ATACHMENT 5.3

X-RAY ANALYSIS USING SYNCHROTRON RADIATION

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(i) Short summary of work related to methodology and applications of nuclear spectrometry

The X-ray group of the Atominstitut in the research area " Radiation Physics based Analytics and Radiochemistry" is working since years on the development of special techniques in X-ray Spectrometry. Research is done in the field of TXRF, angle resolved grazing incidence XRF for depth profiling and Synchrotron radiation induced XRF, both TXRF and microanalysis. Investigations range from environmental samples, Si wafer surfaces, medical samples to fine art samples.

(ii) Scientific scope of your project under the CRP

Topic of the proposed research will be the integration of specific analytical X-ray techniques using Synchrotron radiation as excitation source. It should cover Synchrotron radiation TXRF, micro X-ray fluorescence analysis (μ-XRF) in confocal as well as conventional mode for elemental 2D and 3D X-ray imaging. Both variants of XRF should be combined with absorption spectroscopy in fluorescence mode for chemical speciation (XANES)

(iii) Detailed work plan for the first year

Year 1:

SR-TXRF: aerosol analysis with SR-TXRF and integrated speciation of Fe by XANES at trace levels.

μ-XRF: determine the distribution of Pb in different samples of human bone and cartilage, integrated speciation with XANES to characterize the oxidation state Pb.

(iv) Results obtained till now under the CRP

Analysis of atmospheric aerosols with SR-TXRF: new direct calibration using pico droplets (pL) generated by ink-jet printers and speciation of Iron with SR- TXRF-XANES [1]

This research is done with U.Fittschen and J.Broekaert from Inst. Of Anorganic and Applied Chemistry at the University of Hamburg.

In SR-TXRF the outstanding features of synchrotron radiation such as natural collimation, high intensity and low background allow for the detection of trace and ultra trace absolute amounts (pg, fg) of most medium Z elements. However, an accurate and reliable calibration of SR-TXRF analysis of particulate samples until now is often problematic. As calibration with nano-droplets (10-50 nL) was found to give excellent results in the determination of trace impurities with TXRF in semiconductor material[2], we developed a calibration suitable for atmosphericaerosol analysis with SR-TXRF by decreasing the droplet volume to the pL range[3] . Ink-jet printers are used to generate 5 to 130 pL droplets. The reliability of the printing of a certain amount of a single element standard solution was studied and related to common calibration in TXRF. The performance to print one and more droplets on a certain place was tested (Figure 1, right). The results showed that droplets generated by inkjet printersare smaller in diameter (between 50 and 200 µm depending on the cartridge type) than the width of the Synchrotron beam used in the experiments. The reliability of the dosing of single element standard solution is comparable to common calibration in TXRF and the printing of patterns in the µm range is satisfying. This new calibration technique was applied aerosol characterization. It is still a challenge to characterize aerosols after a short samling time (1h and less). Size classification of aerosols is a very important feature to determine toxicity and atmospheric behaviour of atmospheric aerosols. Especially small particles, fine dust (PM10, Particulate matter < 10 µm, aerodynamic particle size) and ultra fine dust (PM2.5) are subject of many studies and have been related to severe health

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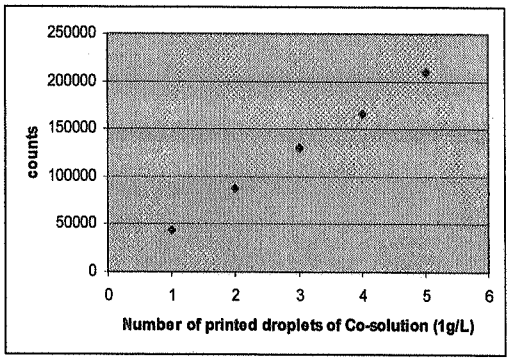
[1] U. E. A. Fittschen, G. Pepponi[1]; F. Meirer[2], S. Hauschild,S. Förster, C. Streli[2], P. Wobrauschek[2], G. Falkenberg[3] and J. A. C. Broekaert, Hasylab Annual Report 2006,

[2] T. C. Miller, C. M. Sparks, G. J. Havrilla, M. R. Beebe, Spectrochim. Acta, Part B 59, (2004), 1117-1124

[3] U. E. A. Fittschen, S. Hauschild, M. A. Amberger, G. Lammel, C. Streli, S. Förster, P. Wobrauschek, C. Jokubonis, G. Pepponi, G. Falkenberg, J. A. C. Broekaert, Spectrochimica Acta Part B 61 (2006) 1098 – 1104

damage[4].



