantial (0.000257), which simplifies use of schlieren imaging. A double-pass schlieren system has been constructed around an atmospheric-sampling time-of-flight mass spectrometer in order to gather plasma support-gas and ion-identity information simultaneously. Correlation of the two kinds of information will aid in improving reproducibility while elucidating mass-transport processes. Sample introduction through melting-point capillaries (MPCs) and sample surfaces will be examined. Both MPCs and surfaces affect the spread of helium flow, and optimal positioning for each will be described.

(528) **Femtosecond Laser Vaporization of Complex Molecules: Nonequilibrium Electrospray Ionization Preserves Noncovalent Interactions**; Robert Levis; [1]Center for Advanced Photonics Research, Temple University

The analysis of complex mixtures of macromolecules with no sample manipulation is an important capability for mass spectrometry and biological science. Such methods pave the way to imaging biomarkers directly from tissue, cells, and biological fluid. As a means to accomplish such analysis, the vaporization of biomarkers including lipids, sugars, and proteins from the solution phase and solid phase is performed using ultra-intense laser pulses. Vaporization with intensity of 1013 W cm-2 using a pulse duration of 80 fs results in an extraordinarily soft release method for mass spectrometry when combined with atmospheric pressure electrospray ionization. We will present an overview of the laser electropray mass spectrometry (LEMS) technique with application to analysis of biomolecules in the native state, determination of protein conformation in solution and solid phase, and prospects for imaging mass spectrometry. In this presentation, we will present our measurements of the intact state of proteins and other biomolecules after interaction with such ultra-intense laser pulses using pulsed deflection, time-of-flight mass spectrometry. The capability for directly determining the conformation of proteins (folded or unfolded) in a given solution or material using LEMS will be presented as will the prospects for quantitative analysis of biomarkers. Finally, the nonequilibrium release and droplet entrainment mechanism will be discussed to understand the laser vaporization experiments.

(529) **An Optical Fiber-Based Sensor Array For Multi-Elemental Analysis in Aqueous Environments**; Steven Kopitzke[1], Peter Geissinger[1]; [1]University of Wisconsin-Milwaukee

Both zinc and copper are essential nutrients to support life. However, at high concentrations both of these elements exhibit toxicity to the same species. Due to inappropriate disposal methods, these elements may enter environmental waterways. Consequently, the ability to accurately, easily and, when possible, remotely monitor these pollutants is crucial. The sensors described here offer applicable detection limits reflecting elemental toxicity and fast response times for real-time monitoring in aqueous environments. Sensing is based on the changes in the luminescence of sensor molecules when the analyte of interest is present. Many sensor regions can be created along a single fiber, offering the possibility of multi-analyte sensing with a single fiber. Each region on the fiber can be separated temporally allowing for a specific sensor to be measured. Our novel sensor design requires two perpendicularly laid fibers. The excitation of the sensor molecules is through the evanescent fields of the laser pulses propagating through the first fiber. The sensor luminescence pulses are coupled into the second fiber (also through evanescent fields) and detected at the end of that fiber. This allows for high spatial resolution of sensor arrays and, consequently, for a compact sensor platform. The sensor molecules employed here exhibit high specificity for either zinc or copper. While the copper sensor molecules are covalently attached to the bare fiber core, the zinc sensor requires impregnation within a polyethylene glycol diacrylate polymer. In order to match the fast response time (<30 sec) of the copper sensor, the zinc sensor matrix undergoes a microsphere templating procedure creating micro- and nanoscale channels within the polymer allowing for rapid transport of zinc to the sensor. The copper sensor is sensitive to low mg/L levels, whereas the zinc sensor can detect concentrations between 0.05 mg/L and 7 mg/L depending on the concentration of sensor molecules. Both sensors are easily regenerated and last approximately 3-4 weeks. While each sensor functions individually, an important point is that these sensors can be incorporated into an array for multi-analyte sensing. Current research has focused on developing a platform capable of monitoring zinc and copper simultaneously.

(530) **Fiber-Optic Probes with Microscale Optics**; Francis Esmonde-White[1], Cynthia Cipolla[1], Michael Morris[1], Robert Kennedy[1]; [1]University of Michigan, Dept. of Chemistry

Many applications in spectroscopy are moving towards small optical probes. Difficulties inherent in scaling optical systems down include the difficulty of assembling multiple small parts and encapsulating them into a small package while maintaining robust alignment. We have adapted the mature soft-lithography technology commonly used to fabricate microfluidic systems in order to directly fabricate optics on the tips of optical fibers. These monolithic microprobes enable tiny probes with complex optical designs, yet do not require rigorous optical micro-assembly steps. These probes can be used in a broad range of applications as modular detection systems, such as simplified optical detection modules in microfluidic platforms and as disposable probes for biomedical spectroscopy. We will present details regarding the design, fabrication and characterization of these probes, as well as specific applications in fluorescence and Raman spectroscopy. While these probes offer a novel and versatile method for creating modular probes, they also introduce a set of new challenges unlike those faced in traditional micro-optical systems. These new challenges and the approaches for overcoming them will also be discussed.

(531) **An Anisotropic Virtually Imaged Phased Array (VIPA) Spectral Disperser for Raman and Brillouin Spectroscopy**; Rajesh Morampudi[1], John Turner[1]; [1]Cleveland State University

The chemical conformation and mechanical properties of polymers are closely related to their functional capabilities and are important considerations when developing high performance devices such as artificial tissue implants and prosthetics. Noninvasive and nondestructive methods are needed to evaluate polymer performance during manufacture and use, which may include in-vitro and in-vivo testing. Raman scattering spectroscopy is ideal for nondestructively characterizing polymer composition, conformation, and crystallinity and requires little or no sample preparation, but mechanical properties such as elastic modulus are difficult to infer. Another type of inelastic scattering, Brillouin scattering, provides a more direct measure of sample elasticity and results from the interaction of light with time dependent optical density (refractive index) variations imparted by acoustic phonons. Brillouin scattering is, therefore, a useful method for quantifying mechanical integrity as well as characterizing other polymer properties such as piezoelectricity. Achieving the necessary spectral resolution for Brillouin spectroscopy (FWHM<<1nm) is challenging, and conventional grating monochromators are often replaced with cascade series of Fabry-Perot filters. A more recent technology, the virtually imaged phased array (VIPA) is capable of passbands well below 1nm and exhibits high angular dispersion. The compact device is not appreciably polarization sensitive and its use in demanding applications like wavelength division multiplexing has already been demonstrated. In the work presented here we demonstrate high

resolution Raman and limited Brillouin spectroscopy using a novel gold-film VIPA which allow us to indirectly measure the elastic (Young's) modulus of samples using Brillouin scattered light and to measure the long-range crystalline order using Raman scattered light. The VIPA design, theory, and data analysis are presented.

(532) **Low-Frequency Raman Spectroscopy - Enabling Affordable Access to the Terahertz Regime**; James Carriere[1], Frank Havermeyer[1]; [1]Ondax

Spectroscopic measurements of low-energy rotational/vibrational modes are of increasing interest for many applications, since these spectra can reveal unique and important structural information about a wide range of materials. These modes correspond to low-frequency Raman ($10cm^{-1}$ - $100cm^{-1}$) or Terahertz frequencies (300 GHz-3THz), that have been traditionally difficult and/or expensive to access through conventional techniques. We report a new, inexpensive, and highly efficient approach to gathering low-frequency Raman spectra on a broad range of materials, opening potential new applications and analytical tools for both chemical/structural analysis and detection. Terahertz spectroscopy can directly measure these low-energy modes by emitting radiation in the 300GHz to 3THz frequency range and detecting the corresponding absorption spectrum. However, source and detector availability and expense have limited the potential sensitivity, resolution, and/or economics of using this technique. Raman spectroscopy can also observe these modes (for Raman active materials) by exciting them with a more conventional visible or NIR laser and measuring the induced frequency shift in the $10cm^{-1}$ to $100cm^{-1}$ region. Unfortunately, traditional edge filters used to block Rayleigh scattered light remove most, if not all of these low-frequency Raman signals, as well as the entire anti-Stokes region. To capture these low-frequency Raman signals, multi-stage spectrometers (which don't require the edge filters) can be used, but they tend to be large and expensive, while significantly attenuating the overall Raman signal. Recent developments in ultra-narrow band notch filter systems can now bridge this gap in capability, and fully enable high-throughput, low-frequency Raman measurements in a compact, economical and easy to use system. We demonstrate the ability of these filters to measure low-energy rotational/vibrational modes in a variety of materials of interest to the pharmaceutical, homeland security, oil & gas and scientific communities. Example applications include phase discrimination in sulfur and polymorphic materials; measurement of surrogate compounds to high explosives and radionuclides in radioactive waste; localized temperature measurements of gases; and measurements of mono- and multi-layer graphene structures. These are all shown to exhibit characteristically different low-frequency Raman peaks that can be exploited for chemical analysis, identification, monitoring, contamination and defect detection.

(533) **The Multi-channel FTIR, a New Interferometer Solution for Fast and Pulsed Spectral Sensing**; Sascha Pierre Heussler[1], Herbert Oskar Moser[2]; [1]SSLS/NUS, [2]KIT/NES IMT

For about two decades, micro technology has demonstrated its capability to reduce the dimensions of analytical tools. The ability to miniaturize offers the attractive potential for science and industries to build small and cost-effective devices for application fields previously not conceivable with large size, lab-bound tools. Spectrometers, in particular, in the field of molecular spectroscopy, have benefited from this development, and a plethora of small, hand-held devices are currently being developed for applications ranging from quality control to the detection of glucose levels in blood serum. In their physical operation, most of these spectrometers are either based on the dispersion of a grating or on the shifting of the phase between two interfering beams as in the case of Fourier transform spectrometers with the latter having advantages with regard to signal-to-noise ratio and spectral range, but shortcomings concerning time resolution as discussed in literature. Here, we introduce an interferometer which overcomes such shortcomings. We name it the Multi-channel FTIR interferometer or spectrometer (MC-FTIR). Its core is a static, micro-machined, multi mirror array (MMA) that divides the incident beam into many sub-beams that are phase-shifted with respect to each other. Additionally, a lamellar grating structure acts as a wavefront division beam-splitter and reference plane for the phase. Both are merged together into one microstructure to form the MMA. Avoiding any moving parts, the MC-FTIR offers ultra-fast spectral sensing and single pulse detection capability. Set in a Czerny-Turner-like optical layout, the multi-channel FTIR lends itself to field deployable applications. We present a prototype spectrometer working in the mid-infrared spectral band from 1000 to 4000 cm^{-1} generating 1600 spectra per second at a spectral resolution of 100 cm^{-1}, currently, which can be upgraded to <10 cm^{-1} within our micromanufacturing process.

(534) **Role of Plasmon Interactions in Surface-Enhanced Raman Scattering Immunoassays Based on Labeled Gold Nanoparticles**; Marc Porter[1]; [1]University of Utah

Immunoassays based on surface-enhanced Raman scattering (SERS) are capable of ultralow level detection of antigens. This presentation describes the results from an in-depth analysis of the plasmonic coupling that is essential to the reliable application of this readout methodology. Results indicate that coupling between labeled gold nanoparticles (i.e., extrinsic Raman labels or ERLs) and a planar gold substrate, as well as between neighboring ERLs, play important roles in the strength and reproducibility of the response. Moreover, the extent of ERL-ERL plasmonic coupling and substrate-ERL coupling is affected by the presence of the antibodies immobilized on the two types of surfaces. Lower surface concentrations of antibodies lead to an increase in antigen binding capacity, which decreases the gap between the ERLs and substrate, and thereby increasing the SERS response. Interestingly, the formation of small ERL aggregates appears to also magnify the observed signal, but the formation of larger aggregates has the opposite effect. The implications of these results, which are also examined theoretically, will also be discussed.

(535) **What is "Robust Surface Chemistry" for LSPR Sensors?**; Amanda Haes[1]; [1]University of Iowa[4]

Monitoring the interactions between and functions of biological molecules in a personalized yet sensitive, specific, and quick manner for disease understanding and/or treatment is one of the ultimate goals in LSPR sensor development. Typically, antibodies and nucleic acids are used to facilitate detection specificity but are limited by their inherent binding affinity to target molecules, instability/tendency to denature in experimental conditions, epitope binding affinity changes when bound to solid substrates, limited availability and high cost, as well as storage limitations. In this presentation, bio-mimic surface chemistries will be exploited using engineered silica/polymer recognition layers. These surface chemistries will be compared to traditional receptor surface chemistries for small molecule detection using LSPR signal transduction. Applications related to the direct and quantitative detection of small molecules will be discussed. Improvements in understanding the relationship between robust nanoparticle surface chemistry and LSPR signal transduction will have ultimate implications on the detection of target biological and environmental toxins.

(536) **Spatial Control of Light at the Nanoscale Using Plasmonic Nanocrescents**; Cindy Cooper[1], Cara Barnes[1], Christopher Gore[1], Jennifer Shumaker-Parry[1]; [1]University of Utah

Noble metal nanostructures are of great interest due to their localized surface plasmon resonances (LSPR) and the resulting enhanced electric fields that have been exploited in both spectroscopic and

microscopic applications. Nanocrescents are of special interest due to their highly tunable physical structure as well as multipolar and polarization dependent resonance modes. Polarization dependence allows for the selective excitation of distinct resonance modes which occur over a broad spectral range and can be used to control the spatial location of field enhancement. This field enhancement can be further strengthened or spatially extended via coupling of adjacent fields. This interparticle coupling is currently the main focus of our research and utilizes nanocrescents in array organization. The fabrication procedures used to control nanocrescent structure and organization, the resulting plasmon resonance modes and implications for applications of these structures will be discussed.

(537) **Gold Plated Filters for Minimizing Time and Complexity of a SERS-based Immunoassay**; Jeremy Driskell[1], David Drake[1]; [1]Illinois State University

Immunoassays are standard bioanalytical techniques because of the specificity imparted by antibody recognition of target antigen. However, long incubation times that are required for analyte and label binding limit the utility of immunoassays for time sensitive analyses. To address this limitation, we explore the use of a porous antibody-modified gold plated filter membrane as a flow-through capture substrate to enhance antibody-antigen binding kinetics. A surface-enhanced Raman scattering (SERS)-based readout strategy was used to provide the requisite low level detection and potential for multiplexed analysis that is desirable for bioanalytical assays. A thin layer of gold is plated onto commercially available polycarbonate track-etched nanoporous membranes via electroless deposition. Capture antibody is immobilized onto the gold plated filter and functions as a capture substrate. A syringe is then used to actively transport the analyte and extrinsic Raman labels through the capture substrate. The fabrication of the gold plated membrane is thoroughly investigated and preliminary results establish proof-of-principle for the flow-through SERS-based immunoassay. Efforts to systematically investigate the effect of flow rate during sampling, labeling, and rinsing will also be presented.

(538) **Patterned Plasmonic Arrays with Differential Resonance for High-Performance SPR Analysis**; Quan Cheng[1], Matthew Linman[1], Abdennour Abbas[1]; [1]University of California Riverside

Surface plasmon resonance imaging (SPRi) has gained considerable interest in the BIA community. The ability of label-free multi-analyte interrogation and high throughput detection offered by SPRi has led to a wide variety of applications. However, there are still challenging issues for SPR imaging methods, in particular the acquisition of quality raw data/images. This talk discusses the new development in the design of high performing SPR biochips using lithographic approaches. The first example is the fabrication of patterned plasmonic arrays based on the spatial variation of the metal thickness and resonance confinement. The key innovation is the manipulation of the metal film to attenuate the evanescent field in the background area, while enabling the excitation of surface plasmons inside the desired patterns. The second method involves the etching of the glass substrate that induces a variation in the resonance condition and thus in the resonance angle between the etched wells and the surrounding area, leading to the isolation of the array spot resonance with a significant reduction of the background signal. Analytical performance of the two chips will be broadly discussed.

(539) **Ash Composition Analysis of Herbaceous and Woody Biomass Using Laser-Induced Breakdown Spectroscopy (LIBS)**; Tyler Westover[1], Garold Gresham[1], Richard Boardman[1]; [1]Idaho National Laboratory

As much as one-fifth of herbaceous biomass is composed of inorganic constituents, commonly known as ash. These inorganic components are important not only during the life of plants as nutrients but also affect numerous applications for harvested biomass materials. For example, in converting biomass to biofuels, the elements Si, K, Ca, Na, S, P, Cl, Mg, Fe and Al are particularly problematic and are known to influence reaction pathways, contribute to fouling and corrosion, poison catalysts, and impact waste streams. Current methodologies to measure the concentrations of these elements, such as inductively coupled plasma optical emission spectrometry/mass spectrometry (ICP-OES/MS) are expensive in time and reagents. This study demonstrates that a new methodology employing laser-induced breakdown spectroscopy (LIBS) can rapidly and accurately analyze the inorganic constituents in a wide range of biomass materials, including both woody and herbaceous examples. This technique requires little or no sample preparation, does not consume any reagents, and the analytical data is available immediately. In addition to comparing LIBS data with results from ICP-OES methods, this work also includes discussions of sample preparation techniques, calibration curves for interpreting LIBS spectra, minimum detection limits, and the use of internal standards and standard reference materials.

(540) **Uranium Isotope Detection in Standard Reference Material Glasses with femto-Second Laser Ablation Multicollector Mass Spectrometry**; Gregory C. Eiden[1], Andrew M. Duffin[1], Garret L. Hart[1]; [1]Pacific Northwest National Laboratory

Femtosecond laser ablation multicollector inductively coupled mass spectrometry (fs-LA-MC-ICPMS) is a powerful technique for direct analysis of solid samples, and we have utilized this technique to determine uranium isotope ratios in a series of standard reference material glasses (NIST 610, 612, 614, 616).

(541) **The Effect of Sample Composition on the Interaction between Laser Generated Aerosol and the ICP**; Luca Flamigni[1], Olga Borovinskaya[1], Joachim Koch[1], Detlef Günther[1]; [1]ETH Zurich

Since the early days of LA-ICP-MS, many efforts have been made to optimize ablation, aerosol entrainment and aerosol transport. Nowadays, modern laser ablation systems produce fine aerosols containing small particles (< 100 nm), which are efficiently transported by a stream of gas (argon or helium) into the ICP [1]. External calibration strategies employing matrix-matched standard reference materials are successfully applied for the quantification using LA-ICP-MS [2]. However, for the majority of real-life samples, no matrix-matched standard exists and therefore accurate quantification still remains a challenge. To overcome this problem, a better understanding of the physicochemical processes taking place during a LA-ICP-MS analysis is required. This work focuses on the role of the ICP in the matrix-effects encountered during LA-ICP-MS. Space- and time-resolved optical emission measurements were used to determine cloud size and to detect the onset of vaporization, which was found to depend on the sample matrix. Further, it was found that the sample material (matrix) contributes significantly to the shift of the vaporization onset. A computational approach based on the work by Horner et al. [3] was then applied to simulate melting, boiling and atomic cloud expansion of nanoparticles in a temperature gradient and the calculated results confirm our experimental findings. As an additional validation of the optical measurements, the duration of the signals originated from single ion clouds was measured using LA-ICP-MS. Consequences arisen from matrix-dependent diffusion-driven analyte losses in the plasma, which limit the accuracy of current LA-ICP-MS analyses, will be discussed in detail.

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(542) **Preparation of Surrogate Standards for Trace Element Analysis of Biological Tissues via Laser Ablation Inductively**

Coupled Plasma Mass Spectrometry; Jenee Jacobs[1, 2], R. S. Houk[1, 2]; [1]Iowa State University, [2]Ames Laboratory

Surrogate standards of biological matrices were investigated for elemental quantification in biological tissue samples using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). The main surrogate matrix examined was liquid egg whites. Liquid egg whites were spiked with various elements of interest (0-50 µg g-1), solidified via heating, and sliced into flat cylindrical discs. An ICP magnetic sector mass spectrometer (Element 1, Thermo) coupled with a femtosecond laser ablation system was used for analysis. Carbon-13 was used as an internal standard to accommodate for variation in the amount of material ablated. The liquid egg white surrogate standards exhibit homogeneity allowing for reproducibility. They also demonstrate strong correlation (R^2 > 0.98) and low limits of detection. The results of these surrogate standards as well as other possible biological matrices will be discussed.

(543) **Diagnostic and Modeling of Laser Induced Breakdown Spectroscopy Based on Optical Tomography**; Igor Gornushkin[1], Sergei Shabanov[2], Ben Smith[3], Nicolo Omenetto[3], Sven Merk[1], Alexander Demidov[1], Ulrich Panne[1, 4]; [1]BAM Federal Institute for Materials Research and Testing, [2]Department of Mathematics, University of Florida, [3]Department of Chemistry, University of Florida, [4]Humboldt-Universität zu Berlin, Department of Chemistry

In this work, diagnostics of laser induced plasma are carried out based on experimental data and plasma modeling. Abel inversion (AI) and Radon transform (RT) methods are used to reconstruct spatial distributions of plasma parameters, i.e. plasma temperature and densities of plasma species. The RT is used to reconstruct emissivity distribution in a single- (SP) and double-pulse (DP) laser induced plasmas. The orthogonal DP plasma is especially suitable for RT because it is intrinsically asymmetric. Additionally, symmetry of the SP plasma is investigated by comparing data from the multi-angle Abel inversion and Radon reconstruction. The multi-angle measurements are used to estimate the Abel reconstruction error. Time-resolved Radon reconstruction in white light is performed for the DP plasma to study the effects of ablated aerosol and asymmetric compression shock on the formation of air plasma. The observations are supported by computer simulations using a collision-dominated plasma model. The interaction of two orthogonal plasmas is also studied by spectrally resolved Radon reconstruction revealing the complex distribution of target and ambient species inside the plasma at all delay times investigated. Overall, it is demonstrated that Radon-based tomography is an informative tool to study transient asymmetric laser induced plasmas.

(544) **What Lies Beneath: Broadened Absorption Spectra of Biomolecules Exposed**; Hannah Wagie[1], Bradley Moran[1], Jörg Woehl[1], Peter Geissinger[1]; [1]University of Wisconsin-Milwaukee

Sprawling spectral bands in the UV–VIS region as seen for example in biomolecules are often considered inconvenient because they can obscure sharp transitions and blur identifying features. However, the broadening phenomena store a great deal of information on dynamical processes and structural properties of a system. We will describe line-narrowing spectroscopies such as hole-burning spectroscopy that allow for revealing individual components of broadened spectra. The transition energies of individual chromophores are homogeneously broadened, reflecting dynamical processes in their environment on time scales within the excited state lifetimes. The corresponding homogeneous linewidths show a strong temperature dependence. In addition, the chromophore transition energies may be distributed, because of structural disorder in the local chromophore environment , which in turn leads to the magnitude of the chromophore-host interaction to vary for different chromophore. This inhomogeneous line-broadening may be dominant, particularly at low temperatures. Moreover, the distribution of transition energies is not static, because structural relaxations of the chromophore environment may occur over long time scales and may change the transition energies. Broadened spectra contain a signature of each chromophore's immediate environment and can provide an energetic map of the wide range of matrix conformations. Line-narrowing spectroscopies can reveal homogeneous line shapes and provide access to information on chromophore-host dynamics, structure, and interaction. Proteins are rich and varied examples of such systems. A polypeptide matrix surrounding a functional active site provides the required specificity in environment for biological function. The distribution of charges around the chromophore (frequently the active site) gives rise to an internal electric field at the active site, which may be important for biological function. Hole-burning and single molecule spectroscopies allow for the determination of these internal electric fields. Moreover, a typical biological environment exists with great deal of physiologically meaningful conformational entropy; structural fluctuations may be important for biological function as well. This means that internal electric fields may fluctuate as well, but the biological relevance of these field fluctuations has largely been unexplored. We will discuss approaches to extract information on the electrostatic structure of the chromophore environment and how the field fluctuation may be measured.

(545) **Chemical Imaging Beyond the Diffraction limit: Experimental Validation of the PTIR Technique**; Andrea Centrone[1, 2], Basudev Lahiri[1, 2], Glenn Holland[1]; [1]NIST, Center for Nanoscale Science and Technology, [2]University of Maryland, Institute for Research in Electronics and Applied Physics (IREAP)

Photo Thermal Induced Resonance (PTIR), is a new technique that attracted great interest for enabling chemical identification and imaging with nanoscale resolution. PTIR uses a tunable pulsed laser for sample illumination in ATR configuration and an AFM tip in contact mode to measure the sample instantaneous thermal expansion induced by light absorption. Infrared spectra are obtained by plotting the amplitude of the tip deflection with respect to the laser frequency. Our set up requires placing the sample over an optically transparent prism. PTIR was previously used for nanoscale chemical characterization under the assumption that the PTIR signal is proportional to the energy absorbed. However, this assumption was not previously verified experimentally, nor was proved that PTIR can be used for quantitative chemical analysis at the nanoscale. In this work, electron beam nano-patterned polymer samples were fabricated directly on ZnSe prisms using customized adaptor pieces to evaluate the PTIR lateral resolution, sensitivity and linearity. The samples analyzed here can be grouped into 2 categories: samples with constant thickness patterned with features of various size and samples with variable height patterned with lines. Results shows that PTIR lateral resolution for chemical imaging is comparable to the lateral resolution obtained in the AFM height images, up to the smallest feature measured (100 nm). Spectra and chemical maps were produced from the thinnest sample analyzed (40 nm). Additionally, we demonstrate, for the first time, that the intensity of the PTIR spectra of thin films (< 1 µm) depends linearly on the sample thickness. This is arguably the most important contribution of this work since it proves that PTIR spectra and imaging can be effectively used for quantitative analysis at the nanoscale. Finally, by analyzing samples with an extended range of thicknesses we demonstrate that the PTIR signal is proportional to the local energy absorbed, to the thermal expansion and to persistence time of the thermal excitation in the sample, as previously predicted theoretically. We believe that our findings provide experimental evidence of PTIR usefulness, allowing its use for quantitative characterization in a variety of nanotechnology applications.

(546) **Nano-FTIR: Infrared Spectroscopic Chemical Identification of Materials at Nanoscale**; Florian Huth[1, 2], Alexander Govyadinov[1], Martin Schnell[1], Jesper Wittborn[3], Nenad Ocelic[2], Sergiu Amarie[2], Wiwat Nuansing[1], Fritz Keilmann[4], Rainer Hillenbrand[1], ; [1]CIC Nanogune Consolider, [2]Neaspec GmbH, [3]Infineon Technologies AG, [4]Dept. of Physics and CeNS, Ludwigs-Maximilians-Universität

Fourier-transform infrared (FTIR) spectroscopy is an established technique for characterization and recognition of inorganic, organic and biological materials by their far-field absorption spectra in the infrared (IR) fingerprint region. However due to the diffraction limit the conventional FTIR is unsuitable for nano-scale imaging or spectroscopy. Here we apply the principles of FTIR to the scattering-type scanning near-field optical microscopy (s-SNOM). The s-SNOM employs an illuminated sharp metallic tip to create a nanoscale hot-spot at its apex. The light backscattered from the tip transmits the information about tip's near-field interaction with the sample to the far zone where the FTIR spectra can be recorded. The result is a novel nano-FTIR technique, which is able to perform near-field infrared spectroscopy. We show that nano-FTIR is capable of nanosale resolved mapping of infrared phonon and plasmon spectra, even when employing the weak but broadand radiation from an incoherent thermal source. We further demonstrate that nano-FTIR can acquire near-field absorption spectra of molecular vibrations throughout the mid-infrared fingerprint region at a spatial resolution of 20 nm. To that end we employ a novel laser-based continuum source and perform spectroscopic imaging of a (poly(methyl methacrylate), PMMA), which is a typical polymer sample. Finally, we provide experimental and theoretical evidence that the near-field absorption spectra match well with conventional (far-field) FTIR absorption spectra. This relates, in particular, to the spectral line positions, line widths and line shapes, and therefore allows for direct chemical recognition of nanoscale materials by consulting standard FTIR databases. We envision that nano-FTIR will become a powerful tool for chemical identification of nanostructures, as well as for non-invasive measurement of the local free-carrier concentration and mobility in doped nanostructures.

(547) **Whispering Gallery Mode Imaging for Biomarker Detection**; Robert Dunn, Sarah Wildgen, Heath Huckabay; [1]University of Kansas

The confinement of light within transparent materials through total internal reflectance is well known and exploited in applications ranging from telecommunications to microscopy. This process can also lead to the efficient confinement of light within small optical resonators. When light is coupled into dielectric microspheres, resonances are observed at frequencies where the circumnavigation distance around the sphere is an integer multiple of the coupled wavelength. At these resonances, known as whispering gallery modes, light is efficiently coupled into and trapped within the resonator. Whispering gallery mode resonators are emerging as powerful platforms for the development of biosensors. These approaches take advantage of the dependence of the WGM resonant wavelength with effective refractive index. When sensing elements such as antibodies are immobilized on the resonator surface, binding of their associated antigen will alter the effective refractive index surrounding the resonator leading to shifts in the WGM resonance. This leads to a label-free approach for biosensing that offers many advantages. Recently we reported a method for detecting WGM resonances based on fluorescence imaging that overcomes many of the difficulties encountered when using microsphere resonators in sensing platforms. The approach takes advantage of the evanescent field created at the sphere surface upon excitation of a WGM resonance, which can excite fluorescent dyes attached to the outer surface of the resonator. When a particular sphere comes into resonance, an enhanced ring of fluorescence is observed which enables the WGM resonance from each sphere in the field of view to be simultaneously measured. This approach, therefore, potentially enables large scale multiplexed detection of biomarkers in a label-free format. We have demonstrated the utility this method by quantifying biomarkers of ovarian cancer in buffer, serum, and patient serum samples. Having validated the approach, we are currently working to maximize sensing performance and reduce interferences from non-specific binding. This work is progressing through several studies that range from single molecule fluorescence measurements of immobilized antibody orientation to thin film engineering at the nanometer dimension to increase resonator performance. Developments in these areas will be discussed.

(548) **IRENI - Synchrotron-based Wide-Field Infrared Spectrochemical Imaging at the Diffraction Limit**; Kathleen Gough[1], Carol Hirschmugl[2]; [1]University of Manitoba, [2]University of Wisconsin-Milwaukee

Synchrotron based spectrochemical imaging, as recently implemented at the Synchrotron Radiation Center in Stoughton, WI, demonstrates the new capability to achieve diffraction limited chemical imaging across the entire mid-infrared region. With IRENI, we overcome the trade-off between the number of pixels, acquisition time and signal-to-noise ratio by coupling multiple low-étendue synchrotron beams with a large FPA detector. The relevant advantages will be illustrated through results for our most recent work, with a particular emphasis on analysis of fresh, unfixed biological samples, primarily central nervous system tissues in healthy and diseased animal models, and live cell imaging. This new method, including source arrangement and optical design implemented in IRENI, advances the conceptual basis of IR imaging and is critical to achieving improvement in image quality compared to current state of the art. Many biochemical and biomedical studies require detection of changes that occur at the cellular and sub-cellular level. The spatial oversampling for all mid-IR wavelengths makes the IRENI data ideal for spatial image restoration techniques. Examples will be presented to show how diffraction-limited spectrochemical imaging can be achieved through Fourier-based deconvolution algorithms with well-defined PSFs. Further enhancements and the development of medium-cost instruments will create the opportunity for novel experiments in many disciplines and bring this tool into mainstream diagnostic laboratories.

(549) **Levitated Drops as Microreactors: How Far Did We Get?**; Alexander Scheeline[1], Edward Chainani[1], Khanh Ngo[1], Woo-Hyuck Choi[1]; [1]University of Illinois at Urbana-Champaign

Levitated drops are attractive candidates for use as microreactors. Their volume is a factor of 5 or more smaller than is typical of micro stopped flows. While mixing time for drops formed by fluids effusing from bundled capillaries or colliding droplets is of the order of a few seconds, modulation of an ultrasound field can accelerate mixing so that homogeneity is accelerated by at least a factor of 2. Mass transfer between gas and solution phases is facile. Most importantly for the study of reactions involving free radicals, there are no solid/liquid interfaces except by choice, e.g., when introducing electrochemical probes. We report our progress in developing optical and electrochemical diagnostics in levitated drops, and suggest directions in which this technology may develop.

(550) **Spectroscopic Analysis in Acoustically Levitated Droplets**; Merwe Albrecht[1], Jonas Schenk[1], Arne Stindt[1], Jens Riedel[1], Ulrich Panne[1, 2]; [1]BAM Federal Institute for Materials Research and Testing, [2]Humboldt-Universität zu Berlin, Department of Chemistry

In the field of droplet-based microfluidics acoustic levitation allows for contact-free handling of solid or liquid samples. Levitated droplets serve as microreactors and for contact-free handling of small sample volumes in the µL range and are therefore valuable for the design and development of miniaturized techniques in analytical

chemistry. Contamination and analyte adsorption at container walls are eliminated and the sample is easily accessible to analytical tools. The acoustic levitator enables online reaction monitoring and in situ investigations of concentration induced effects such as aggregation and crystallization. On the other hand, evaporation of the solvent, interactions with the surrounding atmosphere, and possible influences of the ultrasonic field have to be taken into account. The ultrasonic field is characterized by sound pressure measurements in this study. To analyze reactions in small sample volumes, time resolved and sensitive techniques are required. In this study, hyphenation of UV/Vis and Raman spectroscopy is used for simultaneous measurements to investigate the formation and aggregation of hydroxylamine reduced silver nanoparticles in levitated droplets. The sensitivity of Raman spectroscopy is increased by the application of nanoparticles for surface enhanced Raman scattering (SERS) and the colloidal solution is ideal for the investigation by UV/Vis spectroscopy. The coupling of the two methods allows for the investigation of the plasmonic properties of metal nanoparticles during their application for SERS, providing additional information on the interactions between SERS substrate and analyte molecules. In addition to aqueous solutions, imidazolium-based ionic liquids were used as solvent. They are suitable for the application in levitated droplet experiments because of their low vapour pressure and are intensively studied due to their adjustable properties like viscosity, polarity, and conductivity. A constant volume of the droplet is important for reliable reaction monitoring. However, interactions with the surrounding atmosphere have to be considered. Therefore, also the interactions of levitated ionic liquid droplets with the humidity of the surrounding air are investigated in this study.

(551) **Partial Coalescence of Charged Droplets for Reagent Delivery in Water-in-Oil Microfluidics**; Carina Minardi[1], Mazdak Taghioskoui[1], Kaveh Jorabchi[1]; [1]Georgetown University

Droplet-in-oil strategies have gained considerable attention in recent years. These developments aim at using small droplets as reaction vessels where chemical and biochemical reactions can be monitored in a high-throughput fashion. Potential applications for these technologies include high-throughput pharmaceutical screening and single-cell analysis. The general workflow in these strategies consists of three main steps: 1) pico- to nano- liter droplet generation, 2) reagent delivery to droplets, and 3) detection of reaction products in droplets. Here we focus on reagent delivery. An ideal delivery method must reproducibly inject multiple reagents into the droplets without a large change in droplet volume. Considering the minute size of the droplets, this entails delivery of pico-liter and smaller volumes. We present a novel approach for this task based on partial coalescence of oppositely charged droplets. In our approach, nano-liter droplets are generated in silicone oil by pulsing high voltage to a needle carrying a flow of reagent solution. The charged reagent droplets are repelled by the potential on the needle towards a recipient droplet in contact with a grounded electrode. At sufficiently high electric fields, the reagent droplet undergoes charge exchange with the recipient droplet upon collision, resulting in charge inversion of the reagent droplet. This leads to attraction of the reagent droplet by the needle, separating the two droplets prior to complete coalescence. In other words, the reagent droplet bounces off of the recipient droplet, injecting a fraction of its volume. The injected volume is characterized by extracting the recipient droplet from oil followed by mass spectrometric analysis. We demonstrate that the bouncing can reproducibly inject as low as 0.1% of the reagent droplet into the recipient droplet using a solution of amino acids in water. Moreover, the rate of volume transfer is controlled by bouncing conditions (e.g. reagent droplet velocity and charge exchange rate), which in turn are regulated by experimental parameters (e.g. oil viscosity and electric field). This provides tunability of the volume transfer rate. Furthermore, we have verified that the bouncing occurs for pico-liter reagent droplets, extending the applicability of this method to even smaller volume transfers.

