Atomic spectrometry update–X-ray fluorescence spectrometry

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This comprehensive review covers the latest published activities using XRF techniques. X-ray analytical equipment continues to be integrated with X-ray emission/diffraction/absorption techniques with the growing use of synchrotron radiation (SR) sources reflected in the literature. This integration trend was also prevalent in the development of small-scale laboratory equipment. X-ray detectors have advanced with pixellated systems, micro-calorimeter types and the now established silicon drift detectors being readily used by many authors. Matrix correction and calibration procedures have developed to accommodate instrumental developments related to micro-beam and bulk analysis. SR-based micro-techniques for two and three dimensional imaging were reported in research activities in applications for clinical, biological, environmental and cultural heritage studies as well as investigations of extraterrestrial material. Sample preparation developments continue, especially for TXRF. The extension of TXRF to measure the angle dependence fluorescence signal (GI-XRF, XSW) showed increased interest with several groups applying the technique to depth profiling and thin layer analysis of nano-particles. More applications were reported this year for the reversed technique (GE-XRF) combining micro-beam analysis with surface sensitivity. Geochemical mapping of the moon is reported after space flight measurements used the Sun as a radiation source. The literature reflects increasing quantitative analysis using portable XRF with a welcomed growth in acceptance by the Food and Drug authorities and other applied users. This year's Update offers dietary delights for those who enjoy crab meat and an insight into the eating habits of elephants. Advice for gardeners contemplating a green roof is reported along with analysis of the wood treatments used in the manufacture of Stradivari and Guarneri violins. XRF has also played its part in the development of self-cleaning fabrics.

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1   Introduction and reviews

This Update refers to papers published approximately between April 2009 and March 2010 and continues the series of Atomic Spectroscopy Updates in X-ray Fluorescence Spectrometry[1] that should be read in conjunction with other related reviews in the series.[2–6] As this journal celebrates 25 years in print, it is perhaps interesting to *track the developments in XRF instrumentation*. Energy dispersive configurations have benefited from dramatic improvements in their detection systems. In 1985, most EDXRF systems were floor-standing or needed substantial benches and the detector was a bulky lithium-drifted Si(Li) detector that

required cooling with liquid nitrogen (LN). Start-up times were a matter of hours and failure to keep a system cool often resulted in an expensive and lengthy repair at a distant facility. Those detectors were, however, very good spectroscopy devices with good X-ray stopping power, energy resolution as low as 140 eV for premium systems at low count rates (<5 kcps) but often in the 170 to 200 eV range for practical purposes. Nowadays, the Peltier-cooled Si PIN or Si Drift detector (SDD) is most commonly used. Such detectors are the size of a matchbox, require only electrical power and are ready to use in a couple of minutes. In addition to these huge strides in operational simplicity, the modern SDD offers an excellent energy resolution of <130 eV energy resolution at count rates of at least 50 kcps and is even now to be found in the latest models of handheld EDXRF system. Excitation in EDXRF has also seen substantial changes and where most compact systems of 25 years ago used radioisotope sources for excitation; most systems nowadays employ compact, low-power X-ray tubes that require no liquid cooling and can operate at voltages up to 50 kV. The latest hand held systems are equipped with very compact, light and frugal X-ray sources that are still able to deliver 50 kV and 50 μA. Equally impressive on the benchtop has been the deployment of polarized X-ray excitation and Cartesian geometry using X-ray sources delivering only 50 W of beam power. Such systems yield XRF spectra with extremely low background and have improved EDXRF detection limits by at least one order of magnitude for several key applications. The use of Fundamental Parameter (FP) computations has transformed XRF analytical software. Massive on-line disk storage, fast CPU's and staggering amounts of RAM have brought real-time FP analysis to most modern XRF systems and this capability is particularly valuable for the analysis of unknown samples for which Reference Materials and calibration samples are unavailable. Advances in X-ray optics have given the analyst smaller beams with higher spatial resolution. With the number of Synchrotrons increasing worldwide, SR systems coupled to μ-XRF configurations now benefit from beam sizes in the range below 1 μm and down to 10 nm. New detectors enable the processing of higher count rates thereby providing lower detection limits. The combination of various techniques at one beamline now bestows comprehensive characterisation of samples. SR in combination with X-ray absorption spectroscopy has transformed chemical speciation from the adventurous exploits of the few to valuable data for the many. Total reflection XRF (TXRF) has proved to be a boom for the semiconductor industry where wafer surface characterisation is commonplace. In recent years TXRF instrumentation now includes portable systems that extend applications out into the field. Grazing incidence systems (GI-XRF) enable comprehensive depth profiling and thin film characterisation whereas the grazing emission (GE-XRF) combination offers the user spatial resolution and nanometer depth information. The powerful combination of TXRF using SR as the excitation source offers lower detection limits that have proved especially interesting in aerosol analysis. The SR-TXRF-XANES configuration offer direct sampling in a short time on only small amounts of sample and give new insights for environmental applications. The literature also reflects the increasing use of imaging techniques that provide either 2D or 3D mapping facilities for a range of applications.

Advances in the "family" of XRF techniques were described by Wepasnick et al.[7] in a review of the chemical and structural characterisation techniques available to assess carbon nanotube surfaces. Sitko[8] described the difficulties and possibilities for quantitative XRF analysis of samples with less than infinite thickness. Matrix correction methods, including fundamental parameters, Monte Carlo simulations, influence coefficients algorithms and methods based on X-ray transmission measurements were reviewed. Margui et al.[9] described sample preparation procedures, trends and future possibilities for the determination and quantification of metals in vegetal materials.

2 Instrumentation

2.1 General Instrumentation and excitation sources

An overall trend in publications this year in the development of X-ray analytical equipment was the integration of X-ray emission/diffraction/absorption techniques and the growing use of synchrotron radiation sources. This integration trend was also prevalent in the development of small-scale laboratory equipment.

A number of reports on the construction of new or modified instrumentation were devoted to the *synchrotron beam line set ups* utilising highly collimated and focussed X-ray beams. Matsuyama et al.[10] evaluated the performance of a newly constructed scanning XRF microscope applying Kirkpatrick-Baez mirror optics at 15 keV to produce sub-100 nm beam spots. The set up, implemented at SPring-8 synchrotron facility in Japan, was used to visualise distributions of chemical elements in biological samples with single cell resolution. Alberti et al.[11] and Gianoncelli et al.[12] reported a new addition to the European TwinMic X-ray microscope established at the Italian synchrotron facility ELETTRA, comprising a low-energy (280–2200 eV), microbeam X-ray fluorescence spectrometer (LEXRF) with sub-100 nm resolution. The LEXRF utilises multiple, windowless, large area silicon drift detectors (SDD) with customised pre-amplifiers and a fast multi-channel acquisition system. The main advantage of this combined set up is that the absorption and phase contrast images of morphological structures can be superimposed with simultaneously collected elemental maps. Kaulich et al.[13] performed pilot experiments utilising the Twin-Mic and the LEXRF set-up to correlate the distributions of essential trace elements with the lateral distributions of trace nutrients in zooplankton and wheat seeds. The description of another newly commissioned, advanced, synchrotron beam line set up for high spatial resolution X-ray absorption spectrometry was given by Fink et al.[14] This instrument, PolLux-STXM, dedicated to scanning transmission X-ray micro-spectroscopy (STXM), was established at the Swiss Light Source synchrotron facility and utilised Fresnel zone-plate optics to produce spot sizes equal to about 20 nm. In operation, low energy X-rays were applied to give access to 1s absorption edges of low-Z elements such as C, N, and O. Kunz et al.[15] described a new μ-XRD strain measurement and μ-XRF instrument established at the advanced light source of the Lawrence Berkeley National Laboratory in the USA. A focal spot of one micrometer was obtained with Kirkpatrick-Baez mirrors equipped with active temperature stabilisation. In the XRD mode with a white beam, the achieved

resolution was 5×10^{-5} in the strain units. XRF scans could be performed in continuous mode with speeds up to 300 points per second. De Nolf et al.[16] performed a comparative assessment of a combined XRF/XRD powder diffraction micro-beam set up established at the Hamburger Synchrotronstrahlunglabor (HASYLAB, Germany) Beamline L to that available at the European Synchrotron Radiation Facility (ESRF, France) beam line ID18F/ID22. The HASYLAB instrument achieved a typical angular resolution in the range 0.3–0.5 degrees as compared to 0.1–0.15 degrees at the ID18F/ID22. The authors demonstrated the capabilities and limitations of the μ-XRF/XRD Beamline L instrument and presented two case studies involving identification of heavy metal phases in polluted soils. Also a review, of the design and performance of a micro-focus X-ray beam line established at the Diamond Light Source, UK, was published by Mosselmans et al.[17] This micro-beam facility comprised X-ray fluorescence (XRF), extended X-ray absorption fine structure (EXAFS), and X-ray diffraction (XRD) spectrometers. The achieved spot size was equal to about 3 μm and the energy range 2–20.7 keV. Another synchrotron facility and another review article was presented by Erko and Zizak,[18] this time on the capabilities of hard X-ray beam lines at the synchrotron ring BESSY II, Germany. They demonstrated a number of micro-beam X-ray spectrometric techniques that can be applied with micro- and nanometer-spatial resolution, including combined XRF/XRD analysis with X-ray beam induced current (XRBIC) measurements. They also described a confocal depth-resolved μ-XRF instrument, and a set up for performing single nanometre depth-resolved μ-EXAFS analysis with standing wave excitation. In Japan, at the 2.5 GeV Photon Factory synchrotron facility, Suzuki and co-workers[19] established a system for X-ray magnetic diffraction (XRMD) analysis of ferromagnets with a high count rate capability of up to 10^5 counts per second and high magnetic field strength over 20 kOe. The details of the newly upgraded system were presented in their report. In Campinas, the Brazilian Synchrotron Light Laboratory (LNLS), Pereira et al.[20] implemented an instrument capable of simultaneous X-ray transmission/XRF μ-CT with the aim of correlating the distributions of selected elements with the observed pathological changes in breast tissue samples. The transmission data were used to correct the absorption effects in XRF tomography. Back in Europe, Meirer et al.[21] compared the grazing exit (GE) versus grazing incidence (GI) measuring geometry combined with XAFS analysis on Beamline L at the HASYLAB synchrotron facility in Germany. They concluded that GE geometry was less sensitive as compared with GI excitation and, therefore, less suitable for the analysis of trace amounts of elements. They also confirmed that self-absorption effects were more severe in GI as compared to that observed in GE geometry.

Although not X-ray excitation, innovative developments in X-ray spectrometers have been reported in related particle and ion beam excitation techniques. Thus, Beyer and a large group of collaborators[22] built a custom, twin-crystal spectrometer for spectroscopic measurements produced by heavy ion beams at the GSI Helmholtz Centre for Heavy Ion Research in Germany. The twin crystal optics was coupled to a 2D position-sensitive X-ray detector allowing high spectral resolution measurements of X-ray emissions from fast moving, highly ionised atoms in the ion beam. They reported the results of test measurements.

Raepsaet et al.[23] gave an overview of a unique nuclear micro-probe facility of the Pierre Sue Laboratory in France devoted to the analysis of small quantities of radioactive samples. The available analytical techniques included elastic recoil detection analysis (ERDA), Rutherford backscattering spectrometry (RBS), nuclear reaction analysis (NRA), and particle induced X-ray emission (PIXE). An overview of the programs related to nuclear research was given in the report.