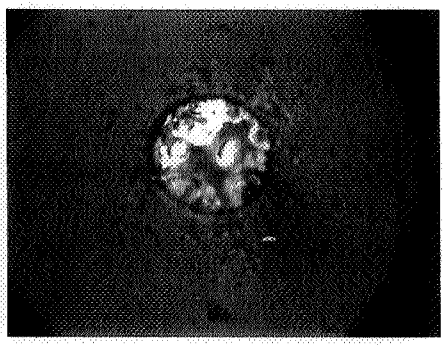


Fig. 1: Left:. Five times 1 droplet of a 1g/L Co standard solution was printed successively with HP 500C on a quartz reflector . Right: pico-droplet (Co 1g/L) printed by a modified HP500C on a silicon wafer investigated with a light microscope, droplet size about 20 µm.

For size fractionized aerosol sampling impaction devices with different specification varying in the number of stages and air throughput are in use. In this study a 12-stage Berner impactor which enables sampling particles of 60 nm aerodynamic particle size was used. Atmospheric aerosols were collected with the aid of a Berner impactor on Si-wafer reflectors for 20 min and 60 min at the University of Hamburg. One droplet of a cobalt standard solution (1 g/L) containing 160 pg cobalt was spotted on the aerosol with an ink-jet printer for quantification. Fig. 2 shows a spectrum.

In atmospheric aerosol research, element speciation is important to assess their origin, toxicity and potential to influence climate processes. A major challenge in element speciation is to avoid chemical transformation during analyses. This easily occurs during sample preparation as used e. g. in fractionated solvent extraction or in applying chromatographic techniques. XANES measurements allow element speciation without dissolving the samples. As Si-wafers can be used as aerosol collection plates in an impaction device and as sample carrier for XANES measurements, no additional step is necessary for sample preparation. The same aerosol samples described above were analyzed by TXRF-XANES to determine the oxidation states of iron before the internal standard was added not to change the oxidation state by adding the internal standard..

As shown in Fig. 2 the TXRF-XANES measurements at the Fe K edge revealed that the oxidation state of iron is the same for different particle size fraction.

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[4] U. Lahl, W. Steven, Pneumol. 59, (2005) 704-714

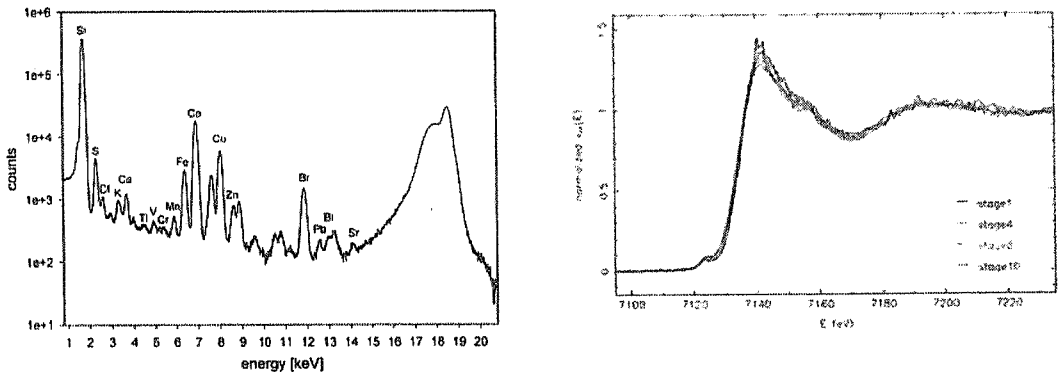

Figure 2: (left) Spectrum of an aerosol- stage 4 (2-0.130 µm), 20 minutes samling time, multilayer monochromator, 1000 s measuring time. (right). Iron K-Edge XANES spectra from aerosol samples (60 min sampling time) for stage 1, stage 4, stage 8 and stage 10.