(552) **Bioparticle Capture in a Sawtooth Dielectrophoretic Microchannel**; Paul Jones[1], Mark Hayes[1]; [1]Arizona State University

The objective of rapid bioparticle analysis has driven profuse and divergent analytical research over the past several decades. Much has been accomplished, but new techniques and applications continue to emerge. Such innovations may soon enable the development of rapid, on-site bioanalysis devices that improve the availability, accuracy, and scope of clinical diagnosis. Microfluidic electrokinetic approaches provide unique advantages over many entrenched diagnostic technologies, including short analysis times, microliter sample and reagent volumes, potentially low cost, and portability. The work presented here utilizes a single, continuous microchannel in which opposing electrokinetic and dielectrophoretic forces create multiple and distinct bioparticle traps. Specifically, it focuses on the isolation and concentration of bioparticles using DC insulator-based gradient dielectrophoresis in a converging, sawtooth-patterned microchannel. The channel design enables localized isolation and concentration of specific particles by exploiting variations in their characteristic physical properties. Experiments have succeeded in dielectrophoretic capture of human blood cells from dilute whole blood. Mature amyloid protein fibrils have also been captured and concentrated. In each case, reproducible capture occurred at specific locales within the sawtooth channel. Lastly, differentiable capture of three live Escherichia coli serotypes has been demonstrated.

(553) **Variability in Single Cell Phytoplankton Fluorescence**; Joseph Swanstrom[1], Tammi Richardson[1], Timothy Shaw[1], Michael Myrick[1]; [1]University of South Carolina

We are developing a phytoplankton classification method using multivariate optical computing (MOC) in which an imaging photometer in required. We have explored the source of measurement variability in our imaging photometer and characterized as many sources of variability due to instrumentation as possible. In this report, we show the dominant source of variability in the florescence signal of a single phytoplankton cell does not originate from instrumentation and is seven times greater than expected from photon counting statistics. Preliminary results indicate the source may originate from the phytoplankton cells themselves. Additional measurements exploring the individual phytoplankton "noise" will be presented. These include a study of the time-dependence of phytoplankton fluorescence, a determination of the autocorrelation function for fluorescence intensity, and a study of the dependence of this fluorescence variability with excitation intensity. Potential sources of the unexpected "noise" in phytoplankton fluorescence will be discussed.

(554) **Determination of Polymer Entities in Complex Systems using Near Infrared Spectroscopy And Chemometrics**; Yusuf Sulub, Ph.D.[1], James DeRudder, Ph.D.[1]; [1]SABIC

There has been increased need in recent years to develop polymers with myriad of properties that can be used in automotive, electronic, and construction businesses. To achieve this objective, chemical companies either have to develop new polymers or resort to blending several polymers. Most chemical companies resort to the latter because not only does it combine the individual polymer properties, this approach is less risky from a business standpoint and is easy to scale up and commercialize. However, because several components are blended into one product, there is a need to deploy a reliable, robust, precise and accurate measurement system that will determine the relative amounts of all the components within the blend. Near-infrared (NIR) is a widely used analytical measurement tool in chemical, pharmaceutical, petroleum, and agricultural industries. The technique requires little or no sample preparation and is nondestructive, reagentless, simple and fast. In addition, NIR

spectroscopy exhibits the capability to extract quantitative information of several species within a sample from a measured spectrum thereby making this approach ideal for multicomponent determination of complex matrixes. The principal drawback to this method is the occurrence of broad and highly overlapping spectral bands in the NIR region. In a complex sample, it is very unlikely that selective quantitative measurement can be made on the basis of a single wavelength. Consequently, quantitative information must be made on information at multiple wavelengths, thereby requiring the use of multivariate chemometric methods. The research presented here will examine the use of NIR combined with chemometrics to determine the amounts of a complex polymer blend that is composed of one single component and three copolymers.

(555) **Characterization of Mechanical Deformation in Crystalline Poly(ethylene) Films Using Vibrational Spectroscopy**; Gloria M. Story[1], R. Thomas Cambron[1]; [1]P&G

Plastic deformation of crystalline poly(ethylene) invariably produces changes in the morphology and crystalline properties of the material. Methods based on x-ray scattering, differential thermal analysis, density, isotropic index of refraction, infrared spectroscopy, and Raman spectroscopy have been developed. Each methodology yields a different estimate of crystallinity. Reports in the literature have shown differences by up to a factor of two on the same samples. No method has been demonstrated more accurate than others. However, it is widely accepted that trends observed within each measurement methodology can be used to rank crystallinity in polymer materials. In these experiments, we will describe the use of Raman spectroscopy, polarized mid-infrared imaging, and near-infrared imaging to characterize changes in film thickness, morphology, and crystallinity distributions in mechanically-deformed poly(ethylene) films.

(556) **Soil Analysis with Infrared Spectroscopy**; Hui Li[1]; [1]Bruker Optics, Inc

Parameters such as soil texture and organic matter are very important for us to assess soil quality. Soil texture, determined by the percentages of sand, silt and clay in mineral soil, controls physical processes like the drainage rate, water holding capacity and porosity, which affect root development and crop yields. Together, soil texture and organic matter content control key chemical reactions like the cation exchange capacity and the pH buffering capacity, which govern nutrient availability for crop uptake and fertilizer use efficiency. There is an increasing global interest in developing rapid, cost effective methods to measure those parameters and in turn use them to maintain and increase agricultural production while avoiding contamination of ground and surface waters by over-applications of fertilizers. Infrared spectroscopy has been used as one of the most promising techniques since multiple properties can be simultaneously determined with one single measurement which can be done within 1 minute. Research has been carried out in this field with both mid and near infrared spectroscopy; furthermore, both ATR and diffuse reflectance measurements have been studied with mid-IR. In this study we will analyze soil samples collected from farms across eastern Canada using both mid and near infrared spectroscopy and exploit which one is more suitable for in-field soil analysis to rapidly assess soil fertility without resorting to the use of laboratory techniques.

(557) **Real-Time Monitoring of a Continuous Pharmaceutical Blend Process by FT-NIR Spectroscopy**; Chris Heil[1], Dave Drapcho[1]; [1]Thermo Fisher Scientific

One of the challenges with continuous processing is attaining accurate, robust and timely analysis of key product components to guarantee the process is running in control. Process Analytical Technology (PAT) tools, such as NIR spectroscopy, overcome these challenges allowing the process to be monitored continuously in order to detect any out-of-specification conditions. This study shows how a NIR process analyzer, with fiber optic reflection probe, successfully monitored the API level of a pharmaceutical product exiting a continuous blender. Continuous processing has several key economic advantages when compared to batch processing including increased production capacity, reduced facility work hours and reduced cost of analytical tests. On-line analytics, such as NIR spectroscopy, are allowing quality control testing to be moved from the laboratory to the production line making real-time monitoring and control of continuous processes a reality.

(558) **Internal Multiple Scattering Hole Enhanced Raman Spectroscopy: Improved Backscattering FT-Raman Sampling in Pharmaceutical Tablets Utilizing Cylindrical -Conical Holes**; Peter J. Larkin[1], Matthew Santangelo[2], Slobodan Sasic[3]; [1]Bristol-Myers Squibb, [2]Pfizer Pharmaceuticals, [3]Vertex Pharmaceuticals

The benefits of Raman signal enhancement and improved measurement precision are demonstrated using 180° backscattering FT-Raman spectroscopy from drilled cylindrical-conical holes within pharmaceutical tablet cores. Multiple scattering of the incident laser light within the holes results in an increased Raman signal due to larger Raman sample volume. This is important for overcoming typical sub-sampling issues encountered when employing FT-Raman backscattering of heterogeneous pharmaceutical tablets. Hole depth and diameter were found to be important experimental parameters and were optimized to yield the greatest signal enhancement. The FT-Raman spectra collected using backscattering from cylindrical-conical holes is compared to typical 180° backscattering from flat surfaces using tablet cores of Excedrin® and Vivarin®. Raman chemical images are used to establish a representative sampling area. We observe a three- to five-fold increase in the Raman intensity and a two-fold improvement in the measurement precision when sampling from cylindrical-conical holes rather than classic backscattering from flat tablet cores. Self-absorption effects on analyte band ratios are negligible in the fingerprint region, but are more significant at the higher NIR absorbances found in the CH/OH/NH stretching region. The sampling technique will facilitate developing quantitative FT-Raman methods of pharmaceutical tablets using the fingerprint spectral region.

(559) **Ultrasound Enhanced ATR mid-IR Fibre Optic Probe for Spectroscopy of Particles in Suspensions**; Cosima Koch[1], Maria Reyes Plata Torres[1], Stefan Radel[1], Bernhard Lendl[1]; [1]Vienna University of Technology

Attenuated Total Reflection mid-infrared (ATR mid-IR) spectroscopy in combination with a fibre optic probe or an optical conduit probe, respectively, has successfully been used for in-line bioprocess monitoring. It currently allows for quantification of dissolved analytes like substrates or extracellular metabolites. Spectroscopic measurements of the cells themselves which give information on the physiological state of the cells, however, are not possible. We have successfully combined an ATR mid-IR spectroscopy with ultrasonic particle manipulation, which is a recognised technique for filtering and sorting of small particles or cells in suspension by acoustic standing waves. Placing an ultrasonic transducer directly opposite the ATR element of a mid-IR fibre optic probe, we are able to build up an acoustic resonator between them. By tuning the ultrasound frequency, we are able to actively keep yeast cells (*S.cerevisiae*) away from, or push them into, the evanescent field of the ATR element. Thus, we acquired spectra of the particles only, and of the medium only, respectively. Yeast cell undergoing nitrogen limitation during the fed-batch phase of fermentations change their chemical constitution by building and agglomerating storage carbohydrates (trehalose and glycogen). This is reflected by changes in the carbohydrate region of FTIR spectra. Results obtained during fed-

batch fermentations of *S. cerevisiae* (*strain: CBS 8340*) with the prototype in-line probe will be compared to reference spectra of samples drawn from the fermentation. Furthermore, HPLC-RI measurements were performed for identification and quantification of sugar content (trehalose, glucose, mannose) and correlated with spectral changes. Total protein and total carbohydrate content were determined as well.

(560) **Validating *in vivo* Transcutaneous Raman Spectroscopy of Bone for Humans**; Francis W. L. Esmonde-White[1]; [1]University of Michigan

Raman spectroscopy enables the non-destructive measurement bone properties. Over the past several years, Raman spectroscopy has been demonstrated for measuring the properties of bone in animal tissues, animal cadavers, human tissues, human cadavers, and even living animals. We have developed a methodology for validating non-invasive Raman measurements of bone in humans. These validation measurements involve measuring a transcutaneous Raman spectrum of the proximal tibia, followed by measurements of a nearby region of the proximal tibia bone exposed in vivo during a surgical procedure, and further follow up with comparison to Raman microscopy measurements of bone fragments recovered from a nearby region of the tibia. The transcutaneous and exposed-bone in vivo measurements use a low power density to minimize patient risk. Some of the difficulties and corresponding solutions for performing these in vivo measurements will be described, including safety precautions for integrating Raman spectroscopy into an operating room, and methods for dealing with the required room light during these long measurements (60+ second integration times).

(561) **Gone in 60 Milliseconds:Fast IR with a Planar Array Spectrograph**; Bruce Chase[1], Dan Frost[1], John Rabolt[2]; [1]Pair Technologies LLC, [2]University of Delaware

Infrared spectroscopy is a powerful tool for identification and quantitation of chemical species. By far, the most common instrumental approach to these measurements uses an interferometer. The performance and sensitivity of these FT-IR spectrometers is excellent and they have served as the workhorse for four decades. However, there are significant obstacles to measuring transient, non-repeatable events with an FT-IR. The use of focal planar array detectors in a dispersive spectrograph overcomes these difficulties. PA-IR (planar array infrared) spectrographs can be used to obtain spectra on timescales as short as a millisecond with a spectral coverage of 800 cm-1. The instrumentation and approach to these types of measurements will be described.

(562) **Following Catalytic Processes in both Solution and Solid State with Fast Time-Resolved Infrared Spectroscopy**; Michael W. George[1]; [1]University of Nottingham

This lecture will show how the combination of photochemistry and fast time-resolved IR (TRIR) spectroscopy initiated either photochemically or thermally in both the solid state and in conventional and supercritical fluids is used to shed new light on chemical processes. Fast time-resolved infrared Spectroscopy is a powerful tool for the detection of reaction intermediates and the elucidation of reaction mechanisms. Examples will be given following reactions on a range of timescales ranging using either transmission or diffuse reflectance. Examples will include Organometallic Alkane Complexes [1], Noble Gas Complexes [2] and C-H Activation [3] together with the interrogation of electron transfer and isomerisation processes inside MOF environments. [4]

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Process in both Solution and Solid State with Fast Time-Resolved Infrared Spectroscopy

(563) **Infrared Spectroscopic Imaging: the Next Generation**; Rohit Bhargava[1]; [1]University of Illinois at Urbana-Champaign

Infrared spectroscopic imaging promises the best capabilities of optical microscopy and vibrational spectroscopy. Here we present the state of the art in technology and explore emerging trends. In particular, we describe the effect of theory and simulation on the design and validation of instruments. We first describe a new theoretical framework based on scalar wave theory that allows for the design of optimal instruments and enables new capabilities. We also describe how spectral properties of domains in complex materials or samples with or nano- to micron- scale dimensions affect the recorded data. The relationship between structure and properties can now be predicted and the framework used to recover absorption and morphology from recorded data. In summary, integration of new understanding with instrumentation can provide the next phase of development for both spectrometers and for our understanding of data they acquire.

(564) **Towards Portable Diagnostics: Development of Colloidal SERS Assays**; Patrick Johnson[1], Ashley Driscoll[1], Jing Neng[1], Hao Zhang[1]; [1]University of Wyoming

Colloidal based SERS bioassays have distinct advantages for use in portable diagnostic systems. Nanoparticles in solution allow for both a freely diffusing sensor surface and a high surface area to volume ratio. Therefore colloidal systems are not impacted by mass transfer limitations, allowing for the rapid analysis of small sample volumes. In addition, paramagnetic capture assay schemes provide both separation and concentration mechanisms, minimizing signals from non-specific interactions. Recent developments in the fabrication of gold-coated magnetic nanoparticles provide an alternative single nanoparticle assay scheme. The nanoparticles function as SERS substrates while simultaneously allowing for manipulation by a magnetic field. Detection strategies have been demonstrated for the sensitive detection of Rift Valley Fever virus and West Nile virus nucleic acids and proteins in multiplexed formats. In addition, considerations of the advantages of using colloidal systems over surface-based systems for biological assays will be discussed through insights derived from modeling.

(565) **Novel Detection of MRSA using Surface Enhanced Raman Scattering (SERS)**; Mhairi Harper[1], Karen Faulds[1], Duncan Graham[1]; [1]University of Strathclyde

Surface enhanced Raman scattering (SERS) is an optical spectroscopy technique which has become competitively exploited as a DNA detection method. SERS is a hugely beneficial technique owing to its multiplexing capabilities, low sensitivity and the molecularly specific identification which can be obtained. Thus, the development of SERS as a quantitative analytical method, in particular for the detection of DNA, has rapidly progressed. We have developed a novel assay which detects specific DNA sequences through the exploitation of SERS. The principle of the assay is based on the generation of a SERS signal following sequence specific hybridisation and enzyme digestion to qualitatively determine the presence of specific target DNA. A combination of a TaqMan assay coupled with SERS achieved accurate and sensitive detection of methicillin-resistant Staphylococcus aureus (MRSA) sequences. Through use of the beneficial insight we have into the effects of SERS, low picomolar concentrations of target has been detected to

date, however, lower detection limits are currently being progressed. The assay has also been designed to enable the potential for multiple strains to be identified within a single sample.

(566) **Identifying the Genetic Markers of Highly Pathogenic Influenza by SERS**; Richard Dluhy[1]; [1]University of Georgia

There are several highly pathogenic influenza strains that are able to infect humans and are considered as potential precursors for future influenza pandemics. Unfortunately, to date there is no rapid and multiplexed method to screen for the biochemical markers of influenza virulence. A high sensitivity method capable of identifying and classifying highly pathogenic influenza would impact areas such as biomedical diagnostics, vaccine development and bioterrorism security. We have developed a rapid, sensitive, and specific SERS-based assay allowing detection, identification, and assessment of virulence factors associated with pathogenesis in influenza virus. The assay consists of an oligonucleotide-based array immobilized on the surface of a Ag nanorod substrate that allows detection of various influenza RNA strains containing a gene mutation coding for the PB1-F2 protein associated with high virulence. Hybridization of the DNA probes to their complementary RNA sequences was probed using surface-enhanced Raman spectroscopy (SERS) and accomplished without amplification or labeling. The spectral signature due to their highly selective interaction was differentiated from that of the immobilized DNA probes alone or the DNA probes incubated with non-specific RNA targets and based on their intrinsic SERS spectra. Multivariate statistical methods were employed to differentiate the spectra of the complementary DNA probe-RNA target hybrid from those of non-complementary sequences. This approach has the potential to provide scientific foundation for the development of new screening methods critically needed for risk assessment in human influenza infections. The successful development of a rapid and sensitive method for screening of highly pathogenic influenza virulence factors would significantly improve our ability to identify emerging strains with a risk of high mortality, and allow public health professionals to effectively respond to prevent widespread infection and/or death.

(567) **Challenges in Moving SERS-based Diagnostics from the Analytical Chemistry Laboratory to the Clinic**; Marc Porter[1]; [1]University of Utah

Several research laboratories around the globe are examining the merits of surface-enhanced Raman scattering (SERS) as a new addition to the bioanalytical sciences toolbox. Impetus for these efforts reflects, in part, the ever-increasing demand for ultrasensitive, high-speed diagnostic tests with respect to platforms for cancer, infectious disease, and homeland security. However, fully harnessing the potential detection advantages of nanotechnology-based phenomena like SERS still faces many of the obstacles that have plagued the performance of most traditional diagnostic methodologies like ELISA and microarrays. This presentation will describe several of the challenges our laboratory has encountered in attempting to develop platforms and readout methodologies that couple nanometric labeling concepts with surface-enhanced Raman scattering and giant magnetoresistance readout methodologies. Examples include the dependence of performance with respect to sample matrix (e.g., serum, urine, and cerebral spinal fluid); nonspecific adsorption and cross reactivity; and sample storage/stability, preparation, rinsing and other processing steps. How several of these factors affect analytical metrics of performance (e.g., analytical and clinical sensitivity) will be discussed.

(568) **Alternative Desorption/Ionization Processes of Low-Temperature Plasma Probe Mass Spectrometry**; Joshua Wiley[1], Jobin Cyriac[1], Jacob Shelley[1], R. Graham Cooks[1]; [1]Purdue University

Plasma-based ambient ionization mass spectrometry has been an emerging field since its onset with direct analysis in real time (DART). Of the many different ambient ionization techniques, nearly one third take advantage of the excellent ionization capabilities of various ambient discharges. While little work has focused on elucidation of desorption mechanisms for the various plasma-based ambient ionization sources, literature suggests that many have thermal desorption as the only relevant mechanism with no apparent evidence for non-thermal desorption mechanisms. Furthermore, it is widely believed that thermal desorption is followed by commonly-known atmospheric pressure chemical ionization (APCI) reactions, such as proton and charge transfer from capable reagent ions (formed from ambient air molecules in the discharge). The work at hand suggests that non-thermal desorption processes take place with an ambient plasma ionization source in addition to the widely accepted thermal desorption. In this study, a room temperature plasma known as the low-temperature plasma (LTP) probe was used in conjunction with a Thermo LTQ ion trap mass spectrometer to examine various non-volatile samples. Samples ranged from thermally stable self-assembled monolayers (SAMs) to pre-charged organic salts to long chain polymers. Ions were detected in the mass spectrum for the LTP interrogation of each category of non-volatile sample. For the SAMs and the long chain polymers, the desorption process necessarily involved breaking chemical bonds through a higher energy process. Fragments of nonvolatile pre-charged samples were also readily detected with LTP-MS. An attempt to explain the non-thermal desorption process will be presented through correlation of the types of molecules that were capably desorbed/ionized and the spectra acquired for each. Further mechanistic elucidation will also be discussed through the interpretation of studies in which the sampling environment was controlled and varied in terms of temperature and gas composition.

(569) **Nanoscale Molecular Cartography: Towards Combined Topographical and Chemical Imaging using Atomic Force Microscopy and Mass Spectrometry**; Olga S. Ovchinnikova[1], Gary J. Van Berkel[1]; [1]Oak Ridge National Laboratory

There exists a clear need to extend the limits of our understanding of chemical and physical phenomena of materials and biosystems at the nanoscale. Currently available techniques usually face a trade-off between spatial resolution and chemical information. The goal of atmospheric pressure chemical imaging at the nanometer scale with mass spectrometry has been until now approached by our group using near field effect laser desorption and proximal probe thermal desorption for surface sampling followed by a secondary ionization process like electrospray. Each of these sampling approaches can be coupled with an AFM platform to give a multimoldal, physical and chemical, imaging platform. The thermal desorption approach allows for the easy scaling of the technique all the way from the millimeter to the nanometer regime. In the nanometer regime an AFM platform with silicon based heating AFM probes is used to locally desorb material from a surface with ~250 nanometer spatial resolution. The latest results from our group in these two areas will be presented. The future of all these techniques and the potential of high resolution chemical imaging via mass spectrometry using other sampling approaches combined with AFM will be discussed. This work was supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, United States Department of Energy. ORNL is managed by UT-Battelle, LLC for the U.S. Department of Energy under contract DE-AC05-00OR22725.

(570) **Characterization and Application of Microplasma Devices for Ambient Mass Spectrometry and Surface Analysis**; Joshua Symonds, Reuben Gann, Thomas Orlando; [1]Georgia Institute of Technology

In ambient mass spectrometry, ionization sources with broad chemical compatibility, low fragmentation, and high reliability are

one of the keys necessary to enable effective and rapid analysis of unknown samples. One such approach, employing ambient-pressure electrical discharges broadly termed "microplasmas," has demonstrated itself to be a promising technique with a variety of successful applications and results. This class of devices holds a competitive edge over alternative ionization methods when cost and portability are a concern: microplasmas typically require only modest electrical power and minimal gas flows to operate. We have developed our own such devices and methods, and look more closely into the physical nature of what makes particular designs successful. We focus on using these devices to perform mass spectrometry imaging in tandem with optical microscope imaging of samples at ambient pressure. Additionally, we investigate a specific use of microplasmas for the production of VUV photons, another highly effective ionization source.

(571) **Paper Spray Ionization Mass Spectrometry Mechanism: So much more than a Variant of Electrospray**; Ryan Espy[1], Ariel Muliadi[1], Zheng Ouyang[1], R. Graham Cooks[1]; [1]Purdue

Paper spray is an ambient ionization method used for analyzing complex mixtures by mass spectrometry. As an ambient ionization technique, paper spray analyzes samples in their native environment in the open air external to the mass spectrometer, with no sample preparation or pre-separation required. New Images and droplet size experiments show that paper spray operates under two distinct spray modes. Mode 1 is described as a solvent-rich system which creates multiple Taylor conejets and subsequently produces multiple droplet sizes. Mode 2 is a low solvent flow rate, higher current (1 uA) source which is characterized by a Taylor conejet and corona discharge. Distinguishing features in both modes of paper spray are the influence of the microfiber structures to create a field-enhanced spray, as well as a fixed droplet velocity independent of droplet size. The cause of these unique spray modes and potential applications will be discussed.

(572) **Paper-SAW: Surface Acoustic Wave MEMS Devices for the Rapid Aerosolization and Ionization of Liquid Samples**; David Go[1]; [1]University of Notre Dame

While surface acoustic wave devices have been around for the better part of four decades in applications ranging from electronics communications to gas sensing, these microelectromechanical systems (MEMS) have also been recently developed as ionization sources for mass spectrometry. A surface acoustic wave is a high-frequency (~MHz) mechanical wave that propagates on the surface of a piezoelectric crystal. When the wave interacts with a liquid droplet or film, it can cause the liquid to stream, and at sufficient energy, disperse into droplets that, notably, carry charge. This has been termed surface acoustic wave nebulization (SAWN) and can be used as an atmospheric pressure ionization source for mass spectrometry akin to the classic electrospray ionization technique. Further, SAWN can be easily coupled to paper devices that serve as a simple and rapid sample delivery platform. Since the paper has natural filtering properties, raw samples, such as blood and plasma, can be directly analyzed using a paper-SAW approach. This talk will discuss the fundamental mechanisms of the coupling of paper to SAW devices for ambient ionization. Using high-speed imaging, SAW was revealed to pump fluid out of the paper to create a thin liquid film on the SAW substrate. Different regimes of liquid film development, from a stable film through the progression to droplet formation were identified and compared to a simplified analytical model. The implications of these studies will be discussed within the context of ionization and utilizing paper-SAW for ambient mass spectrometry.

(573) **New Directions in Plasmonic Materials and SERS Applications**; George Schatz[1]; [1]Northwestern University

This talk will describe a number of advances in the development of plasmonic materials with emphasis on substrates for SERS and its applications. While anisotropic nanoparticles have long been of interest for SERS applications, an important new generation of SERS substrates is based on gold nanoparticles with a small gap (<1nm) as this leads to enhancement factors of >10^8, the structures can be stabilized using silica shells, and they can used for both solution and surface-based measurements. The talk will discuss some of the fundamental theoretical issues involved underlying SERS for these structures, and it will describe recent applications using these and other substrates for analytical applications.

(574) **Localized Surface Plasmon Resonance Properties of Gold Nanoplates Coupled with Gold Nanopartcles at Edge Sites**; Francis Zamborini[1], Lanlan Bao[1], Srinivas Beeram; [1]University of Louisville

We recently developed a method for the synthesis and purification of Au nanoplates grown directly on surfaces by a chemical seed-mediated growth method. A ligand-exchange reaction led to the selective attachment of antibodies to the edges of Au nanoplates as determined by atomic force microscopy (AFM). The localized surface plasmon resonance response (LSPR) of the Au nanoplates is significantly more sensitive to antibody (and subsequent antigen) binding on the edges of nanoplates compared to terraces. Using the same ligand-exchange reaction, we recently attached Au nanoparticles selectively onto the edges of the purified Au nanoplates. Through controlling the exchange time, we have selectively attached Au nanoparticles to the vertices, edges and the terraces of the nanoplates. The attachment of Au nanoparticles onto the edges of the Au nanoplates led to strong plasmon coupling between the nanostructures and a red shift in the LSPR band. This research provides a better understanding of the effect of binding location and particle-particle coupling location on the optical properties of the metal nanostructures for optical-based sensing and plasmonics applications.

(575) **Sensing of Nucleic Acids using Fluorescent Plasmonic Core-Shell Nanoparticles**; Denis Boudreau[1], Olivier Ratelle[1], Marie-Christine Dorais[1], Luc Rainville[1], Danny Brouard[1], Félix-Antoine Lavoie[1]; [1]Département de chimie and Centre d'optique, photonique et laser (COPL), Université Laval

Photophysical studies of metal nanoparticles and their application to the design of optical nanoprobes is an active field of research. In particular, it has been shown that the range and efficiency of Förster resonant energy transfer (FRET) can be enhanced in multilayer core-shell nanoparticles, and that plasmonic coupling of shell-encapsulated dyes with the metal cores increases their brightness and photostability for bioanalytical detection at ultralow concentration levels [1]. In this presentation, we will present the progress accomplished in the synthesis, characterization and application of multilayer core-shell plasmon-enhanced fluorescent nanoprobes. In particular, we will describe how these highly luminescent nanoparticles can be used for the ultrasensitive detection of DNA material from clinical samples. This detection scheme is composed of core-shell multilayer dye-doped acceptor nanoparticles (NP) grafted with ssDNA probes and complexed with a cationic conjugated polymer (CCP) donor. This approach exploits the transduction mechanism of the CCP based on intensity and spectral changes in absorption and luminescence caused by conformational changes upon electrostatic binding to DNA strands. Each hybridization event is signalled by a potentially large number of excited reporters following the plasmon-enhanced energy transfer between the target-activated polymer and fluorophores embedded in the silica shell [2,3], thereby amplifying the optical signal generated by DNA hybridization events and improving the overall detection sensitivity. Photophysical properties of this system were studied by time-resolved and steady-state fluorescence, imaging flow cytometry and darkfield microscopy. Furthermore, results on the application of this sensing scheme to the detection of specific

sequences from human genomic DNA extracted from clinical samples will be presented.

[1] M.L. Viger, M. Rioux, L. Rainville, D. Boudreau, "FRET Enhancement spot in Multilayer Core-Shell Nanoparticles", Nano Letters (2009) 9, 3066-3071. [2] D. Brouard, M.L. Viger, G. Bracamonte, D. Boudreau, "Label-Free Biosensing Based on Multilayer Fluorescent Nanocomposites and a Cationic Polymeric Transducer", ACS Nano (2011) 5, 1888-1896. [3] M.L. Viger, D. Brouard, D. Boudreau, "Plasmon-Enhanced Resonance Energy Transfer from a Conjugated Polymer to Fluorescent Multilayer Core-Shell Nanoparticles: A Photophysical Study", J. Phys. Chem. C. (2011) 115, 2974-2981.

(576) **Plasmonic Properties of Silver Nanocube Monolayers on High Refractive Index Substrates**; Anatoli Ianoul[1], Adam Bottomley[1], Daniel Prezgot[1], Alyssa Staff[1]; [1]Carleton University

Extinction spectra of nanocubes supported by a symmetry breaking dielectric substrate are very different from those in solution. In this work we varied the refractive index of the substrate in order to optimize the refractive index sensitivity (RIS) of supported silver nanocube monolayers. We found that on thin (5-7 nm) silicon films the RIS is characterized by the figure of merit (FOM) for the quadrupolar plasmonic mode as high as 5.0, making silicon supported silver nanocube monolayers a promising sensing platform.

(577) **Competitive Organothiol and Protein Adsorption onto Gold Nanoparticles**; Karthikeswar Vangala[1], Siyam Ansar[1], Dongmao Zhang[1]; [1]Mississippi State University

Protein and organothiols are known to have high binding affinity to gold nanoparticles (AuNPs). Extensive research has been conducted to study protein interaction with AuNPs, organothiol interaction with AuNPs and protein interaction with organothiol functionalized AuNPs. We recently studied organothiol interaction with protein functionalized AuNPs. Presented in this work is our study on the competitive protein and organothiol interaction with AuNPs in which protein and organothiol are added simultaneously into colloidal AuNP solutions. Bovine serum albumin (BSA) was used as the model protein, and a series of thiopurines and endogenous amino acids including cysteine, homocysteine and glutathione as model organothiols. The thiopurines differ in the position and/or the number of thiol or amino groups attached to the purine ring. Time-resolved UV-Vis, dynamic light scattering, and time-resolved surface enhanced Raman spectroscopic measurements were used to study the competitive protein and organothiol binding onto AuNPs. It was found that the stability of AuNPs in protein and organothiol mixtures depends strongly on structure and concentration of organothiols. Those results provide critical new insight regarding the kinetics and thermodynamics of protein and organothiol binding to AuNPs.

(578) **Spatial Heterodyne Raman Spectrometer for Wide-Area Standoff Detection**; Mike Angel, Nathaniel Gomer, Nirmal Lamsal; [1]Univ. of South Carolina, Dept. of Chem. & Biochem

NASA has stated a desire for small, space-flight capable instruments with minimal or no moving parts to detect organic molecules and biomarkers on other planets. Raman spectroscopy is an ideal technique for this application and a standoff instrument is desirable to maximize the measurement area. Recently we developed a new type of FT- Raman spectrometer, the Spatial Heterodyne Raman Spectrometer (SHRS). The SHRS does not require an entrance slit and has a large optical etendue, can resolve off-axis contributions up to 10° and has no moving parts. The SHS measures all optical path differences in its interferogram simultaneously with a detector array, so the technique is compatible with gated detection using pulsed lasers, important to reject ambient background and mitigate fluorescence that might be encountered on a planetary surface where samples are uncontrolled. In the SHRS the spectrum is heterodyned around the laser wavelength, making it particularly suitable for Raman measurements. UV Raman is a particular technical challenge for space applications because dispersive (grating) approaches require large spectrographs and very narrow slits to achieve the spectral resolution required to maximize the potential of Raman spectroscopy. The heterodyne approach of the SHS has only a weak coupling of resolution and throughput, so a high resolution UV SHS can both be small, and employ a wide slit to maximize throughput. This talk will include a brief overview of standoff Raman detection, and will focus on wide-area measurements using the SHRS.

(579) **Vapor Generation - Make it Your Second Thought for Sample Introduction**; Ralph Sturgeon[1]; [1]National Research Council of Canada

The overwhelming majority of samples interrogated by atomic spectrometry are presented in their liquid form for introduction into the various sources. Although minimally demanding of resources and advantageous from a throughput perspective, direct nebulization and aerosol formation is inefficient in its utilization of analyte. Not only does typically more than 95 % not reach the source, enhancement of detection power or pre-treatment strategies undertaken to reduce matrix effects or spectroscopic interferences require significant intervention by the analyst. With a similar expenditure of resources, conversion of many analytes to stable atomic or molecular forms can be accomplished that simultaneously achieves all of these objectives. The modern toolbox of vapor generation techniques has expanded in the past 40 years to encompass an enhanced suite of elements, including several transition and noble metals, making VG an attractive alternative for many practical analytical problems. The field of VG will be briefly reviewed and several of the more recent, intriguing approaches arising from our laboratory highlighted.

(580) **Investigating the Performances of Transition Metal Cyanide Complexes for Determination of Cadmium by Vapor Generation ICP-MS**; Zikri Arslan[1], Vedat Yilmaz[2], LaKeysha Rose[1]; [1]Jackson State University, [2]Erciyes University

Vapor generation is an attractive approach for determination of hydride/vapor forming elements by atomic spectroscopy techniques. The generation of cadmium vapor is a challenging task unlike that for many other hydride/vapor forming elements. Difficulties mainly associate with the inefficient vapor generation and interferences of transition metal ions, such as Cu and Ni. Chelating or complexing agents have been utilized to alleviate the interferences. Nonetheless, vapor generation has not been a robust approach for cadmium determinations due to the inherent difficulties demanding either standard additions analysis or control of matrix precisely for accurate results. In this study, the performances of cyanide complexes of several transition metal ions, including Ti, V, Cr, Mn, Co, Ni, were examined for generation of cadmium vapor. Studies were conducted with off-line and on-line approaches. In the former, cyanide complexes of particular metal ions were prepared and reacted with the acidic sample solutions. In the latter, aqueous solutions of the metal ions were reacted with potassium cyanide solution and then interacted with acidic sample solution. Cadmium vapor was generated by reaction of the reaction contents with $NaBH_4$. Experimental variables, including sample acidity, concentrations of the transition metal ions and potassium cyanide solution, sodium borohydride solution were examined. The results indicated that cyanide complexes of Ti, V and Cr performed better than those of Co, Mn and Ni. An improvement up to a factor 20-30 was achieved. The interferences from transitions metals ions including, Co, Cu, Fe, Mn, Ni, and Zn were not significant up to 0.5 µg/mL levels. No interferences were observed from alkali and alkaline earth elements up to 1000 µg/mL levels. The method was applied to the determination of Cd from seawater and various calcium-rich samples by ICP-MS.

(581) **"Microarc" Discharge for Solution Sampling into an Inductively Coupled Plasma Mass Spectrograph**; Jeremy Felton[1], José A. C. Broekaert[2], Steven J. Ray[1], Roger P. Sperline[3], M. Bonner Denton[3], Charles J. Barinaga[4], David W. Koppenaal[4], Gary M. Hieftje[1]; [1]Indiana University, [2]Universität Hamburg, [3]University of Arizona, [4]Pacific Northwest National Laboratory

An argon direct-current microarc discharge is utilized for introducing microliter volumes of solution samples into an inductively coupled plasma (ICP) mass spectrograph. The discharge is sustained between a filament cathode, which acts as a sample loop, and a rod anode. Sample loops can be designed to hold as little as 1 µL of a solution, which is dried after being deposited onto the sample loop. Dried salts of sample solutions are removed from the cathode by the discharge through both thermal and sputtering processes and sent directly into the ICP. Signals produced by this discharge are transient in nature and are about five seconds in duration. Reproducibility, detection limits, and isotope-ratio precision of signals generated by this method will be discussed.

(582) **prepFAST Inline Auto Calibration, Variable Auto Dilution, and Auto QC Dilution for ICP and ICPMS**; Nathan Saetveit[1], Paul Field[1], Austin Schultz[1], Daniel Wiederin[1]; [1]Elemental Scientific

New ICP and ICPMS sample introduction instrumentation that performs inline auto calibration, variable auto dilution, and auto QC dilution is described. Dilution has long been a primary approach to many problems with sample introduction for ICP and ICPMS. Manual dilution is a time-consuming and contamination-prone process that uses excess chemicals and lab resources. Some "online" dilution systems require additional sample handling and separate vials to perform dilutions. This method is excessively slow and prone to failure due to vial contamination. The prepFAST, a recent advance in FAST sample introduction technology, performs inline variable dilution that overcomes the limitations of manual dilution or "online" dilution in a separate vial. Undiluted sample is loaded into the sample loop where high purity syringe pumps push carrier, diluent, and internal standard at variable flow rates to achieve the desired dilution. Custom valve designs provide low dead volume mixing at variable dilution factors up to 200x. The prepFAST can operate in various modes of automated, inline dilution. For example, all samples and standards may be auto diluted by the same factor, or a dilution factor may be prescribed on a per-sample basis during an automated run. Samples for which measured concentrations exceed defined limits may be immediately resampled and diluted. Furthermore, calibration curves may be built automatically from a single standard, eliminating the majority of standard preparation and the associated analytical error.