Finally in this section but not of least importance, a few projects introducing new or updated small-scale laboratory equipment were described in the literature. Thus, Bozek et al.[24] constructed a new multi-purpose X-ray microprobe system based on a microfocus X-ray tube source (spot size 1 μm, maximum power 6 W). The spectrometer could be used in a few dedicated modes of operation: μ-CT, μ-XRF, μ-TXRF, as well as the irradiation of mammalian cells. The latter was devoted to research on the damage induced in individual cells by X-ray radiation. The basic characteristics of the system and its construction details were given in the report. Another article by the same research group with Bielecki as principle author[25] gave more details of the spectrometer with preliminary results of μ-CT measurements. Yang et al.[26] built a new glancing incidence X-ray fluorescence (GIXRF) spectrometer by collimating the incident beam using a parallel polycapillary lens. By applying a zirconium filter in the primary beam of the X-ray tube source, they obtained a semi-monochromatic, highly-collimated, incidence beam and described an application of the new spectrometer for the characterisation of crystal and a thin film samples. Matsuda et al.[27] constructed a μ-XRF spectrometer equipped with two X-ray focusing elements arranged in series. The radiation emitted by the X-ray source was first focused by a polycapillary lens, after which a glass conical pinhole was mounted to achieve a finer focused beam of spot diameter 25 μm with a gain from the combined optics of approximately 1400. Maeo et al.[28] reported the construction of a multi-target, micro-focus X-ray tube with maximum power of 50 W and three selectable anode targets made of Cr, W, and Rh. The tube could serve as an energy tuneable source for laboratory "desktop-sized" micro-beam X-ray instruments. A spectrometer utilizing the tube was presented by the same group in another report.[29] The radiation emitted by the tube was focused by a customised, doubly curved crystal (DCC) with construction details reported along with performance of the system, in terms of spatial resolution and the detection limits of elements. Sitko et al.[30] assembled a μ-XRF spectrometer comprising a low-power air cooled Rh-anode X-ray tube, Si-PIN detector and a set of pinhole collimators with diameters varying from 50 μm up to 2 mm. The evaluation of the X-ray beam spot size and the influence of the beam collimation on the spectral distribution of photons in the primary beam was presented. A rather rare combination of techniques in one instrument was presented by Procop et al.[31] They installed a miniature, micro-focus X-ray tube in a scanning electron microscope (SEM) equipped with standard energy dispersive X-ray detector system. The X-ray tube was optimized for low-Z element excitation. The X-ray photons emitted by the tube were focused by a custom designed polycapillary lens optimized for transmission at 5 keV. By utilizing L-series emission from Mo and Rh tube targets, 1% m/m detection limits for Na_2O in a glass sample was achieved. Specialised instrumentation utilising XAS

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for the characterization of inertial confinement fusion (ICF) targets was built by Fong et al.[32] The system was capable of determining the aerial density of any element with atomic number Z > 17 with 3% (one sigma) accuracy without the need for a reference standard. Results of measurements of a number of ICFs and high energy density targets were presented.

2.2 Detectors

The area of perhaps the most interest and activity during the review period was that of *pixellated X-ray detectors*. An evaluation was reported[33] of a so–called controlled drift detector (CDD) that was a 2–dimensional, energy dispersive X-ray detector with a design and characteristics related to a silicon drift detector (SDD). The detector comprised a 36 mm² active area of 300–450 μm thick, fully depleted silicon with a pixel size of 180 × 180 μm². When cooled to −34 °C by means of a simple, single stage Peltier cooler, the detector achieved an energy resolution equivalent to 267 eV at 5.9 keV, although a second device with reduced leakage current was able to provide energy resolution of 198 eV. The drift time and read-out channel location provided the 2D capability which was demonstrated in applications of X-ray absorption edge contrast imaging, XRF imaging and diffraction enhanced breast imaging. In the area of XRF imaging, a laboratory set up comprising a high-power X-ray tube and polycapillary optics fitted to both the incident and fluorescence X-ray paths enabled imaging of the 300 μm copper tracks on a PCB at a claimed effective pixel size of 35 μm in an acquisition time of 8 min; a performance that is attractive for laboratory XRF imaging. Although being tested for robustness to proton radiation damage during a space mission to the Moon (Chandrayaan-1), the swept charge device (SCD) X-ray detector[34] had attractive characteristics for XRF imaging. The SCD is closely related to a CCD and comprised a large active area of 1.1 cm² with both spatial and energy resolving capabilities. When cooled to −20 °C the energy resolution was shown to be <150 eV at 5.9 keV rising to around 400 eV following a high energy proton irradiation equivalent to the expected 1.5 year mission duration. The energy resolution was shown to improve to 350 eV when the detector was cooled to −40 °C. Undeterred by the dreadful energy resolution of 2000–3000 eV at 8 keV of their programmable pixel readout chip for arrival time, energy and/or photon counting measurements ("TIMEPIX") CCD X-ray detector, Zemlicka and co-workers[35] evaluated this detector for direct XRF imaging of simple systems such as a PCB and a coin. The spatial resolution was limited by the pinhole used, to around 200 μm and the abysmal energy resolution made it impossible, despite some valiant attempts at spectrum modelling and processing, to separate the K lines of Cu, Ni and Zn. However, the authors did achieve some success in separating the rather more distant Pb L and Sn K series lines. This work underlines the very limited energy resolution of CCD's and the reason they are more often used in conjunction with X-ray scintillators or as straightforward, though highly effective photon counters with minimal direct energy discrimination.[36,37] The future needs of 2D X-ray detectors for the European Free Electron Laser in Hamburg were briefly discussed by Graafsma,[38] who identified a clear need for a new generation of 2D detectors. The needs of the space community for high

performance pixellated detectors was described by Treis et al.,[39] who identified the novel dual energy pixellated X-ray detector for the SIMBOL-X instrument on a novel multi-satellite high performance X-ray telescope. This instrument comprised a 128 × 128 DEPFET (depleted P-channel field effect transistor) pixel array for the lower energies and a pixellated CdTe detector for the higher energies of up to 80 keV. The authors also noted the use of a similar DEPFET array for the impressive mercury imaging X-ray spectrometer (MIXS) instrument for XRF imaging of Mercury on the European Space Agency (ESA) BepiColombo mission that is currently being built. A study was conducted by Meuris and colleagues[40] of charge-sharing in the spectacular 16384 channel pixellated CdTe X-ray detector designed for "SIMBOL–X". The detector comprised a mosaic of 64 sensors, each of 1 cm² active area and 1 or 2 mm thick, which were themselves segmented to obtain 256 pixels of 625 μm pitch with an associated guard ring. Split charge due to charge sharing and X-ray fluorescence of the Cd and Te elements of the detector itself were studied and the authors reported charge loss to be negligible and developed a model to successfully correct for the split events. This impressive XRF camera was reported to exhibit an energy resolution of 722 eV at 13.94 keV when operated at −10 °C and successfully met all specification requirements for the intended mission.

The review year saw a minor resurgence in *high resolution cryogenic detectors* and in this regard Ohno and co-workers[41] reported the development of a new transition edge sensor (TES) for a microcalorimeter. The design aimed to increase simultaneously the sensitivity, the geometric efficiency and the output count rate, the latter of these being a particular limitation for conventional microcalorimeters. The new TES employed a novel thermal feedback system and comprised a 150 × 150 μm² gold film absorber, which met the criterion of "large" for a microcalorimeter. The detector exhibited an energy resolution of 34 eV at 5.9 keV and a thermal decay time of 150 μs, that may lead to count rates of a few thousand cps, which is attractive when compared to the 100 cps often reported as the maximum attainable for conventional microcalorimeters. Despite these improvements and the use of an SRXRF beam line at the SPring-8 facility, the authors reported the rather unimpressive ability of the device to resolve the main XRF peaks from a stainless steel sample, which is a routine application for thousands of lab and handheld XRF systems. In a separate attempt[42] to improve sensitivity and geometric collection efficiency, a thick gold absorber layer was fabricated as the cap of a mushroom shape on a Ti/Au bilayer sensor but, at the time of writing, there were no results available from a detector incorporating this new sensor structure. Tanaka et al.[43] demonstrated a high-energy resolution, microcalorimeter type, energy dispersive X-ray detector. The detector, a transition edge sensor (TES), was operated below 200 mK. It used a cryogen-free dilution refrigerator. The reported energy resolution of the detector was equal to 12.8 eV. The TES could be mounted inside a scanning electron microscope (SEM). The TES-EDS enabled high-energy resolution analysis in SEM under low acceleration voltage, typically less than 5 kV. In another work reported by Li et al.,[44] the TES-EDS, installed in an SEM, was applied successfully to resolve spectral interferences between S Kα and Pb Mα, Zn Lα and Na Kα, as well as Ti Kα and Ba Lα peaks in the analysis of individual grains

of air particulate matter deposited on polycarbonate membrane filters.

The development of an interesting new silicon-based microcalorimeter was described,[45] the aim of which was to provide high energy resolution array X-ray detectors for future space missions. The new device comprised a tantalum absorber bump-bonded with indium bumps onto a fabricated silicon thermistor. The fabrication technique offered advantages for the effective production of a pixellated array that was claimed will yield higher geometric collection efficiency than previously available and we await results on how well such sensors perform as X-ray spectrometers. A second approach involved the use of micro-calorimeters giving higher collection area and pixellated high resolution X-ray spectrometers was reported by Smith,[46] who described the implementation of a complex signal processing algorithm for enhancing energy and position resolution of position-sensitive TES detectors. In this design a pixellated absorber layer was connected to one or more position-sensitive TES pixels to reduce the number of readout channels required. The algorithm developed by the author provided the photon energy and positional information. At this stage only theoretical data were reported but they indicated that a 3×3 pixel array configuration would be able to provide an energy resolution of <8 eV and position sensitivity down to energies of a few hundred eV. While we wait for the demonstration of real improvements in microcalorimeters from the aforementioned work, Friedrich and co-workers[47] reported substantial practical improvements to the other type of cryogenic high resolution X-ray detector, based upon superconducting tunnel junction (STJ) sensors. The detector system used a cryogen-free cooling solution comprising in two-stage pulse-tube cooler in combination with a two-stage adiabatic demagnetisation refrigerator (ADR) that achieved the required operating temperature of around 300 mK at the push of a button. The X-ray detector itself was an array of 36 pixels, each 200×200 μm^2 and fabricated as Nb–Al–AlO$_x$–Al–Nb with a 165 nm thick, niobium absorber layer. This convenient system permitted a cold finger length up to 40 cm and delivered an energy resolution of 10–20 eV at energies <1 keV and, unlike micro-calorimeter systems, could be operated with count rates up to 10^6 cps. Such count rates are now routinely available and are used for SR X-ray applications.

Conventional *Silicon Drift Detectors* (*SDDs*) are now routinely used in many types of commercially available XRF systems and there was nothing of note published in this area during this review period. That said, Carini and co-workers[48] fabricated and tested hexagonal SDD arrays comprising 14 independent SDD detector structures (pixels) and two additional test pixels. In addition to providing a very large effective area, these devices also had an entrance window that was optimized for low-energy (<1 keV) detection. Details of this interesting SDD operating regime were covered and results were repeated for measurement on an NSLS X-ray beam line of X-ray energies in the range 550 to 900 eV. A monolithic 7-element SDD was also reported by Welter *et al.*,[49] who used the device as an EXAFS detector that required operation at very high count rates and still provided a high geometric collection angle and an energy resolution of 250–300 eV at 5.9 keV. In a further novel use of an SDD, Pausch and co-workers[50] optically coupled a single SDD to a LaBr$_3$(Ce$^+$) scintillating crystal to provide an effective dual

energy range photon detector. The SDD "native" output was used for energies up to about 100 keV and provided excellent energy resolution. The derived output from the coupled scintillator-SDD was used for energies >100 to 1 MeV giving, according to the authors, an excellent overall performance for nuclear safeguard and homeland security applications. The authors used straightforward pulse shape discrimination to separate the signal from the native SDD and the SDD-scintillator coupled modes of operation.