Elemental Mapping of Human Bone by Confocal SR micro-XRF and Pb speciation by micro-XANES in Fluorescence mode

One of the main threats to human health from heavy metals is associated with exposure to lead (Pb), which is associated with chronic diseases in the nervous, hematopoietic, skeletal, renal and endocrine systems. Once incorporated through ingestion or inhalation, Pb accumulates in the skeleton. However, little is known about how Pb is distributed in calcified tissue on the microscopic level. Therefore our group studied the distribution of Pb in human bones slices using synchrotron radiation induced micro X-ray fluorescence analysis (SR µ-XRF) in scanning and tomographic mode. The project is performed in cooperation with the IAEA Seibersdorf Laboratories, XRF Group, Instrumentation Unit, Seibersdorf, Austria, the Ludwig Boltzmann-Institute of Osteology, Vienna, Austria as well as with the two German Synchrotron radiation facilities HASYLAB at DESY, Hamburg and ANKA, Karlsruhe.

The latest results were obtained by using the confocal microbeam setup at HASYLAB beamline L. With this setup a quasi-cubic detection volume, defined by the overlap of the focal cones of the two x-ray optics (one in the primary beam, the second one in front of the energy-dispersive x-ray detector) was used for analyses. Since this variant of SR µ-XRF offers the possibility to perform depth sensitive analysis it was used to determine the three-dimensional distributions of Pb and other (trace) elements in human bone (Figure 3) with an resolution of about 10- 20 µm (lateral and in depth).

The region for the scan in human patella was chosen to contain non-mineralized articular cartilage, mineralized articular cartilage and subchondral bone.

From this measurement a very local distribution of Zn an Pb at the tidemark (the border between non-mineralized and mineralized cartilage) could be detected[5]. These novel results of the specific accumulation of Pb in the tidemark of human bone may lead to further understanding and research on the effects of Pb on cartilage, bone biology and biomineralization.

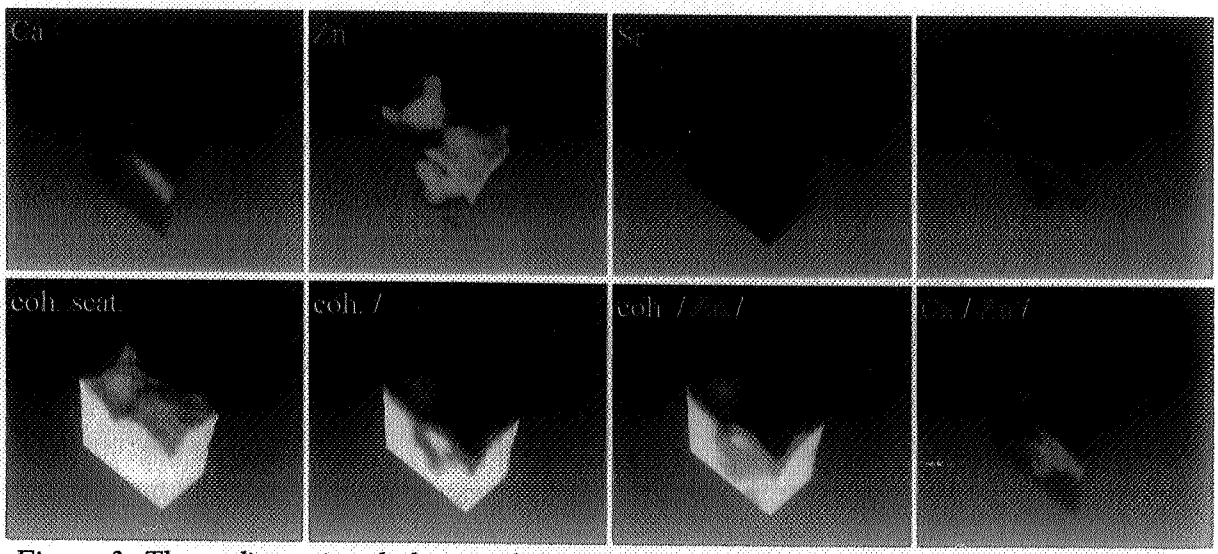

Figure 3: Three-dimensional elemental distribution in a human patella sample. Distance of measurement pixel: 10μm (lateral and in depth); measurement time per pixel: 5s; scanned volume: 200 x 200 x 160 μm³; total number of spectra: 7497.