(583) **Metal Determination in Cosmetics by ICP – Comparative Study between Borate and Peroxide Fusions using TheOx Electric Fluxer**; John A. Anzelmo[1], Janice Pitre[1], Melanie Bedard[1]; [1]Claisse, Corporation Scientifique

It is well known that heavy metals are found naturally in the environment in rocks, soil and water, and therefore exist in the manufacture of pigments and other raw materials in all industries including the cosmetics industry. Some of these metals have been used as cosmetic ingredients in the past. Some measures have been implemented to reduce the amount of heavy metals to which users are exposed, including prohibiting their use in cosmetics. Lead, arsenic, cadmium, mercury, antimony and chromium are the main heavy metal ingredients prohibited in cosmetics in most countries. Cosmetic manufacturers have the responsibility to ensure their products do not contain any of these metals. Metal determination in samples is often done by ICP or ICPMS and it requires the samples to be in dissolved form. Commonly, acid digestions are the method of choice but seeing as many samples contain an important amount of silica, alumina and magnesium, some aggressive acids, such as HF must be added. Knowing the risks associated with the use of HF, many laboratories look for alternative methods for obtaining full dissolution of their samples while optimizing the uptime and productivity. The proposed methods describe alternative ways to determine the concentration of elements of interest as well as confirm the absence of heavy metals contained in cosmetics using borate fusions and peroxide fusions for ICP-OES determination.

Materials and Methods

Two reference materials were tested: NCS DC60132 and USGS SDC-1 as well as 5 different cosmetic samples. All fusions were performed on a Claisse TheOx six position electric Fluxer using alternatively sodium peroxide fusions and lithium borate fusions. Quantitative analyses were performed using an ICP-OES. All calibration standards were matrix matched using the same fluxes used for the fusion of the samples. Acids were of the trace metal grade. Background corrections (BGC), multi-component spectral fitting (MSF), and inter-element spectral corrections (IEC) were performed to deal with the multiple interferences. ICP-OES parameters were adjusted to minimize torch effects with the RF Power adjusted at 1500 W, argon flow at 16 L/min, and sample flow below 1.0 mL/min.

Significance

The significance of this research resides in the simplicity of the methods, their speed (complete sample dissolution in less than 15 min), the absence of harsh acids as well as the advantages offered by the automation and flexibility of the multi-position electric Fluxer.

(584) **Achieving a Hotter Plasma with an All-Ceramic Torch**; Ryan Brennan, Jerry Dulude, Jol Desmarchelier; [1]Glass Expansion

Torches for ICP-OES and ICP-MS have traditionally been composed of quartz. Since quartz has a melting point of 1700C and the plasma reaches temperatures in excess of 6000C, a significant cooling sheath is required. This is normally accomplished with a stream of argon gas between the outer and intermediate tubes. We designed and built an ICP torch with ceramic intermediate tube, alumina injector and sialon (sintered silicon nitride) outer tube. Sialon has a melting point over 2100C and therefore needs much less cooling. We therefore ran the all-ceramic torch with reduced argon coolant and measured the change in intensities for both ICP-OES and ICP-MS. We did not find a marked enhancement in intensity for ICP-OES but expect to find a significant increase in ion generation for ICP-MS. Plasma robustness was also measured. Two of the most significant advantages of the all-ceramic torch were the decrease in argon consumption and the dramatically increased lifetime of the outer tube, especially in the presence of high salt samples which cause severe devitrification of quartz.

(585) **Chemical and Petrochemical Applications of Microwave Plasma – Atomic Emission Spectroscopy (MP-AES)**; Doug Shrader[1], Steve Wall[1], Phil Lowenstern[1]; [1]Agilent Technologies

This poster describes the analysis of chemical and petrochemical samples using the new Agilent 4100 MP-AES, Microwave Plasma – Atomic Emission Spectrometer. The Agilent 4100 MP-AES produces a robust and stable nitrogen plasma using magnetically coupled microwave energy and provides superior detection limits and extended working range compared to flame atomic absorption. A nitrogen gas generator can be used to feed the plasma and source lamps are not required, significantly reducing operating costs while improving laboratory safety by eliminating flammable and oxidizing compressed gases. The design and operation of this new instrument for elemental determinations will be discussed. For organic matrices, solvent resistant tubing, a double-pass spraychamber, inert OneNeb nebulizer, an external gas control module (EGCM) and low load conditions were utilized. Methods developed for the MP-AES system will be presented along with results obtained for the multi-element determination of metals in ethanol, diesel and oil samples.

(586) **Automated, Syringe-Based Preconcentration, Matrix Removal, and Calibration for ICP and ICPMS**; Nathan Saetveit[1], Daniel Wiederin[1]; [1]Elemental Scientific

The determination of trace metals in high saline matrices is challenging by ICPOES and ICPMS. Dilution or method of standard additions (MSA) has been used to attenuate or correct for matrix effects, but other techniques are required to achieve the best detection limits. Preconcentration with matrix removal is a proven technique to improve detection limits by eliminating matrix effects and reducing instrument drift, but it is often done using manual sample preparation or peristaltic pump-driven systems. A fully automated, syringe-based, inline system eliminates contamination from peristaltic pump tubing, increases throughput, and allows greater control over the column chemistry. Advanced automation capabilities enable autocalibration from a single standard and variable sample autodilution. New advances in ICPOES and ICPMS hardware and software will be discussed. Automated calibration of low-ppt level transition metals in undiluted seawater and recoveries of trace elements in certified reference materials will be shown.

(587) **Advances in Enhanced Productivity Sample Introduction Accessories for ICP Spectrometry**; Ryan Brennan[1], Jerry Dulude[1], Scott Bridger[1], Vesna Dolic[1]; [1]Glass Expansion

We will focus this presentation on recent advances in the design and functionality of accessories that combine a switching valve with flow injection technology. Foremost is the development of a new 6/7-port valve with a removable T-piece designed to switch easily between internal standard (or dilution) mode and straight sample mode. The new design cuts down on the components required, reduces the swept volume of the sample from the valve to the nebulizer, and allows for online addition of an internal standard without the need for a second sample loop. Many laboratories use high uptake rates to reduce the time for filling and emptying the sample line, but the higher rate results in wasted sample and reduced lifetime of the peristaltic pump tubing. A built-in positive displacement pump rapidly fills the sample loop and allows the analyst to run at lower sample uptake rates without sacrificing valuable analysis time. The Time in Sample (TIS) and bubble injection features of the software speed washout, reduce carryover and analysis time, and conserve sample. Lastly we will focus on the benefits of replacing the use of a peristaltic pump with a precision syringe drive to provide the highest level of accuracy, stability, and sample throughput. The precision achieved with the customized valve and syringe drive is compared to that of natural aspiration and the use of peristaltic pump sample delivery. In addition, stabilization times associated with a 2, 5, and 20 fold online dilution can be achieved in less than 10 seconds.

(588) **Coupling of an Inert Ion Chromatographic System with ICP-Q-MS for Robust and Accurate Metal Speciation Analyses**; Lothar Rottmann[1], Daniel Kutscher[1], Shona McSheehy[1], Julian Wills[1]; [1]Thermo Fisher Scientific, Bremen

The coupling of IC with ICP-MS has great potential in many fields where trace elemental speciation is of concern. Many physicochemical parameters such as toxicity, reactivity and mobility are strongly dependent of the elemental compound rather that the concentration of the element itself. A new speciation package is used to demonstrate the rapid and accurate analysis of sub-ppb levels of elemental compounds, including hexavalent chromium that are regulated in drinking waters or arsenic species in food. With this combination unattended routine speciation analysis is possible with simple hardware coupling and by use of a new software platform fully integrated control, dedicated chromatographic integration, data processing and compound specific QC is offered.

(589) **Improved Throughput for Analysis by ICP-OES Using Next Generation Sample Introduction Technology**; Steve Wall[1], Doug Shrader[1], Phil Lowenstern[1]; [1]Agilent Technologies

This poster describes the analysis of oil and water samples using the Agilent SVS2, a new and innovative sample introduction system for the Agilent ICP-OES, to improve sample throughput. A typical sample analysis cycle using an ICP-OES involves sample uptake at high pump rates from the autosampler to the plasma, followed by a stabilization delay to allow the plasma to return to equilibrium. The sample is then measured and rinsed from the system. The SVS2 improves sample introduction efficiency by greatly reducing sample uptake and washout times. This can more than double sample throughput, and significantly reduce operating costs. In addition, as there is a constant flow of solution to the plasma, plasma stability is improved and stabilization times are reduced. Instrumentation and operation of this new sample introduction system will be discussed. Methods developed for the SVS2 / ICP-OES system will be presented along with results obtained for the high throughput simultaneous multi-element determination of metals in oil and trace elements in water.

(590) **Analysis of Fish Otoliths by Cold Vapor Generation ICP-MS for Mercury- Could Mercury be a Useful Tracer of Fish History?**; Zikri Arslan[1], Mehmet Ates[1], Erdal Kenduzler[2]; [1]Jackson State University, [2]Mehmet Akif Ersoy University

Fish otoliths are calcium carbonate minerals in the head of fish. These minerals grow throughout the life of fish and accumulate trace elements from the water. Research have shown that the concentrations of the trace elements vary with chemical composition of the outside water, and thus play an important role in elucidating the life history of fish groups. Mercury (Hg) is a toxic trace element that mostly bio-accumulates in tissues as methyl mercury. To date there has not been any data on concentration of Hg and Hg species in fish otoliths. Thus it is not known if Hg could be a key element in otolith microchemistry for discriminating the fish groups to their natal origins. In this study, a cold vapor generation method is developed for determination of Hg in fish otolith by ICP-MS in an attempt to investigate the uptake pathways and distribution of Hg species. Experimental conditions were optimized for selective detection of inorganic and total Hg in solutions acidified by hydrochloric acid (HCl). Sodium borohydride was used the "only" reducing agent and the concentration was optimized to discriminate inorganic and total mercury. At 1x10-4% (w/v) $NaBH_4$, only inorganic Hg reacted to produce Hg vapor. For complete reaction of organic Hg species, a NaBH4 concentration of 0.2-0.5% (w/v) was required. Higher HCl concentration of about 5% v/v was found to be optimum that also resulted in the reduction of Hg signals from CH_3HgCl in at low NaBH4 level. Memory effects were alleviated with bu using potassium ferricyanide as washout solution. The detection limits achieve for a sample solution 3.8 ng/L for inorganic Hg and 6.2 ng/L for total Hg. The analysis of otoliths samples from pacific halibut (*Hippoglossus stenolepis*) and emperor snapper (*Lutjanus sebae*) indicate that Hg levels in the otoliths are very low ranging from 15 to 45 ng/g (ppb). Majority of Hg in the otoliths are in the form of organic Hg with trace levels of inorganic Hg (2-6 ng/g).

(591) **Advancements in ICP-OES Plasma Generation and Application to Environmental Sample Analysis**; Laura Thompson[1], Angela LaCroix-Fralish[1]; [1]PerkinElmer, Inc

Most areas of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) technology have remained virtually unchanged since the first commercial instruments were introduced ~40 years ago. Plasma generation has been traditionally accomplished with a helical coil design which provides a stable plasma for routine analytical analysis, but requires maintenance and a

significant amount of argon gas to function. This work utilizes a new technological breakthrough designed to improve ICP-OES performance without any reduction in application capability. This is the implementation of a new plasma generation technology which uses flat induction plates to produce a symmetrical, dense, robust plasma. This plasma is matrix-tolerant and capable of operating at lower plasma gas flows resulting in a reduction in argon consumption by almost 50%. For environmental analysis labs, cost-effective analytical techniques are highly desirable. An ICP-OES equipped with both Flat Plate™ plasma generation would provide a considerable cost reduction due its high level of performance and reduction in argon consumption. The analysis of environmental samples following EPA Method 200.7 was successfully conducted. Quality control samples are analyzed and found to be within limits and long-term stability is demonstrated.

(592) **Tissue-dependent Metal Ion Affinity for a Datura Innoxia Biosorbent**; Richie Eriacho, Jessica Moore, Debbie Serna, Gary Rayson; [1]Department of Chemistry and Biochemistry, New Mexico State University

Use of plants to enable the selective removal, sequestration, and transport from its roots to its leaves of toxic metals (phytoextraction) is an attractive approach to remediation of contaminated soil and water. Unfortunately, most extracted metal ions remain in the roots. Our laboratory continues to investigate the chemical interactions of heavy metal ions with plant-derived materials (Datura innoxia). The present work discusses the extension of that work to the investigation of metal ion passive binding to various tissue materials (i.e. roots, stems, leaves, and flowers). Past efforts using regularized regression analysis of binding isotherms has revealed the presence of both "high" affinity and "low" affinity binding sites. Current work expands these efforts to includes not only Eu3+, an Am3+ surrogate, but also Pb2+, Cu2+, Zn2+, Ni2+, and Cd2+. Carboxylates have been identified in the binding of Cd2+, Eu3+, and Pb2+ to the culture cell biosorbents. Generation and analysis of metal ion binding isotherms for each tissue type enables assessment of variations in binding mechanisms in extraction of each metal ion and its subsequent migration (i.e., roots to leaves). The impact of these results on metal binding mechanisms and the use of phytoextraction remediation will be discussed.

(593) **Tissue Chemical Variability in Eu(III) Passive Binding Thermodynamics to Datura innoxia Biosorbents**; Gary Rayson[1], Jessica Moore[1], Debbie S[1], Richie Eriacho[1], Fengshan Jiang[1]; [1]Department of Chemistry and Biochemistry, New Mexico State University

Phytoextraction of metal ions from contaminated soil and water offers the potential for a cost-effective approach to remediation of large areas. Realization of this potential requires efficient uptake and transport of these metal ions into and through the plant with final concentration in its shoots and leaves. Unfortunately, relatively little is understood regarding the chemical interactions involved as the metal ion moves through the various plant tissue types. D. innoxia exhibits several desirable characteristics for metal ion phytoextraction: it is an arid land, metal tolerant perennial plant that naturally resists herbivory. Previous investigations in our laboratory involved use of luminescence spectroscopy and analysis of affinity spectra to study Eu(III) binding to cultured anther cells of this plant. The present study expands those efforts to elucidation of chemical interactions responsible for binding this Am(III) surrogate by various tissue types. These include elucidation of some thermodynamic parameters governing the process (e.g., ΔG, ΔH, and ΔS). Results of these studies will be described. Their implications regarding metal-ion phytoextraction will be discussed.

(594) **Solid Sampling High-Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry to Monitor the Ag body Burden in Individual Daphnia Magna Specimens Exposed to Ag Nanoparticles**; Esperanza García-Ruiz[1], Ana Cristina Lapeña[1], Miguel Angel Belarra[1], Martín Resano[1]; [1]University of Zaragoza

In this work, the potential of solid sampling high-resolution continuum source graphite furnace atomic absorption spectrometry (HR CS GFAAS) for the direct determination of the Ag body burden in individual specimens of Daphnia magna (small aquatic invertebrates of approx. 2 mm length that are widely used in ecotoxicological research) exposed to different Ag species - particularly to Ag nanoparticles (NPs)- is investigated. It is shown that this technique offers very interesting features for this type of application, permitting the direct analysis of these invertebrates in a very straightforward way (approx. 2-3 min. are required for the measurement of every individual) and constructing the calibration curve with aqueous standards. Moreover, the judicious selection of the detector pixels used for signal quantification makes it feasible to achieve a very broad linear range for any set of experimental conditions, contrary to what occurs for traditional line source-GFAAS. This feature is particularly important for this application, as every Daphnia magna specimen can be measured only once and its Ag content is not known in advance. In this case, the use of central and/or side pixels permits achieving a working range between 3 pg and 1 μg for the 328.068 nm Ag line, thus allowing analysis of all the samples of interest with the same experimental settings. The results obtained in this study demonstrate that Ag body burden for Daphnia magna specimens exposed to the same amount of Ag, either as AgNO3 or AgNPs, is very different, as exposition to AgNPs results in significantly higher Ag accumulation. However, it is also apparent that different Daphnia magna individuals show a very dissimilar behavior from one another. Therefore, the use of a technique that can analyze these individuals in a fast and simple way seems very valuable to obtain conclusions of ecotoxicological relevance.

(595) **ICP-MS and HPLC-ICP-MS Used as a Tool to Monitor Trends in Inorganic Contaminants in Mussels from a Previously Polluted Fjord**; Daniel Fliegel[1], Astrid J. Meyer[1], Sylvia Frantzen[1], Joar Øygard[1], Kåre Julshamn[1], Amund Maage[1]; [1]National Institute of Nutrition and Seafood Research

Cheap and accessible hydropower at the oceanic coast in proximity to central Europe lead to a historic settlement of heavy industry such as smelters, chemical industry and metallurgical industry in Norwegian fjords. One fjord, where in the past especially metallurgical industry was concentrated, is the Sørfjord in Western-Norway. The Sørfjord is a long and narrow sidearm of the important cultural heritage Hardanger fjord. In the beginning of the last century, up to the mid of the century, the Sørfjord ecosystem was severely polluted by heavy metal emission (Cd, Cu, Zn, As, Pb and Hg) and thus, the Sørfjord was one of the most polluted industrial areas in the early to mid 20th century. In this study Q-ICP-MS and HPLC-Q-ICP-MS is used to determine elemental concentrations and iAs (inorganic arsenic) in blue mussels (Mytilus edulis) as a biomonitoring organisms to evaluate the environmental quality of the Hardangerfjord-Sørfjord from 1986-2006. Additionally, from September 2005 to October 2006 a detailed, monthly resolved, study of contaminants in Mytilus edulis from Sørfjord and Hardanger fjord was conducted. The results show a significant decrease of contaminant levels since 1986. Furthermore, seasonal variation especially in Cd, Hg and Pb levels are liked to seasonal water chemistry and dynamics such as fresh water influx and stratification. The study further demonstrated that concentrations of Cu and Zn are bioregulated within the mussels' tissue and the iAs (as Σ(AsIII + AsV)) level is also influence by fresh water discharges into the fjord. These results can be used to predict the future environmental quality of the Hardanger-Sørfjord system

but also may indicate important aspects for seafood safety/production in contaminated marine ecosystems.

(596) **Silver Nanoparticle and Ion Toxicity in Saltwater Alga Skeletonema Costatum**; Nicole Hanks[1]; [1]University of Cincinnati

In the past fifty years, silver has been engineered into structures from 1 to 100 nm in size or now known as nanoparticles. Due to their small size, nanoparticles have a high ratio of activation value to weight due to the amount of surface area. Silver nanoparticles (Ag-NPs) are now in many common products including detergents, clothing, and kitchen appliances. These nanoparticles exhibit stronger antibacterial and antimicrobial properties than bulk silver sources, causing them to continue to gain popularity for commercial applications. With increasing usage, these nanoparticles will lose adhesion to the product and escape into the environment. Their small size allows for easy penetration into the cells of organisms and small ecosystems. Despite the vast usage of Ag-NPs, the toxicity of these particles is poorly understood and poses a threat to the environment. More research is required to understand the process that actually causes these particles to be hazards to biological systems. The research presented shows preliminary total metal analysis of silver within algal cultures of Skeletonema costatum when doped with various concentrations of silver chloride and silver nanoparticles. This research provides an understanding of the algal intake of silver and how it may affect the algal culture's survival. All results are accomplished using an Inductively Coupled Plasma-Mass Spectrometer for total metal analysis. Cell counting and UV-Vis analysis are also utilized to evaluate the vitality of the cells within the culture during harvest.

(597) **Characterization by HPLC-ICP-MS of Algal Extracts and Water in Evaporation Ponds**; Christopher M. W. Medley[1]; [1]University of Cincinnati

Abstract: Arsenic is a toxic element and its affects on humans, animals and other organisms are well documented. A method to accurately determine the concentration and speciation of arsenic in highly complex evaporation pond water will be discussed. These ponds are shallow man-made ponds designed to harvest salt from sea water. The sea water is fed into large ponds and water is drawn out through natural evaporation, which allows the salt to be subsequently harvested. Interestingly, microorganisms are thriving in evaporation ponds that have high levels of arsenic, which is unusual for microorganism to survive. This study shows nine different arsenic species including the most common: AsB, As^{III}, MMA DMA, As^{V}, and four different arsenosugars. The ultimate goal of this project is to determine if algae from these evaporation ponds may effect oxidation of the most toxic As^{III} to the less toxic As^{V}.

(598) **Solid Phase Extraction, QuEChERS Cleanup with LC-MS/MS as an Improved Method for Analyzing Five Estrogens in Wastewater**; Sameera Gunatilake[1], Shelby Steelhammer[1], Todd Mlsna[1], Kang Xia[3], Jeong-Wook Kwon[2], Kevin Armbrust[2]; [1]Department of Chemistry, Mississippi State University, [2]Mississippi State Chemical Laboratory, [3]Department of Crop and Soil Environmental Sciences, Virginia Polytechnic Institute and State University

Substances having the capability to interfere with human and wildlife endocrine system, even at extremely low concentrations are commonly known as endocrine disrupters (EDs). According to current perspective, the most potent active EDs present in the environment are steroid estrogens as they show the highest affinity for the estrogen receptors. Modern society uses considerable amounts of estrogens in human medicine to diagnose, treat or prevent diseases. These substances are excreted in urine and faeces and will eventually be discharged into municipal wastewaters. Therefore, method development for the detection of estrogens in environmental waters has become a popular research interest. We present an improved method which includes sample preparation using solid-phase extraction followed by a "QuEChERS" (Quick Easy Cheap Effective Rugged Safe) cleanup, and a liquid chromatography/tandem mass spectrometry detection for estriol (E3), estrone (E1), 17α-estradiol (αE2), 17 β-estradiol (βE2), and 17α-ethinylestradiol (EE2) waste waters. Solid-phase extraction was carried out using Oasis HLB cartridges (500 g). Subsequently, the QuEChERS cleanup was done by performing dispersive solid phase extractions with homemade cleanup packs containing $MgSO_4$, PSA and C-18. Resulting extract was then derivatized with dansyl chloride. Separation was achieved on an Agilent Zorbex Extend C-18, Narrow Bore RR, (2.1 x 100mm, 3.5 μm) column with 0.1% formic acid and acetonitrile as the mobile phase. Quantification was accomplished in the positive ion mode using selected ion monitoring. The cleanup method was quick, efficient and inexpensive. Reliable linearities were obtained for all the calibration curves ($r2 > 0.9975$) Matrix effects calculated were less than 20% for all the analytes and hence, matrix matched calibration curves were not needed. The recoveries for the estrogens were ranged from 77 – 103% with a high repeatability (n=3, RSD ≤ 9%). Even with less sample volumes (200 mL), low limits of quantification were obtained (0.6 – 0.9 ppt). The method was used to analyze effluent and influent waste waters from Starkville, Columbus and Jackson waste water treatment plants.

(599) **Pharmaceuticals and Phytosanitary Water Pollution: Combined Raman Spectroscopy and Multivariate Data Analysis**; Ivana Durickovic[1], Mario Marchetti[1]; [1]CETE de l

Water pollution has become an important issue in the last decade. With the enlargement of human activities and city size, the waste quantities become more important leading to a continuously increasing environmental pollution and impacts. Many documents are written with the objective to put a legislation on the waste disposal, with a special accent on chemical species inducing severe environmental impacts. Pharmaceuticals and phytosanitary products are identified as a major issue and particularly important to survey. The French ministry of Ecology has thus established plans for the reduction of the water pollution caused by these products. Nowadays, the surveillance of the quality of water courses is performed by laboratory analysis of field samples. The information on the water quality is therefore obtained with a rather heavy chemical procedure and an important temporal delay. In order to identify the presence of pollutants in running waters as soon as it appears, it is necessary to dispose of a technique permitting quick analysis. Raman spectroscopy constitute such a technique as it is appropriate for water analysis and for in situ measurements. The combination of this technique with the Multivariate Data Analysis permits the improvement of the signal treatment and thus of the detection limit. Moreover, the in situ aspect of these combined techniques will help to determine the chemical and biological dynamics of the pollutants. In this work we will present the first results on the analysis of water pollution by the combined approaches of Raman spectroscopy and of Multivariate Data Analysis. The final objective is to develop a contactless technique permitting an in situ detection of the water pollution.

(600) **Quantification of Dicyandiamide (DCD) in Fresh Water Environment**; Shelby Steelhammer[1], Todd Mlsna[1], Dongdi Sun[1], Sameera Gunatilake[1]; [1]Mississippi State University

Quantification of Dicyandiamide (DCD) in Fresh Water Environment

The pollution of New Zealand stream waters has become a growing concern as intensive fertilizer use has caused excessive nitrogen pollution in these environments. Fertilizers containing Dicyandiamide (DCD) used in high application rates promote extenuating environmental consequences associated with the high levels of nitrogen subsequently found in aquatic environments. DCD is a nitrogen containing compound that is easily leeched into these

waters due to high water solubility. This is of great environmental concern because when introduced into water streams, they present an inhibitory effect on microbial nitrification that in turn leads to an increase of the inorganic nitrogen species in addition to the accumulation of ammonium in the environment. Literature suggests that the presence of DCDs in fertilized pastures is one of the major sources of these effects. New Zealand stream water samples have been collected and the concentration of DCD quantified via HPLC and LC-MS. Water samples are spiked before LC-MS analysis using DCD standard in matrix samples to determine detection limits. A calibration curve is obtained by spiking DCD standards in pure water and is used to determine the concentration of DCD in real water stream samples. Details on the quantification method and field results with be presented.

(601) **Interaction Study of Bovine Serum Albumin with Formaldehyde by Flow Injection Chemiluminescence Analysis**; Xijuan Tan[1], Zhenghua Song[1]; [1]Northwest University

Formaldehyde is receiving great concern in public due to it is a potential causative agent of leukemia and nasopharyngeal cancer in humans upgraded by the International Agency for Research on Cancer. The interaction of bovine serum albumin (BSA) with formaldehyde has been reported by fluorescence spectroscopy, however the binding mode has not been clarified. In this work, the interaction of BSA with formaldehyde was investigated by flow injection (FI) chemiluminescence (CL) analysis using luminol as a luminescence probe. It was found that formaldehyde can obviously enhance the CL intensity from luminol–BSA reaction and the increment was linear with formaldehyde concentration in the range of 7.0 to 1000 pmol L−1, giving the calibration equation of $\Delta I = 0.59C + 61.85$ ($R = 0.9981$) with the detection limit of 2.7 pmol L−1 (3σ) and the relative standard deviation (RSD) less than 4.5% ($n = 7$). The binding constant K (1.89×106 L mol−1) and the binding site number n (0.86) were obtained by homemade FI-CL model. The thermodynamic parameters (enthalpy change ΔH, entropy change ΔS, and free energy change ΔG) were estimated by performing the experiment at different temperatures. The values of ΔH and ΔS were −101.87 kJ mol−1 and −225.30 J mol−1 K−1 with ΔG of −36.99, −34.73 and −32.47 kJ mol−1 at 288, 298 and 308 K respectively. The negative sign of ΔH, ΔS and ΔG suggested that hydrogen bond and van der Waals force play major roles in the spontaneous formation of the 1:1 complex of BSA with formaldehyde. This proposed method was also successfully applied to formaldehyde determination in beer with recoveries of 98.0% to 106.4% and RSDs lower than 4.2%.

(602) **Determination of Methane and Formaldehyde Concentrations in Jonesboro, AR**; Sindhu Kaimal[1], Scott Reeve[1]; [1]Arkansas State University

A graphical user interface (GUI) has been developed in the MATLAB environment that provides an automated determination of species concentrations from a fit to observed infrared spectra obtained with a Difference Frequency Generation (DFG) laser based spectrometer. Quantitication is currently limited to molecules that have been catalogued in the HITRAN database. High resolution infrared spectra (0.0001 cm^{-1} per point) for methane and formaldehyde were collected at known concentrations and the consistency of the measurements was assessed. Methane and formaldehyde concentrations in ambient air at various locations in Jonesboro, AR, were determined. We have also examined human breath and vehicle exhaust using this approach. The results of the tests give assurance that the algorithm could be used in semi-automated continuous online quantification of species with minimal operator intervention. This abstract has been approved as Distribution A: unlimited public release.

(603) **Assessment of possible Impact of Industrial Activities and the Use of Agrochemicals on the levels of Toxic Chemicals in the Natural Environment.**; ElMukhtar Belgasem; [1]Tripoli University

The boom in some of chemical industries and the wide excessive uncontrolled long term use of enormous varieties of agrochemicals, especially in Libyan coastal areas drove us to carry out an extensive study to assess the possible impact of those uncontrolled notorious human activities on the levels of some toxic chemicals in the natural environment. Therefore, an enormous number of environmental samples known to be especially subject to possible rain and air born contamination, were carefully analyzed for some the most common chemical pollutants relevant to the industrial and agrochemical activities in the area around Tripoli city. Special emphasis was given to the analytical methodology such as sampling, sample preparation and evaluation of the analytical data such as reproducibility, recovery and linearity. The important role of chemical research and science policy to monitor the environmental samples is briefly discussed in this paper.

(604) **Measurement of Nitro-Compounds in Automobile Exhaust with IR CRDS Method**; Hiroyuki Yamada[1]; [1]National Traffic Safety and Environment Laboratory

Measurements of nitrogen dioxide and nitromethane from a light duty truck exhaust gas were performed with continuous wave infrared cavity ring down spectroscopy. 1600 cm-1 quantum cascade laser was adopted for light source. Detection limits of the measurement system for NO2 and nitromethane were 700 ppt and 2 ppb respectively, with 99.98 % reflectivity CRDS mirrors. Interferences from water and particles were removed using gas dryer and HEPA filter respectively. NO2 spectrum obtained with CW-CRDS system was in good agreement with that simulated with HITRAN. 1599.8cm-1 was used for NO2 measurement and 1599.55cm-1 for nitromethane. Maximum emission of NO2 in JC08 mode was 15 ppm, and that of nitromethane was 50 ppb. These results are consistent with the former studies

(605) **Determination of Ester Content in Biodiesel -- Modification in the Existing EN 14103 method**; Dheer Singh[1], Anju Chopra[1], A.K. Tewari[1], M.I.S. Sastry[1], M.B. Patel[1], B. Basu[1]; [1]Indian Oil Corporation Limited

Biodiesel, a fuel from natural oils such as jatropha oil, soybean oil, rapeseed oil or animal fats, is a substitute for petroleum-diesel fuel. The quality criteria for the production of biodiesel are specified in EN 14214 specifications. Within EN 14214 specifications, EN 14103:2003 method determines the fatty acid methyl ester (FAME) and linolenic acid methyl ester content. This method employs an internal standard, methyl heptadecanoate (C17:0), to quantify the total fatty acid methyl ester and linolenic acid content of the biodiesel. Vegetable oil based biodiesels do not contain naturally occurring methyl heptadecanoate (C17:0) and are therefore not affected by this test method but animal based biodiesels have been found to contain naturally occurring C17:0 methyl ester. This results in erroneously low results of ester content. Another error arising in this method is because of the assumption that all the fatty acids have a linear detector response. In the modified EN 14103 method introduced in 2011, C 19:0 is used as an internal standard and it also includes the whole range (C6-C24) methyl ester in the calculation of ester content. This method is also silent about the response factors of individual methyl esters present in the biodiesel and thus does not give accurate value of total ester content. The values estimated by this method in biodiesel samples were lower than the actual value, therefore, the results obtained by this method indicated that majority of the biodiesel samples were not meeting the EN 14214 specifications (< 96.5%). In this present work, a new method is developed for the determination of ester content of biodiesel by applying the corrected response factors of fatty acids. In this method,

a whole range of fatty acids (C6-C24:1 methyl esters) have been included in the calculation of the ester content. Methyl nonadecanoate (C19:0) was used as an internal standard for the estimation of ester content in biodiesel. The response factors of both the saturated (C6:0, C8:0, C10:0, C12:0, C14:0, C16:0, C18:0, C19:0, C20:0 C22:0 and C24:0) and unsaturated (C16:1,C18:1,C18:2,C18:3,C20:1 and C24:1) methyl esters were estimated. These methyl esters cover the entire range expectedly present in the different biodiesel samples. It was found that the response factors vary from 0.89 to 1.01. The ester content was calculated after applying the response factors of each methyl ester. The results showed that the ester content of different kinds of biodiesel samples was more accurate as compared to the EN 14103 method and meet the biodiesel specification for ester content (> 96.5 wt %) as per EN14214. The results were also validated by the ASTM D7371 method based on mid-infrared spectroscopy.

(606) **Challenges and Opportunities in On-Line Monitoring of Thermochemical Biomass Processes**; Daniel Carpenter[1], Marc Pomeroy[1]; [1]National Renewable Energy Laboratory

Thermal conversion of biomass, e.g. for the production of advanced biofuels, results in a complex gas mixture that contains hundreds of chemical species, the composition and properties of which vary markedly with biomass feedstock and process conditions. Gasification at high temperatures produces a syngas that primarily contains H2, CO, CO2, H2O, and CH4; unwanted byproducts include light hydrocarbons, heavy tars (including sulfur- and nitrogen-substituted compounds), and inorganic gas-phase components containing sulfur (H2S, COS), nitrogen (NH3, HCN) and chlorine (HCl). Lower temperature pyrolysis processes generally seek to maximize yield of bio-oil, which results in a product gas containing many of the same permanent species, but with up to 70% condensable, reactive hydrocarbons. The long-term economic viability of either process will depend heavily on technologies for in-situ catalytic processing of the product gas for downstream use, whether by removal/conversion of unwanted gasification byproducts, or by selective de-oxygenation of pyrolysis vapors. Real-time gas analysis at various points in a process has the obvious benefit of capturing transient events, such as catalyst deactivation or changing process conditions. Additionally, a detailed chemical characterization of byproduct species is important for accurate elemental mass balances and because different classes of compounds have unique operational and environmental impacts. While techniques for online measurement of permanent gas components and light hydrocarbons are widely used, methods for direct analysis of compounds in hot, untreated gas streams are considerably less developed. The National Renewable Energy Laboratory (NREL) has been developing methods to achieve comprehensive, real-time analysis of biomass-derived products from thermochemical processes for several years. Some of these techniques, including molecular-beam mass spectrometry and advanced gas chromatography, have been employed in a 0.5 ton/day, pilot-scale Thermochemical Process Development Unit. An overview of NREL's online analytical capabilities is given, including advantages, limitations, and future needs. Instrumentation includes a transportable molecular-beam mass spectrometer; high-resolution mass spectrometer; and a custom, dual-GC system for analysis of hydrocarbons and condensable sulfur and nitrogen species. Experimental results are presented from analysis of raw syngas derived from biomass feedstocks.

(607) **Defining the Relationships between Fuel Composition and Performance Properties Using Compound Profiles and Shape-Based Analysis of GC-MS Data**; Jeffrey Cramer[1], Robert Morris[1]; [1]U.S. Naval Research Laboratory

The relationships between the chemical constituency of a mobility fuel and resultant properties and performance are being investigated for the purposes of comprehensive fit-for-purpose (FFP) fuel modeling. The goal of this research is to develop an understanding of the relationship between the composition of a fuel and its resultant properties. Our approach is based on statistical correlations of comprehensive compositions of a large set of worldwide fuels, determined with gas chromatography–mass spectrometry (GC-MS), and known performance properties. In this manner, we are developing models that will predict how any fuel would perform in any given application, on the basis of a single compositional analysis. This approach will address the limitations of current property specification-based fuel assessment methodologies and provide a framework for determining the FFP parameters of a fuel in any engine or system, regardless of fuel type or source. In order to address such a wide-ranging goal, a comprehensive analysis strategy must first be developed that accurately correlates fuel compositional information to known performance properties. This presentation will compare the results obtained from two separate strategies. In the first strategy, a compositional profiler was used to identify and quantify the chemical compounds found within GC-MS fuel data, and said compositions were then correlated to specification fuel properties using partial least squares (PLS) regression modeling. In the second strategy, the GC-MS compositional information was abstracted into data shapes that were assessed in a direct fashion to intelligently select data subsets for subsequent PLS regression modeling. The capabilities of the two strategies with respect to producing accurate fuel property models that are also chemically meaningful will be compared.