The review period provided an interesting mixture of papers on the use of *other materials and techniques* for X-ray detectors. Cadmium zinc telluride (CZT) remains an attractive detector material for operation at room temperature. Crystals of CZT were grown using a newly-developed boron encapsulated vertical Bridgeman method to provide 2-inch detector-grade material.[51] High resistivity was attained by means of indium doping of the melt and detectors could be made following surface passivation and with the use of a guard ring. When operated at room temperature, the detectors yielded an energy resolution of only 4.9% at 59.5 keV and may be of use in some gamma-ray detector applications but are of no real use for EDXRF spectrometry due to the dismal energy resolution and very high level of incomplete charge collection. In a further related paper[52] it was shown that leakage current in a CZT detector could be reduced by surface passivation with an aqueous solution of NH$_4$F/H$_2$O$_2$ and by use of a guard ring. Although the work of Kim *el al.*[53] was aimed at studying sonoluminescence, one of the detectors to be used in that study was a CdTe detector. In studying the spectroscopic response at room temperature for three radioisotope sources (^{57}Co, ^{133}Ba and ^{241}Am) the authors obtained distorted spectra and opted to use Monte Carlo (MC) simulation in order to establish the true detector response function. It was also concluded by Stankovic *et al.*[54] that numerical simulation tools such as MC were likely to be essential for the understanding and design of diamond-based X-ray detectors. A detailed study by Kostamo and co-workers[55] of the structural and electrical characteristics of TlBr crystals for X-ray detectors identified small-angle grain boundaries in the material, which were shown to be correlated with detector performance. Crystals with the most pronounced grains boundaries had the lowest sensitivity and gave detectors with the worst spectroscopic properties. When operated at −8 °C, the best energy resolution obtained was only 1.8 keV at 59.6 keV. X-ray detectors are, by definition, often working in harsh radiation environments, but the specific demands of space exploration are very high and led to the study by Lees *et al.*[56] of silicon carbide as an X-ray detector material. The authors reported an energy resolution of 1.3 keV at 5.9 keV that degraded to 2.5 keV after irradiation with a high dose of high energy protons. While unattractive for terrestrial EDXRF applications, the sensor showed the key benefit of radiation hardness that was expected to be needed on a mission to the extremely harsh Jovian planetary system. For the harsh nuclear environment of a new materials testing reactor, a new type of GaAs detector was planned by Kotiluoto and co-workers.[57] Finally, an exotic X-ray detector using surface plasmon resonance was proposed[58] for its time and spatial resolution that are expected to be better than conventional X-ray detectors for ultrafast X-ray pulse measurements in high energy physics/X-ray laser applications.

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An interesting new type of micro-pattern *gas proportional X-ray detector* was described by Silva *et al.*[59] The xenon-filled detector used a two-dimensional micro-strip charge collection structure in order to provide a single photon detector with both energy dispersive and position sensitive capabilities. The detector energy resolution was measured to be about 850 eV at 5.9 keV and was able to separate Fe K and Pb L series XRF lines from simple ceramics irradiated with a standard small spot 50 keV X-ray tube operated at 20 kV and up to 1 mA. The simple setup used a 200 μm tungsten pinhole arranged to provide a magnification of 2 to 2.5 times. The detector strip had a non-uniform response that required a correction procedure but that correction gave a useful improvement in energy resolution from 25% to 17% at 8 keV. Two-dimensional XRF images were shown of some historical ceramic artefacts that demonstrated the ability of the system to reveal variations in lead glaze on the ceramics, although only the separation of lead from iron was shown. Any presence of copper was needed as *a priori* information as there was insufficient ability to resolve the Fe and Cu K lines. This detector setup is interesting although of limited real or wider applicability due to its poor energy resolution, which will likely thwart the authors' intended future use of it at lower X-ray energies. Members of the same Coimbra, Portugal group also studied various argon-xenon Penning gas mixtures in gridded microstrip gas detectors.[60] A 95% Ar-5% Xe gas mixture was shown to provide a tenfold improvement in charge multiplication gains and an improved energy resolution of 12.5% at 5.9 keV over a pure xenon gas fill. A slight improvement in energy resolution to 12.3% was achieved with the addition of 9.5% methane quench gas. A significant upgrade to the OD-3M one-dimensional gas proportional X-ray detector was reported. The complete electronics system for the 2048 channels of this parallax-free strip detector was configured from a massive computer automated measurement and control (CAMAC)-based system to a compact, fast digital systems based on field programmable gate array (FPGA) technology. The benefits for wide angle X-ray scattering and high-resolution XRD measurements were demonstrated with results collected on an X-ray beamline at the VEPP-3 SR facility in Novosibirsk, Russia. A spatial resolution of 470 μm was reported for the updated detection system.

3 Spectrum analysis, matrix correction and calibration procedures

As *an overview*, important contributions this year were made by a number of research groups to fundamental parameter based methods, improved and more accurate values of X-ray production cross-sections, the use of X-ray emission signals in combination with other analytical techniques and quantification procedures tailored for micro-beam analysis. In addition, exotic interfering effects were treated successfully and a few authors adapted empirical approaches to quantitative analysis.

Fundamental parameter (*FP*) *methods* were extended to the analysis of Z < 10 elements and *in situ* excitation geometry by Pavlinskii and Vladimirova.[61] They demonstrated that the ionisation of elements such as carbon and oxygen by photo- and Auger-electrons should be taken into account in the FP models when relevant. Pavlinskii *et al.*[62] published another article on the

contribution of the photoelectric effect, Auger- and Compton-generated electrons to the bremsstrahlung radiation produced in the sample during irradiation by X-rays. They found that the contribution from the Compton electrons was of importance for monochromatic primary radiation of high-energy photons, whereas contribution of photo- and Auger-electrons was significant for excitation with the primary radiation from X-ray tubes. They identified the regions of the X-ray spectra where the intensity of the electron bremsstrahlung was greater than the intensity of the primary X-ray tube radiation scattered by the sample. A FP approach was adapted by Gherase and Fleming[63] to determine As in skin. The FP model usually assumes a parallel primary beam and parallel collimated radiation emitted by the sample. In the model developed by Gherase and Fleming, the primary beam photons could travel in any direction. The detected X-ray fluorescence signal explicitly depended on the length of the detector collimator, the detector size, position, and orientation and the model was used for predicting optimum position and orientation of the detector and collimator assembly in the arsenic in skin application.

An *empirical approach* to the correction of matrix effects in the analysis of samples comprising low-Z elements that can be considered to be "infinitely thick", was elaborated by Bansal and Mittal.[64] In their work, the absorption and enhancement correction terms were correlated with element concentrations based on experimental data and correlations were obtained for different types of samples. Another empirical approach to the correction of matrix effects was presented by Tuo *et al.*[65] using binary samples (Ti–V, Ti–Fe, and V–Fe) to determine experimentally the enhancement and absorption correction coefficients in the analysis of Ti–V–Fe systems. The empirical model was validated using three groups of Ti–V samples and observed relative errors of Ti and V determinations were less than 0.2%. Oskolok and Monogarova[66] proposed an algorithm utilising the concept of effective or equivalent wavelength. They developed a method of matrix effect correction for XRF analysis with polychromatic excitation source, applicable to samples of any composition and thickness.

A *combination of gamma ray and XRF spectrometer* was presented by Yucel and Dikmen,[67] who elaborated a method for the determination of ^{235}U enrichment in depleted uranium samples and in uranium ores using the ratio of the self-induced characteristic K-series X-ray radiation of uranium to the 92 keV gamma ray. The elaborated method produced more accurate results compared with the standard multi-group gamma-ray analysis method for uranium (MGAU) enrichment determination.

The development of quantification procedures dedicated for *micro-beam techniques* was reported in a number of papers. In a report by Schaumann *et al.*,[68] the preparation of a set of polymer-base reference samples, doped with silica and zinc oxides, was described. These reference samples were produced in the form of layers with alternating and varying concentrations of the added elements. After preparation, the samples were characterised using a number of micro-analytical techniques to verify the concentration profiles and thickness of layers. The reference set was used to validate measurement of concentrations of elements in stratified samples by the confocal μ-XRF technique. Sokaras and Karydas[69] examined XRF enhancement effects in confocal μ-XRF and μ-PIXE. They calculated the contribution

from enhancements effects to the overall confocal X-ray intensity profiles for typical samples. In another article by Sokaras et al.[70] a theoretical model of the elemental profiles obtained by confocal μ-PIXE was discussed in detail. Layered as well as concentration-gradient samples were investigated and the advantages and limitations of the technique were explained based on these examples. In a work on a similar topic, Zitnik et al.[71] applied a confocal μ-PIXE technique to obtain 3D images of the concentrations of Ca, Fe, and S, as well as the surface profile of silicon, in air aerosol particulates with a μm resolution. The determination of the chemical composition of individual air aerosol particles by μ-XRF spectrometry was carried out by Sun et al.,[72] taking into account the Gaussian distribution of photons in the beam spot. The accuracy of the chemical compositions was determined to an average accuracy of 25% and a precision better than 5%. A comprehensive review of developments for the measurement of aerosols and particles is given in section 9.3.2 of this review.

A fresh look at exotic *interference effects* as well as further *improvements of fundamental parameter databases* were investigated by a number of authors. Fernandez and Scot[73] published a detailed investigation of an interesting self-enhancement effect that occurred due to the finite line width of X-ray characteristic lines. They presented the results from calculations of the effect in pure element samples in the atomic number range $Z = 11–92$. Improved, more precise and more accurate values of the so-called fundamental parameters are always looked for by the X-ray analytical community. In work related to the determination of X-ray production cross-sections, Mainardi[74] criticised the work published earlier by Özdemir,[75] negating the results on angular dependence of the differential atomic cross-sections for inner atomic shells. Mainardi claimed that in the referred article the description of the experimental set up was incomplete, many assumptions were made on dubious grounds, and the reported data were not evaluated with appropriate statistical tools. In another article to improve the estimation of X-ray production cross-sections, Muller et al.[76] carried out an accurate determination of nickel L^{III} X-ray transition probabilities by employing a wavelength dispersive spectrometer and a plane grating monochromator at the BESSY II SR facility in Germany. The applied methodology did not require reference samples and had a well characterised uncertainty budget that allowed reliable results to be obtained. Following the efforts towards the more accurate determination of fundamental parameters, Pia et al.[77] performed a systematic validation of K- and L-shell X-ray transition probabilities according to different theoretical models against experimental data. They found that the Hartree–Fock approach produced the best approximation of the experimental results. With the same goal in mind to improve the accuracy of the fundamental parameter data, Casteleiro et al.[78] used the multi-configuration Dirack–Fock method to predict K-shell transition probabilities in Cd, Hg and Zn. Based on the obtained values, corresponding fluorescence yields were calculated and compared with existing semi-empirical and experimental results. To yield accurate results in μ-XRF analysis with the FP algorithms, an accurate model of the primary X-ray spectrum modified by the focusing lens is required. Hodoroaba and Procop[79] proposed a method in which the transmission function of the lens was determined by calculating the ratio of the

experimentally measured, scattered primary beam spectrum (with the X-ray lens installed in the spectrometer) to a theoretically calculated one where the capillary was substituted by a well defined collimator. This approach was tested by comparing the results with the directly measured X-ray tube spectra obtained by installing a miniature X-ray source in a scanning electron microscope equipped with an efficiency calibrated X-ray spectrometer. Good agreement was observed between the calculated and experimentally determined transmission factors.