To obtain informations about the oxidation state of Pb at the tidemark, experiments have been carried out at the SUL Beamline at ANKA using μ-XANES in fluorescence mode. The continous X-ray spectrum from the wiggler has been monochromatized by a Si(111) double crystal monochromator. Focusing of the primary beam to a spot size of about 250 x 250 μm was accomplished by KB optics. μ-XRF line scans across the border between non-calcified and calcified cartilage have been performed to determine the position of the tidemark, which was the measurement position for the μ-XANES experiments. X-ray absorption spectra have been recorded by tuning the excitation energy in 0.5 eV steps across the L_3 absorption edge of Pb (13035 eV) while measuring the Pb-La fluorescence signal with an 7-element SiLi detector

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[5] N.Zoeger, P. Roschger, J.G. Hofstaetter, C. Jokubonis, G. Pepponi, G. Falkenberg, P. Fratzl, A. Berzlanovich, W. Osterode, C. Streli and P. Wobrauschek, Lead accumulation in tidemark of articular cartilage , Osteoarthritis and Cartilage 14 (9), 906-913 (2006)

First results have been obtained at the tidemark of a femoral head and patella,. Additionally, a set of standard materials, namely Pb-hydroxyapatite (pb ha), PbO, PbS, PbCO3, and PbSO4 (pressed pellets), have been analyzed for comparison. While the standard materials could be measured with sufficient counting statistics, the measurement in the tidemark, where only traces of Pb are present, show reasonable statistics. Due to the low count rates obtained in the subchondral region of the bone (10 times lower than in the tidemark) XANES scans in this region were not feasible. Nevertheless, the micro μ-XANES spectra obtained in the tidemark are in good agreement with spectra obtained from the hydroxyapatite standard materials, which suggests that Pb in tidemark and therefore in calcified cartilage is bond to hydroxyapatite as it is .known for subchondral bone

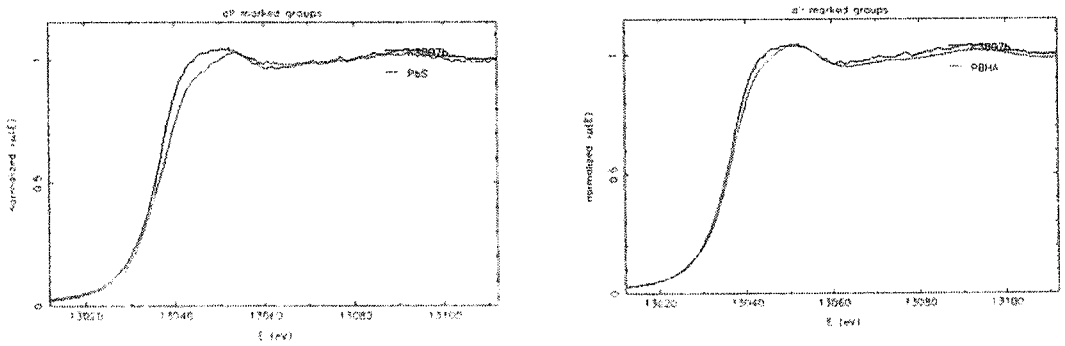

Fig.4 XANES spectrum from a PbS standard in comparison to Pb at the tidemark(left) Pb-Hydroxyapathite standard in comparison to Pb at the tidemark (right)

(v) Work plan of your project for the coming years.

Year 2:

SR-TXRF: Speciation of Fe on Si wafer surfaces with SR-TXRF XANES

μ-XRF: Determination of the oxidation state of Pb in articular cartilage

Year 3:

SR-TXRF: Depth profiling and absolute dose determination of Indium implants in Si wafers

Characterisation of Arsenic Ultra Shallow Junctions by Grazing Incidence Fluorescence EXAFS,

μ-XRF: Determination of the distribution of oxidation state of Pb in bone and cartilage of patients suffering from bone diseases.