(608) **Quantification of Rubber in High Impact Polystyrene by NMR, Raman Spectroscopy and Chemometrics. Confrontation Fitting Method and Chemometrics**; Nadège Brun[1], Patrice Bourson[1], Samuel Margueron[1]; [1]LMOPS - University of Lorraine

An analytical method for detection and quantification of polybutadiene in High Impact Polystyrene (HIPS) is proposed. The percent of rubber contained in a HIPS pellets determine the properties of the material. More the material is concentrated with rubber, more it presents mechanical resistant. Analytical method currently used to estimate the proportion of rubber in HIPS pellets is Nuclear Magnetic Resonance (NMR). The application of Raman spectroscopy in polymers become most and most popular because of the sensibility of the Raman spectroscopy to the vinyl bond C=C. This technique offers various advantages as no sample preparation, no destructive measurements, reproducibility of the methods, and information about conformations of polybutadiene which can be easily accessible. The purpose of this paper is to compare two different quantitative procedures and evaluate which one is the best way to estimate the percent of rubber in High Impact Polystyrene pellets, by Raman spectroscopy. The first traditional method is based on the fitting of Raman spectra and yielded good prediction with a regression coefficient R2 equal to 0.96, versus the second which is based on chemometrics techniques with a R2 equal to 0.98. The goal of this paper is to compare these methods and to highlight the best way for quantitative analysis of HIPS pellets by Raman spectroscopy.

(609) **Establishment of Patterns and Control of high Temperature Oxidation Flaws of Low-Density Polyethylene with the Raman Spectroscopy**; Vietmann Marie[1, 2], Jumeau Richard[1, 2], Bourson Patrice[1], François Lahure[2], Michel Ferriol[1]; [1]LMOPS University of Lorraine, [2]1Total Petrochemicals France, Usine de Carling - Saint-Avold, RN33

Low-Density Polyethylene (LPDE) is the most popular used thermoplastic in the world, with a wide range of applications, particularly in flexible packaging. Two kinds of flaws can occur during the polymerization: the "unmetled flaws" which affect the structure of the polymer itself (over cross-linkage and oxidation) and the "agglomerated flaws" which are generally a mix of two polymers

with different Melt Flow Index (MFI). The ability to identify and quantify specific flaws is a major issue in the polymer industry. In this study we suggest a method to determine the degree of flaw that can occur during polymer processing due to oxidation. We have reproduced different kinds of oxidation flaws in the laboratory. Measurements were made on several samples, each sample was oxidized with air and exposed to 150°C in an oven for variable time duration and then characterized by Raman spectroscopy. By using statistical tools as chemometrics on these spectra, we built a model able to predict the oxidation degree of flaws. Indeed, the evolution of the crystallized carbon group and the carbonyl functions in the Raman spectra allowed us to follow the oxidation in the sample. Finally, other characterization methods such as Infra-Red spectroscopy, Differential Scanning Calorimetry (DSC), and X-Ray Diffraction (XRD) were used in combination with Raman spectroscopy in order to determine the high temperature oxidation mechanism in LPDE To conclude, we developed a system able to identify and quantify oxidation flaws in Low-Density Polyethylene in order to understand how such properties will be affected by the imperfection.

(610) **Variable Temperature Raman Spectra, Structural Parameters and Vibrational Assignments of Ethylenediphosphine**; Savitha S. Panikar[1], James R. Durig[1], Victor F. Kalasinsky[2]; [1]University of Missouri-Kansas City, [2]Armed Forces Institute of Pathology

Infrared spectra (3600 - 500 cm-1) of gas, amorphous, crystalline solid and Raman spectra (3000 - 200 cm-1) of liquid and solid were recorded. Variable temperature Raman spectra (30 to -38°C) of liquid were recorded which indicates the presence of significant amounts of six conformers at ambient temperature. Rotation about C-C bond gives Trans (T) and Gauche (G) conformers and rotation around both C-P bonds gives trans (t) and gauche (g) forms. Enthalpy differences for five of the lower energy conformers w.r.t. the lowest energy tTt form were determined to be 272 ± 39 cm-1, 434 ± 40 cm-1, 443 ± 30 cm-1, 663 ± 60 cm-1 and 671 ± 34 cm-1 for g′Tt, g′Tg′, g′Tg, tG′g′ and tG′t conformers, respectively, which are in the increasing order of energy. Ab initio calculations with various basis sets up to aug-cc-pVTZ were performed and to support the spectroscopic studies MP2(full)/6-31G(d) was used to predict Raman activities, infrared intensities, vibrational frequencies and band contours. By utilizing the previously reported microwave rotational constants along with MP2(full)/6-311+G(d,p) predictions, adjusted r0 parameters were obtained for two Trans and two Gauche (C-C bond) conformers. The determined heavy atom structural parameters for g′Tt [g′Tg′] {tG′g′} |tG′t| conformers are: distances (Å) P1-C2 = 1.870(3) [1.866(3)] {1.858(3)} |1.859(3)|, C2-C3 = 1.535(3) [1.536(3)] {1.534(3)} |1.536(3)|, C3-P4 = 1.863(3) [1.866(3)] {1.866(3)} |1.859(3)|, and angles (°) □P1C2C3 = 110.5(5) [110.4(5)] {117.0(5)} |118.5(5)|, □C2C3P4 = 115.5(5) [110.4(5)] {113.7(5)} |118.5(5)|. The results are discussed and compared to the corresponding properties of some similar molecules.

(611) **Intermolecular Vibrations of poly-(R)-3-hydroxybutyrate in Low-Frequency Raman and THz Time-Domain Spectra Explored by DFT Calculation with Cartesian Coordinate Tensor Transfer**; Shigeki Yamamoto[1], Yusuke Morisawa[1, 2], Hiromichi Hoshina[3], Shinya Ishii[3, 4], Harumi Sato[1], Chiko Otani[3], Yukihiro Ozaki[1]; [1]Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, [2]Department of Chemistry, School of Science and Engineering, Kinki University, [3]RIKEN, 519-1399 Aramaki-Aoba, [4]Miyagi University of Education, 149 Aramaki-Aoba

Vibrational bands in low-frequency region below ~300 cm^{-1} can be informative not only on the intrinsic molecular interactions via covalent bonds and hydrogen bonds in a molecule, but also on the intermolecular interactions such as weak hydrogen bonds and Van der Waals interactions among the molecules. This low-frequency region is called Terahertz (THz) region in a field of the THz time-domain (TD) spectroscopy. Although assignments of the vibrational modes in this region have been desired for understanding of the weak intermolecular interactions mentioned above, however, it was quite difficult if based on the experiments, because these bands are expected to be highly delocalized in the molecule, and to be mixtures of some fundamental vibrations. In this study we compared both of the experimental THz absorption spectra and the low-frequency Raman spectra of lamellar crystal poly(3-hydroxybutyrate) (PHB) with the quantum-mechanically calculated spectra. The calculations of the spectra with the aid of the Cartesian-coordinate tensor transfer (CCT)[1,2] method were applied successfully, which include the explicit consideration of the intermolecular interactions, in order to verify the assignments of the vibrational bands in THz region and to confirm the experimentally suggested route of the bands, the weak intermolecular interactions among PHB chains via hydrogen bonds between the methyl hydrogens and the carbonyl oxygens. The agreements between the experiments and the calculations were good in both of the THz-TD and Raman spectra. The results obtained here confirmed a sensitivity of the vibrational bands in the THz region to the intermolecular interactions including weak hydrogen bonds among polymer chains.

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(612) **Raman Spectroscopy and High-Resolution Transmission Electron Microscopy as Complementary Techniques to Investigate Natural nm Thin Graphitic Films**; Daniel Fliegel[1], Mark van Zuilen[2], Richard Wirth[3], Aivo Lepland[4], Yuangao Qu, Anja Schreiber, Alexander E. Romashkin, Pascal Philippot[2]; [1]National Institute of Nutrition and Seafood Research, [2]Equipe Géobiosphère, Institut de Physique du Globe de Paris - Sorbonne Paris Cité, Université Paris Diderot, [3]GeoForschungsZentrum Potsdam, Telegrafenberg, Chemistry and Physics of Earth Materials, [4]Geological Survey of Norway, Leiv Eirikssons vei 39

Materials science studies have shown that 2-dimensional (2D) crystals of graphene can be produced artificially by growing a monolayer of carbon on top of another 3D crystal. Here we use first-order and second order Raman spectra together with focused ion beam followed by high resolution transmission electron microscopy (HR-TEM) to describe the natural occurrence of near 2D carbonaceous structures on mineral surfaces in metamorphosed organic-rich rocks of the Zaonega Formation, Russia. Analysis by Raman spectroscopy (RM) and HR-TEM reveals 7-35 nm thick stacks of highly ordered graphene layers (here defined as graphite films - GF) that completely envelop small quartz crystals, and occur on specific crystal faces of chlorite. To our knowledge this study demonstrates for the first time a combined RM – FIB -TEM approach in order to investigate natural ordered nm thin graphitic layers on top of mineral surfaces. The existence of these structures can be explained by passive and active mineral-template induced graphitization in a bitumen-rich fluid. The active process involves adsorption of polar organic macromolecules on charged surfaces, followed by heat-induced graphitization. Deep understanding of these natural templating processes will have a strong impact on the production of structured carbonaceous materials and will open a new field of geo-nano-science. We envisage that the combination of RM and FIB-TEM will play an important role in the investigation of natural carbon-based analogue materials.

(613) **Raman and X-Ray Diffraction Studies of Cadmium Zinc Telluride (CZT) and Ambient Temperature and Pressure Effected Chemical Contaminants**; Dale L Perry[4], Daniel Sneed[1], Andrew Knudson[2], Lewis Jones[3], John W Farley[1]; [1]University of Nevada, Las Vegas, [2]Sierra College (CA), [3]Morehouse College, [4]Lawrence Berkeley National Laboratory, University of California

The use of cadmium and zinc in cadmium zinc telluride (CZT) has demonstrated the solid-phase material's usefulness as a type of very important multipurpose semiconductor. The photonic properties of the zinc telluride crystal also make the material very useful in laser optics and solar panels. Unlike other materials that require extensive cooling, cadmium zinc telluride is a room-temperature semiconductor radiation detector. This work centers on the Raman and X-ray diffraction (XRD) analyses of CZT in order to determine its chemical contaminant properties, with special focus on contaminants that are formed during processing and ambient temperature and pressure. Support for A.K. and L. Jones under an NSF Research Experience for Undergraduates under Grant DMR-1005247 is gratefully acknowledged.

(614) **Using FT-IR to Investigate the Behavior of Carboxylate Based Monolayers on Titanium Dioxide at High Temperatures**; Catherine G. McKenas[1], Karla S. McCain[1]; [1]Austin College

FT-IR spectroscopy was used to examine the behavior of carboxylate based monolayers of varying alkyl chain length on titanium dioxide at high temperatures. Titanium dioxide has many applications, which include being a UV-resistant material in sunscreen, a semi-conductor in dye-sensitized solar cells, and a photocatalyst. By better understanding the behavior and properties of these surface modifications, titanium dioxide's performance in these applications could be enhanced. Titanium dioxide nanoparticles (10-25 nm) were stirred in ethanolic solutions of alkyl carboxylic acids, centrifuged into a pellet, and heated in a 100o C oven for varying number of days. Infrared spectra of the derivitized nanoparticles were acquired using a single point ZnSe ATR accessory. It was found that the length of time the nanoparticles were heated affected the mode of surface adsorption of the carboxylate group to the surface of titanium dioxide. This change in modes of surface adsorption was found to correlate with changes in the conformational ordering of the alkyl chain of the carboxylic acid. Carboxylic acids with longer alkyl tails rearranged on the surface more slowly than carboxylic acids with shorter alkyl tails, with all surface rearrangements requiring about a three-day induction period. Future work includes examining the effect of temperature on this behavior in order to gain insight into the activation energy of this process.

(615) **Electric Field Effect on the Infrared Spectra of Ferroelectric Poly(vinylidene fluoride-hexafluoropropylene) (PVDF/HFP) and Nylon 11 Films**; Hayato Isoda[1], Yukio Furukawa[1]; [1]Graduate School of Advanced Science and Engineering, Waseda University

We present the study of external electric field effect on the infrared spectra of ferroelectric uniaxially stretched PVDF/HFP and nylon 11 films with the polarization perpendicular to the draw direction using transparent gold electrodes. A PVDF/HFP film contains a polar β phase and an amorphous sate. The unit cell of the β phase has two polymer chains taking all-trans structure. Since an infinite poly(vinylydene fluoride) polymer chain has the C_{2v} symmetry, we will analyze the spectrum of PVDF/HFP with C_{2v} symmetry. Infrared spectra of a PVDF/HFP film were stepwise measured in the range of electric fields from 1.4 to −1.4 MV/cm. The intensity changes of the a_1 bands (2979, 1432, 1279, and 842 cm^{-1}), b_1 bands (1403 and 1073 cm^{-1}), and b_2 bands (3017, 1185, and 880 cm^{-1}) were plotted against the electric field strength. Each band showed a butterfly-shaped hysteresis loop characteristic of ferroelectrics. The a_1 and b_2 bands have transition dipole moments perpendicular to the polymer chain, whereas the b_1 band parallel to the chain. The intensity changes due to the a_1 and b_2 bands can be explained by the rotation around the polymer chain axis. On the other hand, the intensity changes due to the b_1 bands can be explained by the rotation of a polar crystallite. The infrared spectra of a nylon 11 film were measured in the range of electric fields between 1.4 and −1.4 MV/cm. Observed intensity changes of the NH stretch and amide I (C=O stretch) bands are large, whereas those of the CH stretch of the $(CH_2)_{10}$ group small. This result indicates that only the amide group re-oriented upon an electric field. The amide I band was decomposed into four bands; two bands at 1638 and 1646 are attributed to the crystalline and amorphous regions, respectively. Since the C=O group has a local permanent dipole moment, the amide I band may be a marker of the polarization properties of nylon 11. Butterfly-shaped hysteresis loops were observed for both crystalline and amorphous components. This molecular re-orientation mechanism in nylon 11 is quite different from that of PVDF/HFP.

(616) **Thiol on Gold Stability and Impact on Atom Transfer Radical Polymerization (ATRP) of Styrene at Various Temperatures**; Richard Osibanjo[1]; [1]University of California Davis

Thin film sensors are developed for aqueous systems to monitor water quality and for biosensing. Growth of well-controlled polymer brushes in solution is an established technology. In this study, we explore the in situ monitoring of surface initiated polymerization of styrene on germanium+gold substrate by attenuated total reflectance Fourier transform Infrared (ATR-FTIR). Atom transfer radical polymerization (ATRP) was used to start the polymerization process using 11-Mercaptoundecyl bromoisobutyrate as the initiator. Changes in the surface composition with time is characterized by ATR-FTIR. Comparison is made between the polymerization of styrene on surfaces with initiator deposited from solution or initiator synthesized in situ on the surface. The initiator was synthesized and characterized with H-NMR and ATR-FTIR.

(617) **Reverse Engineering of Polymeric Multilayers using AFM-based Nanoscale IR Spectroscopy and Thermal Analysis**; Mike Lo[1], Tom Eby[2], Usha Gundusharma[2], Khoren Sahagian[1], Curtis Marcott[3], Kevin Kjoller[1]; [1]Anasys Instruments Corp., [2]Kimberkley Clark Corporation, [3]Light Light Solutions, LLC

Using atomic force microscopy (AFM)-based nanoscale infrared (IR) spectroscopy and thermal analysis (TA), analysis of the cross section of an intact multilayer polymeric film with the smallest features being approximately one micrometer is now possible. Since these techniques employ AFM tips, which typically have radii of tens of nanometer, the AFM-IR and AFM-TA measurements readily achieve 100 to 200 nm in actual spatial resolution. Nanoscale infrared spectroscopy relies on the rapid local thermal expansions of the material upon absorbing 10 ns pulses of radiation from a tunable infrared source. Such expansions are detected using an off-the-shelf AFM tip in the form of ringing motions, which are proportional to the absorptivity of the sample. Measuring the amplitude of the ringdown across a range of wavenumbers would generate AFM-IR spectra that are similar to conventional infrared spectroscopy. Nanoscale thermal analysis uses a specialized probe that has a resistive heating element directly at the tip of an AFM cantilever. As the tip heats up with an increasing voltage, the material in contact with the tip would expand and the deflection of the AFM tip would increase until there it reaches a softening point. This is defined as the transition temperature, which correlates favorably with bulk thermal analytical techniques. Since the above Ñmentioned techniques do not require physically extracting each layer of the film, these localized analyses ensure the chemical integrity of the film as well as the exact placement of the components in space in an AFM image. In this poster, we demonstrate the combined AFM-TA and AFM-IR analyses of each layer of the multilayer film with 1 μm inclusions.

All measurements are correlated to the corresponding AFM topographic image.

(618) **External Electric Field Effect on the Infrared Spectra of Ferroelectric Vinylidene Fluoride/Trifluoroethylene Copolymer Thin Films**; Kenji Takashima[1], Yukio Furukawa[1]; [1]Waseda Univ

The external electric field effect on the infrared spectra of thin films of ferroelectric vinylidene fluoride/trifluoroethylene copolymer (P(VDF/TrFE)) (molar ratio, 75:25) has been studied. A cell having the structure of BaF_2/Al/P(VDF/TrFE) (350 nm)/Al was made. A P(VDF/TrFE) film was prepared by spin-coating. Transparent Al electrodes were made by the vacuum deposition method. The observed infrared bands are attributable to the β phase, a polymer chain takes the all-trans extended structure (C_{2v} symmetry). After polling the film, an external electric field was applied stepwise between 3.0 and −3.0 MV/cm across the film; an infrared spectrum was measured at each electric field. Intensity changes of infrared bands were observed. We will discuss the infrared spectrum of P(VDF/TrFE) under the C_{2v} symmetry. Transition dipole moments associated with the a_1 and b_2 modes are perpendicular to the polymer chain, whereas those of the b_1 modes are along the polymer chain. The transition dipole moments of the a_1 bands are along the permanent dipole moment of a CF_2 group, which is the origin of ferroelectric properties. The intensity changes of each band were plotted as a function of external electric fields. The plots exhibited the butterfly-type hysteresis curve characteristic of ferroelectrics. The hysteresis curve had a maximum or a minimum at about ±0.6 MV/cm, corresponding to the coercive electric field in the literature. The intensity change of each of the a_1 and the b_2 modes was larger than those of the b_1 bands. This result suggests that the polymer chains are rotated along the polymer chain axis by the electric field. The intensity changes of b_1 bands probably originate from the orientation of polar crystallites. At 0 MV/cm, the intensity change of each band did not return to zero, indicating that the orientation change of the polymer chains remained. Time dependence of the intensity of each band was measured after the removal of an electric field 3.0 MV/cm. The intensity of each band decreased to a constant value. The decay has two components: few seconds and very long lifetime.

(619) **Crystallinity Evaluation of a Biodegradable Polymer by using the new NIR Camera (Compovision) Developed for High Speed Wide Area Measurement**; Daitaro Ishikawa[1], Takashi Nishii[1], Fumiaki Mizuno[2], Harumi Sato[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]Sumitomo Electric Industries, Ltd

This study reports the validity of the new NIR Camera (Compovision) developed for high speed measurement under various practical situations by Sumitomo Electric Industries, Ltd. The several characteristics of Compovision were described in another study. In order to evaluate the performance of Compovision, this study focused on the distribution analysis of crystalline parts in a biodegradable polymer such as poly-L-lactic acid (PLLA). Although investigations were carried out for spectral behavior of biodegradable polymers, unfortunately, distribution evaluation method of fracture or decomposition degree based on NIR imaging has not been fully established yet. Polymer samples should have different crystallinity depending on the annealing conditions and the spatial distribution within the sample is also affected by the difference in the conditions. Therefore, it is thought that it does not only derive in-depth understanding of the conformation and spatial distribution of the PLLA films, but also provide a good opportunity for the evaluation of Compovision. The films were hot-pressed well above its melting temperature at more than 15kg/m2. To make different crystallinity, annealing time changed several intervals. The NIR image consisted by the diffuse reflectance spectra in the 1000 - 2300 nm region was measured by using Compovision. All the spectral data were collected with a 6 nm spectral resolution. The data were collected by the NIR analysis program, and converted into text files per pixel for spectral analysis. The peaks observed at 1690 and 1730 nm may be assigned to the first overtone of CH stretching vibration of the PLLA sample. A peak at 1920 nm may be assigned to the first overtone of CO stretching vibration. It is important note that the peak at 1730 nm decreased with the annealing time and the peak at 1920 nm increased. That is, it is thought that these bands may show the contribution from the amorphous and crystalline structure, respectively. Consequently, the image, defined as these peak intensities, becomes a useful index to estimate the relative population of the crystalline structure. Thais result suggested that the evaluation of the biodegradable polymer is possible by using Compovision.

(620) **Conformational and Structural Studies of n-propylamine from Temperature Dependent Raman and Far Infrared Spectra of Xenon Solutions and ab initio Calculations**; Ikhlas Darkhalil[1], Joshua Klaassen[1], Wouter Herreboutb[2], Johan Domb[2], Benjamin van der Vekenb[2], James Durig[1]; [1]Department of Chemistry, University of Missouri-Kansas City, [2]Department of Chemistry, Universitair Centrum Antwerpen

The Raman and infrared spectra (4000 to 50 cm-1) of the gas, liquid or solution, and solid have been recorded of n-propylamine, CH3CH2CH2NH2. Variable temperature (-60 to -100oC) studies of the Raman (1175 to 625 cm-1) and far infrared (600 to 10 cm-1) spectra dissolved in liquid xenon have been carried out. From these data, the five possible conformers have been identified and their relative stabilities obtained with enthalpy difference relative to Tt of 79 ± 9 cm-1 (0.9 ± 0.1 kJ/mol) for Tg ≥ 91 ± 26 cm-1 (1.08 ± 0.3 kJ/mol) for Gg > 135 ± 21 cm-1 (1.61 ± 0.2 kJ/mol) for Gg' ≥ 143 ± 11 cm-1 (1.71 ± 0.1 kJ/mol) for Gt. The percentage of the five conformers is estimated to be 18 % for the Tt, 24 ± 1 % for Tg, 23 ± 1 % for Gg, 18 ± 1 % for Gg' and 18 ± 1 % for Gt at ambient temperature. The conformational stabilities have been predicted from ab initio calculations utilizing several different basis sets up to aug-cc-pVTZ from both MP2(full) and density functional theory calculations by the B3LYP method. Vibrational assignments have been provided for the observed bands for all five conformers which are supported by MP2(full)/6-31G(d) ab initio calculations to predict harmonic force constants, wavenumbers, infrared intensities, Raman activities and depolarization ratios for both conformers. Estimated r0 structural parameters have been obtained from adjusted MP2(full)/6-311+G(d,p) calculations.

(621) **Local Structure Determination of Thin-Film Boron Carbides**; Wenjing Li[1], Michelle Paquette[1], Sky Driver[1], Sudarshan Karki[1], Bradley Nordell[1], Anthony Caruso[1], Nathan Oyler[1]; [1]University of Missouri-Kansas City

Boron-rich carbides have brought attention of scientists in different fields due to their unique thermal, electrical, and mechanical properties. However, the molecular structure and the mechanism of thin-film boron carbides formation remains a question, which is inhibits our understanding and applications. In this project, amorphous hydrogenated boron carbide thin-film was made by the plasma-enhanced chemical vapor deposition (PECVD) method from the single-source precursor orthocarborane (C2B10H12). To investigate local physical structure of a-BxC:Hy thin-films we applied solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR) methods along with elemental analysis and Fourier transform infrared (FT-IR) spectroscopy. Ab initio calculations were performed to compare with the experimental results in order to propose a structural model.

(622) **Applications of Headspace GC/MS Methods for Assessment of Polymer Aging**; James Lewicki[1], Rebecca Alba[1], Cynthia Alviso[1], Robert Maxwell[1]; [1]LLNL

Headspace sampling paired with gas chromatography/mass spectrometry (HS-GC/MS) is common technique for analyzing evolved volatiles in difficult to analyze samples, such as polymers. HS-GC/MS can provide a rapid and non-destructive method for assessing polymers' health, age, and possible sources of chemical degradation. Polymers are extremely difficult to analyze due to their considerable molecular weight and low solubilities. When polymers are exposed to various external contaminants (i.e. residual acids/bases, humidity, heat, etc.), they can react resulting in unfavorable changes to the properties of the polymer. In addition to these external factors, as polymers age, physical and chemical changes can occur which also affect the performance of the polymer. Monitoring the offgassing of volatile compounds from polymeric materials can be useful to understanding the aging, degradation chemistry, and relative stability of these materials, which is extremely important for lifetime prediction and stability/compatibility assessment. HS-GC/MS provides a technique to assess both the stability and 'health' of complex polymeric systems by monitoring offgassing species, however there are several technical challenges that have to be overcome if a robust and quantitative analytical methodology is to be developed. Difficulties in the analysis and quantitation include understanding the complexity of the system and in optimizing methods for the key offgassing compounds for the materials. This presentation will address some of the complications in polymer offgassing analysis and how these issues were addressed. Various analytical techniques to improve sample analysis were explored including using various collection methods, solid phase microextraction vs. direct headspace analysis, and headspace derivatization to improve compound volatility and reduce polarity of analytes of interest. Additionally, the use of cryogenic trapping and subambient GC separation allowed for speciation of broader molecular weight ranges and peak focusing to increase limits of detection. The methods presented were used to characterize the offgassing of well-defined model PDMS systems, thermally aged and exposed to various external factors (i.e. residual acid/bases, humidity) which can be used to model more complex polymeric systems. Prepared by LLNL under Contract DE-AC52-07NA27344

(623) **Analysis of Inorganic Anions in CVD snd ALD Precursors gor Semiconductor Industry**; Abul Azad[1], Hugh Gotts[2]; [1]Balazs Nanoanalysis, Air Liquide Electronics U.S. LP, 13546 N. Central Expressway, [2]Balazs Nanoanalysis, Air Liquide Electronics U.S. LP, 46409 Landing Pkwy

Semiconductor device fabrication produces integrated circuits on highly purified and well defined silicon substrates. A variety of metallic and silicon compounds are used to create thin films on surfaces for specialized applications. The precursor compounds used in the semiconductor industry are extensively purified, and both metallic and inorganic anion impurities should be tightly controlled in these chemicals. Due to the high reactivity and interference effects of the decomposition by-product, analysis of precursor compounds is a challenge for the analytical chemist. In this paper a simple ion chromatographic method for analysis of inorganic anions in precursor compounds has been reported, in which hydrolyzed precursor compounds were analyzed. The effect of pH of the hydrolyzed sample, soluble decomposed product and soluble metal hydroxide on analysis of inorganic anions in precursor compounds had been investigated. The % recovery for several 0.1 ppm anion spiked precursor samples were in the range of 90-95%. The method was successfully applied to silicon and other metal containing precursor compounds.

(624) **Optimization and Validation of a Solid-Phase Microextraction Method for Determination of Volatile Organic Compounds from Aspergillus Flavus by Gas Chromatography Mass Spectrometry**; Dongdi Sun[1], Alicia Wood-Jones[2], Todd Mlsna[1], Richard Baird[2]; [1]Chemistry Department, Mississippi State University, [2]Department of Entomology & Plant Pathology, Mississippi State University

Aflatoxin-producing members of Aspergillus flavus are universal and widespread in nature. They can colonize and contaminate corn before harvest or during storage. Aflatoxins are toxic to humans and animals, and are one of the most carcinogenic of all natural compounds. The studies of volatile organic compounds (VOCs) metabolites from different fungi using Solid Phase Microextraction (SPME) or Purge and Trap methods has been accomplished by many research institutions, however, none of them has systematically developed a method for qualitative and quantitative analysis of VOC metabolites produced by the fungus. This sort of quantitative information is required for early identification of the presence of Aspergillus flavus. In this study, 15 standards which were reported by previous researchers as being produced by this fungus are tested using headspace solid-phase microextraction (HS-SPME) combined with Gas Chromatography Mass Spectrometry. The results have been used for method development in the identification of the fungus. A PDMS/CAR fiber has been shown to provide the best efficiency for extracting alcohols, ketones and hydrocarbons produced by Aspergillus flavus at lower concentrations. The limits of detection of 15 standards are also determined for quantification analysis of VOCs from aflatoxins producing fungi. The headspace analysis of volatile fungal metabolites in corn media confirmed that the SPME-GCMS technique is a suitable monitoring technique for the fast detection of aflatoxins producing fungi.

(625) **Effect of Iron on Volatile Organic Compounds Produced During Pineapple Fermentation Using HS-SPME and GC/MS**; Matthew Essandoh[1], Jon Deweese[1], Todd Mlsna[1]; [1]mississippi State University

The aroma and thus the quality of wines are impacted by the volatile organic compounds produced during the fermentation process. The main objective of this work is to study the effect of different concentrations (0 to 24 ppm) of iron added to the wort on ethanol and other volatile organic compounds produced during pineapple wine fermentation. Headspace solid phase microextraction (HS-SPME) and direct gas injection in collaboration with gas chromatograph – mass spectrometry (GC-MS) was performed to study the volatile profile produced during phase one (aerobic) and phase two (anaerobic) of the fermentation process. Many classes of compounds were produced during phase one and phase two. A critical study of when and which compounds are produced indicates that there are certain chemicals that are distinct to certain phases. For example, 2, 3, 4 -trimethyl pentane, 2 – methyl propanal, ethyl 2 –methyl butane, methyl ethanoate, methyl 2 - methyl propanoate, methyl pentanoate, methyl propanoate are compounds that were produced only in phase 1 while 2–methyl-1-butanol, 3-methyl-butyl octanoate, 3-methyl butyl hexanoate, 3-methyl butyl pentadecanoate, decanoic acid, ethyl heptanoate, ethyl dodecanoate, ethyl nonanoate, octanoic acid and phenyl ethanol are compounds that were produced only in phase 2. Of the compounds produced and collected in the headspace, 7.41% were alcohols, 2.47% aldehydes, 13.5% alkanes, 6.17% alkenes, 9.88% carboxylic acid, 50.62% esters, 1.23% ketones and 8.64% miscellaneous compounds. Specific gravity determination shows that as the concentration of iron increases the specific gravity increases indicating less production of ethanol. Analysis of the volume of the gas produced during fermentation is underway to quantify how the rate of carbon dioxide or ethanol production changes with different iron concentrations.

(626) **Determination of Ascorbic Acid, Sugars, Organic Acids and Total Phenols of Different Cultivars of Citrus Fruits**; Jose-Luis Todoli[1], Silvia Carballo[1], Soledad Prats, Salvador Maestre[1], Amanda Terol[1]; [1]University of Alicante

Fresh citrus fruits and its derivatives are products with a high-market consumption and production all over the world. Ascorbic acid, sugars, organic acids and total phenols are studied because of its importance on organolpetic and nutritional quality, and its beneficial health effects. In this study ascorbic acid, sugars (glucose, fructose and sucrose) and organic acids (citric and succinic acids) were determined by High Performane Liquid Chromatography (HPLC) in twenty-eight cultivars of sweet oranges (Citrus sinensis) and tangerines (Citrus reticulata and Citrus hybrids). All the samples were collected at the optimum maturation stage and cultivated in the same experimental orchard. Juice of samples was extracted and stored at -18ºC on PVC tubes. Before analysis juice was defrosted, centifugated and and diluted on Milli-Q water. Separation and detection of interested components was performed using a Zirchrom SAX column and a Photodiode Array Detector (PDA) at a 254 nm wavelength for ascorbic acid determination, a Hamilton RCX-10 column for sugars determination coupled to a Refractive Index Detector (RID) and a Rezex RHM-Monosaccharide and a PDA at a 210 nm for organic acid analysis. Total phenol determination was obtained by the Folin-Ciocalteau's method. Some basic parameters like edible portion, juice percentage, titratable acidity and ºBrix (total soluble solids) also are described. The results have shown that ascorbic acid acid varies in high degree among varieties from 22 up to 85 mg/100 mL. For organic acids, citric reaches levels up to 20 g/L whereas 2,9 g/L are found for succinic acid. Phenol total analysis have shown concentration values ranging from 25 to 72 mg gallic acid/100 mL. As was expected the blood type sample Sanguinelli orange has the highest concentration in this compound, 67,4 mg galic acid/100 mL. In relation to the basic parameters determined, edible portion shows no significant differences between oranges and tangerines. Highest variation is shown on juice percentage and acidity. From the data obtained, it is possible to establish a classification of the samples as a function of their similarities or differences in terms of concentration in ascorbic acid, sugars, organic acids, total phenolic components and some basic parameters studied.

(627) **Wheat Early Generation Desirable Wheat Glycolipid Quality Prediction from 100 mg of Wheat Endosperm as a Boon to Breeding for End Use Quality**; David Wetzel[1], Allan Fritz[1]; [1]Microbeam Molecular Spectroscopy Laboratory and Agronomy Dept., Kansas State University

Revealing the level of desirable glycolipids that enhance the breadmaking quality of new experimental lines in the breeding program has been laboriously achieved in the past with extraction fractionation and either liquid or supercritical chromatography. We describe ranking new lines of wheat cultivars two generations earlier than previously possible. Using tandem mass spectrometry on lipid total extract enables analyzing 100 mg or less of combined endosperm obtained from dissection of 5-7 individual wheat kernels. The sensitivity of MSMS not only accommodates the smaller samples, but the sequential concentration, collision, and programmable selectivity for the glycolipid fraction of interest eliminates the previous lengthy stepwise procedure. For decades, elevated digalactosyldiglyceride (DGDG) content has been used as an important predictor of eventual quality for end use in breadmaking. A two-fold range of DGDG occurs even within only two breeding nurseries and is greater for a single year among all experimental wheat lines produced. The practicality of DGDG determination was formerly limited because of time; initially 22 hours and subsequently 38 minutes with selective supercritical extraction followed by LC and SFC. This is the practical method for large scale, seasonal desirable lipid screening of breeding lines.

(628) **Flour Stream Purity Determination via Quantitative Near Infrared Chemical Imaging**; Tyler Nickoley[1], Mark Boatwright[1], David Wetzel[1]; [1]Microbeam Molecular Spectroscopy Laboratory, Kansas State University

Individual flours streams from a commercial wheat milling operation are combined to maximize patent flour yield, while meeting the purity specifications expected by the buyer. Whereas traditional analyses of flour purity measure sample impurity, we propose direct measurement of the flour product (endosperm). For this experiment, quantitative near infrared imaging was used to calculate the percentage endosperm of twenty three flour streams collected from the Kansas State University Pilot Mill. By using the recently developed quantitation of endosperm and measurement of flour stream flow rates, a cumulative endosperm curve was created showing the weighted combination of successive ordered streams.

(629) **FT-IR Spectral Studies on the Identification of Organic Foreign Matters in Food**; Joon Shik Park[1], Sung Chel Shin[1], Ju Young Lee[1], Kyeon Yeol Kim[1], Sheen Hee Kim[1], Woo Seong Kim[1], Ki Seoung Kwon[1]; [1]Busan Regional Korea Food and Drug Administration

The presence of foreign matters in food is of major concern to both producers and consumers. After discovering them, rapid identification of their nature is necessary to help to eliminate or reduce their presence and improve food quality with consumers satisfied. Fourier transform–infrared (FT-IR) spectroscopy is ideal for use in the non-destructive identification of the various types of matters swiftly and easily. It is widely used to confirm, identify, and detect matter in many applications. Also, it is effective for the analysis of foreign matter analysis. We investigated the applicability of FT-IR for the chemical identification of a wide variety of organic foreign matters that can be present in food and made a variety of spectra in a searchable spectral database including natural and artificial organic materials in order to identify foreign matters in food later.

(630) **Application of Handheld and Portable Infrared Spectrometers in Bovine Milk Analysis**; Poliana Macedo dos Santos, Edenir R. Pereira-Filho, Luis Rodriguez-Saona; [1]Universidade Federal de São Carlos, [2]The Ohio State University

Milk is one of the most important natural food, composed by essential nutrients (water, carbohydrate, fat, protein, minerals and vitamins) that provide great nutritional relevance for human, particularly during childhood. In 2007–2008, the problem of milk adulteration gained substantial notoriety with the addition of melamine. Nowadays, the occurrence of milk adulteration is a major issue in the dairy industry, and has been causing concerns among costumers and food manufacturers. The objective of this study was examined the feasibility and compare the performance of handheld and portable infrared spectrometers (IR) to identify and quantify milk adulteration using pattern recognition techniques including soft independent modeling of class (SIMCA) and partial least squares regression (PLSR) algorithm. Milk samples were purchased from local supermarkets (Columbus, OH, USA) and spiked with tap-water, whey, hydrogen peroxide, synthetic urine, urea and synthetic milk in different concentrations. Spectral data was collected using portable and handheld mid-infrared (MIR) and near-infrared (NIR) spectrometers. Classification models based on SIMCA exhibited tight and well-separated clusters allowing the discrimination of control samples (unadulterated) from adulterated milk. PLSR models showed high coefficients of correlation ($r > 0.98$) and relatively low standard error for cross validation (SECV < 1% (v/v)). Results obtained indicated that the MIR was superior to the NIR systems to detect and quantify adulteration in milk. These study confirm the feasibility to apply portable and handheld MIR spectrometers to check milk authentic and the method can provide an alternative methodology to

the dairy industry for screening potential fraudulent practice for economic adulteration of cow's milk.