As all analysts know from experience, every matrix correction procedure has its *limitations, often related to the nature of the sample*. It is crucial to realise where the limits are, especially during *in situ* measurements with limited or no control on the analysed sample. Naranen et al.[80] tackled the impact of interfering effects on the results of X-ray fluorescence analysis of planetary regolith. They used two laboratory facilities to measure an analogue for the lunar regolith with different particle-size ranges. The influence of the surface roughness and regolith porosity was examined and results are of interest for future planetary missions carrying on-board X-ray emission spectrometers. Sample micro-heterogeneity and grain size effects were discussed in a work by Smagunova et al.[81] They concluded that due to a number of different factors, such as moisture and the presence of different particle phases, it is extremely difficult to create a theoretical model for correcting the micro-heterogeneity/particle size effects in routine XRF analysis. In another article related to evaluation of X-ray data from planetary missions Campbell et al.[82] proposed a new fundamental parameter calibration procedure for the Alpha Particle X-ray Spectrometer (APXS) on the Mars Exploration Rovers. The algorithm fully combined the XRF and PIXE methodology and the main aim of the work was to characterise fully the spectrometer and to test the new fundamental approach by using a flight spare instrument.

A number of authors adapted *Monte Carlo (MC) algorithms* to quantitative analysis and instrument characterisation. Aiming at optimisation of miniaturised XRD and XRF instruments for planetary missions, Hansford[83] developed a ray-tracing Monte Carlo code. The code contained several variance reduction techniques minimizing its execution time. The author observed good agreement between experimental data and the code output. MC simulation models were also developed by Gardner and Xu[84] to create a so-called MC library least-squares (MCLLS) database. The MCLLS was used in prompt gamma ray neutron activation analysis, EDXRF analysis, and in carbon/oxygen tool analysis by a linear least-squares deconvolution approach to determine contributions of individual elements to the unknown sample. In their work, the current status of the ongoing project was reported. MC models can be validated not only by comparing the results of simulation with the experimental data, but also with the results of already tested analytical solutions. Kocar[85] proposed such a solution to the scalar photon transport equation applied to the EDXRF measurements. The details of the solution were presented, with the analytically-calculated energy current compared with the results of the MC simulation.

The development of quantitative analysis methods was also coupled with the *development of data acquisition system*s and the optimisation of the X-ray detection systems. Papp et al.[86] made a significant advance in X-ray spectra acquisition and processing as well as in fundamental parameter methodology by developing

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digital signal processing hardware/software that accounted for all events collected by the detector, including, pile-up and noise events which are usually rejected by other data acquisition systems. All collected information was used in the developed FP XRF analysis program. They also developed and implemented in computer code, an inverse fundamental parameter method which allowed the characterisation of the X-ray tube spectrum based on the measurements from reference samples. More details of their developments can be found in another publication by the same authors.[87] In two contributions, Portnoi et al.[88,89] investigated the signal-to-background behaviour of an energy dispersive Si(Li) type X-ray detector. By modelling radiation transport in both the sample and the detector as well as the transport of electrons in the detector, they predicted signal-to-background ratios and compared modelled results with experimental data. They found that, depending on the detector thickness and the characteristics of the primary radiation source, the signal-to-background ratio could vary by several orders of magnitude. The authors concluded that, depending on the measuring conditions, Si- or Ge-type detectors should preferably be used.

4 X-ray optics and micro-fluorescence

Just a few articles discussed the research on the development on *new X-ray optics and optics characterization* as compared to the numbers of reports in which already well developed X-ray focusing devices were applied to new or upgraded instruments. Bingolbali and MacDonald[90] carried out a simulation of the defects and misalignment of doubly curved crystal (DCC) X-ray optics and investigated the impact of these defects on focusing properties. A simple operator-independent alignment procedure for ensuring optimal beam intensity was developed and good agreement was observed between the results of the simulations and the experimental data. Wolff et al.[91] characterised the performance of the so-called half-polycapillary lens, applied either as the primary beam focusing optic or the detector collecting lens. The tests were performed with a point source of X-rays obtained using proton and electron beams. They observed differences in focus size and transmission between the focusing and collecting modes of operation of the lens. Another characterisation of X-ray focusing polycapillary optics was carried out by Sun et al.[92] Their X-ray optics was installed in a micro-beam confocal XRF instrument utilising a low power X-ray tube. The energy dependence of the lens acceptance angle and focal spot size were determined as well as the detection limits of elements. Bjeonmikhov et al.[93] published a review article on the use of capillary optics (mono- and poly-capillary) at SR beam lines as well as using laboratory sources. Details were given of an XRD module insertion for SEM and its applications were described.

5 Synchrotron radiation

5.1 Instrumental developments, fundamental studies and reviews

Only one *new instrument* was reported within the current review period; the imaging system for XRF micro-tomography at the Brazilian Synchrotron Light Laboratory (LNLS), Campinas by Pereira et al.[20] An X-ray transmission micro-tomography (CT)

system combined with an X-ray fluorescence micro-tomography (XRF-CT) system was implemented in the LNLS. In this paper the determination of the elemental distribution maps, for both reference samples and breast tissue samples, was reported in order to verify the concentration of some elements correlated with characteristics and pathology of each tissue observed by transmission CT. More applications concerning element distribution in breast cancer tissues can be found in section 9.6.

Fundamental studies on reconstruction mechanisms for XRF-CT were performed. An exact analytical reconstruction and an approximated version were reported by Miqueles and Pierro.[94] XRF-CT is a relatively new synchrotron-based imaging technique aimed at reconstructing the distribution of non-radiative elements within a sample irradiated with high-intensity monochromatic X-rays. In this paper the authors compared the earlier work of La Riviere's approximated inversion method with recently derived 'exact' analytical formulae for the generalised attenuated radon transform. However, during this review period La Riviere et al.[95] published their results on region of interest (ROI) reconstruction in XRF-CT for negligible attenuation. The authors argued that one limitation of XRF-CT was the long image acquisition time needed to acquire a complete set of line integrals, one-by-one. Even if only a portion of a slice through the object was of interest, measurement lines were acquired spanning the entire object at every projection view over 180 degrees, to avoid reconstructing images with so-called truncation artefacts. The authors showed that when attenuation was negligible, recent developments in tomographic reconstruction theory could be used to reduce the scanning effort required to reconstruct regions of interest within the slice. The new theory provided welcomed explicit guidance as to which line integrals need to be measured for a given ROI. It also provided a back-projection-filtration reconstruction algorithm that averted the truncation artefacts that typically plagued such data. This was successfully demonstrated through simulation studies and with real synchrotron-based XRF-CT data. This technique seemed to be economical in terms of beam-time usage. Toque and Ide-Ektessabi[96] published a new technique for the reconstruction of elemental distribution images from XRF spectra of trace elements. The proposed technique featured interpolation and background subtraction using matrix transformations of the spectral data in order to produce an enhanced distribution image. It was achieved by employing polychromatic or monochromatic colour assignments proportional to the fluorescence intensities for the display of single-element or multiple-element distributions respectively. The authors claimed that the elemental distribution images produced by this study have better quality when compared with those produced using other analytical techniques.

A quarter-century of metrology using synchrotron radiation at the Physikalisch Technische Bundesanstalt in Berlin was *reviewed* by Beckhoff et al.[97] In the beginning, the work was focused on fundamental radiometry, *i.e.*, using the storage ring as a primary radiation source with standard and operating beam-lines for source and detector calibration in the vacuum ultraviolet spectral range. The activities have now extended to include an impressive broad range of fundamental and applied photon metrology from the far infrared to hard X-rays, such as cryogenic radiometry, reflectometry and XRF.

5.2 New applications

The combination of μ-XRF, μ-XRD, μ-XANES and μ-EXAFS, highlighted in last year's reviews, has seen further development this year, in particular for more comprehensive characterisation of samples. Also X-ray scattering techniques and Raman scattering have been combined with SR-techniques. Another trend was observed, where μ-SRXRF moved towards the nano-scale as SR-beams were reduced in size, offering new exciting opportunities for interdisciplinary applications. The majority of SR applications can be found in the dedicated application sections in part 9 of this review, reflecting the popularity of SR based techniques and the additional SR facilities with dedicated beam lines that are available for both research and established studies.

The number of *medical applications* increased significantly within the review period and most of these can be found in the application section 9.6. Rat bone and lumber vertebra of different age groups were investigated by Rao *et al.*[98] at the new hard X-ray microprobe X27 at NSLS that offers a spot size of 10 μm using energies of 8, 10 and 12 keV and a 13 element Ge detector. With this spatial resolution and high flux throughput, the authors identified trace levels of Ca, Fe, Ni, and Zn as well as Cr, Mn and Ti.

As in last year's review, several groups analysed *star dust mission samples*. Schmitz *et al.*[99] used confocal high resolution SRXRF to detect two highly refractory cometary dust fragments in samples of comet 81P/Wild 2 in the impact track 110 [C2012, 0, 110, 0, 0]. The authors reported an impressive improvement in the confidence of particle measurements by removing the contribution from the surrounding aerogel using a confocal high resolution arrangement. For two of the largest particles in the track, the terminal particle and a second particle along the impact track, the Ca concentration was found to be up to 30 times higher than that of Cl. Titanium was enriched by a factor of two compared to Cl. Using high resolution SRXRF mapping, the authors revealed that the highest concentrations of Ca, Fe, Ni and Ti measured within each grain belonged to different areas of the respective maps indicating that the particles were composed of several chemically diverse mineral phases. Furthermore the authors concluded that the detection of fragments of new calcium- and aluminium-rich inclusions in the coma dust of comet 81P/Wild 2 strengthened the observation that strong mixing effects and, therefore, mass transport before or during comet formation must have occurred within the region where Kuiper Belt comets formed. Tsuchiyama *et al.*[100] examined 3D structures and elemental abundances of four impact tracks in silica aerogel of Stardust samples from comet 81P/Wild 2 (bulbous track 67 and carrot-type tracks 46, 47, and 68) using SR μ-CT and XRF-CT. Track features, such as length, volume and width as a function of track depth, were obtained quantitatively by CT. A bulbous portion was determined near the track entrance even in carrot-type tracks. The authors concluded that each impact of a cometary dust particle resulted in its disaggregation into small pieces that were widely distributed not only on the track walls but also at its terminal. Ca, Fe, Ni, S and eight minor elements were found to be concentrated in the bulbous portion of track 68 as well as in the terminal grains. It was confirmed that bulbous portions and thin tracks were formed by disaggregation of very fine fragile material and relatively coarse

crystalline particles, respectively. From the almost constant ratio of whole iron mass to track volume, the authors concluded that the track volume was almost proportional to the impact kinetic energy. Ebel *et al.*[101] reported the analyses of aerogel tracks using XRF-CT, laser confocal scanning microscopy (LCSM) and SRXRF of particles and their paths resulting from simulated hyper-velocity impacts and a single (~1 mm) aerogel track from the Stardust cometary sample collector. A 3D deconvolution method using an estimated point-spread function for aerogel was presented, allowing basic corrections of LCSM data for axial distortion. The authors concluded that LCSM allowed rapid, comprehensive, non-destructive, detailed analysis of tracks in aerogel keystones, prior to destructive grain extraction and SRXRF. This allowed spatial correlation of grain size, chemical, and mineralogical data. The authors claimed that these data were fundamental to the understanding of hypervelocity particle-aerogel interaction histories of Stardust grains.

Several significant papers in the field of *biology* are reported within the review period. SRXRF imaging of human cells labelled with CdSe quantum dots were reported for the first time by Corezzi *et al.*[102] The authors explored the potential of SRXRF for chemical nano-imaging with a 100 nm spatial resolution (nano-XRF) of human cells through the use of functionalised CdSe/ZnS quantum dots (QDs). They concluded that nano-XRF using QD-based markers could be very effective at co-localising specific intracellular targets with elements naturally present in the cell. This might be complementary to confocal fluorescence microscopy in a synergistic fashion. Synchrotron X-ray 2D and 3D elemental imaging of CdSe/ZnS quantum dot nano-particles in *Daphnia magna* was reported by Jackson *et al.*[103] The potential toxicity of nano-particles into aquatic organisms is of concern. *Daphnia magna* was exposed to both red and green QDs and SRXRF was used to study the distribution of Zn and Se in the organism over a time period of 36 h. The QDs appeared to be confined to the gut and there was no evidence of further assimilation into the organism. Zinc and Se fluorescence signals were highly correlated, suggesting that the QDs had not dissolved to any extent. There was no apparent difference between red or green QDs, as there was no effect on QD size. The potential power of the technique was demonstrated in that 3D tomography confirmed that the QDs were exclusively in the gut area of the organism. Ortega[104] reviewed the use of SRXRF for direct analysis of metallo-proteins on electrophoresis gels as an alternative approach to the standard method that used high resolution chromatography for metal analysis in solutions. SRXRF was successfully employed for sensitive metal identification, with XAS for metal local structure speciation in proteins.

Progress in *geological applications* included Schmitz *et al.*[105] who reported chemical uranium-thorium-lead dating of monazite by 3D μ-SRXRF. A confocal set-up was used at the mySpot beamline at BESSY II, Berlin, Germany, with a probing volume of approximately 21 × 21 × 24 μm for W Lα using an excitation energy of 19 keV. The relative detection limits particularly for Pb were found to be below 10 μg g^{-1}. This impressive set-up was tested on monazites that were characterised by isotopic techniques and had a wide range of ages, varying from 20 Ma to 1.82 Ga. The average 3D μ-XRF dates reproduced the reference ages with discrepancies of 1 to 4%.

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6. TXRF

6.1 Fundamental TXRF research and instrumentation

This review period again demonstrated the *widespread field of research* covered by TXRF with fundamental investigations, sample preparation, thin film characterisation, chemical speciation by TXRF-X-ray absorption (XAS) measurements plus applications in environmental and medicinal studies featuring in the literature. A review of TXRF and related methods covering the literature of four decades was presented by Von Bohlen[106] in which new developments and trends were discussed in all fields of science related to emerging nano-technologies. An interesting application took advantage of the phenomenon of X-ray standing waves (XSW), where the interference field of X-rays was used as a very fine and sensitive measure for the characterisation of surface layers to determine nanometer modifications perpendicular to the surface. Horntrich et al.[107] also dealt with fundamental aspects of TXRF in their study of how total (>200 ng) amounts of sample caused deviations from the linear relationship between fluorescence intensity and sample mass. Samples with different total amounts of arsenic were prepared for the determination of the upper limit of sample mass where this linear relationship between fluorescence intensity and sample amount was no longer certain. A simulation model, developed to calculate the influence of the absorption effects, found that the relationship between fluorescence intensity and sample amount was linear up to 100 ng of arsenic. One of the key parameters required to obtain good agreement between model and experiment turned out to be the density of the element in the dried residues. Another interesting fundamental study[108] on the influence of the coherence length on TXRF and X-ray standing waves (XSW) refuted the approach that the full intersection area of reflected and incident beam can be used as the interference area. Chemical characterisation and a study of the morphology of very fine fractions of nanoparticles on surfaces were shown to be deducible from XSW experiments. New theoretical aspects were introduced and discussed including coherence length of X-rays from different sources, particle shape and size distribution. This was the first time that numerical simulations for modelling of particles were compared with experimental data obtained from SR-XSW experiments. Improvements in the instrumental capability of a genuine portable TXRF instrument of only a few kg in weight were described by Kunimura and Kawai.[109] The interesting step forward made by this instrument was the collimation of incident X-rays by a simple X-ray optic. The simplicity of the X-ray refractive lens was ingeneous, as it comprised only two sections cut from a gramophone record that were held apart by spacers. In comparison with a conventional X-ray waveguide using optical flats, the vertical angular divergence was improved by the refractive lens and thus a better signal to background ratio was achieved. Placing this lens in a light weight portable TXRF instrument permitted detection limits in the sub-ng range for 3d transition metals to be obtained.

6.2 Chemical analysis and speciation using TXRF

When discussing chemical speciation, the conventional approach typically uses X-ray absorption near edge spectrometry (XANES) spectra around the K- or L-edge of the chemical element. In a publication by Kallithrakas-Kontos et al.[110] an interesting simple approach was described in which *selective membranes and TXRF* were directly combined. In this arrangement the membrane was placed on the reflector surface and then immersed for many hours in aqueous solutions containing low concentrations of chromium salts. Completely selective membranes for Cr^{VI}, a known carcinogen, and the less hazardous Cr^{III} were prepared for measurement by TXRF yielding detection limits <0.6 ng ml^{-1} in drinking water. Fernandez-Ruiz presented a study[111] on the influence of deposition morphology on the analytical quality of direct solid suspension measurements. Three cases were investigated: direct solid analysis of reference clay, solid suspension of magnetite nanoparticles and Ru and Se impregnated in carbon nanoparticles. In the first case, for depositions obtained from water or toluene liquid media, a strong dependence of the results on the microscopic morphology was observed. In the second case, the evaporation process and type of sample carrier used gave a significant variation on the Fe uncertainty but did not affect the given value. In the third case the ultrasonic modifications of the particle size caused drastic consequences on the uncertainties associated with the metallic content. In an extended article by the same author and two others,[112] a study was presented of Ru and Se impregnated nanoparticles currently used as an alternative voltaic system. Conventional analytical techniques such as AAS or ICP spectroscopy can produce deviations, as high as 50%, in the metallic contents of this material due to recovery problems (mainly associated with Ru) in the acid leaching process. An alternative approach with direct solid analysis of metallic impregnated carbon nanoparticles by means of TXRF was therefore developed. Basically the suspension conditions were optimised by the use of ultrasonic pulses that checked the particle size distribution of the solid deposition on the reflector by SEM. The important outcome was the strong correlation found between particle size distributions and the homogeneity of the depositions with respect to the uncertainty of the Ru and Se TXRF measurements, but not with respect to their nominal values. The ICP results indicated that adequate modification of the fundamental ICP-MS parameters such as dilution factors, RF power and nebulizer gas flow could be an initial way to improve the analytical results of ICP-MS. Results from experiments for the direct determination of trace elements in boron carbide powders with different particle size distributions were reported by Amberger et al.[113] Samples were prepared as slurry and stability was monitored by measuring the zeta potential for different pH values and different concentrations of polyethylenimine (PEI). The elements Ca, Co, Cr, Cu, Fe, Mn, Ni and Ti were determined by TXRF and ICP-OES after wet chemical digestion of the samples. Results of both techniques were in good agreement at the 2–1200 μg g^{-1} level. Correlation coefficients of the determinations by both techniques for Fe and Ti in seven different boron carbide powders were found to be practically equal with R = 0.996 for ICP-OES and R = 0.997 for TXRF. Another interesting approach was suggested by Aretaki and Kallithrakas-Kontos[114] to determine trace levels of Se ^{IV} collected on TXRF-reflectors after reduction using ascorbic acid. More specifically, the reflectors were immersed in water solutions, containing low concentrations of Se ^{IV}, the reducing reagent was added and colloidal Se adsorbed onto the reflector.

No interference with other metals present was observed and detection limits of 0.8 ng mL^{-1} were achieved. The method was reported to be applicable to seawater samples. Chloride determination in acidic media by TXRF was reported by Misra et al.[115] from the Bhabha Atom Research Centre, India. The method was based on the precipitation of silver chloride following the addition of a known excess of AgNO$_3$ solution to the sample containing Cl. This interesting approach was followed by the TXRF determination of Ag in supernatants after filtering, employing Cd as an internal standard. Tungsten continuum excitation at 50 kV and 38 mA was used for the measurements with Ag Kα line of the analyte and Cd Kα line of the internal standard. Samples of different molarity were prepared in HNO$_3$ media ranging from 1 to 60 μg mL^{-1} with chlorine detection limits of 5 μg mL^{-1} and a precision of better than 10% claimed. Another article by Kallithrakas-Kontos and Hatzistavros[116] dealt with the determination of ultra trace levels of Co, Cu, Ni and Zn complexed using anionic ligands (CN–, etc.) which were then immobilised by means of anion selective membranes. These membranes were directly produced from a few micro grams of complexing reagents in a polyvinylchloride matrix on the reflector. The membranes were then immersed in water solutions and after reaching equilibrium, the reflectors were left to dry and analysed by TXRF. Impressive detection limits at the 1 ng mL^{-1} level of were reported for the metallic cations of interest.

6.3 Surface analysis

An interesting area of development has seen the determination of thin films in the nm region, based on scanning over the incident angle from zero to the critical angle and above. The standing wave phenomenon above the surface of the reflector may be used to determine the thickness of layered structures that are in most cases a silicon wafer. This approach is called grazing incidence XRF (GIXRF) and is excellent for ultra shallow junctions and nm layers but it is time consuming. In contrast, the direct approach is to use TXRF measurements at a small fixed angle and detect the fluorescence signal, which is correlated to the thickness of the layer. In order to further reduce the line-widths and the device size for the semiconductor industry, a substitution of gate oxide materials such as silicon dioxide with high-k dielectrics was proposed. Unfortunately, the poly-silicon gate and the high-k dielectric reacts and could possibly lead to pinning effects, one material preventing these effects is La$_2$O$_3$. A paper by Lee and Lim[117] described TXRF as the method of choice to determine and monitor the thickness of such sub-nanometer scale La$_2$O$_3$ films deposited on the surface of a device. Using the W-L$_{\beta1}$ for excitation at an angle of 0.008° for 100 s and taking the fluorescence signal of the L$_\alpha$-L$_{\beta1}$ line resulted in excellent agreement with thickness measurements performed with TEM. Bennun et al.[118] presented results from thickness measurements of amalgamable metallic films by TXRF. In this case the peaks intensity in the TXRF spectra were directly related to the surface density of the sample. Taking the relative peak intensity of a specific metal line of a thin film of amalgamated metal, the layer thickness could be accurately obtained. An amalgamated gold film created additional problems, as the mercury and gold L-series lines overlap strongly, leading the authors to develop a general data processing scheme to achieve accurate results. The

growing of layers by atomic layer deposition was studied by Sioncke et al.[119] in research to create a good dielectric layer on gallium arsenide (GaAs) substrates. A promising candidate was shown to be alumina (Al$_2$O$_3$) on GaAs substrates, leading to investigations on the influence of the growing process itself (thermal vs. plasma enhanced) and also the influence of the initial surface treatment (no clean vs. partial removal of the native oxide layer). Ellipsometry and TXRF were used to study the growth whereas angle-resolved X-ray photoelectron spectroscopy served for the determination of the interlayer composition. Thermally deposited layers were reported to show better electrical characteristics, which could be linked to thinner inter-layers achieved with thermal deposition. However, pinning effects were observed, so the authors suggested more work be done on passivating the interface between GaAs and the high-k layer.

Baake et al.[120] reported the chemical characterisation of SiC$_x$N$_y$ nanolayers by four techniques, Fourier Transform Infrared Spectroscopy (FTIR), Raman spectroscopy, XPS and near edge X-ray fine structure investigations with TXRF. The results were compared with those obtained from standard samples of SiC and Si$_3$N$_4$ and literature spectra. The first results identified two or more compounds containing Si–N bonds, one compound with a Si–C bond and graphitic carbon.