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(631) **Using Infrared Spectroscopy to classify types of grape and regions in Peru's Piscos**; Marçal Plans Pujolras[1], Beatriz Hatta-Sakoda[2], Juan Carlos Palma[2], Luis Rodríguez-Saona[1]; [1]The Ohio State University, [2]Universidad Nacional Agraria La Molina

Pisco sprit is the most consumed distillate drink in Peru and Chile obtained by batch distillation and vaporization of wine made from different varieties of Muscat grapes, being considered a high-quality product of economical importance for the region. Pisco is an eau-de-vie obtained exclusively through the distillation of recently fermented fresh musts of grapes, governed by denomination of origin and varieties of grape that may be grown for Pisco. The most representative varieties of Peruvian pisco are Italia and Quebranta. Our aim was to develop a rapid FT-IR method in combination with multivariate data analysis to classify Peruvian Pisco spirit based on grape variety and production region. A total of 42 Pisco samples were provided by the Universidad Nacional Agraria (UNALM, Lima, Peru) that included Puro Italia (23) and Puro Quebranta (19). Among these samples, we had Pisco samples of known denomination of origen from Lima (n=8) and Ica (n=12). Samples were dried with a rotavapor and registered with FTS 3500GX with Attenuated Total Reflectance (ATR). Soft Independent Modeling of Class Analogies (SIMCA) algorithm was used to classify groups. Our results showed that FT-IR was able to classify the Muscat grape varieties Quebranta and Italia (interclass distance, ID=2.7). SIMCA also showed good discrimination power to classify Pisco samples by region (ID=3.5). Interestingly, we found large variability in copper content among Pisco samples ranging from 0.53 to 8.19 mg Cu/L. FT-IR combined with pattern recognition (SIMCA) analysis showed potential as a discrimination tool for differentiating samples based on production region and Muscatel's grape source.

(632) **Finding Metal-protein Binding Constants Under Equilibrium Conditions Using Separation by Ultracentrifugation and Detection by ICP-MS**; James Holcombe[1], Isaac Arnquist[1]; [1]University of Texas at Austin

The coupling of separation by preparative ultracentrifugation and metal detection by inductively coupled plasma mass spectrometry (ICP-MS) has been explored for metal-protein equilibrium determinations. This study characterizes the stoichiometry as well as apparent (K_{app}) and intrinsic (K_{int}) binding affinities of the metal-protein association for a model protein. In particular, the affinity of Cu^{2+} for the high affinity binding site in bovine serum albumin (BSA) is determined. Once equilibrium is established between Cu^{2+} and BSA, preparative ultracentrifugation moves the metalloprotein away from the meniscus, leaving unbound copper that was previously in equilibrium with the BSA in the protein free solution. Since the initial (total) concentrations of purified BSA and Cu^{2+} can be determined, the free copper concentration at equilibrium can also be determined by taking a small aliquot above the sedimenting boundary for analysis using ICP-MS. This analysis allows for the determination of free Cu^{2+} ion, which is identical to the equilibrium concentration prior to ultracentrifugation. From these data apparent (K_{app}) and intrinsic (K_{int} , viz., pH-independent K) equilibrium binding constants were determined. The Tris buffer also participates as a Cu binding ligand and is accounted for in the calculations. log K_{app} values of 17.6 and 14.6 were determined at pH 9.53 and pH 7.93, respectively. Furthermore, pH-independent log K_{int} values of -1.43 and -1.04 were determined at pH 9.53 and 7.93, respectively. While the log K_{int} at pH 9.53 was in good agreement with literature values obtained from alternative methods, K_{int} at pH 7.93 was about 2.5x larger than previously reported. BSA undergoes a structural rearrangement between pH 7-9, and the generally accepted pH-dependency of protein tertiary structure may be responsible for the variations in the "intrinsic" binding constant. The Cu-BSA binding affinity was also monitored in 100 mM Tris 0.1% SDS solution at pH 7.93 in order to determine the effect of a denaturant on metal binding. This study validates and shows the efficacy of combining preparative ultracentrifugation with ICP-MS detection for interrogating metal-protein associations while causing minimal equilibrium perturbations as a result of the separation and measurement processes. Impact of SDS and DTT on binding will also be discussed.

(633) **Cooking Solid Samples in a Graphite Furnace. A Story of Metals, Non-Metals and Nanoparticles**; Martin Resano[1], Maria R. Flórez[1], Engracia Mozas[2], Eduardo Bolea, Maite Aramendía[3]; [1]University of Zaragoza, [2]Technological Institute of Aragón (ITA), [3]Centro Universitario de la Defensa, Zaragoza

The use of direct solid sampling techniques provides important advantages in terms of sample throughput and limits of detections, but typically brings about more possibilities of suffering from spectral overlaps, owing to the presence of all the matrix components. Thus, the success of these techniques depends to a large extend on the possibilities to improve their resolution. If we focus on electrothermal atomic absorption spectrometry (ETAAS), the recent development of high-resolution continuum source (HR-CS) represents a significant step forward in this direction [1,2]. This technology has brought new possibilities to the field. Among the main benefits of the novel HR CS ETAAS technique, the following can be listed: i) improved correction of complex and rapidly changing background structures; ii) potential for expanding the often very narrow linear range of the technique; iii) possibilities for monitoring molecular lines for elements for which the measurement of atomic absorption is complicated. iv) potential for simultaneous monitoring of several lines. The purpose of the work is to discuss in detail these new characteristics and discuss how these advantages open new opportunities for the analysis of complex matrixes, particularly for situations in which analysis of solid samples containing nanoparticles or direct analysis of nanomaterials is aimed at.

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(634) **"Cold" Methods for ADME (Absorption, Distribution, Metabolisation and Excretion) Studies of Candidate Drugs using ICP – Mass Spectrometry**; Frank Vanhaecke[1], Björn Meermann[1], Andrei Izmer[1], Deepti Gholap[1], Sylvia Van Dorpe[2], Filip Cuyckens[2]; [1]Ghent University, Department of Analytical Chemistry, [2]Drug Safety Studies, Janssen R&D

In pharmaceutical R&D, it is common practice to label a candidate drug compound with a ^{13}C- or ^{3}H-radiolabel to facilitate quantitative determination of its metabolites and to realize visualization of its distribution over the body tissues of a test animal. For both purposes, the use of a radiolabel can be avoided, provided that a "hetero-element" that can be monitored using ICP – mass spectrometry is present in the active component. Present-day ICP-MS instrumentation not only enables monitoring of metals and metalloids, but also of several non-metals, such as some halogens, sulfur and phosphorus. In this presentation, the successful use of reverse phase liquid chromatography (RP-HPLC) hyphenated to ICP-MS in an actual clinical study with human volunteers will be reported on. The administration of ^{14}C-labeled drug was not advisable in the context of the study as a result of the long tissue half-life of the drug compound. On-line species-unspecific isotope dilution as a powerful way for handling the variation in sensitivity accompanying the use of

gradient elution provided reliable quantification. As avoiding radiolabeling renders the "cold" approach more straightforward and less expensive, it can also already be deployed at an earlier stage of the drug development. In case also endogenous compounds containing the target element are present in the sample studied, a version of the drug molecule containing the hetero-element in a non-natural isotopic composition can be administered to unequivocally identify the compound-related components. Finally, also the capabilities and limitations of the combination of laser ablation (LA) and ICP-MS for visualization of the distribution of the hetero-element present in the drug compound over the body tissues in a thin section of test animal will be covered.

(635) **Matrix Interferences in ICP-AES: How to Recognize and Eliminate Them**; Gary Hieftje[1], George Chan[1], Yan Cheung[1]; [1]Indiana University

Ralph Sturgeon has made many key contributions in several fields of atomic spectrometry, notably in electrothermal vaporization and in photochemical vapor generation. Perhaps not surprisingly, Ralph has avoided when possible the use of inductively coupled plasma–atomic emission spectrometry (ICP-AES). After all, that method is known to suffer from several kinds of matrix interference, and there is ordinarily no way to tell if such interferences are present or what their magnitude might be. The poor analyst is faced with the choice of tolerating the interference and the error it causes, or resorting to time-consuming and laborious procedures such as matrix matching, standard additions, and internal standardization. What would be desirable is to have available a method that flags when an interference exists and, even better, to indicate experimental conditions under which the interference is minimized or, ideally, eliminated. In the present study just such a method will be introduced, described, and evaluated. It relies upon the fact that atomization, ionization, and excitation conditions vary from location to location in an ICP. As a result, the severity of matrix interferences is also spatially dependent. An indication of this behavior can be found in the classical study by Blades and Horlick[1], in which a "crossover point" in the vertical spatial emission pattern was found; at this point, the interference is absent. Regrettably, the crossover point differs from element to element and from sample to sample, so a single location cannot be used. Here, a more general approach is used; the spatial emission pattern of the calibration samples is compared with that of a new sample; if the patterns do not match, the samples are behaving differently and an interference can be inferred. Importantly, the method is rather general; it can be used to flag spectral, sample-introduction, drift, and ICP excitation interferences. It also can be applied to both end-on or side-on viewing of an ICP and to use of either aqueous or organic solvents. In an extension of the method, it allows the interference-free crossover point to be determined if one exists.

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(636) **Electrothermal Vaporization or Atomization on Tungsten Coil for Analytical Atomic Spectrometry**; Xiandeng Hou[1]; [1]Sichuan University

Tungsten coil device has been used in analytical atomic spectrometry for approximately 40 years for sample vaporization or atomization. These vaporizers/atomizers can be easily electrically heated up to over 3000 K at very high heating rates, with a simple power supply, and the whole device can be very compact. Here we report our recent work using tungsten coil as an electrithermal vaporizer for sample vaporization into atomizers such as new plasmas and flames, and as an atomizer or excitation source, for atomic spectrometry.

(637) **Single Cell Raman Micro-Spectroscopy – a Powerful Tool in Biophotonics**; Juergen Popp[1, 2], Michael Schmitt[2], Benjamin Dietzek[1], Ute Nerugebauer[1], Christoph Krafft[1], Petra Roesch[2]; [1]Institute of Photonic Technology, [2]Institute for Physical Chemistry and Abbe Center of Photonics, Friedrich-Schiller University Jena

Raman spectroscopy has been recognized to be a powerful tool to study biological cells. One challenge in Raman microspectroscopy of biological cells is the analysis of the spectra. Since Raman spectra of biological samples like cells or tissue are superpositions of the molecular information from all components within the laser focus special statistical / chemometrical methods to properly analyze the data are necessary. Here we describe briefly some of our latest results concerning the application of Raman microspectroscopy in combination with innovative chemometrics to characterize prokaryotic and eukaryotic cells for biomedical applications. The first part reports about the great potential of Raman microspectroscopy in combination with modern chemometrics for a rapid microbial analysis i.e. the identification of single bacterial cells without the need of pure cultures or any cultivation step. For real samples like e.g. soil or blood, the localization of single bacteria in the vicinity of different abiotic particles is challenging. One way for the localization of bacteria is the use of active fluorescent staining methods. The main focus within the second part of this presentation is concerned with Raman studies on eukaryotic cells for biomedical applications. Due to the larger size of eukaryotic cells, sub-cellular features such as nucleus and vesicles can be resolved using Raman microscopic imaging. In particular we will report about the development of classification algorithms capable of distinguishing between normal and tumor cells based on their biochemical composition. Thereby cellular Raman spectra were recorded after drying, in laser tweezers or trapped in a microfluidic environment.

(638) **Investigation of Single Cell Raman Spectroscopy as a Tool for Monitoring Radiation Therapy Treatment Progression**; Andrew Jirasek[1], Quinn Matthews[1, 2, 3], Julian Lum[3], Alexandre Brolo[2]; [1]University of Victoria, Dept. Physics and Astronomy, [2]University of Victoria, Dept. Chemistry, [3]BC Cancer Agency, Vancouver Island Centre

Currently, dose prescriptions for radiation therapy cancer treatment are derived from statistically based prior population outcomes, with limited ability to tailor these prescriptions to any given individual. As such, biologically adaptive radiotherapy stands as a potentially large step forward in modern radiation therapy treatment of cancer. In this talk, we investigate the possibility of utilizing single cell Raman spectroscopy for identifying, characterizing, and monitoring radiation damage in irradiated biological material. The prospects of utilizing Raman spectroscopy as an augmentative technique in the goal of personalized therapy outcome prediction and treatment monitoring are investigated.

(639) **Raman Study of Colorectal Cancer in Live Mouse Model and Cells**; Hidetoshi Sato[1], Akinori Taketani[1], Kosuke Hashimoto[1], Yui Maeda[1], Mika Ishigaki[1], Bibin B. Andriana[1]; [1]School of Science and Technology, Kwansei Gakuin University

Many researchers pay keen attention to Raman spectroscopy for cancer detection and diagnosis. Some clinical application studies demonstrate high performance of Raman spectroscopy in the cancer diagnosis. It is important to know the origin of molecular compositional changes which is observed with Raman spectroscopy in the cancer tissues. In the present study, we undertake basic researches on advance and cure of tumor using live colorectal cancer mouse models and cells. It was succeeded to monitor Raman spectra of the advancing tumor using miniaturized Raman endoscope for a several months. The data shows continuous alteration in molecular composition in the tissue. The most remarkable change is decrease in collagen concentration. It may suggest the expansion of cellular part

in the lesion along with the increase in its size, or the decomposition of collagen by the tumor cells. We are currently working on the histopathological observations of the tissues and cellular study to find out its mechanism. In contrast to molecular biology and biochemistry, Raman spectroscopy can detect total molecular changes in the tissues and cells. The basic research is important to relate the Raman data to knowledge of biology.

(640) **Multiplexed 3D Raman and SERS Imaging of Cells**; Sarah McAughtrie[1], Katherine Lau[2], Karen Faulds[1], Duncan Graham[1]; [1]University of Strathclyde, [2]Renishaw plc

Surface-enhanced Raman spectroscopy (SERS) is an optical spectroscopy technique which has recently found application in the field of intracellular imaging. Although still an emerging technique, the ability to measure SERS spectra inside cells is a potentially powerful application of the technique, especially since sensitive and reliable imaging is required for a whole host of diagnostic and therapeutic applications. Traditionally, fluorescence spectroscopy has been the technique of choice within this area but SERS confers numerous advantages over fluorescence namely the ability to obtain specific molecular information, its multiplexing capability and high sensitivity. In the specific case of intracellular disease it has long been recognised that no single targeting agent can provide the information needed to fully characterise or detect a disease process. As a result, recent research has focussed on the development of a multi-marker approach to improve the sensitivity and specificity with which cellular diseases are detected. With these criteria in mind, we have developed a range of SERS nanoprobes which could be detected within single cells and cell populations, in a multiplexed fashion. We have also used confocal 3D Raman and SERS imaging for the simultaneous confirmation of cellular inclusion and multiplex detection thus avoiding the need for expensive transmission electron microscopy (TEM) images. At present the nanoprobes are un-functionalised, but it is anticipated that following functionalisation with organelle specific peptide sequences we will demonstrate their ability to function as targeting agents for the detection of early cellular disease markers.

(641) **Non-Invasive Single Cell Cytometry Using Label-Free Biophotonic Techniques**; James Chan[1]; [1]University of California, Davis

Cytometry, the analysis of single cells and its subcellular components, is a powerful and essential technique in all areas of fundamental and applied biological, biomedical, and clinical research. Traditional cytometry, whether implemented as an imaging or flow-sorting platform, is largely dependent on the use of exogenous fluorescent dyes for labeling specific molecules to obtain biochemical information of the cell. Despite its prevalence, there are several drawbacks of using fluorescent labels for cytometry, such as (i) photobleaching of the signal that limits the ability to study long-term cellular dynamics, (ii) the lack of defining cellular markers that can be labeled for identifying cell phenotypes, (iii) perturbation of the native biological system, and (iv) low multiplexing capabilities for assessing different chemical species simultaneously due to the limited number of labels that can be detected or imaged at the same time. My research interest is in advancing the field of cytometry through the development and application of novel biophotonic technologies for single cell analysis. These technologies all have a common theme: they enable the direct acquisition of biochemical information from the cell without requiring any exogenous labeling or genetic modification of the sample. The introduction of these non-invasive, label-free capabilities to cytometry would enable new ways of detecting cells and analyzing their biochemical and dynamic properties. This would signify a major paradigm shift in the field that ultimately will enable important biomedical problems to be solved. This talk will focus primarily on our development and application of laser tweezers Raman spectroscopy (LTRS) for identifying cells and characterizing their chemical properties. In addition to highlighting past applications of this technology for discriminating cancer cell populations, identifying stem cells and their progeny, and monitoring cellular response to drugs, we will also present a novel application of LTRS for studying the biochemical response of cells to mechanical forces. For the first time, we show the use of LTRS to measure a force induced deoxygenation of red blood cells (RBCs) and the ability to discriminate normal and diseased RBCs based on this unique behavior.

(642) **Photoacoustic Tomography: Ultrasonically Breaking through the Optical Diffusion Limit**; Lihong Wang[1]; [1]Washington University in St. Louis

Photoacoustic tomography (PAT), combining optical and ultrasonic waves via the photoacoustic effect, provides in vivo multiscale non-ionizing functional and molecular imaging. Light offers rich tissue contrast but does not penetrate biological tissue in straight paths as x-rays do. Consequently, high-resolution pure optical imaging (e.g., confocal microscopy, two-photon microscopy, and optical coherence tomography) is limited to depths within the optical diffusion limit (~1 mm in the skin). Ultrasonic imaging, on the contrary, provides good image resolution but suffers from poor contrast in early-stage tumors as well as strong speckle artifacts. In PAT, pulsed laser light penetrates the tissue and generates a small but rapid temperature rise, which induces emission of ultrasonic waves due to thermoelastic expansion. The ultrasonic waves, ~1000 times less scattering than optical waves in tissue, are then detected to form high-resolution images at depths up to 7 cm, breaking through the optical diffusion limit. Further depths can be reached by using microwaves or RF waves as the excitation source. PAT, embodied in the forms of scanning photoacoustic microscopy or photoacoustic computed tomography, is the only modality capable of imaging across the length scales of organelles, cells, tissues, and organs with consistent contrast. Such a technology has the potential to enable multiscale systems biology and accelerate translation from microscopic laboratory discoveries to macroscopic clinical practice. PAT may also hold the key to the earliest detection of cancer by in vivo label-free quantification of hypermetabolism, the quintessential hallmark of cancer. The technology is commercialized by several companies.

(643) **Advanced Image Reconstruction Methods for Photoacoustic Tomography Brain Imaging**; Mark Anastasio, Chao Huang, Lihong Wang; [1]Washington University in St. Louis

Photoacoustic tomography (PAT) is an emerging soft-tissue imaging modality that has great potential for a wide range of biomedical imaging applications. It can be viewed as a hybrid imaging modality in the sense that it utilizes an optical contrast mechanism combined with ultrasonic detection principles, thereby combining the advantages of optical and ultrasonic imaging while circumventing their primary limitations. The goal of PAT is to reconstruct the distribution of an object's absorbed optical energy density from measurements of pressure wavefields that are induced via the thermoacoustic effect. In this talk, we describe innovative advancements in practical image reconstruction approaches for PAT in heterogeneous acoustic media. Such advancements include physics-based models of the measurement process and associated inversion methods for reconstructing images from limited data sets. Applications of PAT to transcranial brain imaging are presented.

(644) **Photoacoustic Contrast Imaging of Biological Tissues with Nanodiamonds Fabricated for High Near-Infrared Absorbance**; Xinmai Yang[1]; [1]University of Kansas

Radiation-damaged nanodiamonds (DNDs) are potentially ideal optical contrast agents for photoacoustic imaging in biological tissues due to their low toxicity and high optical absorbance. We synthesized a new DND by He+ ion beam irradiation with very high near-infrared

absorption. These DNDs produced a 71-fold higher photoacoustic signal on a molar basis than similarly dimensioned gold nanorods, and 7.1 fmol of DNDs injected into rodents could be clearly imaged 3 mm below the skin surface. Experiments with live animals bearing head-neck cancer and breast cancer showed significant enhancement in imaging contrast.

(645) **Polarization-Sensitive Optical Coherence Tomography**; Gang Yao[1]; [1]University of Missouri

Optical Coherence Tomography (OCT) is a non-invasive optical imaging technique that can provide real time depth-resolved sample structural images with high resolution. Based on optical coherence domain reflectrometry (OCDR), OCT utilizes broadband light in an interferometer configuration to detect light echoes from reflective/scattering interfaces at different depths inside sample. Two or three-dimensional images are acquired by combining one-dimensional OCDR with sequential transverse scans. Polarization-sensitive optical coherence tomography (PSOCT) is an extension of conventional OCT by incorporating polarization measurements. Many tissues such as muscle, tendon and cartilage have highly organized structures and show strong intrinsic polarization properties such as birefringence and diattenuation. Such structure related polarization properties can be altered by medical conditions and thus are sensitive markers for disease diagnosis. Being able to measure depth-resolved polarization parameters, PSOCT has been proven useful in many biomedical applications as well as in material characterization. However, due to the round-trip reflectance measurement in OCT, conventional PSOCT measurements provide only integrated results from the sample surface to a particular measurement depth. When the optical axis varies with sample depth, the true local polarization properties cannot be directly calculated from the integrated measurements. We have developed novel algorithms to systematically reconstruct the sample Jones matrix from which the true local polarization properties can be obtained. This new methodology for PSOCT has been demonstrated in both *in vitro* and *in vivo* imaging examples.

(646) **A History of Analytical Chemistry in the Midwest: Regional Performance with Global Impact**; James Spigarelli; [1]Midwest Research Institute (Retired)

The decade of the 1970's, ushered in a period of rapid development of the measurement tools available to analytical chemists. The advancement of these tools and techniques allowed applied analytical chemistry to play a key role in shaping and ensuring compliance with national policy for protecting the environment and people. The formation of the United States Environmental Protection Agency (EPA) in 1970 was a seminal driving force in providing target requirements and standards of performance through various acts including the Clean Air Act (1970), Clean Water Act (1972), Toxic Substances Control Act (1976) and other crosscutting acts and agreements. The impact of these acts on other agencies and the private sector spurred funding on applied research and development in industry and the Department of Defense. This presentation will describe a number of key studies performed in the Midwest that provided the quality data needed to set national emission standards, determine maximum achievable control technologies, determine health risks, and monitor large scale waste destruction to ensure public safety. New methods requiring detection in the parts per million and parts per trillion levels of a wide variety of toxic materials in complex matrices were required to meet the changing standards for public health risk. For the Department of Defense and State Department, methods were developed and applied to support policy on chemical warfare treaty negotiations and potential exposure of troops to Agent Orange. Advances in applications of mass spectrometry, chromatography, atomic spectroscopy and statistical methods are highlighted.

(647) **Identification of Multiple Conformers of Molecules which Associate by Utilizing Rare Gas Solutions with Variable Temperature Vibrational Spectroscopy**; James R. Durig[1], Joshua J. Klaassen[1], Ikhlas D. Darkhalil[1]; [1]University of Missouri - Kansas City

There were a large number of conformational stability studies carried out in the 1960's and 70's which were determined from variable temperature solutions with non-polar solvents or in some cases the pure liquids. Many different techniques were used but infrared and Raman spectroscopy were the most popular. At that time period there were many reasons for obtaining the most stable conformer such as the structure, steric effect, chemical association, to name a few. However the reasons for determining conformational stabilities have drastically increased from the field of biochemistry and nano-chemistry. These areas have caused a great deal of interest in conformational stability due to its effects on binding sites of proteins in biochemistry and the use of conformer interchange to drive molecular motions and shapes in nano-chemistry. Specifically the conformation of organoamines is currently at work in every human alive with this arising from the amino acids in proteins and the substituted bases in DNA and RNA. The importance of conformational stability is further demonstrated in biological systems by enzyme binding where the conformational changes of the protein can change the binding site either enhancing or deactivating the enzyme. The problem of conformational interchange in organoamines though is complications due to self-association even in the simplest forms so by using analogues of the more complex organoamines such as ethylamine can result in a difficult experiment. Dimer, trimer, and larger complexes are found for many amines even in vibrational spectra of the vapor phase at moderate pressures. The presence of these complexes not only complicate the spectra but will cause any temperature dependent determination of the enthalpy difference value significantly higher than is realistic for a conformational interchange. This association may be avoided by utilizing extremely low pressures with very long path lengths or solutions of the organoamine with a solvent that has little to no interaction with the sample. An excellent solvent for this purpose is xenon. Our research group has been determining the conformational stabilities of many substances by variable temperature infrared spectra of xenon solutions and recently with Raman spectra.

(648) **Enhanced Detection of Trace Elements in High-Purity Sulfuric Acid Uing Ultrasonic Nebulization with ICP-AES Detection**; Fred Smith[1]; [1]CETAC Technologies

Water quality is a critical issue in boiler water reactor (BWR) nuclear power plants. Plant water for steam generation is analyzed after passage through sampling filters to check for indications of corrosion. Corrosion particulate matter can cause numerous problems, including reduced water flow rates, increased pump head pressures, and loss of heat exchange efficiency due to solids buildup on metal surfaces. These problems can all lead to expensive component repairs and/or replacements. The filters in the water filter packs are periodically removes and digested in a sulfuric acid solution to check for indications of corrosion. This paper will examine the use of an efficient ultrasonic nebulizer (USN) with ICP-AES to improve trace element detection in a 7.5%(v/v) high-purity sulfuric acid matrix. Elements of interest include Al, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Ti, W, Zn, and Zr. A particular goal is to lower instrument detection limits (IDLs) for K and Na below 0.1 microgram/L in this matrix. Figures of merit using the USN for introduction of the diluted sulfuric acid include IDLs, calibration, and analyte recoveries.

(649) **Determination of Pollutant Concentration in Spiked Wastewater Samples through Multivariate Regression Modeling of UV-visible Spectral Data**; Amy Fine[1], Bridget O[1], Jemima Ingle[1]; [1]University of Saint Mary

The Environmental Protection Agency (EPA) designates 126 pollutants as priority pollutants, mandating acceptable levels for wastewater; many others are regularly monitored. Such pollutants include phenol and ammonia. In this paper, we describe continuing studies in the development of a method for determining concentration of phenol and ammonia in wastewater using multivariate regression modeling of UV-visible spectral data. Although established methods currently exist for these determinations, these methods involve time-consuming, costly, and/or environmentally unfriendly complexation steps. The goal of this project is to devise a more efficient and cost-effective method of determining the concentration of these pollutants. Previous work had demonstrated the viability of this technique for samples of phenol and ammonia in distilled water and tap water. In this study, samples of effluent wastewater were taken from a local wastewater plant. These samples were analyzed for their phenol or ammonia content, and the samples were then spiked with additional pollutant. The UV-visible spectrum of each sample was obtained, and the spectral data subjected to a PLS-1 regression analysis. The regression models were used to predict the concentration of pollutant in unknown samples. The results of these studies continue to be promising. This paper will discuss the methods and results for the compounds and conditions studied to date.

(650) **Semi-Micro Mid-Infrared Analysis of 100 mg of Composited Wheat Endosperm Enables Protein Content Ranking with a Generational Leap**; David Wetzel[1], Mark Boatwright[1], Allan Fritz[1]; [1]Microbeam Molecular Spectroscopy Laboratory and Agronomy Dept., Kansas State University

Wheat breeders traditionally use multigenerational grow-outs of new breeding lines to obtain a sufficient quantity of flour by small-scale milling for physical dough testing and experimental baking. Sensitive semi-micro chemical compositional analysis by mid-infrared spectroscopy enables ranking the relative protein to starch ratio of nursery breeding lines a generation earlier than previously possible. This provides objective selection criteria for the breeders. Using only 100 mg of wheat endosperm from 5-7 kernels with a typical weight of 30 mg each provides a sufficient flour blend to enable mid-infrared scanning. A system is described for fine powder compaction that has been developed to achieve optical contact for diamond internal reflection. Practical ranking by selective relative protein to carbohydrate band ratioing is shown for early generation breeding lines from Kansas Agricultural Experiment Station nurseries. To the best of our knowledge, the Kansas Agricultural Experiment station is the first wheat breeding group to employ this small sample, early generation method. Ranking of protein content with a generational leap potentially enables breeders to eliminate inferior cultivars of one experimental crop year. Efforts of successive generations can then be concentrated on genetically worthy candidates.

651) **Screening Counterfeit Drugs Using Portable NIR Spectrometer**; Ravi Kalyanaraman; [1]Ravi Kalyanaraman

Counterfeit and adulterated drugs have caused a serious threat to patients in the US after the recent Avastin® injection incident and they have entered the pharmaceutical supply chain due to increasing international trade and sales via the internet. Due to this infiltration, pharmaceutical manufacturers are finding ways to authenticate and identify their product by various technologies. One of the effective ways to authenticate and verify the contents in a pharmaceutical product is by using portable Near Infra-red (NIR) spectrometer to obtain a unique fingerprint of the drug product itself. Using these product fingerprints, it is possible to test a suspect sample and identify if it is a counterfeit and also to authenticate if it is a legitimate product. Solid (tablets, capsules and powders) dosage forms were analyzed directly through packaging, such as glass and blister packs and were non-destructive with no sample handling or preparation required. Examples of counterfeit drugs identified using portable NIR spectrometer and the strategy used to develop, validate and maintain the NIR fingerprint will be discussed. These devices can potentially be utilized as a screening tool in the field and the decision making process in identifying a counterfeit drug can be vastly improved in terms of time, cost and efficiency.

(652) **Rapid Screening of Illegal Weight-Loss Substances in Dietary Supplements using a Hand Held Ion Mobility Spectrometer**; Laura Mecker, Jamie Dunn, Connie Gryniewicz-Ruzicka, John Kauffman, Benjamin Westenberger, Lucinda Buhse; [1]US FDA/Division of Pharmaceutical Analysis

In recent years, there have been several reports describing the detection of synthetic weight-loss drugs in dietary supplements marketed for the treatment of obesity and weight-loss purposes. Herbal products have been adulterated with not only pharmaceutical products (fenfluramine, fluoxetine, phentermine, sibutramine, sertraline, orlistat), but also with synthetic analogues of these drugs, such as desmethylsibutramine and didesmethylsibutramine. The presence of these illegal adulterants in dietary supplements poses a serious health risk to consumers and has prompted the FDA to develop rapid and reliable screening methods to assess the quality and safety of dietary supplements and pharmaceutical products. Ion mobility spectrometry (IMS) is an ideal screening tool for the detection of weight-loss adulterants in dietary supplements because hand held formats are available and samples can be analyzed on-site with analysis times on the order of minutes. This presentation will describe the development of a rapid and reliable IMS screening method for the identification of illegal weight-loss substances in dietary supplements. It will discuss the factors that influence the sensitivity of this method with respect to illegal adulterants as well as highlight the current success of field deployment for on-site sample analysis at U.S. mail import facilities.

(653) **Implementation of a Portable Raman Device in the Pharmaceutical Laboratory**; Jeff Denault[1], Michael Dotlich[1]; [1]Eli Lilly and Co

Current regulations requiring container level identification testing for raw materials used in the manufacture of pharmaceutical products has the potential to significantly increase the workload required of the Quality Control Laboratory. Conventional methods for identification of raw materials are often time consuming and require a variety of chemical reagents to execute. Additionally, many materials require multiple identification tests due to the non-specific nature of any individual test. The use of a handheld Raman system provides a unique solution to material identification. For many Raman active materials, the assessment of selectivity may result in multiple methods being replaced, thereby replacing a significant number of test methods. Based on the portable nature of the device, the choice of test location, i.e., in the laboratory or warehouse, presents its own opportunities and challenges in implementation. This talk will address technical and logistical opportunities and challenges in developing, validating, transferring, and implementing a portable technology in a Pharmaceutical manufacturing facility.

(654) **A Portable Gas Chromatograph for the Monitoring of Biomass Gasification**; Bidhya Kunwar, Todd Mlsna; [1]Mississippi State University

Fossil fuels, coal, oil and natural gas are non-renewable sources of energy that are being consumed by the world at an unsustainable rate. The consumption of fossil fuels is also a major source of environmental pollutants and greenhouse gases. Therefore, biofuel can be a renewable environmentally friendly alternative for fossil fuel. In order to reduce transportation cost, mobile technology is

required that is capable of converting biomass to fuel at the source of the biomass. Presented here is the development of an autosampling, portable gas chromatograph for the continuous online monitoring of biomass gasification during the production of synthesis gas (primarily CO and H2). For improved portability and ease of use, the system was designed with the ability to operate with ambient air as a carrier gas and without the requirement of an oven. For automated operation a six port valve with a gas sampling loop is included. The detector for the chromatograph is a commercial-off-the-shelf metal oxide-based detector and the entire system fits into a portable weatherproof case for field use. Design features, calibration, and results of pilot scale testing are presented. Intelligent control is needed to consistently manage the biomass gasification process to yield a syngas composition matching downstream process needs and preventing excessive tar levels and unwanted emissions. Most of the parameters affecting product composition can be readily controlled but the feedstock composition and moisture content are naturally variable and very difficult to measure continuously. Because of the varied composition of biomass, refinery output is highly sensitive to the naturally variable feedstock characteristics. A robust, feed-stock composition sensitive control system would greatly improve biorefinery efficiency.

(655) **Improving Excipient and Raw Material Screening through Portable Near Infrared and Raman Spectroscopic Methods**; Jason Rodriguez[1], Connie Ruzicka[1], Derya Cebeci Maltaş[1], John Kauffman[1], Lucinda Buhse[1]; [1]FDA, Division of Pharmaceutical Analysis

Over the past few years, FDA's Division of Pharmaceutical Analysis has reported on the sensitivity of library-based spectral correlation methods and their transferability between different portable spectrometers. Library-based spectral correlation methods are qualitative techniques that allow for rapid, nondestructive screening of pharmaceutical materials. In addition, they typically do not require sample preparation and can be easily used by investigators in the field with little or no expertise. Despite these promising attributes, traditional library-based spectral correlation methods which utilize the hit quality index (HQI) are much less sensitive to the presence of contamination/adulteration than latent variable-based methods. We will report on our efforts to enhance the sensitivity of near infrared and Raman library-based verification and identification methods using latent-variable procedures and our attempts to assess their sensitivity towards detecting economically-motivated adulteration levels in pharmaceutical raw materials.

(656) **Plasmonic Nanoparticles in Biosensing and Bioimaging**; Li-Lin Tay[1]; [1]National Research Council

Resonance excitation of the localized surface plasmon resonance and its coupling in closely interacting (aggregated) plasmonic nanostructures is known to generate intense SERS activity. This unique optical property coupled with the well established surface chemistry of noble metal nanoparticles enables these nanostructures as optical labels for a variety of sensing, imaging and bioanalytical applications. Furthermore, the large electron density of the labeled Au nanoparticles doubles as the contrasting agent in electron microscopy, thus providing additional characterization options in ultramicroscopy. While the sensitivity of SERS rivals that of conventional fluorescence labeling techniques, its chemical specificity and the possibility of spectral multiplexing must be considered to be its greatest strengths. In this presentation, we will outline our recent effort in employing the plasmonic nanoparticles as SERS label in imaging of cell surface receptors of mammalian cells and sensing of pathogenic microorganisms. We will also show that combined imaging by optical and electron microscopies of the plasmonic nanoparticles labeled cells allows us to quantify the receptors as well as to reveal their nanoscale interactions. The design incentives for SERS labels required for receptor imaging and pathogen detections are also quite different and also will be discussed in this presentation.

(657) **New Insights in Single Molecule SERS**; Alexandre Brolo[1], Marica L. A. Temperini[1,2], Diego P. dos Santos[1,2]; [1]University of Victoria, Department of Chemistry, [2]University of Sao Paulo, Department of Chemistry

Surface-enhanced Raman scattering is among the few optical methods that allow single-molecule detection. The single molecule signature of SERS is now well-established by a series of bianalyte experiments. Among the main characteristics of a single molecule SERS experiments is the fluctuations in SERS intensities. However, the variations in SERS intensities are accompanied by variations in the Stokes/anti-Stokes ratios. In this work, we will show how the analysis of this ratio can lead to new ways to infer the single molecular characteristic of SERS. We will also described how the analysis of the statistics of this ratio can provide insights into the energy of the local resonances at the hot-spots that enable single-molecule SERS.