6.4 New applications

The region of the Toledo River, Parana, Brazil is characterised by intense anthropogenic activities. Espinoza-Quinones et al.[121] used synchrotron radiation TXRF (SR-TXRF) to measure the river's metal concentrations in order to complete an environmental evaluation. Monthly samples were collected during a one year period at seven different sites from the source down to the river mouth. Physico-chemical variables were determined, with major metallic ions measured by SR-TXRF. The results were statistically analysed and showed a strong correlation for sites 1 and 7, suggesting that organic pollutants were mainly responsible for the decline in the Toledo river water quality. Macedo-Miranda et al.[122] compared analytical data of water samples measured by AAS and TXRF. The metal concentrations in the samples analysed by both techniques were in good agreement. The variation coefficient between the results with both techniques was <14% and the authors concluded that AAS and TXRF are appropriate for regulatory measurement techniques. A feasibility study to determine the botanical origin of honey samples by means of elemental content was presented by Necemer et al.[123] A total of 264 major types of honey from various places in Slovenia, harvested during 2004, 2005 and 2006 were analysed by TXRF. The country is small in terms of surface area but it is pedologically and climatically diverse, thereby offering interesting opportunities to study the influence of such diversity on the elemental content of natural products. By employing principal component analysis (PCA) and regularised discriminant analysis (RDA), it was found that only four key elements Cl, K, Mn and Rb could be used to effectively discriminate the origin of honey. The authors concluded that the inexpensive, simple and fast multi-element TXRF analytical approach and the evaluation of data by chemometric methods had the potential to discriminate the botanical origins of various types of honey. Whilst TXRF is well established for chemical

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analysis of samples deposited as a thin layer, Borgese et al.[124] emphasised that TXRF has reached such a maturity that it could be considered a sufficiently practical, accurate and reliable technique and that it should become an officially recognised analytical technique, although it is not yet accepted as a standard reference method. The authors used a portable TXRF system for their work on environmental monitoring of an industrial site, comparing analytical data from bioindicators (lichens) measured by AAS and TXRF. This comparison highlighted the versatility of the compact, economic TXRF instrument as it allowed more rapid and simultaneous element detection. The results suggested that this portable TXRF system could be suitable for regulatory work and used to produce certificated analysis for some elements with concentrations in the ng g^{-1} region. As a general remark, the use of the earlier developed, luggable TXRF instruments operating with air cooled low power X-ray tubes and electrically cooled detectors, are in strong competition to traditional TXRF instruments as they produce excellent analytical results with respect to accuracy, detection limits and elemental sensitivities. A portable instrument was also used by Juvonen et al.[125] to study the As and trace metal concentrations in the Haveri Au–Cu sulfide mine tailings, leached with aqua regia and in those waters affected by acid mine drainage. Results for 12 water and 16 tailing samples were compared with accredited methods such as ICP-OES and ICP-MS. Certified reference samples of water and sediments were analysed for validation purposes. As expected, detection limits for the elements As, Cr, Pb and Zn were 20 µg L^{-1} and for Co, Cu, Ni, V and Mn, 5–10 µg L^{-1}. Random error of determination varied from 12–20%. The use of the highly monochromated Mo anode X-ray tube lines did not permit excitation and determination of Cd, Mo, Nb, Tc and Zr by the intense K-lines. In contrast to some other authors, these authors concluded that TXRF can be used merely as a preliminary technique for selecting samples, which is a conclusion your reviewer finds very surprising. In expanding the range of detectable elements by TXRF, Ovari et al.[126] determined C in natural freshwater films showing that there was growing interest in the determination of low Z elements such as C or P in biological samples. Biofilms can be used for monitoring the aquatic environment, in addition to trace metals, the carbon content is important for a better understanding of the early stage of biofilm formation. A special TXRF spectrometer was developed for this investigation by the Atominstitut group in Vienna with a chromium-anode X-ray tube for effective excitation of the low Z elements and the detector was equipped with an ultra thin entrance window. Biofilms were grown on two different artificial supports (granite and plexiglass) then freeze-dried and suspended in high purity water prior to analysis. The natural Ti content of the biofilm was used as an internal standard. For this challenging analysis it was pleasing to note that the accuracy of the TXRF method was in agreement with total carbon measurements by a carbon combustion analyser.

Finally in the *area of health and medicine analysis* we find that biocompatibility of advanced prosthetics is a current problem faced by medical researchers. The challenge was to find materials and processing techniques that allowed the production of extracellular matrices to mimic scaffoldings that promote cell growth and organisation into a specific architecture. Hydroxyapatite (HA) is a natural ceramic responsible for the strength and stability of the human skeletal system and Balazsi et al.[127] used this as a biocomposite coating to improve biocompatibility of implant substrates. This HA coating was prepared from low cost natural Ca sources, such as egg shells, and its composition was measured by TXRF and PGAA. The determination of trace elements by TXRF and XRF in Syrian medicinal plants and their infusions was described by Khuder et al.[128] Elements in the Z range from K to Sr were measured and the accuracy and precision verified by analysing Standard Reference Materials, SRM 1647 and SRM 1515. Good agreement was found between measured concentrations and certified values with errors less than 10.7% for TXRF and 15.8% for XRF. The XRF methods showed very good applicability for Br in infusions of different Syrian medicinal plant species, namely anise (*Anisum vulgare*), licorice root (*Glycyrrhiza glabra*) and white wormwood (*Artemisia herba-alba*).

6.5 Related techniques

Awane et al.[129] used *grazing exit micro XRF* (µ-GEXRF) to study hazardous metals in plant leaves. Using a polycapillary X-ray lens to produce a micro beam, the authors expected to selectively detect X-rays emitted at low exit angles near to zero degrees, as the X-rays emitted from inside the specimen should have been absorbed and attenuated within the specimen. However, they found that X-rays emitted from inside aqueous organic material such as a plant leaf were scarcely absorbed because such absorption in aqueous organic samples was much smaller than in most metallic and semiconductor materials analysed by this technique. Therefore, the workers developed a novel µ-GEXRF method in which a chip of a silicon wafer was placed between the analysed leaf and the X-ray detector to act as an absorber of the X-rays emitted from inside the leaf. The method gave enhanced peak to background ratios when compared with conventional XRF techniques. The results were successfully validated using electron microscopy.

Studies of *the surface of silicon wafers* have benefited from advances in synchrotron excitation for X-ray techniques that this review has followed in recent years. In order to evaluate the interactions between Au/Cu atoms and clean Si(lll) surfaces, de Carvalho et al.[130] used SR-GIXRF combined with theoretical calculations. With optimised geometries and energies on different adsorption sites, the study showed that the binding energies at the different adsorption sites were high, suggesting a strong interaction between the metal atoms and the silicon surface. The Au atom showed higher interaction than the Cu atom. It was pleasing to note that the theoretical calculations were in good agreement with the experimental data. Kabala-Kukus et al.[131] demonstrated that ultra-low level Al impurities can be measured on a silicon surface using the high resolution offered by SR-GEXRF. This approach offered a sensitive tool for the study of wafer surfaces and nano-structures. Baake et al.[132] reported their work on the speciation of BC$_x$N$_y$ films grown by plasma-enhanced chemical vapour deposition using trimethylborazine as precursor and with H$_2$, He, N$_2$ and NH$_3$, respectively as auxiliary gases. The films were characterised by SR-TXRF combined with NEXAFS and XPS. The B–N bonds were found to be dominant and independent of the auxiliary gas with B–C and N–C bonds also identified. Lin and colleagues[133]

examined the structure of self-assembled mono-layers in silicon using XSW, X-ray reflectivity (XRR), XRF, atomic force microscopy, XPS and density function theory (DFT). The combined data from XSW and XRR ruled out two alternative bonding models predicted by DFT. The greater rigidity in the molecular structure was correlated to a C=C bond at the root.

7 Portable and mobile XRF

Over recent years, portable XRF, especially in its hand-held form, has become much more widely available. This section covers *developments in instrumentation* and technique and some novel applications, with more routine use of this technology discussed in the relevant application section. Although not normally recognised as an instrument with portability characteristics, further work was undertaken by Kunimura et al.[134] in the optimisation of the glancing angle for a portable total reflection X-ray fluorescence spectrometer. This instrument incorporated a 1 W X-ray tube and the optimum grazing angle was reported to be 0.13 degrees below the critical angle for total reflection (0.20 degrees), achieving detection limits of sub- to 10 ng for elements such as Cr, Fe, Mn, Ni, Sc, Ti and V. Pifferi et al.[135] described a new portable XRF/XRD instrument for *in situ* measurements in which data collection was achieved using a Si solid state detector to count X-ray photons scattered from the sample as a function of both energy and angular step. The development of a portable X-ray diffraction/X-ray fluorescence combined-spectrometer capable of analysing by the two techniques the same small spot selected on the surface of an irregularly shaped sample was described by Yamashita et al.[136] In their work they presented applications of the spectrometer for characterisation of a few precious archaeological objects including the golden mask of the Tutankhamun from the Museum of Egyptian Antiquities. Buzanich et al.[137] described a new portable XRF instrument designed for the analysis of art samples at the Kunsthistorisches Museum, Vienna. This instrument was fitted with a vacuum chamber with a kapton window to minimise absorption losses in air and allow determination of elements from Na upwards in the periodic table. Excitation was achieved with both Mo-anode and Cr-anode low power X-ray tubes with an excitation beam which could be focused to a spot size of 150 μm by means of a poly capillary lens. The instrument was designed to access concave parts of artefacts. Detection limits for a range of elements were cited, ranging from 7.7% m/m for Na to 6 μg g^{-1} for Cu and Zn.

One of the earliest applications of portable XRF was in the *analysis of soils* and Hurkamp et al.[138] described the two and three dimensional quantification of Pb contamination in alluvial soils and sediments associated with a historic mining area (Vils River, near Freihung, Eastern Bavaria, Germany). Water content (not surprisingly) was found to be one of the main factors that caused a bias between field and laboratory measurements, for which a correction factor could be calculated. The concentration of Pb ranged from less than 500 mg kg^{-1} to 6000 mg kg^{-1} and this approach was successful in characterising metal contamination in this floodplain environment. A hand-held XRF was used by Huang et al.[139] to measure the concentration of Pb in soil samples, results being compared with ICP data and an AAS method. Heavily polluted soils are associated

with the silver mining area in Ireland and Radu and Diamond[140] measured As, Cu, Pb and Zn using a laboratory AAS reference method and compared results with both radioisotope and miniature tube handheld instruments, reporting an excellent correlation between AAS and XRF results. Weindorf et al.[141] evaluated the use of portable XRF for the *in situ* quantification of gypsum in soils of West Texas and southern New Mexico, comparing field measurements with laboratory XRF scanning. On average, field PXRF provided results within 6% of determinations against the current laboratory standard for gypsum quantification. A second study by Zhu and Weindorf[142] looked at Ca in soil to assess fertility. The effect of a number of variables was evaluated leading to the conclusion that field portable XRF could provide data on the total Ca content of soil rapidly, accurately and consistent with reference methods. Another study of mining pollution was undertaken by Haffert and Craw,[143] in this case the result of mining and roasting arsenopyrite ore in the Waiuta region of New Zealand. Field portable XRF measurements were interpreted in relation to arsenic mineralogy and the likely mechanisms for the dispersion of arsenic by run off and by the atmospheric fall out of dust.

A relatively innovative application of portable/hand-held XRF is for the *analysis of food stuffs*. After reviewing the theory, instrumentation, spectra and expanding range of applications of these instruments, Palmer et al.[144] described the field use of portable instrumentation for the rapid screening of toxic elements in (US) Food and Drug Administration regulated products, commenting on the value of this approach for both routine and non-routine measurements. Anderson[145] described the use of a portable X-ray tube-based analyser for screening foods, thin-films and ceramic glazes for toxic elements. Examples given include distinguishing a beverage spiked with As, Cr and Cu and cocoa powder spiked with As and Pb from unadulterated products when analysed through the original container walls, the determination of Cd and Pb in thin films (15 and 0.2 to 15 μg cm^{-2} detection limits, respectively) and Pb in ceramic glazes (2 μg cm^{-2} detection limits). Bromine was determined in regulated foods by field portable XRF also by Anderson.[146] By using a calibration based on INAA results for Br in reference materials, accurate results could be obtained in flour, bakery products, malted barley and US Food and Drug Administration total diet study foods and other food products. The use of conventional WDXRF for the determination of bromates in bread is covered in section 9.5. By contrast, Rao et al.[147] used portable XRF to provide a heavy metal fingerprint of tea samples of different origins to distinguish them by pattern recognition. The aim of this work was to provide information on the identification of tea from different regions (the rate of error was 4.2%) and to identify fraudulently presented tea.

In terms of the *innovative space use of portable XRF systems*, Swinyard et al.[148] described results from the compact imaging spectrometer which flew on the European Space Agency's Smart-1 mission to the Moon, describing observations made during two solar flare events that occurred during the mission (January 2005-September 2006). The first detection of Ti Kα from the lunar surface was reported and the geological implications discussed as well as lessons relevant to the design of spectrometers for future missions. Another space flight instrument was the XRF spectrometer designed for the *in situ* geochemical analysis

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on Mars that was flown as part of the unsuccessful Beagle 2 mission. Talboys *et al.*[149] undertook a comparison of the analytical performance of a flight spare instrument with a portable XRF instrument designed for terrestrial fieldwork and a laboratory WDXRF instrument, particularly with respect to fitting precision, accuracy and detection limit capability. Overall, the Beagle 2 instrument was found to have a favourable analytical performance compared to the benchmark spectrometers despite the considerable constraints in design required for space flight. Fortes *et al.*[150] described the scientific case for the preliminary design of an instrument to characterise the elemental abundance and mineralogy of the surface of Titan using a combination of EDXRF and XRD. The specification of the XRF instrument was to permit the determination of the elements $16 < Z < 60$ to detection limits of better than 10 μg g^{-1} and better than 0.01 to 1% m/m for the lower atomic number elements down to $Z = 6$ (C). This instrument was designed also to permit detection of the atmospheric noble gases and the scientific aims of the mission were described in detail. Grande *et al.*[151] described a compact UK-built X-ray spectrometer developed for India's Chandrayaan-1 mission to the Moon. The spectrometer collected data during the Moon's orbit, on the surface abundance of major rock-forming elements (Mg, Al, Si, Ti, Ca, and Fe) with a spatial resolution equal to about 25 km. More details about the design of the spectrometer were published by Howe *et al.*[152] The Chandrayaan-1 mission ended on 29 August 2009 due to loss of radio contact with the spacecraft but almost all goals of the project were accomplished. A similar X-ray spectrometer to that of the Chandrayaan-1 was described by Peng *et al.*[153] The spectrometer will be launched onboard the Chinese lunar satellite Change-2 at the end of 2010. The main task is to collect the data from the Moon's orbit on the surface abundances of Mg, Al, Si, Ca, Ti, and Fe with slightly coarser 100 km spatial resolution. The authors simulated the lunar X-ray spectra to be collected by the spectrometer during its mission.

A number of *other applications* of portable XRF have been reported during the current review period. Lawryk *et al.*[154] evaluated the performance of this instrumentation in the determination of Cr, Cu, Fe, Mn, Ni, Pb and Zn in air sample filter media used to monitor the workplace. They concluded that accuracy estimates met the (US) National Institute for Occupational Safety and Health criterion for nearly all element and concentration combinations indicating that this approach showed the potential to be useful in assessing worker inhalation exposures to other metals in addition to lead.

8   On-line XRF

Once again, we believe that on-line applications are seriously under-represented in the literature. However, Haavisto and Hyotyniemi[155] employed multivariate statistical analysis techniques and visible and near-infrared reflectance (VNIR) spectrometry to complete the data usually obtained by X-ray fluorescence analysis during on-line monitoring of a mineral flotation process. They applied a partial least-squares (PLS) model for predicting the slurry contents. The model can recursively adapt to real process data variations.

9   Applications

9.1   Sample preparation and preconcentration techniques

Many readers will be familiar with challenges associated with the analysis of small amounts of sample. However, with the increasing popularity of μ-XRF configurations, a small sample is all that is required. Fittschen and Havrilla[156] published their assessment of a prototype pico-litre pipette, based on thermal inkjet technology, for the preparation of *liquids* for subsequent analysis by μ-XRF. Unlike conventional inkjet printer heads, this instrument allowed the user to control functions such as time settings and energy. The authors found that a strategy was needed to reduce evaporation as this had a major influence on the deposition of such pico-litre volumes of sample. They were successful in preparing calibration samples from 1 to 300 pL and 1 to 2000 pg elemental deposits and quoted limits of detection, focal spot size, sensitivity and precision data for the calibration of a μ-XRF spectrometer. The accuracy of this dried spot approach was demonstrated by comparing multi-element deposits on AP1 film with NIST SRMs 1832 and 1833 thin film reference materials available for micro-analysis work. The deviation from SRM certificate values was reported to be better than 10%. Yamini *et al.*[157] offered a simple and inexpensive method for the simultaneous determination of trace levels of Co, Cr, Cu, Fe, Mn, Ni, V and Zn in natural water using WDXRF. Samples were preconcentrated onto silica gel powder using 1-(2-pyridylazo)-2-naphthol as a chelating agent. The effect of parameters such as pH, temperature, stirring time, amount of ligand, breakthrough volume and the limit of detection were all considered. Nakano *et al.*[158] chose agar, a natural polymer, for their preconcentration procedure prior to XRF analysis of trace levels of elements in environmental waters. Limits of detection for measurements on the agar thin films were 0.26 μg mL^{-1} for Ca, 0.20 μg mL^{-1} for Cd, 0.030 μg mL^{-1} for Cu, 0.11 μg mL^{-1} for Fe, 1.4 μg mL^{-1} for K, 0.029 μg mL^{-1} for Mn, 0.016 μg mL^{-1} for Ni, 0.066 μg mL^{-1} for Pb, 0.088 μg mL^{-1} for V and 0.017 μg mL^{-1} for Zn. Khamizov *et al.*[159] offered a mass-transfer kinetic model for an embedded sorption accumulation micro-system based on polycapillary lenses for the XRF analysis of elements in multi-component solutions. Experimental data were presented for the sorption of Cu, Fe, Mn, Ni and Zn. Petitgirard *et al.*[160] presented a new diamond anvil cell for the SRXRF analysis of trace elements in fluids under high pressure and high temperature (up to 10 GPa and 1273 K). The characteristics of the cell provided optimised shielding and collection geometry in order to reduce the spectrum background. When tested at the ID22 focusing beamline at the European Synchrotron Radiation Facility in Grenoble, France, detection limits of 0.3 μg g^{-1} were calculated for the measurement of Rb, Sr, Y and Zr. The cell was also suitable for XRD studies over the same high pressure-temperature range and will be of interest to geochemists.

Finkelshtein and Brjansky[161] estimated the influence of particles size on the XRF intensity from *powders*. They developed an expression based on a simple modification of the Berry-Furuta-Rhodes formulae for powders consisting of various sized particles randomly distributed in a sample volume. Shibata *et al.*[162] reported a method for the quantitative analysis of As, Cd, Cr, Hg, Se and Pb in soil by WDXRF with samples presented as

either pressed powder pellets or as loose powders. Soil samples containing these hazardous metals for use as calibrators were prepared by adding appropriate amounts of aqueous standards to base soil and then drying and homogenising them. The base soil powders were ground to less than 12.5 μm particle size, a key step in this preparation routine that has eluded many workers in the past. Powder pellets were pressed into aluminium rings and the loose powder was presented to the spectrometer in 31 mm diameter polyethylene cups fitted with 6 μm polypropylene film. Line overlap corrections were applied for Se Kβ on Pb Lβ and Pb Lα on As Kα. Corrections with Compton scattering for As Kα, Cd Kα, Hg Lα, Se Kα and Pb Lβ and with background scattering for Cr Kα were effective and produced good calibration curves. The development of commercially viable transformations of biomass components into platform chemicals is often hampered by poisoning of the metal catalysts assisting such conversions. Sulfur present in small amounts in biomass is a typical catalyst poison. Robinson et al.[163] developed an EDXRF method to measure low μg g^{-1} levels of sulfur in biomass feedstock and in pre-treatment residues. Pressed powder calibrators were prepared from milled biomass mixed with micro-crystalline cellulose and standard additions to cover a concentration range from 2 to 2250 μg g^{-1}. Wang et al.[164] prepared Ti-doped MgO powders by chemical coprecipitation using magnesium nitrate hexahydrate and titanium tetrabutoxide as starting materials and ammonium hydroxide as precipitator. The influence of the Ti-doping on the structure and morphology of the MgO powders was investigated by XRD, XPS and TEM prior to XRF analysis. The Ti^{4+} ion was reported to be successfully incorporated into the MgO crystal lattice as shown by the change in lattice parameter.

There are only two papers to mention in this review concerning the *fused bead preparation technique*. Valle et al.[165] published their method for the analysis of laser active lanthanides (Ln) in NaTm$_{1-x}$Ln$_x$(WO$_4$)$_2$ crystals. A method was developed to circumvent precipitation problems, involving lanthanides and tungsten, experienced during wet chemical dissolution. Three calibrators were prepared with near-to constant Na and W concentrations so that matrix effects for the determination of Tm and Yb from beads fused with Li$_2$B$_4$O$_7$ could be addressed. Vinklerova[166] compared fusion techniques; the so called one-phase method, where the sample was fused in a borate flux and cooled down in the same Pt/Au crucible and the conventional two-phase method whereby the melt was poured from the crucible into a Pt/Au casting dish prior to annealing. Alumino-silicate CRMs were used to compare the two fusion techniques. The single-phase method may be of interest to those analysts challenged by tight budgets. However, melts of many materials that require the addition of agents to eliminate surface tension problems will doubtless continue to support the use of a casting dish.

Other sample preparation methods published during this review year included studies by two Russian workers[167,168] for the analysis of cow's milk. Samples were prepared as freeze-dried residues and presented to a WDXRF spectrometer as 4 g pressed pellets. Calibrations were developed using both plant and milk CRMs with matrix correction based on the Compton scattered intensity. The method was offered for the analysis of different types of milk, dairy products and infant formulas with the advantage of no limitations related to the milk fat content. The

problem of collecting PM 2.5 aerosols from inhospitable regions was solved by Prendez et al.[169] who used a solar powered sampler installed during the summer periods of 2006 and 2007, some 2.5 km from the B. O'Higgins Chilean base in Antarctica. The collecting point was chosen to avoid possible air contamination from oil and gas burning electric power stations and showed the presence of elements typically originating from the Earth's crust and seawater. Dhara and colleagues[170] offered a fast EDXRF method requiring only micro-gram amounts of Th and U in advanced heavy water reactor fuel. A fixed amount of yttrium was added as an internal standard for measurements of 20 μL aliquots on 30 mm diameter filter papers after drying. Calibrations were built from U/Y, U/Th and Th/Y ratios against respective intensity ratios of Th Lα, U Lα and Y Kα. In the first set, U was determined using the Y internal standard, then Th was determined using the calculated U content as an internal standard since the Th and Y concentrations were kept constant in both the calibration solutions and the samples. In the second set, both U and Th were varied and determined using Y as internal standard. The U and Th determinations showed a precision of 3% (1SD) and the results were reported to deviate from expected values by <3% in most cases. This approach offered the advantage that it required only microgram amounts of sample, thereby mitigating radiation hazards associated with the analysis of radioactive materials. Finally in this section, Reiter et al.[171] reviewed sample preparation strategies and methods for the analysis of aflatoxins, naturally occurring mycotoxins, in food and feed. Aflatoxins are known to cause liver cirrhosis and primary liver carcinomas and have been shown to be immuno-suppressive. The EU has set maximum levels, as low as reasonably achievable, to protect consumers, thereby generating a need for a robust method that provides reliable results throughout the analysis chain.