(658) **Imaging SERS Hot Spots with Super-Resolution Microscopy of Multiple Analytes**; Katherine Willets[1]; [1]University Of Texas at Austin

Surface-enhanced Raman scattering (SERS) occurs when a molecule is adsorbed to a nanoscale metal substrate that enhances local electromagnetic fields through the excitation of localized surface plasmons. The region of the SERS substrate that provides the strongest overall enhancement is known as a hot spot. Unfortunately, the size of hot spots are sufficiently small that they are well below the optical diffraction limit, which prevent objects smaller than roughly half the wavelength of light from being resolved. This talk will describe the application of super-resolution microscopy to defeat the optical diffraction limit and probe the size, shape, and local enhancement of nanoparticle-based SERS hot spots with <5 nm resolution. Multiple analytes are introduced to the nanoparticle surface and the origin of the SERS signal from each dye is uniquely resolved, allowing different hot spots to be imaged in a single experiment. The results are then correlated with the structure of the underlying nanoparticle, in order to determine how structural heterogeneity dictates the variable SERS responses from these nanoparticle-based substrates.

(659) **Monolithic Nanoporous Gold Disks as Surface-Enhanced Raman Spectroscopy Substrates**; Wei-chuan Shih[1], Ji Qi[1], Pratik Motwani[1], John Wolfe[1]; [1]University of Houston

Surface-enhanced Raman spectroscopy (SERS) has been widely used for high-sensitivity molecular detection and identification. When a molecule of interest is near the nanostructured surface of a noble metal such as gold or silver, the localized surface plasmon resonance (LSPR) effect can boost the Raman scattering by many orders of magnitude. Because the LSPR is a near-field phenomenon and decays rapidly with increased separation distance between the molecule and the nanostructure, the SERS signal primarily arises from the molecules residing within a few nanometers of the nanostructured surface. Therefore, it is advantageous for a SERS substrate to have a large surface-to-volume ratio from the standpoint of optical sampling efficiency. In this paper, we show, for the first time, that monolithic nanoporous gold disks (NPGD) can be effective SERS substrates with large surface area. The size of NPGD is tunable from 100-500 nm in diameter and 40-100 nm in thickness, resulting in high-density SERS substrates. The average enhancement factor of an individual NPGD is ~100 million. A single NPGD coated with benzenethiol self-assembled monolayer (~10 attmoles) can provide SERS spectrum with a signal-to-noise ratio ~400, resulting in an estimated detection limit ~25 zeptomoles. We characterized the SNR of SERS spectra obtained from individual NPGD using various detector

integration time and detector temperature. We show that a single NPGD can provide SNR ~ 13 dB using an integration time of 25 msec. At 1-sec integration time, a single NPGD can provide SNR ~14 dB using a detector at 25 degrees Celsius.

(660) **Optimizing SERS Tags For Their Applications**; Griff Freeman[1], Michael Natan[1]; [1]Cabot Corporation

SERS tags are novel optical detection labels with a readout based on Raman spectroscopy, with applications in life science (both in vitro and and in vivo diagnostics) and in brand security/anti-counterfeiting. The particles, typically a few hundred nm in diameter, comprise one or more Au nanoparticles, a "reporter" molecule adsorbed to the surface of the particle(s), and a silica shell. Laser irradiation (at wavelengths between 633 and 1550 nm) of these materials yields intense, exceptionally stable Raman spectra of the adsorbed reporter molecules. Combinations of particles with different reporters can be used simultaneously, generating a more complex spectral fingerprint that is easily deconvolved. Over the past decade, synthesis and scale-up of these materials, using many different types of Au particles, different levels of aggregation, and dozens of different reporter molecules have been optimized, and an understanding of the key performance parameters, among the most important being brightness, has been gained. Perhaps the most important result is that the antenna is not made up merely of the Au particles. Rather, antenna must take into account the excitation wavelength, the reporter molecule, and the silica encapsulant. Among the specific materials factors that come into play are the size and aspect ratio of the particles and of the aggregate, the size and shape of the reporter, and the thickness and density of the glass. A SERS tag geometry optimized for a particular reporter at a certain excitation wavelength will not be optimal at a different excitation wavelength, something SERS theorists and experimentalists would know. Surprisingly, that geometry is not optimal at the same excitation wavelength for a different reporter. In other words, the particle and reporter are an inseparable pair that must together be optimized. This presentation will highlight key principles of antenna design, and then describe recent results on rapid assays for three different explosives, on the use of particles for in vivo applications, and for potential opportunities in labeling of pharmaceutical tablets.

(661) **Isotopic Determination of Uranium Samples Using Passive Gamma Spectroscopy with Multiple Detectors**; Steven Horne[1], Brian Dickson[1], Sheldon Landsberger[1]; [1]University of Texas at Austin

Uranium samples of various enrichments have been passively counted on the University of Texas detector system consisting of two HPGe gamma detectors and a NaI(Tl) active shield. By looking at ratios between gamma rays emitted from U-235 and its daughters compared to gamma rays emitted by U-238 daughters and comparing these ratios between standards of known enrichments, we have developed a technique to take a uranium sample of unknown enrichment and passively count it to determine the isotopic concentration, specifically the ratio of U-235 to U-238 in the sample. Because the gamma rays from U-235 are generally in the low-energy regime, there is a strong susceptibility to background interferences, especially from the Compton background produced from higher energy gamma rays. Other interferences, such as those from the decay series of uranium also exist for U-235 gamma rays. In this light, we have collected data using list-mode with digitizers to produce two-dimensional gamma-gamma coincidence spectra, which allows us to gate the low-energy gamma rays from U-235 with gamma rays that are in coincidence. In doing this, much of the low energy interferences are reduced, and one can analyze the U-235 gamma rays with a high degree of precision. A big advantage to this method is the capability for performing this analysis with small (<1 g) samples in a non-destructive and relatively inexpensive manner. If necessary, this analysis can be performed within 24 hours if an urgent nuclear forensics scenario arises.

(662) **Spectroscopic Examination of the Volatile Organic Compounds Comprising the Bouquet of RDX-based Explosives**; Trocia Clasp[1], Taylor Ingle[2], Janet Jamison[2], Roger Buchanan[3], Tiffani Johnson[1], Scott Reeve[1]; [1]Arkansas Center for Laser Applications and Science (ArCLAS), Arkansas State University, [2]Arkansas Biosciences Institute, Arkansas State University, [3]Department of Biological Sciences, Arkansas State University

The detection of v_{28} fundamental band of isobutylene in the vapor signature of polyisobutylene (PIB) were observed using a FTIR spectrometer at a spectral resolution of 0.125 cm-1. The rotational structure of the vapor signature emanating from the PIB sample had a regular pattern in the P and R branches, with an energy level spacing similar to isobutylene. Further analysis of the rotational structure yields a set of molecular constants consistent with v_{28} fundamental band of isobutylene. In addition, higher resolution scans of the vapor signature were recorded with a Pb-salt tunable diode laser spectrometer. In these scans, the spectra collected above the PIB sample were identical with those obtained for a pure sample of isobutylene. The R(3415-3314)/R(3412-3311) transitions were chosen for a limit of detection study. We determined the limit of detection to be 173 ppb (instrumental response) and 210 ppb (area under the curve) respectively. A GCMS was used to detect the signature fractioning pattern of isobutylene collected above RDX-based explosives using solid phase microextraction (SPME) . The base ion peak 41 m/z (99%), molecular ion 55 m/z (16%) and 39 m/z (45%) were used for confirmation. Here we will describe the optical based measurements as well as a series of GCMS measurements which unambiguously identify isobutylene as an explosive bouquet compound. This work has been approved as Distribution A: unlimited public release.

(663) **Towards the Analysis of Forensically Relevant DNA on a Microfluidic Platform**; Claire Lenehan[1], Leigh Thredgold[1, 2], Dmitriy Khodakov[1, 2], Hilton Kobus[1], Adrian Linacre[3], Gunther Andersson[1, 2], Amanda Ellis[1, 2] ; [1]School of Chemical and Physical Sciences, Flinders University, [2]Flinders Centre for NanoScale Science and Technology, Flinders University, [3]School of Biological Sciences, Flinders University

Short tandem repeat (STR) analysis has proven to be a powerful forensic tool for the identification of individuals and wildlife. Currently, this technique is performed on large scale laboratory instrumentation, namely by capillary electrophoresis. The ability to miniaturise this technology onto a microfluidic device has the potential to improve forensic human and wildlife identification in terms of speed, cost and accuracy of results. We have successfully modified PDMS microchannels to attach single-stranded DNA (ssDNA) oligonucleotide capture probes via a thiourea linkage for DNA preconcentration. This presentation details our recent work into the development of on chip portable detection systems based on capacitively coupled contactless conductivity detection (C4D) and LED induced fluorescence detection (LED-IF).

(664) **Accessing the Probative Value of Forensic Evidence with a Ruggedized, Portable Mass Spectrometer Capable of Ambient Ionization**; Christopher Mulligan[1], Kyle Vircks[1], Adam O[1]; [1]Illinois State University

The amount and variety of evidence collected at a typical crime scene is extensive. While many significant analytical methods have been established over the years, forensic laboratories cannot keep up with the demand, and in many cases, significant backlogs of evidence have amassed. While this points to a need for more rapid, streamlined technologies for forensic analysis, a significant reduction in collected evidence, leading to a subsequent reduction in backlogged evidence, would come from the ability to access the probative value of

chemical evidence at the crime scene itself, allowing only pertinent samples to be sent to off-site laboratories for confirmation. In an effort to fulfill the current technological needs of forensic science practitioners, we report the application of a ruggedized, portable ion trap mass spectrometer capable of atmospheric pressure and ambient ionization techniques to the rapid screening of chemical evidence in solid, liquid and gas states with little to no sample preparation. The variety of applicable ionization techniques, including electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), desorption electrospray ionization (DESI), and low temperature plasma ionization (LTP), ensures flexibility towards potential forensic evidence. The instrument has been characterized through the analysis of an array of chemical species, including commonly-occurring classes (illicit drugs, abused pharmaceuticals, accelerants) and others of interest (cutting agents, "bath salts" and other designer drugs, cosmetic traces and dyes, methamphetamine precursors). Initial studies demonstrate broad applicability and exhibit high sensitivity (high pg to low ng detection limits for chemical residues) and selectivity through MS/MS confirmation. As authentic forensic evidence can have complex geometry (e.g. glassware and storage media found at clandestine meth labs) or reside on surfaces that are not amenable to direct analysis, swabbing/physical transfer protocols have been investigated to ensure application to these types of samples, and transfer efficiencies using both wet and dry swabbing have been determined. To allow use by non-technical personnel, "red light/green light" software protocols employing a predetermined mass spectral library have been implemented. Considering the high utility of this technology, the potential impact on criminal justice practice at the local and state level is also examined.

(665) **Time Dependent Particle Characterization of Residual Materials on Fingerprints**; Jason Guicheteau[1], Ashish Tripathi[1, 2], Erik Emmons[2], Steven Christesen[1], Augustus W. Fountain III[1]; [1]USA RDECOM Edgewood Chemical Biological Center, [2]Science Applications International Corporation

We present results from a time-dependent study analyzing fingerprint traces deposited on surfaces after an initial contact with exogenous materials. Fingerprints were initially contaminated with energetic materials and subsequent fingerprint impressions were made onto surfaces at various times over a four hour period. Fingerprint impressions were made on aluminum microscope slides once every hour during this period of time. The person carried on his daily routine during the period of this study. The routine activities included working on a computer terminal, driving, reading, eating, etc. The fingerprints were interrogated for the presence of energetic material residue with a Fiber Assisted Spectral Translation (FAST) Raman Chemical Imaging system. Certain preselected regions of the fingerprint were analyzed. The positive identification of the energetic trace material along with an estimation of its particulate size was obtained. A trend showing particle size dependence with respect to time of deposition was observed.

(666) **Confocal Raman Microscopy to Investigate the Polymerization Kinetics and Properties of Individual Optically Trapped Vinyl-Polymerized Vesicles**; Jonathan Schaefer[1], Joel Harris[1]; [1]University of Utah

Sodium 11-acrylamidoundecanoate (SAAU) is a surfactant with an acrylamide functional group capable of spontaneously forming bilayer structures in water including tubules, rods, and spherical vesicles that can be polymerized using a radical initiator. While the kinetics of SAAU polymerization has been studied in concentrated bulk solutions, there have been no Raman spectroscopic studies of their structure or polymerization kinetics. In this work, individual SAAU particles are optically trapped using a tightly focused 647.1 nm beam from a Krypton laser passed through a high N.A. microscope objective. Raman scattered light from the optically trapped SAAU particle was collected through the same objective and integrated to produce a Raman spectrum. Optically trapped SAAU particles were exposed to a radical initiator at elevated temperature (~50 °C) to initiate the polymerization of the acrylamide functional group, stabilizing the structure. Polymerization of the SAAU particle was measured from structural changes detected in the time-dependent Raman spectra, including the loss of the C=C stretch of the vinyl group at 1628 cm-1. As the SAAU structure is polymerized and the monomers are linked together, a porous particle is formed and stabilized, even at high temperatures (above 50 °C). This attribute makes these structures potentially suitable as a drug delivery vehicle. A series of confocal Raman spectra were collected under z-axis control to estimate the diameter of a polymerized SAAU particle and relative concentrations of Raman active components present inside and outside the particle. The z-scan through the polymerized SAAU particle revealed the particle was solid and SEM images confirmed its uniform porous structure. Confocal Raman microscopy is capable of detecting low concentrations of analyte in small volumes (~1.0 fL), so the adsorption of a payload molecule, dioxybenzone (a sunblock agent) into a polymerized porous SAAU particle interior was examined. Dioxybenzone has a large Raman cross section and accumulates within the porous particle interior, which has a surface area high enough to detect the adsorbate. To our knowledge this is the first direct measurement of the polymerization kinetics and accumulation properties of individual SAAU particles.

(667) **Real time and *in situ* Monitoring of a Polymerization Reaction by Raman Spectroscopy And Rheological Measurements**; David Chapron[1], Marie-Claire Chevrel[1, 2], Sandrine Hoppe[1, 2], Laurent Falk[1, 2], Alain Durand[1, 2, 3], Patrice Bourson[1]; [1]Université de Lorraine, LMOPS, [2]CNRS, LRGP, [3]Université de Lorraine, LCPM, UMR

Kinetics of polymerization reactions are governed by closely linked parameters as temperature, reactants concentrations and viscosity. The real time monitoring of each of these parameters during the polymerization process is fundamental to control and optimize the physical and chemical properties of the final product. The association of a rheometer with spectroscopic measurements could be an exhaustive way to control separately all of these parameters. Moreover, optical measurements provide information on the medium components concentrations without introducing a probe into the reactor which could disrupt the process, in particular the rheological measurements. We present a new coupled Rheo-Raman experiment giving the opportunity to monitor in real time and in situ the medium viscosity and the monomer and polymer concentrations. Rheological measurements were performed continuously with a mixer-type rheometer using the Couette analogy, considering the medium in the Newtonian rheological domain. The reactor was designed to allow non contact Raman measurements. The excitation beam was focused and the backscattered signal was collected through the reactor wall. The reactor was placed in a furnace in order to control the temperature of the reaction. As an example, the results on a free radical polymerization of acrylic acid in aqueous solution will be discussed. The acrylic acid monomer and polymer concentrations were remotely monitored by a Raman spectrometer RXN1 (Kaiser Optical Systems). The intensity decrease of the C=C vibration mode is associated to the monomer consumption and the CH band increase is linked to the polymer synthesis. The correlated results from Raman spectra and viscosity measurements versus reaction time will be presented and the advantages and drawbacks of this coupled Rheo-Raman experiment will be discussed.

(668) **Evaluation of Millimeter-Scale Alignment of Cylindrical Domains in Polystyrene–Poly(ethylene oxide) Diblock Copolymer Films by Single Molecule Tracking**; Khanh Hoa Tran Ba[1, 2], Jason

Finley[1, 2], Daniel A. Higgins[1, 2], Takashi Ito[1, 2]; [1]Kansas State University

Single molecule tracking (SMT) was used to reveal the millimeter-scale alignment of cylindrical microdomains in polystyrene–poly(ethylene oxide) diblock copolymer (PS-b-PEO) films induced by the directional penetration of an organic solvent. The trajectories of individual fluorescent molecules that preferentially partitioned into the cylindrical PEO domains were recorded to assess the alignment of the cylindrical PEO domains in PS-b-PEO films sandwiched between two glass plates. Upon the horizontal penetration of 1,4-dioxane vapor through the film, the majority of probes (≥ 70%) moved in one dimension along the direction of solvent penetration with a high degree of orientation, as represented by the 2D orientational order parameter of ca. 0.9. The highly-ordered, 1D trajectories were found throughout the entire film thickness (ca. 4 μm) over a 2 mm length scale. The domain radius estimated from probe positional error (ca. 11 nm) was close to that (14 ± 2 nm) measured by AFM, suggesting that the 1D trajectories could be used to estimate the radius of the cylindrical PEO domains. In contrast, the penetration of benzene or toluene vapor resulted in observation of 2D molecular motion. The results of this study have demonstrated the usefulness of SMT as a tool to investigate the alignment of nanoscale domains in cylinder-forming block copolymer monoliths under ambient conditions.

(669) **Orientation and Structure of Individual Electrospun Fibers by Raman Microscopy**; Christian Pellerin[1], Marie Richard-Lacroix[1]; [1]University of Montreal

Electrospinning is a widely used technique for producing continuous micro- or nanofibers that can find application in tissue engineering, filtration, biosensing, etc. However, their widespread use is still limited by an incomplete understanding and control of their properties, in part because most characterization techniques can only provide bundle-averaged information about their crystallinity and molecular orientation. Here, we demonstrate that confocal Raman microscopy is a powerful tool for the characterization of individual electrospun fibers using poly(ethylene terephthalate) as a model system. Highly reproducible polarized spectra with good signal-to-noise ratio could be recorded in less than one minute. This allowed extracting quantitative information about the molecular orientation, crystallinity, and conformation. A large distribution of orientation was observed from fiber to fiber, associated with the formation of a highly oriented mesomorphic phase. Our recent work on the influence of the collector on the orientation of electrospun poly(ethylene oxide) fibers will also be presented.

(670) **Scanning Angle Total Internal Reflection Raman Spectroscopy Of Thin Polymer Films**; Matthew Meyer[1, 2], Kristopher McKee[1, 2], Emily Smith[1, 2]; [1]Iowa State University, [2]U.S. DOE, Ames Laboratory

We have established methodology for using a near-infrared scanning angle total internal reflection Raman spectrometer for the analysis of thin polymer films and layers at the polymer-air interface. The ability to collect Raman scatter by precisely controlling the evanescent wave perpendicular to the interface allows for high axial resolution, interfacial chemical content and molecule orientation measurements at the polymer-air interface. Total internal reflection Raman spectroscopy at the polymer-air interface offers the advantage of being non-destructive, no sample change such as swelling and increased Raman scatter compared to other illumination geometries. Different thicknesses of polystyrene were spin coated onto a sapphire substrate by systematically varying the solution polystyrene concentration. The studied polymer films have thicknesses ranging from 1.7 microns to 100 nanometers. Polystyrene films were used to develop models of the experimental data at different incident angles. Specific polymer orientation at the interface has also been deduced by measuring the polarization dependence of the Raman scatter. More complex co-block polymers were analyzed to determine formations of heterogeneous domains at the interface with different film thicknesses. Furthermore, multi-layers were measured to detect the polymer layers as close to 100 nm from the interface. The work shows the ability to simultaneously collect qualitative and quantitative information about thin polymer films to obtain chemical content and thicknesses measurements.

(671) **Far-Ultraviolet Spectroscopy in the Solid and Liquid States**; Yusuke Morisawa[1, 2], Akifumi Ikehata[3], Noboru Higashi[4], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]Kinki University, [3]National Food Research Institute, [4]KURABO Industries LTD.

Far-ultraviolet spectroscopy was studied about the allowed electronic transitions of water and organic molecules, such as Rydberg transitions. Because of large absorption cross section of these transitions, absorption spectra were investigated only in the gas phase. As to condensed phase, only few researches were carried out, thus the absorption spectra in the condensed phase were not understood clearly. To solve the above difficulties of FUV spectroscopy in the wavelength region shorter than 190 nm we recently developed a totally new UV spectrometer based on attenuated total reflection (ATR) technique that allows us to measure spectra of liquid and solid samples in the 140-280 nm region. One must notice that spectroscopy in the wavelength region shorter than 190 nm holds considerable promise not only in basic science but also in applications such as qualitative and quantitative analysis, on-line monitoring, environmental geochemical analysis and surface analysis. In this talk we would like to start from a general introduction and brief history of FUV spectroscopy including development of ATR-FUV spectrometers. Then we will introduce our recent experimental results about assignment of FUV spectra of several kinds of organic liquids with aide of quantum chemical calculations. We also include novel experimental results about surface analysis of polymers.

(672) **Calibration Models using Approximate Light Propagation Theories for Decoupling Absorption and Scattering Effects**; Suresh Thennadil[1], Yi-Chieh Chen[1]; [1]University of Strathclyde

Mulitple scattering of light poses a major challenge in the estimation of chemical properties of particulate systems such as blood, tissue, fermentation broths, and pharmaceutical solids. The scattering effect manifests as changes in spectral slope, baseline and broadening of peak and confounds the chemical absorption effect and thus affects the performance of calibration models built on the spectra. Empirical scatter correction methods are commonly used to remove spectral variation resulting from non-chemical effects by using additive and multiplicative or more complex terms. It is possible to effectively decouple the absorption and scattering effects using the underlying physics of light propagation. This approach would be preferrable since robust calibration models can be built on the "scatter-free" absorption spectra resulting from the decoupling step. An approach based on the exact solution of the radiative transfer equation (RTE) to decouple the two effects, has been shown to have the potential to provide significant improvements in model performance1,2. The decoupling step however involves the inversion of the RTE which is computationally intensive and also prone to errors due to convergence issues. In order to make the approach practical and robust, approximate formulas based on the diffusion approximation and the Kubelka-Munk (K-M) theory are considered in this work. The approximate approaches are tested using a data set collected from samples of a model multicomponent system that mimics optical properties of many biological fluids such as tissue, blood or cell cultures. The system consists of intralipid (fat emulsion) as light scatterer, glucose as the target analyte, and urea as the interference component to break the correlation between the concentrations of the chemical species in the system. Using the exact solution of the RTT

as the benchmark approach for the decoupling step, we compare the performance of multivariate calibration models built to predict glucose concentration from the bulk absorption spectra extracted using the two approximate methods of decoupling the absorption and scattering effects. These results are also compared with the traditional approaches consisting of the application of empirical scatter correction methods prior to building calibration models.

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(673) **Tunable Picosecond Spectroscopy for Detection of NO**; Chakree Tangaroon[1, 2], Christopher Lue[1, 2], Scott Reeve[1, 2], Bruce Johnson[1, 2], Susan Allen[1, 2]; [1]Arkansas Center for Laser Applications and Science, [2]Department of Chemistry and Physics, Arkansas State University-Jonesboro

Nitric oxide (NO) is a major chemical byproduct of many photochemically active nitrogen-containing compounds. As a prototypical free radical with very well characterized high resolution spectrum, NO provides a standard spectroscopic fingerprint for indirect quantitative analysis and detection of a number of low vapor nitroaromatic compounds in air through either direct photochemical decomposition of a parent molecule or from its relatively high vapor pressure chemical constituents. In this paper, we will discuss application of picosecond laser spectroscopy for measurements and detection of NO and the nascent NO generated from photolysis. We will give a general overview of our tunable picosecond laser and detection system that we routinely use for probing and exciting the NO gamma band in the 200 - 300 nm wavelength range. This broad wavelength tuning capability of our laser allows us to set up pump-probe type experiments for detecting blue-shifted rovibronic bands, transferring population via stimulated emission pumping, and probing the relative population distribution for NO. In all cases, experiments were performed using laser pulses with a duration of less than 10 ps. As a result, our measurements could be complete before NO undergoes collisional relaxation. DISTRIBUTION STATEMENT A. Approved for public release; distribution is unlimited.

(674) **Discernment of Foreign Mater in Raw Cotton Using Excitation-Emission Spectra**; Gary Rayson[1], Surja Ghale[1], Elizabeth Gámez[1], Dean Anderson[2], Edward Hughes[3]; [1]Department of Chemistry and Biochemistry, New Mexico State University, [2]USDA-ARS, Jornada Experimental Station, [3]USDA-ARS, Cotton Ginning Laboratory, New Mexico State University

Newly harvested cotton can contain 20-40% foreign mater by weight. Ginning is the process by which cotton fibers can be separated from seeds and other undesirable contaminates. This trash can include leaf and plant fragments, immature seeds, stems, and burr fragments from the cotton boll. This foreign material can significantly degrade fiber quality. Identification of those contaminates prior to processing can significantly enhance the efficiency of the ginning process. Multivariate analysis of excitation-emission spectra from plant extracts using a phosphate buffered saline (PBS) solution has been observed to enable segregation of these trash sources. The results of these investigations will be described and their implication for enhanced cotton processing will be discussed.

(675) **Quantitative Near Infrared Chemical Imaging Enables Revelation of Milled Wheat Fraction Physical Separation Relative to Particle Size**; Mark Boatwright[1], Elieser Posner[2], Jeff Gwirtz[3], David; [1]Microbeam Molecular Spectroscopy Laboratory, Kansas State University, [2]ESP International, Savyon, Israel, [3]JAG Services

In a previous article from our laboratory, the mass balance of wheat endosperm was reported from quantitative near infrared imaging for endosperm content of unit processes and their product and byproduct weights (Wetzel 2010). Sieving is the basis of separation used to segregate the product, wheat endosperm (flour), from the residual material to be reworked. The combination and permutation of various sieve openings in the stack of any sifter section is rated by gauge or the micron dimension of the openings. Traditionally, attempted optimization for purity of the endosperm produced is a trial and error process gauged by the inorganic residue after ignition of the organic content. This chemical imaging approach directly reports the endosperm composition as a function of particle size. The practical purpose is to demonstrate optimization of a selected sieving process by a direct objective measurement.

(676) **The Use of Laser Radiation to Modulate Electron Temperature in the Inductively Coupled Plasma**; Paul Farnsworth[1], Alisa Edmund[1], Kyli Bishop[1], Nicholas Taylor[2]; [1]Brigham Young University, [2]Pacific Northwest National Laboratory

When a laser is tuned to an atomic or ionic transition in an inductively coupled plasma, the excited atoms can lose the energy gained by absorption either by producing fluorescence or by undergoing superelastic collisions that convert internal energy into kinetic energy. The most likely collision partner is an electron, so, in a two-step process, laser radiation can be used to heat the electrons. A pulsed laser tuned to the resonance line of a strong absorber can raise the electron temperature enough to cause a transient doubling of the intensity of emission lines from an analyte species. I will present results demonstrating the heating of electrons by laser radiation and discuss possible uses of the phenomenon to enhance the analytical performance of ICP emission instruments and ICP mass spectrometers.

(677) **Aerosol and Particle Generation, Transport and Fate in the ICP**; John Olesik[1], Fang Liu[1], Patrick Gray[1]; [1]Ohio State University

Generation of aerosols, transport of aerosols to the ICP and sample-plasma processes will be discussed. Approaches to generate and transport sample aerosols with the appropriate size to be vaporized, atomized and ionized in the ICP will be discussed. Experimental measurements of aerosol-plasma and particle-plasma interactions will be presented. The behavior of aerosols that are monodisperse, polydisperse but less than 10 μm in diameter and broadly polydisperse will be compared. Experimental measurement of microparticle and nanoparticle vaporization and ionization in the ICP will also be presented. Implications of aerosol properties on ICP-MS sensitivity and precision will be discussed.

(678) **Graphite Furnace High Resolution Continuum Source Atomic Absorption Spectrometry for the Determination of the Main Components Bi, Sb and Te in Thermoelectric Materials Sampled as Slurries of Nanowires**; José A.C. Broekaert[1], Klaus-Georg Reinsberg[1], Christian Schumacher[2], Katharina Moß[1], William Töllner[2], Sonja Heiderich[2], Kornelius Nielsch[2]; [1]University of Hamburg, Institute for Inorganic and Applied Chemistry, [2]University of Hamburg, Institute of Applied Physics

Since some years high resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS-GF-AAS) is commercially available. It allows the sequential determination of several elements by atomic absorption spectrometry without need for changing the primary source from one element to another but also enables it to go new ways in spectral background correction and for enlarging the linear dynamic range. In this work HR-CS-GF-AAS has been used to determine the main components Bi, Sb and Te in thermoelectric materials on the base of these elements. The samples are nanowires, which are 10 to 40 μm in length and 40 to 300 nm in width. These are produced by electrochemical deposition into an aluminum oxide template and analyzed after a selective removal of the template in the form of slurry samples. The absorbances for the Bi 223.0608 nm, Sb 217.5815 nm and Te 214.2814 nm could be recorded sequentially but

without change of the radiation source. For the Te 214.2814 nm line a background correction with a least squares algorithm was performed. The accuracy of the HR-CS-GF-AAS for concentrations of 10 µg•L1 to 500 µg•L-1 in the analysis solutions or 40 – 70% Te, 16 – 35% Sb or 30 – 85% Bi in the samples was confirmed by comparing the HR-CS-GF-AAS results with those of total reflection X-ray fluorescence (TXRF), for which the sample amounts of 0.8 mg to 2 mg of nanowires in 5 µL of slurry were found to be sufficient, and a good agreement was found to exist.

(679) **ICP Organic and Inorganic Sample Analysis with a High Temperature Micro Sample Introduction System**; José-Luis Todolí[1], Raquel Sánchez[1], Carlos Sánchez[1], Charles-Philippe Lienemann[2], Marco Grotti[4], Francisco Ardini[3], Jean-Michel Mermet[4]; [1]University of Alicante, [2]IFP Energies Nouvelles, [3]University of Genova, [4]Spectroscopy Forever

Correcting for non spectral interferences in ICP techniques has been of great interest in the last times. Our knowledge on plasma effects allows us to mitigate matrix effects by modifying the plasma operating conditions. In general terms, it can be stated that by using a combination of low nebulizer gas flow rates together with high RF power values, a robust plasma (i.e., non sensitive to changes in the matrix composition) is obtained. This makes the analyte excitation and /or ionization yield to be independent on the sample nature. The next step has been to understand the role of the liquid sample introduction system on the extent of the interference. Some studies have proven that, in absence of plasma effects, the spray chamber is the main source of these unwanted phenomena. Aerosol evaporation, coagulation, impact losses and droplets fission are among the most significant processes occurring inside the chamber and being affected by the main sample components. The main issue is that the analyte mass reaching the plasma changes as the sample nature is modified. Therefore, robust sample introduction systems are required. The present lecture shows a recent approach in which a low sample consumption nebulizer has been adapted to a high temperature single pass spray chamber. Samples have been introduced following a segmented flow injection approach in which the sample plug has been injected into an air carrier stream. The results obtained for organic samples, such as petroleum fractions, are highly promising and indicate that a single set of standards can be used to quantify metals in a wide range of fuels. This is due to the fact that the analyte transport efficiency is close to 100% for all the samples evaluated. The proposed approach should not be considered exclusively valid for organic matrices. In fact, as will be demonstrated, inorganic matrices can also be introduced into the plasma with a negligible impact on the accuracy. Finally, the method has additional features such as increased sensitivities, reduced limits of detection or shortened wash out times.

(680) **Alternative Strategies for Sample Introduction: Thermal Inkjet Principle for the Generation of Picoliter Volumes**; Nicolas H. Bings[1], Jan O. Orlandini v. Niessen[1], Jan H. Petersen[1], J. Niklas Schaper[1], Tobias J. Fiedler[1]; [1]Johannes Gutenberg-University Mainz, Institute for Inorganic and Analytical Chemistry, Laboratory for Trace Analysis and Plasma Spectrometry

The introduction of liquid samples into plasma excitation and ionization sources in the field of inorganic trace analysis is commonly established through the continuous generation of aerosols via pneumatic nebulization. It is well known that such aerosols not only show a relatively broad particle size distribution but mostly also result in a too high load for the plasma source (ICP) and thus are not suitable for direct introduction. Various spray chamber designs – e.g. optimized for maximum sensitivity or minimum dead volume and wash-out times – serve to overcome this problem, allowing only the small-sized droplets to pass to the plasma source. However, this might also result in an unfavourable loss of sensitivity. Therefore, the accurate handling of small reagent and sample volumes is of particular importance, not only in the field of hyphenated techniques, based e.g. on the combination of capillary electrophoresis (CE) and plasma source mass spectrometry. Commonly, an additional make-up solvent flow has to be added to the eluent flow to meet the specifications of conventional nebulization systems for sample introduction into the plasma source. A new strategy for direct and flexible introduction of liquid samples is desired, preferably on the basis of small and monodisperse droplets, to minimize the risk of contamination and degradation of chromatographic resolution. The recently introduced approach for the generation of individual ultralow-volume droplets and aerosols from liquid samples by applying the developed drop-on-demand droplet and aerosol generator based on thermal-inkjet technology1 will be presented and further developments will be outlined. Advantages, drawbacks and also its potential for couplings with HPLC and CE will be discussed. A novel dosing frequency-based calibration strategy based on the use of a dual-DOD and its application for the analysis of real samples will be introduced2. Furthermore, the application of the DOD as a tool for precise and accurate transfer of liquid samples in the pL range for calibration and sample transfer in LA-ICP-MS and TXRF will be demonstrated.

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(681) **Computational Optimization of Operating Parameters of ICPMS**; Maryam Aghaei, Helmut Lindner, Annemie Bogaerts; [1]PLASMANT, University of Antwerp

An inductively coupled plasma connected to a mass spectrometer interface (sampling cone) is computationally investigated. The effect of injector flow rate, auxiliary flow rate, applied power and pressure behind the sampler is studied. There is an optimum range of injector flow rate for each set up which guaranties the presence and also proper length of central channel in the torch. The results obtained from our model show that according to any specific purpose, it is possible to control that only the injector gas passes through the sampler orifice or it is accompanied by the auxiliary flow. Moreover, depending on geometry, the variation of outgoing gas rate is much less than the variation of the injector flow rate and it causes higher pressure inside the torch. The general effect of increasing the applied power is a rise in the plasma temperature, which results in higher ionization in the coil region. However, the negative effect is reducing the length of the cool central channel which is important to transfer the droplets to the sampler. Depending on the applied power, the position of efficient power coupling changes. Using a proper applied power can rise the efficiency of the system. Indeed, by changing the gas path lines, it can control which flow (central or intermediate) goes to the sampler orifice. As it is also reported from experiments in literature, the pressure behind the sampler has no dramatic effect on the plasma characteristics.

(682) **Simulation of Electron Collision Processes in an Inductively Coupled Plasma**; Ross Spencer[1], David Perkins[1]; [1]Brigham Young University

The rapid response of atomic level populations to laser-induced perturbations reported in the recent paper of Taylor, et al, (J. Anal. At. Spectrom. 2012, Vol. 27, 857) strongly suggests that electron processes were dominant in these experiments. We have written an electron collision simulation code using the Direct-Simulation Monte Carlo algorithm based on the pioneering work of Nanbu. The code does a good job of simulating energy exchange among electrons, but is much more flexible than Fokker-Planck codes. The effects of electron heating by quenching of excited atomic states and of electron

cooling by various collisional processes between electrons and atoms will be reported.

(683) **Advances in the Development of a Novel Pulsed Radio Frequency Glow Discharge Plasma Source for Imaging Spectrochemical Elemental Speciation Analysis**; Wolfgang Buscher[1], Tobias Steingrobe[1], Volker Hoffmann[2], Maxim Voronov[2], Gary M. Hieftje[3], Andrew P. Storey[3], Steven J. Ray[3], Carsten Engelhard[1]; [1]University of Muenster, Applied Atomic Spectroscopy, [2]Leibniz Institute for Solid State and Materials Research Dresden, IFW Dresden e.V., [3]Department of Chemistry, Indiana University

A pulsed rf glow discharge plasma source was developed that generates a large area homogeneous plasma on surfaces of both electrically conductive and non-conductive samples. By imaging spectrochemical analysis the elements on the sample surface can be measured sensitively and speciation analysis of e.g. individual protein spots becomes possible. The project's aim is highly sensitive and element-selective imaging spectroscopy for the elemental speciation analysis of electrophoretically separated (bio-) molecules. The advances of the project and application results shall be presented.

(684) **Analysis of Single Nanoparticles by a New Time-Of-Flight Mass Spectrometer Coupled to Inductively Coupled Plasma Ionization Source**; Olga Borovinskaya[1], Bodo Hattendorf[1], Martin Tanner[2], Sabrina Gschwind[1], Detlef Günther[11]; [1]Department of Inorganic Chemistry, ETH Zurich, [2]Tofwerk AG

The characterization of inorganic engineered nanoparticles (ENPs) by ICPMS has gained significant attention, due to the high sensitivity that ICPMS offers for elemental analysis [1]. Beside the use of ICPMS in combination with separation techniques, the direct single particle (SP) measurement using a microdroplet dispenser has been recently demonstrated [2]. The capability of determining elemental composition, size and concentration of inorganic ENPs makes SP-ICPMS the technique of choice for their comprehensive analysis. However, the multi-element measurement of sub-millisecond signals (200 µs – 500 µs) generated by single nanoparticles still represents a serious challenge for currently available ICPMS instruments, which are limited by the sequential nature of detection or slow spectra acquisition rates.Simultaneous ion detection over the entire range of relevant m/Q, fast data acquisition and high sensitivity are the properties of an ICP mass spectrometer that are required for the unambiguous characterization of single nanoparticles. Therefore, a new prototype ICPTOFMS was designed and constructed by coupling a TOF mass analyzer (TOFWERK AG, Thun, Switzerland) [3] with the ICP and vacuum interface of a commercial quadrupole-based ICPMS instrument (ELAN 6000, PerkinElmer/Sciex, Ontario, Canada), providing quasi-simultaneous detection at µs-time resolution. Using discrete microdroplets consisting of a multi-element solution and containing nanoparticles the capabilities of this instrument for the analysis of ENPs were characterized and will be discussed in detail.

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(685) **Rapid Uranium Isotope Measurements of Solids by Resonance Ionization Mass Spectrometry**; Michael Savina[1], Kim Knight[2], David Willingham[1], Brett Isselhardt[2], Stanley Prussin[3], Michael Pellin[1], Ian Hutcheon[2]; [1]Argonne National Laboratory, [2]Lawrence Livermore National Laboratory, [3]University of California at Berkeley

Resonance Ionization Mass Spectrometry (RIMS) has the potential to overcome some of the limitations of traditional mass spectrometric techniques, such the inability to resolve isobaric interferences, however the complexities of resonance ionization have kept RIMS from growing into a routine method for isotopic analysis outside of select applications where precision and accuracy are less constrained and sample volumes are limited, such as in the analyses of stellar dust grains or one-time demonstrative analyses. RIMS is a form of mass spectrometry that uses lasers tuned to electronic resonances in an element of interest to achieve selective ionization of a single element. Uranium is among the most challenging elements for RIMS analysis due to large isotope shifts and the strong tendency of uranium to desorb from solids in the form molecular oxides rather than atomic neutrals. We describe the development of RIMS methods for the determination of uranium isotope ratios from solid, unprepared samples of uranium oxide. We characterize various laser-induced ionization pathways and their effects on the isotope ratios observed for analysis of uranium desorbed from UO_2 and U_3O_8 and other solid materials using 2-color and 3-color RIMS laser schemes. Additionally, we demonstrate a rapid, robust method for routine *in situ* measurement of uranium isotopes in solid materials by RIMS based on standard-sample bracketing, and assess sources of error that must be addressed in order to report meaningful data.

(686) **Multimode Imaging in the Thermal Infrared: An Overview**; M.L. Myrick[1], Stephen Morgan[1], Heather Brooke[2], Megan Baranowski[3], Jessica McCutcheon[1], Wayne OBrien[1], Nicholas Boltin[1], Stephanie DeJong[1], Brianna Cassidy[1], Zhenyu Lu[1]; [1]University of South Carolina, [2]Merck, [3]Sandia National Laboratory

Current forensic visualization methods for body fluids are not specific, require dark conditions, potentially contaminate the crime scene, and may not always be sensitive. Infrared diffuse reflection spectroscopy provides a potential tool for detecting proteins on crime scene materials like fabrics. The advantages of infrared diffuse reflection are: examiners are not exposed to chemicals, the technique can be used indoors or outdoors under ambient light, patterns are not smeared, stains are not diluted or altered by chemical reagents, and it is quantifiable (maybe). Instruments for forensic analysis need to be cost-effective, and can't require a Ph.D. to use. We built our first prototype on a lab bench based on mid-infrared (IR) diffuse reflection for visualizing latent blood stains. Lock-in amplifier techniques were used to construct the contrast image of the scene on a pixel-by-pixel basis in real-time. A 1000 W dormitory hot plate was used to illuminate the scene with IR light. This large, diffuse light source was modulated with a modified ceiling fan. This provided conventional thermal images for temperature diagnostics; reflectance imaging for spectrum-based discrimination; and thermal re-emission imaging for density/heat capacity discrimination. Our version 2.0 prototype eliminates the bulky lamp and simplifies the data analysis. In this presentation, I'll discuss what happens when the light source is changed to a laser or a visible lamp, when polarization state is made a variable, and when the angle of incidence is varied. Each of these approaches to modifying image contrast has its own unique applications.

(687) **The LIBS - Raman Connection: A Perspective**; Richard E Russo[1, 2]; [1]Lawrence Berkeley National Laboratory

LIBS (Laser Induced Breakdown Spectroscopy) and Raman have been used in many applications as complementary technologies for improving sample characterization. LIBS provides an elemental signature of a sample with through atomic and ionic emission. Raman provides a measure of the molecular character from the vibrational spectra. Features of each technology will be reviewed and improvements in characterization of analysis will be discussed when data from these two technologies are integrated.

(688) i***n vivo*** **Subsurface Raman Spectroscopy: Hardly Possible without Optical Fibers**; Francis Esmonde-White[1], Michael D. Morris[1]; [1]University of Michigan

Almost all in vivo Raman spectroscopy is performed with fiber optic probes touching or close to the skin of a human subject or animal. Advances in the 1980's and 1990's by Mike Angel and others underlie current probe technology. We will briefly discuss some of these important early advances and show how they led to current probe designs. We will also show how progress in this field has benefited from developments in diffuse fluorescence and near infrared absorption spectroscopy and tomography, as they are practiced in the life sciences. Together, this work has enabled our laboratory and others to use Raman spectroscopy to study processes in humans and animals that require repeated measurements over periods ranging from days to months, including our ongoing studies of fracture healing and related topics in orthopaedics. We will also describe projects that address calibration and validation, which are essential elements of any measurement sciences application.

(689) **UV Raman Studies of Protein and Peptide Structure and Folding Studies**; Sanford Asher; [1]University of Pittsburgh

We developed a powerful method to follow the evolution of secondary structure in peptides and proteins. UV Raman excitation into the ~200 nm peptide bond electronic transitions enhance peptide bond amide vibrations of the backbone. A particular band (the amide III_3) reports on the Ramachandran psi angle and peptide bond hydrogen bonding. This band is Raman scattered independently by each peptide bond with insignificant coupling. Isotope editing of a peptide bond (by replacing the C_{alpha-} H with C_{alpha-} D) allows us to determine the frequency of individual peptide bonds within a peptide or protein to yield their psi angles. Consideration of the Boltzmann equilibria allows us to determine the psi angle Gibbs free energy landscape along the psi (un)folding that connects secondary structure conformations. The psi angle coordinate is the most important reaction coordinate necessary to understand mechanism(s) of protein folding.

(690) **Adsorbate-metal Bond Effect on Empirical Determination of Surface Plasmon Penetration Depth**; Karl Booksh, Laurel Kegel, Nicola Menegazzo; [1]University of Delaware

The penetration depth of surface plasmons is commonly determined empirically from the observed response for adsorbate loading on gold surface plasmon resonance (SPR) substrates. The importance of incorporating an additional adsorbate-gold bonding response in the calculation is shown in the near-infrared (NIR) region with a novel variable angle IR accessory coupled to a commercial FT-IR spectrometer. With this system, the bonding effect is determined from the offset of a SPR shift vs. adsorbate thickness calibration and incorporated into the calculation of penetration depth at various excitation wavelengths. Determination of plasmon penetration depth with and without the bonding response for alkanethiolate-gold is compared and shown to exhibit a significant difference for both of two adsorbate systems investigated; alkanethiolate monolayers and polyelectrolyte multilayers. Additionally, plasmon penetration depth evaluated with bonding effect compensation shows greater consistency over different thicknesses and better agreement with theory, particularly for shallowly penetrating plasmons that have high surface sensitivity.

(691) **Non-invasive Identification of Proteoglycans and Chondrocyte Differentiation State by Raman Microspectroscopy**; Katja Schenke-Layland[1, 2], Eva Brauchle[1, 2], Marieke Pudlas[1], Travis Klein[3], Dietmar Hutmacher[3]; [1]Fraunhofer IGB, Dept. of Cell and Tissue Engineering, Stuttgart, Germany, [2]University Hospital of the Eberhard Karls University Tuebingen, Germany, [3]Institute of Health and Biomedical Innovation, Queensland University, Kelvin Grove, Australia

Proteoglycans (PGs) are crucial extracellular matrix (ECM) components that are present in all tissues and organs. Pathological remodeling of these macromolecules can lead to severe diseases such as osteoarthritis or rheumatoid arthritis. To date, PG-associated ECM alterations are routinely diagnosed by invasive analytical methods. Here, we employed Raman microspectroscopy, a laser-based, marker-free and non-destructive technique that allows the generation of spectra with peaks originating from molecular vibrations within a sample, to identify specific Raman bands that can be assigned to PGs within human and porcine cartilage samples and chondrocytes. Based on the non-invasively acquired Raman spectra, we further revealed that a prolonged in vitro culture leads to phenotypic alterations of chondrocytes, resulting in a decreased PG synthesis rate and loss of lipid contents. Our results are the first to demonstrate the applicability of Raman microspectroscopy as an analytical and potential diagnostic tool for non-invasive cell and tissue state monitoring of cartilage in biomedical research.

(692) **Raman Spectral Imaging of Stem Cell Colonies and Tumour Spheroids**; Max Diem[1]; [1]Northeastern University

We report confocal, three-dimensional Raman spectral images of stem cells, stem cell colonies, embryonic bodies and tumour spheroids, which are models to mimic the growth of solid tumours. In the latter, the level of oxygenation, the pH, and the cellular growth patterns can be monitored by Raman spectral imaging. Major advantages of Raman imaging are its label-free operation, vibrational fingerprint sensitivity, confocality and ability to measure in aqueous media. Disadvantages include the low Raman scattering cross section which necessitates the use of sophisticated image analysis methodology. Yet, the specificity of the Raman signals to distinct biochemical components in stem cells allow the observation of effects that cannot be observed using more conventional methods such as confocal fluorescence microscopy. This presentation will emphasize aspects of cell differentiation into germ layers, the loss of cell synchronization, and aspects of cell growth stimulation and inhibition.

(693) **Label-Free Molecular Characterisation of Live Stem Cells by Raman-Micro-Spectroscopy**; Ioan Notingher[1], Flavius Pascut[1], Adrian Ghita[1], Chris Denning[1], Virginie Sottile[1]; [1]University of Nottingham

Stem cell therapy is widely acknowledged as a key medical technology of the 21st century. These cells have enormous potential for cell replacement therapies in curing age-related illnesses such as Alzheimer's and Parkinson's disease, as well as diabetes and cardiovascular disorders. Label-free non-invasive techniques capable of phenotypic identification of live cells within highly heterogeneous populations are valuable for improving the differentiations conditions as well as developing methods for enrichment of cell populations. Raman micro-spectroscopy (RMS) is a label-free technique which can be used for imaging of live cells. This technique combines the high chemical specificity of Raman spectroscopy with the high spatial resolution of optical microscopy to provide detailed molecular information of complex biological samples. Since RMS has only a minimal background signal from water, it allows repeated observations of viable cells maintained under physiological

conditions. In the first part we will focus on using RMS for detection of molecular markers for individual live cardimyocytes (CMs) derived from human embryonic stem cells (hESCs). The ability to monitor and quantify these spectral markers during differentiation periods as long as 5 days is also demonstrated. The measurements show the ability to monitor the metabolic changes (swithc from glycolytic to oxidative phosphorylation) occuring during the differentiation of the hESCs towards the cardiac phenotype. The prospects of label-free Raman activated cell sorting are also discussed. The second part will present results on using RMS for imaging and quantifying spectral markers in neuronal stem cells (NSCs). Raman spectra of undifferentiated NSCs are compared to those of glial cells derived from NSCs, aimed at identifying molecular markers which can be used for assessing the differentiation status of the NSCs. High resolution spectral maps corresponding to nucleic acids show that NSCs are characterized by increased concentrations of cytoplasmic RNA.

(694) **Measurements of Integrin Mobility in the Membrane of Cultured Cells using Single Particle Tracking (SPT) Technique**; Dipak Mainali[1], Aleem Sayed[1], Emily Smith[1]; [1]Iowa State University

Single Particle Tracking (SPT) experiments were performed to determine if ligand affinity affects the diffusion of an important class of membrane proteins termed integrins. Integrins are an important family of cell surface receptors that maintain a dynamic flow of information between the external and internal environments of the cell for the survival, growth, proliferation, differentiation, and proper functioning of cells. The SPT experiments used functionalized quantum dots with a physisorbed layer of integrin ligand to measure the lateral mobility of wild-type (αPS2CβPS) and high ligand affinity integrin mutant (αPS2CβPS-V409D). The SPT data revealed that integrins exhibit both Brownian and non-Brownian modes of motion similar to those observed in other membrane proteins. The diffusion coefficient was ~4-times slower and the mobile fraction decreased by 22% for the high ligand affinity integrin compared to wild-type integrin. These differences are partially due to the high ligand affinity integrin's increased clustering and may be due to altered interactions with other membrane proteins or cytoskeletal proteins. A 75% decrease in the average diffusion coefficient and smaller mobile fraction was measured by SPT as compared to fluorescence recovery after photobleaching (FRAP) measurement for the high ligand affinity integrin. This difference between the FRAP and SPT results will be discussed. The presented results prove that the ligand affinity of integrins have an affect on the lateral dynamics of a subset of integrins. This research is supported by Iowa State University and the National Science Foundation.

(695) **Chemical Imaging of Live Cells under Autophagy-Inducing Conditions using Raman Microspectroscopy**; Michael Blades[1], Stanislav Konorov[1, 2], Mario Jardon[3], James Piret[3], Robin Turner[2, 4]; [1]Department of Chemistry, The University of British Columbia, [2]Michael Smith Laboratories, The University of British Columbia, [3]Department of Chemical and Biological Engineering, The University of British Columbia, [4]Department of Electrical and Computer Engineering, The University of British Columbia

Autophagy is a cellular process conserved in all eukaryotes whereby targeted intracellular components are sequestered in double-membrane vesicles called autophagosomes which subsequently fuse with lysosomes for degradation. It is primarily a survival response to various kinds of stress, allowing cells to recycle nutrients in conditions of starvation, and to remove damaged organelles, and to clear pathogens or intracellular protein aggregates. Such critical functions of autophagy make this cellular process a topic of major relevance to fundamental and applied biological research [1,2]. So far no group has reported monitoring of autophagy by Raman spectroscopy although a study of apoptosis, which is to some extent linked to autophagy, has been reported [3]. We present preliminary results using mouse and human cancer cell lines that demonstrate the potential to use Raman spectroscopy to detect biologically relevant changes in cells under conditions that trigger autophagy. The response of adherent mouse and human cancer cells to starvation conditions (glutamine deprivation and amino acid deprivation) was probed by Raman spectroscopy and compared to fluorescence microscopy results using autophagy-specific markers. We also demonstrate the capability of Raman spectroscopy to monitor the recovery dynamics of starved cells and to probe the heterogeneity in the response to starvation that can arise in cell populations.

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(696) **Sensor Fusion of FTIR and Image Information for Characterization of Microalgae in Response to Ecological Parameters**; Frank Vogt[1], Morgan McConico-Lewis[1]; [1]University of Tennessee

The assessment of ecological changes induced by chemical shifts in marine ecosystems requires analytical advancements beyond the sole quantification of selected chemical compounds. Microalgae cells are at the bottom of the trophic chain and chemical analyses of their biomass as well as understanding driving forces behind their biodiversity can open the door to ecological investigations of chemical changes in the environment. In order to utilize microalgae cells as bioprobes, chemical shifts in their biomass and the species distribution need to be linked to changes in ambient conditions. Both tasks require fast quantitative chemical analyses of their biomass as well as a qualitative classification of microalgae cells. It has been demonstrated that FTIR spectroscopy is a valuable tool for biomass analyses; however, the number of chemically similar species –which also change their chemical signature as a function of ambient conditions- requires additional information for species classification. We have studied to what extend their physical appearance namely cell size and shape can be utilized to augment spectrochemical analyses. Fusing these two complementary types of information is demonstrated to be valuable for species discrimination and characterization of ambient conditions. For this purpose, microalgae cultures were exposed to different but well-defined environmental conditions. Consequently, the physical cell parameters can quickly be acquired from a large number of cells and linked to ambient conditions. First we will demonstrate the feasibility of utilizing FTIR signatures of selected algae species for quantitative measurements of environmental parameters such as nutrient concentrations. We then present results from image analyses regarding cell size and shape. For the latter task, microscope images of large numbers of microalgae cells were analyzed in order to relate cell size and shapes to species and their growing conditions.

(697) **Temperature Modeling with Near-Infrared Spectroscopy**; Gary Small; [1]University of Iowa

The temperature sensitivity of underlying water absorption bands can create large baseline variation in near-infrared spectra of aqueous samples. These baseline artifacts can negatively impact multivariate calibration models used in quantitative analyses. To address this issue, a common approach is to apply various signal processing methods (e.g., derivative calculations) to suppress baseline variation before submitting spectra to the calibration model. In the work

presented here, an alternative strategy is explored in which an attempt is first made to estimate the aqueous temperature of the sample directly from the spectrum, followed by incorporation of that temperature information into the quantitative calibration model. This approach addresses applications in which it is difficult to obtain an accurate sample temperature with a conventional measurement probe. To estimate the temperatures of aqueous-based solutions, temperature models based on partial least-squares regression combined with the discrete wavelet transform are developed. In initial work, models are developed for pH 7.4 buffer solutions over the 4000 cm-1 - 5000 cm-1 spectral region and the temperature range of 20.0 to 40.5 °C. The long-term predictive ability of the models is assessed by 13 sets of prediction spectra collected over the course of one year. Laboratory-prepared solutions of glucose, mixture solutions of glucose, lactate, urea in buffer, and bovine plasma are also used to assess the predictive ability of the temperature models in increasingly complex matrixes. Given the ability to model sample temperature accurately, strategies to incorporate this information into quantitative models for analyte concentration will be assessed.

(698) **Identification by Transmission Raman of Drug Products and Placebos**; Michael Dotlich[1], Lisa Wenzler[1], Richard Kattner[1]; [1]Eli Lilly & Co

A placebo-controlled study is a way of testing a drug, its indication, as well as the group of subjects that receive the treatment. Placebos are most commonly used in blinded clinical trials where the subjects do not know whether they are receiving the active drug or a placebo treatment. Current placebo identity tests utilize the active's identity HPLC method to confirm the absence of the active (i.e. negative identity). Spectroscopic methods provide several advantages over traditional or compendia type methods (e.g., HPLC, Karl Fischer, UV-Vis). From a productivity standpoint, spectroscopic methods, which can be quantitative or qualitative, provide faster sample throughput and increased ease of use due to the minimal sample preparation required. In this presentation, the development and application of transmission Raman spectroscopy (TRS) for positive placebo identification testing will be reviewed when applied to approximately 12 different drug products including several doses and their respective placebos. Chemometric modeling, PCA and PLSDA, will be utilized to demonstrate the robust nature of the sample predictions as the testing will be applied against several drug products and their placebos. Preliminary results over seven drug product formulations and placebos and using a PLSDA model demonstrated consistent RMSEC, RMSECV, and RMSEP values at 0.085, 0.102, and 0.077, respectively. The model accuracy was 100% for identification of placebo versus active drug products.

(699) **Multivariate Curve Resolution Applied To Bilinear Deep-UV Resonance (DUVRR) Raman Spectra of Proteins**; Renee D. JiJi[1], Olayinka O. Oshokoya[1], Carol A. Roach[1], Christopher M. Halsey[1], Mia C. Brown[1], Jason W. Cooley[1]; [1]University of Missouri-Columbia

The deep-UV resonance Raman (DUVRR) spectra of proteins contain a variety of overlapping modes arising mainly from the peptide backbone amide and aromatic amino acid modes. Proteins adopt three main types of secondary structure, alpha-helix, beta-sheet and disordered structures, which have characteristic DUVRR spectra. Employing a set of globular proteins with varying structural compositions, multivariate methods can be employed to predict each protein's secondary structural content, as well as, the basis α-helix, β-sheet and disordered DUVRR spectra. The intensity of the α-helical amide modes are relatively weak in comparison to β-sheet and disordered amide modes, resulting in poorer prediction of α-helical content using methods such as CLS and PLS. However, inclusion of non-negativity and closure constraints with multivariate curve resolution (MCR) dramatically improves prediction of α-helical content from protein DUVRR spectra. Lowering the prediction errors to at or below 10% for each structural type. Analysis of protein secondary structure via DUVRR spectroscopy can also be complicated by the presence of overlapping aromatic modes. Phenylalanine and tyrosine both contribute to DUVRR spectra at excitation wavelengths below 210 nm. In addition tryptophan modes appear in the DUVRR spectra if lipid soluble proteins. A unique feature of resonance Raman spectroscopy is the spectral dependence on excitation wavelength. Multi-excitation in combination with MCR can be employed to resolve backbone amide modes from aromatic modes in DUVRR spectra of individual proteins. The ability to employ non-negativity, closure and chemically relevant constraints makes MCR a powerful tool for the analysis of two-way (bilinear) DUVRR spectra.

(700) **Near Infrared Spectroscopy Applications in Biofuels Characterization**; Edward Wolfrum[1], Amie Sluiter[1], Courtney Payne[1]; [1]National Renewable Energy Laboratory

Near Infrared (NIR) spectroscopy combined with multivariate statistics to develop rapid calibration models is a well-understood and widely used technique. It has been in the analysis of agricultural products for many years. These rapid calibration models allow the high-throughput characterization of large number of biomass feedstock samples, since the alternative, wet chemical analysis, is far too expensive and time-consuming for application to large numbers of samples. As cellulosic biofuels become more prevalent, there is need for rapid and robust compositional analysis tools to support research, development, and commercialization along the entire value chain of cellulosic biofuels, from crop breeding to process monitoring. This presentation will focus on three areas:

1. Rapid compositional analysis of biomass feedstocks.
2. Rapid compositional analysis of cellulosic ethanol conversion process intermediates, including wet pretreated slurries, liquors, and saccharification and fermentation process monitoring.
3. Exploratory data analysis (EDA) of NIR spectra for agronomic applications.

(701) **Universal Anion Detection by Replacement-Ion Chromatography with a Solution-Cathode Glow Discharge Detector**; Andrew Schwartz[1], Zheng Wang[2], Steven Ray[1], Gary Hieftje[1]; [1]Department of Chemistry, Indiana University, [2]Shanghai Institute of Ceramics, Chinese Academy of Science

Replacement-ion chromatography (RIC) is an alternative detection scheme for ion chromatography (IC). In RIC, analyte ions are detected indirectly after stoichiometric exchange with a "replacement-ion" that can be detected more sensitively than the original sample ions. Further, because each analyte ion is replaced stoichiometrically by a common replacement-ion, each is detected with the same sensitivity and dynamic range independent of its chemical form. This enables quantification of each eluting species from a single calibration curve without knowledge of its identity beforehand. Additionally, because every ion in the original sample is replaced and detected at the same sensitivity, it is possible to determine the relative concentration of each analyte by division of its signal by the sum of all signals from the sample, enabling calibration to be performed in the absence of standards. RIC also offers the potential for uniformly sensitive detection. All chemical species can be quantified with a detector that is optimized to sense the replacement-ion with the greatest fidelity. In the present study a new RIC system has been coupled to an alternative atomic emission source, the solution-cathode glow discharge (SCGD). The SCGD is an attractive detector choice for RIC: it is simple in design, no compressed gases or nebulizer is required and the discharge operates in the ambient atmosphere. Additionally, because the SCGD samples directly a flowing stream of sample solution the detector response is very rapid, promoting chromatographic resolution. Finally, the

SCGD has demonstrated exceptional sensitivity for alkali metals, with detection limits of 5 pg for flow injections of Li^+. Thus, when an alkali metal is selected as the replacement species in an SCGD-RIC setup, the system has the potential to be highly attractive for IC detection. The analytical performance of the new SCGD-RIC system for anion determinations, including universal calibration, repeatability, and sensitivity will be described. Additionally, sources of background inherent to the technique will be characterized and explained.

(702) **Particle and Molecular Species Separation Via Continuous Electroosmotic Flow with Orthogonal Optical Pressure**; Sarah Staton[1], Alex Terray[2], Greg Collins[2], Sean Hart[2]; [1]National Research Council Post-Doctoral Fellow, [2]Naval Research Laboratory

The separation of particles and molecular species is an important first step for complex biological or environmental samples in preparation for analysis by traditional analytical techniques. It is also desirable that this preparation occur in a continuous high-throughput manner without direct manipulation to decrease chances of contamination while maintaining production. A new promising application of electroosmotically induced "plug" flow in combination with an orthogonal optical force on a microfluidic platform was developed. This method selectively removes particle matter from a mixed sample stream of molecular species and variously sized particles. The use of electroosmotic flow reduces cross-sectional velocity heterogeneity while increasing the addressability of laminar layers via optical force. Both experimental and theoretical studies have been performed to evaluate the ability and the accuracy of the method to remove particles from the sample stream while minimizing the effects of diffusion and dilution on the remaining molecular stream. Various sized and refractive indexed particles were combined with a water soluble dye and introduced to a pinched flow microfluidic channel. Along the length of the channel a mildly focused 1064 nm Nd YAG laser applied orthogonally to the fluid flow elicited selective particle movement for all particle types as well as combinations of two particles types with the dye. Theoretical calculations using COMSOL, a finite element multiphysics model, predicted the diffusive losses of the molecular species at less than five percent. This technology along with other applications of optical chromatography allow for complex sample stream separation and purification.

(703) **3-D Imaging of Redox Magnetohydrodynamic Flow in Microfluidic Devices by Fluorescence Correlation Spectroscopy and Particle Tracking**; Colin Heyes[1], Feng Gao[1], Adam Kreidermacher[1], Ingrid Fritsch[1]; [1]University of Arkansas

Microfluidic devices are extremely useful for a range of analytical applications in chemistry, physics and the life sciences. While mechanical pumps are usually used for controlling fluid flow and/or mixing in such devices, they can be quite expensive, are difficult to miniaturize and coupling the pump to the channel is difficult to control. One novel way of achieving controlled solution flow and mixing in microfluidic systems without a mechanical pump (or any moving parts) is by redox magnetohydrodynamics (RMHD). RMHD-based fluid flow is the result of the body force induced by the cross product of an ion flux and a permanent, perpendicular magnetic field. RMHD has the flexibility of creating different flow patterns, switching flow direction easily, creating a range of flow speeds from microns/s up to tens of mm/s, has aqueous and non-aqueous solution compatibility and, since it has no moving parts, has no pulsating flow effects or bubble formation. However, predicting the quantitative flow profiles in a microfluidic system caused by RMHD is not trivial, and detailed experiments are needed to develop and test theoretical predictions. An attractive method to evaluate flow can be accomplished by directly visualizing microbeads in the flow path and using particle image velocimetry (PIV) or single particle tracking (SPT) analysis. While this approach is quite successful, it has spatial resolution limitations. Here we combine Fluorescence Correlation Spectroscopy (FCS) and particle tracking analysis from video microscopy to image flow velocities on the order of 5-50 microns/s in 3 dimensions with micron spatial resolution. We validated that the flow speed evaluated from FCS is the same as that obtained from particle tracking for beads of the same size (1 micron). We then show that reducing the bead size to 100 nm, which is better suited for FCS, but not visible for particle tracking, also recovers the same flow speeds. Obtaining high-resolution flow maps from pumpless microfluidic devices based on RMHD effect will allow us to study in detail the various forces involved which, in turn, will allow us to design, optimize and fabricate advanced microfluidic devices for a wide range of (bio)analytical applications.

(704) **Confocal Raman Microscopy for *in-situ* Detection of Polyaromatic Hydrocarbon Accumulation within Single C18 Silica Particles**; Jay Kitt[1], Joel Harris[1], Marc Porter[1], [1]University of Utah

Solid phase extraction has been used as a method to pre-concentrate analytes of interest typically prior to *ex-situ* quantification. In this work, solid phase extraction is observed *in-situ* within a single, small C_{18}-derivitized chromatographic particle using confocal Raman microscopy. The combination of single-particle pre-concentration and *in-situ* measurement allow detection of nanomolar concentrations of pyrene from small (sub-μL) volume aqueous solutions. It is demonstrated that it is possible to quantify pyrene surface coverage *within the C_{18} particle* by taking the ratio of the pyrene in-plane ring deformation scattering intensity at 1241cm^{-1} to that of the CH_2 twisting mode of surface bound C_{18}-chains at 1303cm^{-1} and comparing to pyrene/hexadecane standards. Control of the adsorption equilibrium is accomplished by varying the methanol/water ratio giving Langmuir adsorption constants which scales exponentially with changing water fraction in the water:methanol source phase, changing from 0.007±0.001μM^{-1} at 40% water to 0.16±0.04μM^{-1} at 95% water. At 95% water, it is possible to achieve 2.5×10^5 fold pre-concentration of pyrene in the volume of the particle relative to the volume of the source phase solution. This level of pre-concentration in a 10μm particle corresponds to a source volume of only 130nL allowing for sensitive detection of analyte from extremely small volume samples. The kinetics of single-particle accumulation depend on the rate of pyrene transfer between solution and solid phases, as well as diffusion along the C_{18} surface. In order to investigate the underlying mechanism of phase transfer and intra-particle diffusion for optimization of single particle solid phase extraction, the three-dimensional spatial resolution of confocal Raman microscopy can be used to measure analyte accumulation kinetics at the center of a single chromatographic particle following time-dependent changes in analyte concentration into particles of different sizes.

(705) **Electrophoretic Exclusion: A Microchip Separation Scheme**; Stacy Kenyon[1], Michael Keebaugh[1], Mark Hayes[1]; [1]Arizona State University

Electrophoretic exclusion is a novel separations technique that utilizes counterflow and differentiates species in bulk solution based upon their electrophoretic mobilities. This is a unique strategy, but grows from several gradient focusing techniques. A key aspect of this method is that separation occurs in a bulk reservoir when the electrophoretic velocity of a species out of a channel is greater than or equal to the hydrodynamic flow into the channel—other species, lower mobilities are allowed to enter. Various types of analytes can therefore be excluded by changing applied electric field strengths. Initial microchip studies on a hybrid PDMS/glass device were able to demonstrate exclusion for a large range of targets: from particles (1 μm sulfated polystyrene spheres) to fluorescent dye small molecules (rhodamine 123) within as little as 10 s at field strengths of 300

V/cm. Current research focuses on developing the simple hybrid PDMS/glass microchip into a more complex array that will allow for the isolation of three species simultaneously. Underlying models suggest extremely high resolution separations are available from this paradigm and these quantitative arguments will be presented.

(706) **Characterization of a Reference-Laser Free Spectrometer**; Kevin Yeh[1, 2], Matthew Schulmerich[1, 2], Rohit Bhargava[1, 2]; [1]University of Illinois at Urbana-Champaign, [2]Beckman Institute for Advanced Science and Technology

Fourier transform infrared (FT-IR) spectroscopy is a widely-used technique for examining the chemical constituents of a sample. Modern FT-IR spectrometers are typically based on an interferometer design that allows the simultaneous measurement of absorption at multiple wavelengths when the interferogram is deconstructed using a Fourier transform. In commercial instruments, a reference laser accurately encodes the position of the moving mirror. However, this laser creates an additional upkeep cost as they need to be replaced every few years. Here, we have built a reference-laser free FT-IR spectrometer and characterized its performance by measuring SU-8 polymer thickness on a Barium Fluoride slide. Errors in measuring stage position over time results in stretching and shifting of the interferogram along the retardation axis. We have demonstrated the absence of a reference laser results in a 2% stretch in the interferogram which proportionally affects the measured polymer thickness. The variation of this measurement, as determined by two standard deviations, increased by 6.3-fold from to 0.3% to 2%. These results summarize the degree in which a reference-laser free approach can be used to approximate spectroscopic data.

(707) **Mapping 3D Molecular Confromations with Multiple-Mode Multiple-Dimensional Vibrational Spectroscopy**; Junrong Zheng[1], Hongtao Bian[1], Jiebo Li[1], Hailong Chen[1], Xiewen Wen[1]; [1]Rice University

The principles of mapping transient and static three-dimensional molecular conformations in condensed phases (liquids, solids, and interfaces) with a multiple-mode multiple-dimensional vibrational spectroscopy will be introduced. The method directly measures the cross angles among vibrations that cover the entire molecular space through vibrational couplings and intramolecular vibrational energy transfers. The vibrational angles are then translated into cross angles among chemical bonds by quantum chemistry calculations. The 3D molecular conformations are therefore determined by these bond angles. The above procedure determines the relative orientations of chemical bonds. The absolute distance between two bonds can also be determined by the mode-specific vibrational energy transfer approach. Because of its intrinsic fast temporal resolution and ease of manipulating light polarization, this new method is able to resolve some molecular structures and conformations that XRD or NMR has difficulties to determine. Applications in these areas will be presented.

(708) **IR Microscopy using External-Cavity Quantum-Cascade Lasers**; Robert Shine[1], Miles Weida[1], Dave Arnone[1], Tim Day[1]; [1]Daylight Solutions

Infrared (IR) micro-spectroscopy has shown itself to be an important tool by providing spectroscopic and chemical analysis in areas as diverse as investigating surface defects in manufacturing to tissue diagnostics at the molecular level. To date, the main tool for performing IR micro-spectroscopy has been the Fourier Transform Infrared (FTIR) microscope, but these have been limited by the relatively poor optical quality of the incandescent light source. Recent work has used synchrotron sources to significantly increase the performance of IR microscopy, but these sources are not commercially viable. The development of broadly tunable, external cavity quantum cascade lasers (EC-QCLs) has created an ideal light source for IR microscopy. Initial results were obtained by coupling an EC-QCL to a commercially available FTIR microscope. Spectral performance and coherence effects were determined by performing scans for different sample materials. Advantages of the EC-QCL based spectra included higher spatial resolution (10 μm vs. 25 μm), higher spectral resolution (1 cm-1 compared to 4 cm-1), and less averaging time (5 sec vs. 1 min). The laser based IR microscope was further improved by coupling to a micro-bolometer FPA detector. Images of approximately 2 mm by 2 mm were obtained for both reference samples and reticles to determine the performance, and results compared well to synchrotron-based IR microscopes. EC-QCL based imaging microscopes stand ready to rival the performance of state-of-the art IR microscopes for a fraction of the cost and complexity.

(709) **Use of NMR to Interpret NIR: Application to Biologics Manufacturing**; Maureen Lanan[1], Amr Ali[1]; [1]Biogen Idec

The use of outer-product analysis1 (OPA) as a data fusion technique is explored using near infra-red (NIR) and 1H NMR spectra. NIR and NMR share characteristics that make them well-suited for data fusion. Both techniques probe the physical and chemical environment of protons with similar sensitivity. They also have important practical issues that hinder more widespread use of each: NIR spectra are 'hard to interpret' and NMR instrumentation is delicate. Exploiting the common chemical sensitivity for the two techniques with data fusion should provide a way to leverage the strengths of each. Spectra obtained with mixtures of amino acids and sugars will be presented to demonstrate how NIR and NMR spectra can be combined using OPA. An application of OPA to raw material characterization will be shown. For example, NIR spectra of media components can be dominated by signals from water, which is not important compared to the entirely aqueous cell-culture process. OPA between NIR and NMR helps identify underlying composition differences between raw material lots that could be related to production variation regardless of nuisance water levels. Ultimately, OPA will provide more robust and interpretable NIR-only analysis with occasional fusion with NMR spectra. This presentation will describe our current understanding of the benefits and limitations of OPA as a data fusion technique and as a strategy to expand the appropriate use of NIR and NMR in a biopharmaceutical setting.

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(710) **Correlation of Quality Measurements to Visible-Near Infrared Spectra of Pasteurized Eggs**; Samantha Hawkins[1], Deana Jones[1]; [1]US. Department of Agriculture-Agricultural Research Services

A twelve week study was conducted on the egg albumen from both pasteurized and non-pasteurized shell eggs using visible-near infrared spectroscopy. Correlation of the chemical changes detected in the spectra to the measurement of Haugh units (measure of interior egg quality) was carried out using chemometric methods. Additionally, the study sought to determine how pasteurization affects both shelf life and egg quality. Eighty-four dozen eggs were involved in this study, with 12 dozen eggs scanned initially and biweekly for the remainder of the study. The samples were divided into two dozen control and two dozen treated samples, run in triplicate, for each day of data collection. The shell eggs were kept refrigerated at 4°C until ready for data collection. The Haugh units were measured followed by the separation of egg components and 60 second homogenization of the egg albumen. Approximately 2 mL of the albumen from each egg was used for spectral data collection in a UV/VIS/NIR spectrometer. The data was then processed and analyzed using chemometric software. Both principal component analysis and principal component regression were used to correlate the spectral data to the other sample variables, i.e. shelf life time and Haugh unit

measurements. The chemometric data analysis demonstrates that chemical changes can be correlated both to the length of time that the eggs were stored and to the egg quality measurements.

(711) **New Frontiers in Handheld FTIR- Instrumentation and Applications**; John Seelenbinder; [1]Agilent Technologies

The last 15 years has shown a marked increase in the availability and applications of hand held molecular spectroscopy techniques. Optical and electronic developments have allowed the creation of new instruments which are smaller, lighter and more rugged than most laboratory users would expect. Equally interesting to the instrumentation developments are the needs of users which are driving these developments. Handheld and portable FTIR spectroscopy provides a range of new capabilities for non-destructive testing, allowing users to qualify materials and assess damage of composites, coatings and polymers. As the range of high performance materials increases, so do the needs for non-destructive testing. Additionally, portable spectroscopy can be used to reduce expense by measuring materials at their source, providing quicker QC and quality control. In this talk we will focus on applications of handheld FTIR for materials analysis of polymers, composites and coatings. We will cover three areas. First, we will cover determination of coatings cure via handheld FTIR spectroscopy. Though many coating processes are automated, proper cure depends on several variables. We will show how handheld FTIR can be used to determine if visibly different spots are fully cured or have other issues. Secondly, we will discuss a new method of identifying elastomers using a handheld FTIR equipped with a Germanium ATR. The use of a Ge ATR to measure carbon filled elastomers is nothing new; however, identification algorithms are often confused by large amounts of filler. We have developed a new algorithm which can easily separate elastomers into one of 10 categories even with different levels of filler. Finally, we'll give an update on continued work done using a handheld FTIR for the measurement of composite damage. In addition to earlier work on heat damage of epoxy composites, we have shown good correlation to heat damage of BMI composites as well. Additionally, we'll speak about work done in mapping heat damage on actual composite parts.

(712) **Compact On-Site NMR Assessment of Acyl Group Quality of Combustible and Edible Glycerides**; David Wetzel[1], Marcelo Coronado[1], Mark Boatwright[1], Jeffrey Sherman[2]; [1]Microbeam Molecular Spectroscopy Laboratory, Kansas State University, [2]picoSpin, LLC[4]

Fatty acid methyl esters from various biological sources constitute biodiesel fuels. Quality factors for their end use such as BTU content, storage, and handling are dependent on the composition of the acyl groups. Similarly, naturally occurring glycolipids in edible plant material, including wheat, contribute to quality for end use in breadmaking. Health concerns also include the lipid composition of edible oils used for cooking. For regular laboratory analysis, esterification followed by gas chromatography has served well. However, with the recent availability of a compact, portable NMR instrument, the picoSpin-45, the acyl group chain length and unsaturation that both affect heat of combustion, stability upon storage and physical characteristics such as sold fat index, could readily be compared to physical or library spectral standards. Spectra of commonly encountered acyl groups of concern are shown to exemplify the utility of this as a practical on-site approach to potential routine measurement of quality for end use. The NMR spectra of acyl group mixtures are used to illustrate how the summation of the molecularly weighted combination of constituents of the mixtures influence its' composite characteristics.

(713) **Opportunities of Portable FT-IR Instrumentation for the Food Industry**; Luis Rodriguez-Saona[1]; [1]The Ohio State University

Optical technology is rapidly developing and instruments are already available commercially as portable, hand-held, and micro- devices that can be used when it is not practical or economical to use the more sophisticated and costly instruments used in research laboratories. There is a need for cutting edge sensor technology for the food industry directed at improving efficiency, throughput and reliability of critical processes. Our aim is to evaluate the feasibility of handheld and portable infrared systems in applications relevant to the food industry. We have evaluated their performance against benchtop systems directed at developing fingerprinting strategies for rapid and specific analysis of food components, providing reliable tools for assessment of quality and safety. Food applications have been targeted at authentication, detection of economic adulteration, detection of chemical food contaminants, monitoring quality parameters associated with product deterioration and quantification of food trait components including proteins, fats, sugars, organic acids and carotenoids. This technology can enable the food manufacturer to rapidly assess the quality of food, allowing for timely correction measures during manufacture. We expect these portable systems to be simple to use and require minimal or no sample preparation, reducing the assay time and helping to streamline the analytical procedure so that it is more applicable to higher sample throughput and automation. The portable infrared technology could save time and money to the food industry helping to implement quality control programs and risk management systems.

(714) **QCL as a Forefront Technology, Rethinking the Limitations of Infrared Spectroscopy**; Frederick G. Haibach[1]; [1]Block Engineering

Interferometers have come to dominate infrared spectroscopy, as the performance complements incandescent sources. Many of the published advantages of interferometers rely on the limitations of the incandescent source. Recent advances in interferometers seek to recapture some of the applications that dispersive instruments proved superior in. Step-scan was the most prominent of these advances. The dominance is so complete, that many modern practitioners of infrared spectroscopy have experience with other spectroscopic instrument designs only peripherally through terahertz, near-infrared or UV-vis. New, brighter sources, like quantum cascade lasers (QCLs) make it possible to rethink how infrared spectroscopy is performed. The four advantages over incandescent sources are that QCLs provide are: orders of magnitude higher spectral radiance, nearly diffraction-limited source size, collimated light and inherently greater than 100:1 polarization. Pulsed mode operation makes it possible to obtain operation across hundreds of wavenumbers in a single unit. Other properties, such as scan rates in milliseconds, miniaturization, low power consumption and ultrahigh resolution spectroscopy depend on the laser packaging. The four advantages enable spectroscopy that is difficult with incandescent sources. Standoff absorbance measurements, efficient fiber and ATR coupling, microscopy and measurements on high-absorbance materials are now possible. These measurements were challenging requiring extensive work around or not previously achievable. Examples and performance of these types of spectroscopy will be discussed.

(715) **Recent Advances in Laser-Based Mid-IR Devices for Spectroscopic Applications**; Leigh J. Bromley[1], Patrick Mock[1], Dave Caffey[1], Timothy Day[1]; [1]Daylight Solutions

With the advent of Quantum Cascade Lasers and new performance from diode lasers, new capabilities in mid-IR spectroscopic techniques have emerged. Enhancements in sensitivity, selectivity, resolution, speed, size, wavelength coverage, frequency stability, and power consumption have come to light. Furthermore techniques such

as infrared microscopy and nanoscale imaging have been enhanced by new performance of these developing light sources. In this paper we will discuss advances in these capabilities. As laser sources transition from laboratory tools to engines in analytical devices broader and broader coverage is required to meet the needs of specific applications. Two approaches have been developed: broader tuning from single chips and the multiplexing of several chips. Multiplexed, broad-tuning systems have been built which provide over 850 cm^{-1} of continuous coverage from 6 to 12 µm. Integrated performance from up to four chips requires overcoming thermal management issues and combining the individual beams. A complete system has been developed and will be presented to provide this performance. In order to obtain fully resolved spectra of light, gas phase molecules, narrow linewidth and strictly continuous tuning are necessary. We have built a new laser cavity with open-loop linewidths as low as 5 MHz over a 100 ms integration time. This cavity tunes continuously and without mode hops over as much as 100 cm-1. The cavity is driven both by a coarse stepper motor and a piezoelectric crystal (PZT) for finer tuning. The PZT bandwidth has been extended over previous versions of this laser to allow for high modulation rates. A Type I GaSb diode has been incorporated into a variation of the cavity discussed above. Over 40 cm^{-1} of mode hop-free tuning was obtained in the 3.3 µm (3050 cm-1) region. This wavelength is centered on the C-H stretch absorption frequency for many hydrocarbons. Performance at this and other newly available wavelengths will be presented.

(716) **Chemical Imaging of Heterogeneous and Rough Surfaces by Means of Infrared Microspectroscopy in Specular Reflection Mode**; Valdas Sablinskas[1], Milda Pucetaite[1], Justinas Ceponkus[1]; [1]Vilnius University

Infrared spectral imaging in specular reflection mode is suffering from the fact that the spectral bands (so called Reststrahlen bands) in the specular reflection spectra resemble first derivative of the absorption spectrum and they are shifted towards lower wavenumbers [1]. Such distortions can introduce serious errors when integral intensities of the Reststrahlen bands are used for estimation of concentration of some chemical compound in particular spot of the imaged surface. This is particularly true in case of the band overlapping. Contour of the overlapped Reststrahlen bands due to the first derivative feature is complicated and the bands are hardly distinguishable. The case is even worse when the imaged surface is scattering the incident radiation and diffuse reflection contour is introduced into the spectrum [2]. Cross-sectioned urinary stones are typical example of such heterogeneous and rough surface. Standard Kramers–Kronig (KK) procedure is not applicable to correct the raw spectra of urinary stones as they contain diffuse reflection component arising from relatively rough surface of the cross-section as well as interfaces between different chemical compounds. This contribution is devoted to the issue of correcting the distorted specular reflection spectra in order to perform quantitative analysis of multi-component urinary stones and create informative chemical (false-colour) images of the stones. The correction was performed by subtracting the diffuse reflection component from the raw reflection spectra of cross-sectioned stones prior the KK transform. The results show that even highly scattering samples, such as urinary stones, can be effectively imaged by using specular reflection infrared microspectroscopy. The modification of the experimental spectra – the subtraction of the diffuse reflection component – is crucial in order to apply Kramers-Kronig transform to the Reststrahlen bands and to restore their peak positions and contour shapes.

[1] M. Claybourn in J. M. Chalmers, P. R. Griffiths (Eds.) Handbook of Vibrational Spectroscopy, Vol 2, John Willey & Sons, Chichester, (2001) 969-981.

[2] B. J. Davis, P. S. Carney, R. Bhargava, Anal Chem 82 (2010) 3487-3499.

(717) **The use of Raman Spectroscopy in Explaining High Speed Friction of Titanium Alloy Against Tantalum**; Patrice Bourson[1], Jean Jacques Arnoux[2], Guy Sutter[2], Gauthier List[2]; [1]LMOPS University of Lorraine Metz, [2]LEM3 University of Lorraine Metz

An original approach is presented to characterize the friction process of the titanium alloy Ti 6Al 4V on tantalum. Very high sliding velocity from 15 to 120 m/s can be reached by using a ballistic set-up based on the principle of hopkinson's bars. During the friction tests, the normal pressure is fixed to 31 MPa following the size of the specimens and a specific load sensor records the friction force. Only a single pass is carried without running-in phase. Although generally used for non-metallic materials or in the case of metallic powder, the Raman spectroscopy and X-ray fluorescence are used to characterize the surface of friction. More conventional means for measuring roughness as an optical interferometer are also used. The tendency of Ti alloys to transfer material on the tantalum specimen is confirmed despite the high sliding velocity. Tribochemical reactions as micro welding are supposed to explain the evolution of the surface roughness. In addition, the high affinity that Ti has for oxygen results of the presence of oxides as TiO2. The crystalline structure of this oxide is proposed as indicator of maximal temperature reached during the process. The generation of very high-localised temperatures during the friction is also confirmed.

(718) **Depth Profiling in Opaque Materials; Applications of Time-Resolved Raman Spectroscopy**; Ingeborg Iping Petterson, Cees Gooijer, Freek Ariese; [1]Vrije University Amsterdam, LaserLaB

Time-resolved Raman spectroscopy (TRRS) allows for depth profiling and provides vibrational information about materials hidden below a non-transparent surface. Signals from different depths within an opaque sample are discriminated on the basis of their migration time; the deeper a photon travels within a scattering sample, the longer it will take to be backscattered to the detector. Through the use of tunable, pulsed laser excitation and gated detection via an intensified CCD camera, we are able to discriminate in-depth on a mm scale within a variety of opaque materials. This technique also considerably reduces interference from fluorescence. Measurements by Spatially Offset Raman Spectroscopy (SORS) are also possible for comparison, or in combination with time resolution, using the same instrumental setup. We have performed proof of principle experiments using TRRS demonstrating the potential for applications in an number of different fields. For example, in studies relevant to industrial catalysis to monitor reactions within catalytic bodies, and for the detection of explosives through plastic packaging materials. This technique also shows great potential for non-invasive biomedical diagnostics, as well as for planetary science studies, for the detection of life biomarkers through evaporitic minerals and blocks of ice. These results will be discussed, along with plans for future studies.

(719) **Transmission Raman Spectroscopy on Freshly Excised Breast Pathology Specimens**; Marleen Kerssens[1, 2], Pavel Matousek[3], Keith Rogers[2], Nick Stone[1, 4]; [1]Biophotonics Research Unit GRH NHS FT, [2]Cranfield University, [3]Central Laser Facility, Rutherford Appleton Laboratory, [4]Department of Physics, University of Exeter

Breast cancer is the most common type of cancer among women and accounts for over 30% of all cancers among women [1]. The prognosis of breast cancer patients is strongly correlated to the stage in which the disease is detected. Early diagnosis allows more conservative treatment. One of the first changes in the breast related to breast cancer that can be observed is the presence of microcalcifications. In our previous work [2-4], we explored the potential to use transmission Raman spectroscopy for the detection of calcifications in breast. Here we present the findings from, a small proof of principle study. Breast tissue specimens were collected from 41 patients who underwent a wide local excision or a wire guided

local excision at Gloucestershire Royal Hospital (United Kingdom) between March and July 2012. Ethical approval was obtained from the Gloucestershire Local Research Ethics Committee and informed written consent was given by the patients involved. After excision, the specimens were brought over to the Biophotonics Research Unit where they were measured on a novel transmission Raman system [3]. The sample was mounted in a sample holder between two glass plates (51x76x1.2-1.5 mm) and the thickness of the sample was recorded. Five measurements were taken from each sample (at different positions) with an accumulation time of 3x60s with an Andor CCD camera. After the measurements the specimens were entered into the standard clinical pathway. The deep Raman measurements were compared to X-ray images of the samples, measured using a faxitron device in operating theatre, which were provided by the surgical staff. We will report progress with the data analysis which is currently underway.

[1] CRUK, CancerStats Incidence 2009, 2012
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[3] Stone & Matousek, Cancer Research, 2008, vol 68, pp. 4424-4430
[4] Kerssens et al, Analyst, 2010, vol 135, pp. 3156-3161

(720) **Cytoplasmic RNA in Undifferentiated Neural Stem Cells: A Potential Label-Free Raman Spectral Marker for Assessing the Undifferentiated Status**; Adrian Ghita[1], Flavius C. Pascut[1], Virginie Sottile[1], Ioan Notingher[1]; [1]University of Nottingham

Raman microspectroscopy (RMS) was used to identify, image, and quantify potential molecular markers for label-free monitoring the differentiation status of live neural stem cells (NSCs) in vitro. Label-free noninvasive techniques for characterization of NCSs in vitro are needed as they can be developed for real-time monitoring of live cells. Principal component analysis (PCA) and linear discriminant analysis (LDA) models based on Raman spectra of undifferentiated NSCs and NSCderived glial cells enabled discrimination of NSCs with 89.4% sensitivity and 96.4% specificity. The differences between Raman spectra of NSCs and glial cells indicated that the discrimination of the NSCs was based on higher concentration of nucleic acids in NSCs. Spectral images corresponding to Raman bands assigned to nucleic acids for individual NSCs and glial cells were compared with fluorescence staining of cell nuclei and cytoplasm to show that the origin of the spectral differences were related to cytoplasmic RNA. On the basis of calibration models, the concentration of the RNA was quantified and mapped in individual cells at a resolution of ~700 nm. The spectral maps revealed cytoplasmic regions with concentrations of RNA as high as 4 mg/ mL for NSCs while the RNA concentration in the cytoplasm of the glial cells was below the detection limit of our instrument (~1 mg/mL). In the light of recent reports describing the importance of the RNAs in stem cell populations, we propose that the observed high concentration of cytoplasmic RNAs in NSCs compared to glial cells is related to the repressed translation of mRNAs, higher concentrations of large noncoding RNAs in the cytoplasm as well as their lower cytoplasm volume. While this study demonstrates the potential of using RMS for label-free assessment of live NSCs in vitro, further studies are required to establish the exact origin of the increased contribution of the cytoplasmic RNA.

(721) **Punctuated Microgradients for Electric Field Separations**; Mark Hayes[1], Stacy Kenyon[1], Paul Jones[1]; [1]Arizona State University

Core to all separations science is resolution: causing important components to move in time or space away from each other. Although a description of core processes controlling resolution across all separations systems does not exist, the most successful techniques are considered to be electrophoretic in nature. Early demonstrations of capillary- and microchip- based electrophoresis have shown absolutely extraordinary resolution using high fields showing deuterated vs. hydrogenated and sub-millisecond separations. These results were obtained in systems operating in a linear mode—spreading and diluting a mixture out along a single axis. Our work, presented for the first time here at SciX 2012 uncovers a radically new approach enabled by the short length-scale of microdevices which exploits local field gradients. The core to this discovery is setting up punctuated microgradients separated by flat field zones. This uniquely minimizes the effects of diffusion by dramatically increasing the local restoring forces. As a result, not only does the resolution increase by a factor tied to the strength of the local gradients, but can be accomplished this in parallel while increasing concentration of the targets (focusing). This opens up several new venues for exploitation, including dynamic and programmable collection of specific analytes at higher resolution than is available from any traditional technique in an array format. Speeds of separations are also dramatically increased. We describe the underlying theoretical principles and provide examples of flow/electric field and electrokinetic/dielectrophoretic devices in a microfluidic format. The underlying models extend to any force which can be induced into dispersed microgradients in the presence of a static counter field.

(722) **Far-field, Sub-diffraction Fluorescence Lifetime Imaging**; Emily Smith[1, 2], Michael Lesoine[1, 2], Sayantan Bose[1, 2], Jacob Petrich[1, 2]; [1]Iowa State University, [2]The Ames Laboratory

We developed a stimulated emission depletion (STED) fluorescence microscope and used it to collect sub-diffraction fluorescence lifetime images. The basic operating principle of STED microscopy is inhibiting the fluorescence at the periphery of a diffraction limited excitation spot by stimulated emission. When coupled to time correlated single photon counting detection, fluorescence lifetime images with 40 nm lateral spatial resolution are measured. This is approximately an 8-fold improvement in the spatial resolution compared to traditional far-field optical microscopy. The same average fluorescence lifetime (2.0 ± 0.1 nanoseconds) was measured for 40 nm fluorescent beads using confocal or STED lifetime imaging, providing validation for the STED lifetime measurement. The three main parameters affecting the performance of the system: beam profile, signal gating, and optical alignment will be discussed. The instrument has been applied to study Alexa Fluor 594-phalloidin labeled F-actin rich projections with dimensions smaller than the diffraction limit of light in cultured S2 cells. Fluorescence lifetimes of the F-actin rich projections range from 2.2 to 2.9 nanoseconds as measured by STED lifetime imaging. The system has also been used to measure the organization of integrin cell membrane proteins and the cellular factors that affect integrin rearrangement.

(723) **Desorption Ionization with the Liquid Sampling-Atmospheric Pressure Glow Discharge Microplasma**; R. Kenneth Marcus[1], Carolyn Q. Burdette[1], Benjamin T. Manard[1], Lynn X. Zhang; [1]Clemson University

The field of ambient mass spectrometry has been a very active area over the last decade, with up to 40 different source geometries described in the literature. Other than the veritable DESI source, all of the other geometries are basically uni-taskers; i.e., they have one specific implementation. The liquid sampling-atmospheric pressure glow discharge (LS-APGD) was initially introduced by Marcus and Davis as a low power, small footprint optical emission source. The source is configured such that an electrolytic liquid (e.g., 1 M HNO3) flows out a small (~100 μm) glass capillary housed within a slightly larger metal capillary, between which a cooling gas is passed. The metallic counter electrode is placed ~2 mm from the liquid surface, with the plasma discharge potential applied to either electrodes while holding the other at ground potential. The i-V characteristics (10 – 50 mA, 200 – 500 V dc) of the device where shown to exist in the

abnormal glow discharge regime of plasma operation. In this configuration, solution flows of up to 0.4 mL min^{-1} could be totally vaporized by the plasma struck to the liquid surface. Advantages of this geometry are the much lower flow rates (down to 0.1 mL min^{-1}), lack of liquid waste generation, and ready coupling to flow injection/chromatography sample introduction without compromise of temporal integrity. Limits of detection on the order of 10 ng for 5 µL injections have been obtained on fairly simple optical detection platforms, while also showing appreciable robustness with regards to addition of easily-ionized matrix species. We describe here the use of the LS-APGD microplasma ion source as a desorption ionization source. This is achieved with NO MODIFICATIONS from the implementation of the devices as an elemental/isotope analysis ion source. There are indeed many other potential advantages of this sources versus the other ambient MS sources, most specifically, the primary desorption current is >10 mA and the local temperature is >200 ^{o}C. We describe here the preliminary characterization of the source and its application in ambient MS.

(724) **Advancing Infrared Microscopy Instrumentation by Theory and Computation**; Rohit Bhargava[1], P. Scott Carney[1], Rohith Reddy[1], Kevin Yeh[1], Thomas van Dijk[1], Matthew Gelber[1], Matthew V. Schulmerich[1]; [1]University of Illinois, Beckman Institute for Advanced Science and Technology

Vibrational spectroscopic imaging, especially based on infrared absorption, was widely believed to be a simple combination of spectroscopy and optical microscopy. Here we first demonstrate that this is not the case. Spectroscopic imaging is considerably more complicated and presents a rich area of investigation. We first present a recently developed theoretical framework to understand light propagation in microspectroscopic imaging systems. The examination of progressively more heterogeneous samples leads to a variety of distortions in the spectrum, which the theory predicts. Application of the theory to recorded data allows for the recovery of correct spectral information in some cases and fits to a generalized model in other cases. The theoretical understanding also leads to the development of instruments with new capability for both IR and Raman imaging. Specifically, we show how unprecedented spatial resolution can be obtained and describe the fundamental limits of information extraction based on rigorous theory. Finally, we demonstrate the experimental realization of the theory and simulation to demonstrate a new capability for IR imaging. In summary, the application of optical theory and modeling to vibrational spectroscopic imaging has allowed us to design and understand instruments with new capabilities, to enhance and interpret spectral data, to realize models for real-world samples and to obtain fundamental understanding of light-matter interaction in complex systems.

(725) **Sudden Impact: Scholarly Publishing and the Day After Tomorrow**; Michael Blades[1, 3], Rebecca Airmet[3], Peter Griffiths[2, 3]; [1]Department of Chemistry, The University of British Columbia, [2]Department of Chemistry, University of Idaho, [3]Society for Applied Spectroscopy

"Publish or Perish" is a phrase with which every assistant professor is familiar. Publications are the main way that researchers communicate the results of their research work to their colleagues and the broader scientific community. About 1,350,000 scholarly articles were published in 2009 and this number is growing at an annual rate of about 2.5%. Librarians, editors and researchers share the perception that there are severe problems facing scholarly publishing as a result of a combination of economic pressures and the emergence of new technologies for disseminating information. We will discuss the following issues with respect to their impact on Applied Spectroscopy.

1. Federal granting agencies are sensitive to the fact that research that they fund should be openly accessible to the taxpayer free of charge. But "open access" does not mean that no costs are involved. We will discuss the current state of open access and its likely evolution.
2. In many cases researchers sign copyright over to for-profit publishers who want to sell that same work back to the institution where the author or reviewer works. Many of those same institutions can't afford to subscribe to all the journals used by their research community which, in part, has led to the "Cost of Knowledge" campaign targeting Elsevier. Where is this headed?
3. The Impact Factor (IP) has become widely used to assess the relative importance of a journal, which has sometimes led journals to adopt practices to artificially boost their IP. We will raise the question of whether a journal's IP really measures the quality and impact of its publications and why academics have allowed this metric to become a dominant force in decisions that affect their livelihood.
4. The increasing demand for publishing has led to the creation of journals that have impressive sounding names and lists of prominent advisory editors. The net result is that there is a "market" for all manner of research no matter how insignificant or bad which has led to a trickle-down phenomenon where authors resubmit their work until they find a journal willing to accept it. Is this good for science?

(726) **Analysis of Polymer-Surface Coatings Using Infrared External-Reflection Spectrometry**; Takeshi Hasegawa[1]; [1]ICR, Kyoto University

Infrared external-reflection (ER) technique should be more used for surface characterization in polymer sciences. It is molecular-orientation sensitive, and the whole cross-sectional image near the surface is readily obtained with an easy experimental skill. In recent years, however, infrared ER is pushed back by the rapid expansion of SFG. Although SFG is a really powerful and sensitive technique to draw molecular information from asymmetric local structure in terms of inversion symmetry, which is often found at an interface, the amount of information is limited due to the strict selection rule: the product of selection rules of infrared and Raman spectroscopies. On the other hand, infrared ER is ruled only by the surface selection rule, and many IR-active normal modes are available. Therefore, the discussion of orientation is quite easy thanks to an IR-specific character: the estimation of the direction of a transition moment is easy. In practice, however, some technical aspects of infrared ER are not described in a comprehensive manner, which may keep the analysts away from the useful technique. In this talk, the surface selection rule and experimental tips of the infrared ER technique is mentioned followed by an application study analyzing spontaneous adsorption of surfactants and cellulose onto a poly(methyl methacrylate) (PMMA) surface in an aqueous solution in an ordered and cooperative fashion induced by hydrogen bonding. The glucose rings of n-dodecyl-β-D-maltoside (DDM) and hydroxyethylcellulose (HEC) stand perpendicular to the surface, H-bond to the surface COOMe groups with their C=O and Me-O bonds parallel to the surface, and form a tight monolayer. The non-H-bonded COOMe groups orient their C=O bonds perpendicular to the surface. In contrast, the glucose rings of hydrophobically modified hydroxyethylcellulose (HMHEC) lie flat with the side chains perpendicular to the surface and H-bond to the perpendicular-oriented C=O groups. The non-H-bonded COOMe groups orient their C=O bonds parallel but Me-O bonds near-perpendicular to the surface for stabilizing HMHEC. The current work provides a detailed picture of how surface-active molecules interact with a solid surface and self-assemble into greatly different architectures.

(727) **Electrophoresis Joins FACSS: History and Newest Results**;
Mark Hayes[1]; [1]Arizona State University

The FACSS community has a new member: The Electrophoresis Society (AES*). After forty successful years of professional and social activities, this group of leading scientists has joined forces with the other Federation members. My talk will weave the story of this society and my own recent work, which directly grows from many of the topics central to the intellectual focus of this organization. The nucleating act of AES started in 1972, in Tubingen, Germany, during a meeting called, "The Blue Fingers", initially focused on Polyacrylamide Gel Electrophoresis and Isoelectric Focusing. These remain—to this day—extremely important tools for analysis of proteins and complex biomolecules. The society was formed and the first meeting held in 1981. The interests of organization have evolved to include all forms of theoretical and experimental manipulations of molecules and particles by flow or electric fields. AES boasts a membership that includes the best and brightest of the field. Core to all separations science is resolution: causing important components to move in time or space away from each other. Although a description of core processes controlling resolution across all separations systems does not exist, the most successful techniques are considered to be electrophoretic in nature. Early demonstrations of capillary- and microchip- based electrophoresis have shown absolutely extraordinary resolution using high fields showing deuterated vs. hydrogenated and sub-millisecond separations. These results were obtained in systems operating in a linear mode—spreading and diluting a mixture out along a single axis. My own work focusses on a new approach enabled by the short length-scale of microdevices which exploits local field gradients. The core to this discovery is setting up punctuated microgradients separated by flat field zones. This uniquely minimizes the effects of diffusion by dramatically increasing the local restoring forces. As a result, not only does the resolution increase by a factor tied to the strength of the local gradients, but can be accomplished in parallel while increasing concentration of the targets (focusing). This opens up several new venues for exploitation, including dynamic and programmable collection of specific analytes at higher resolution than is available from any traditional technique in an array format. Speeds of separations are also dramatically increased. We describe the underlying theoretical principles and provide examples of flow/electric field and electrokinetic/dielectrophoretic devices in a microfluidic format. The underlying models extend to any force which can be induced into dispersed microgradients in the presence of a static counter field.

*The acronym remains AES, the name was recently changed from 'American Electrophoresis Society'. The official name is AES Electrophoresis Society.

(728) **LIBS in Atomic Spectroscopy: NASLIBS in FACSS**;
Richard E. Russo[1, 2], Jhanis Gonzalez[1, 2], Jong Yoo[2], [1]Lawrence Berkely National Lab, [2]Applied Spectra

LIBS (Laser Induced Breakdown Spectroscopy) R&D has grown throughout the scientific community with the latest advance being the incorporation of NASLIBS (North American Society for LIBS) into the FACSS membership. The attributes of LIBS have driven its interest and development. Attributes include the ability to perform rapid direct solid-state elemental analysis, without sample preparation or consumables, and standoff analysis. 2012 is a special year for LIBS as the NASA Rover Curiosity is scheduled to land on Mars in August; the Chemcam instrument on Curiosity includes a LIBS system. This talk will give an overview of LIBS R&D to include capabilities, concerns, applications, commercialization, and maybe results from Curiosity.

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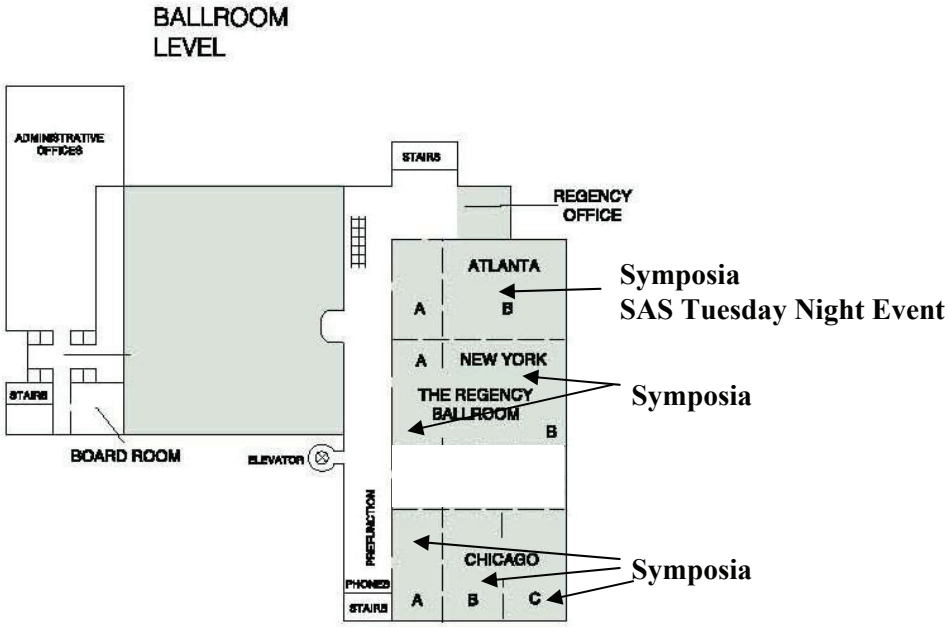

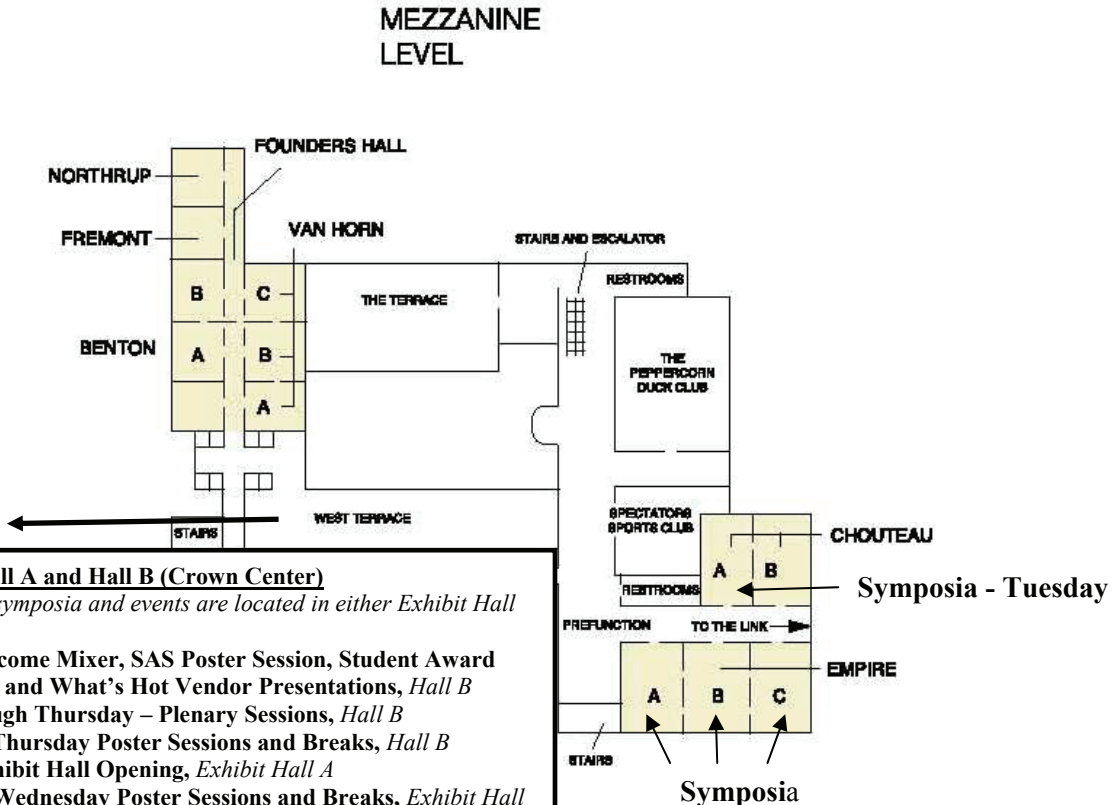

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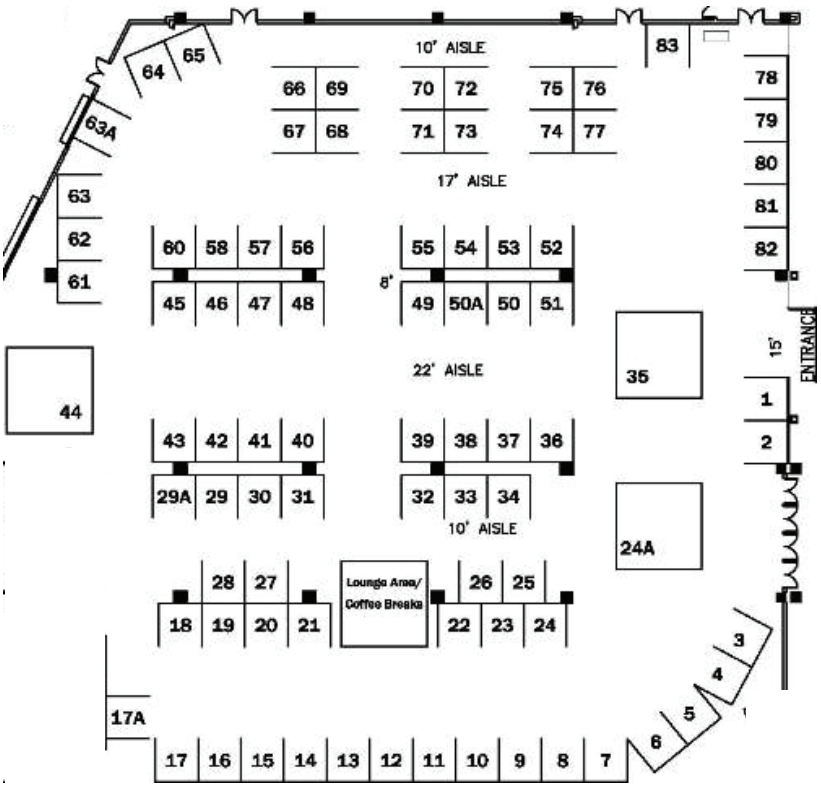

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