9.2 Geological and industrial minerals

XRF has had another prolific year in contributing to the analysis of geological materials and has continued its role as a standard technique for the characterisation of the *major and selected trace elements in igneous rocks* as a contribution to a wide range of geochemical research projects. Applications included characterising 'trap' rocks from the Noril'sk Trough, northwestern Siberian craton,[172] clinoptilolite tuffs in the Central Simav Graben, western Turkey,[173] the eruptive history of the La Garrinada volcano, northeastern Spain,[174] Permian melaphyre lavas, Darmstadt, Germany,[175] beach rock samples from the Andaman Islands,[176] magmatic dyke samples from the Gardar Province (southern Greenland),[177] xenoliths associated with Cenozoic alkali basaltic magma from the Shamah Harrat (southwestern Syria) in which the mean composition was used to estimate the seismic compressional wave velocity giving good agreement with the values reported from seismic studies[178] and the Cluanie granitoid pluton (Northwest Scotland).[179] Two studies of kimberlites were of interest, one to evaluate the diamond potential of kimberlites from the Nyurbinskaya Pipe (East Siberia) that had experienced secondary alteration[180] and the second a study of volcaniclastic kimberlites from the Northern Slave Province (Nunavut, Canada).[181] Staying with the theme of kimberlites, Roy et al.[182] described a rapid and reliable method

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for the quantitative determination of S in geochemical samples by WDXRF. Determinations were undertaken on powder pellets with detection limits claimed to be 0.004% m/m and accuracy affirmed by the analysis of geochemical reference materials and results from an independent method (the Leco S analyser). Finkelshtein and Chubarov[183] revisited what could be described as one of the holy grails of geochemical analysis—the WDXRF determination of the FeO/Fe_2O_{3total} ratio. The $K\beta_{2,5}/K\beta_{1,3}$ ratio was selected as the analytical signal and the authors claimed that in igneous rocks where $FeO/Fe_2O_{3total} > 0.25$, the XRF determination of the FeO content could be performed at an accuracy comparable with that of wet chemical analysis. A geochemical study with a difference was undertaken by Denecke et al.[184] who used μ-SRXRF and μ-XAFS to evaluate the speciation of neptunium in a fractured granite bore core from the Swedish Aspo Hard Rock Laboratory. A confocal irradiation-detection geometry was used to demonstrate that the Np^V tracer was reduced to Np^{IV} and was located in fissures and permeable channels often correlated with the presence of zinc. Hashimoto et al.[185] also undertook a sophisticated use of XRF in the estimation of fluid flux and permeability of a fault zone in the Mugi melange (Shimanto Belt, Southwest Japan) in which a decrease in silica was one of the key parameters in contributing to an estimate of the permeability of the fault breccia.

In *studies related to ore deposits*, Lintern et al.[186] used SRXRF and XANES to show for the first time the distribution of Au in calcrete at the Bounty Gold Deposit (Western Australia) and demonstrated the presence of Au in both particulate and ionic form. These results suggested that biotic influences can affect the mobilisation and distribution of Au in surficial materials with implications from the presence of easily soluble Au in soils for mineral extraction. Menon et al.'s[187] interest lay in a conventional geochemical soil survey at the Tumallpalle uranium mineralisation zone (Cuddapah district, India), in which XRF and ICP-MS were used to compliment an *in situ* radiometric survey to delineate uranium anomalies in soil to optimise exploitation. Sartandel et al.[188] measured the Th and U distribution by gamma spectrometry and the toxic elements Cr and Pb by EDXRF in surface soil and sediment cores around a proposed uranium mining site at Lambapur near the Nagarjuna Sagar Dam, India. Results showed higher concentrations of Cr and Pb in the upper sections of the sediment core indicating the impact of river input on the geochemical character of the dam sediment. Rare earth element ores were of interest to Zuzaan et al.[189] in the development of an EDXRF technique for the determination of Ce, La, Nd and Pr using an instrument fitted with an ^{241}Am excitation source. Back into the field, Singh and Kumar[190] used WDXRF to analyse hand-panned mineral concentrates from riverine placer deposits around the Bastar Craton (Central India) for the elements Ce, Nb, Sn, Ta, Y. Mineral associations were revealed by XRD, but the conclusion was that only localised and uneconomic concentrations of the LREE bearing mineral, monazite were to be found in this placer. Hayes et al.'s[191] interest lay in what happens at the end of the mining process, specifically Pb and Zn contamination in surficial and mine tailings from the Arizona Klondyke State Superfund Site (USA). They used chemical extractions, XRD, μ-XRF and μ-Raman to characterise the availability and mineral associations of these elements over the range of pHs (2.5 to 8.0) found at this site and concluded

that acidification in the tailings diminished the overall liability of the total Pb and Zn contamination. Arsenic mobility and bio-accessibility associated with primary and secondary (weathered) arsenic bearing minerals in the Nova Scotia gold mining districts (Canada) were studied by Walker et al.[192] using XRD, microscopy and EPMA, μ-SRXRD, μ-SRXRF and μ-SRXAS. Their conclusions were that the arsenic mineralogy in weathered mine tailings was highly variable and affected by the presence or absence of mill concentrates, the degree of water saturation and the abundance of relic carbonate minerals with the environmental impact influenced by the variable solubility of these species. The fate of potential contaminants from the weathering of a sulfide ore body was a topic investigated by Courtin-Nomade et al.,[193] based on a multi-technique approach that included μ-XAS and scanning XRF mapping techniques. The elements of interest included As, Cu, Pb and Zn at Leona Heights, California (USA) (in a suburb of the heavily urbanised area of Oakland). A detailed assessment was made of authigenic minerals (sulfates, iron oxyhydroxides and poorly crystallised manganese hydroxides) which indicated that the orebody still represented a significant reservoir of potential contaminants. Pyrite ash waste is created by the roasting of pyrite ores for the production of sulfuric acid and was the topic of a study by Tugrul et al.[194] on the reuse of this waste material in the iron production industry, because of its high Fe_2O_3 content. XRD and XRF used in a laboratory-scale electric arc furnace experiment showed that this oxide could be reduced to a metallic iron phase. Iron oxyhydroxide biomineralisation on iron microbial mat samples from a creek and abandoned mine was studied by Chan et al.[195] using STEM, μ-XRF and high resolution TEM. In both natural and cultured samples, microbial polymers were found to be acidic polysaccharides with carboxyl functional groups, strongly spatially correlated with iron oxyhydroxide distribution patterns. Cherkashina et al.[196] applied WDXRF spectrometry for the determination of trace element concentrations in phosphorite by using a standard background method. Due to the lack of CRMs they used theoretically calculated standard samples. The results of XRF analysis were used for geochemical characterization of rocks. Cui et al.[197] studied the synthesis of lithiophorite, a naturally occurring manganese oxide mineral commonly found in soils and sediments to elucidate from laboratory experiments the factors relevant to the formation of this mineral in the environment. Vazquez et al.[198] used a range of techniques including XRF and XANES to characterise kaolin from a region near to San Luis Potosi (Mexico) and concluded that the high content of volcanic glass and the reddish colour associated with the presence of limonite (FeO(OH)) made the material favourable for use in the cement industry, rather than traditional ceramic applications. XRD and XRF were used by Tongamp et al.[199] to investigate the use of alkaline leaching, using sodium hydrogen sulfide (NaHS), to remove arsenic impurities from copper ores and concentrates. Significant success was reported with over 90% of the As removed after an appropriate period associated with the decomposition or transformation of Cu_3AsS_4 to CuS_2 and Na_3AsS_3 (in solution).

XRF also made a significant contribution to the *analysis of individual minerals*. Thus, Zhang and Sakurai[200] used XRF for the 2D X-ray mapping of bloodstone, identifying elemental correlations and proposing that the bottle green colouration was

associated with a Fe^{2+} or Cu compound, yellow and red with Fe_2O_3 or another Fe^{3+} compound and black with Fe_3O_4. XRF contributed with XRD and SEM to a study of zircon and apatite crystals from the Fish Canyon Tuff (Colorado, USA) in a contribution by Bermudez-Cella et al.[201] to the characterisation of reference materials for use in thermochronology. SRXRF was used by Kolonin et al.[202] to measure the REE and Y content of monazite samples from the Ilmen' Reserve (South Urals, Russia). Polarised EDXRF was paired with confocal Raman spectrometry to demonstrate differences between two antimonide ore samples from Turkey.[203] A multi-technique approach that included XRF was used by Garcia-Guinea et al.[204] to examine the luminescence properties of strontianite ($SrCO_3$) and the way these properties are modified when heated to temperatures up to 500 °C. Bonizzoni et al.[205] used an EDXRF method for the quantitative analysis of corundum to evaluate the effect of trace levels of Cr, Fe, Ti to impart colour on gemstone varieties. SRXRF was used by Dalby et al.[206] to confirm that the red cathodoluminescence emission and the 720 nm X-ray excited optical luminescence intensity observed from albite grains found in the Georgeville granite (Nova Scotia, Canada) were associated with the total iron concentration. XRF was one of the techniques used to examine natural hydrothermal smithsonite by Garcia-Guinea et al.[207] with a particular interest in the effect of heating from room temperature up to 500 °C on the thermoluminescence emission spectrum. Bruthans et al.[208] used XRD and XRF to analyse surficial deposits on salt diapirs in the Zagros Mountains and Persian Gulf Platform (Iran). Their particular interest was the effect of surface deposits containing halite and gypsum on erosion rates, salt karst evolution, land use and the density of vegetation cover.

Minerals have a wide range of *industrial uses*, exemplified by the study by Chen-Tan et al.[209] of Western Australian fly ash using XRF/XRD to quantify the reactive component that can be used in geopolymerisation. With additional data from alkaline dissolution experiments and the use of SEM, it was concluded that amorphous iron does not participate in the geopolymerisation process. XRD and XRF were also used by Velosa et al.[210] to analyse the effect of three different metakaolins processed by a Portuguese factory on mortar characteristics. Their particular interest was to assess the effect of mineral and chemical composition on the mechanical strength of lime mortars. Chen et al.[211] used a combination of techniques, including XRF, to examine the effectiveness of iron montmorillonite as a catalyst for the decolorisation of reactive brilliant orange, X-GN. In a further study, Chen and Zhu[212] investigated the catalytic activity of different iron pillared bentonites in the discoloration and mineralisation of Orange II in the presence of UV light and H_2O_2. A combination of techniques, including XRF was also used by Kaufhold and Dohrmann[213] to assess the stability of bentonites in salt solutions as a buffer for the storage of radioactive waste. This study focused specifically on the effect of exposure to 6 mol L^{-1} sodium chloride solution at 60 °C for 5 months and the influence of carbonates and gypsum on the expected cation exchanges. XRF determinations of Nb, Th, Y and Zr strongly supported the presence of multiple volcanic sources in bentonite beds of the Western Interior Basin of western Canada and northwestern USA in a study by Fanti.[214] Other studies of industrial minerals included the characterisation of magnesium smectite from Jbel Ghassoul (Morocco),[215] sodium-exchanged smectites,[216] zeolitic tuff from Jordan[217,218] and pozzolanic reactions of common natural zeolites.[219]

Turning now to another topic, XRF has continued to be applied to the *analysis of soils*. In this field, XRF was used with wet chemical analysis by Fiantis et al.[220] to study the weathering indices of pyroclastic deposits resulting from the eruption of Mount Merapi (Indonesia). The mechanical properties of weathered soil were measured by Son and Chan[221] using XRF to allow correlation with the degree of weathering. XRF contributed to an interesting study.[222] that evaluated the use of the REE to trace pedogenetic processes (that is the process of soil formation from unconsolidated rock). The study by Chandrajith et al.[223] of soils in the Udawalawe National Park (Sri Lanka) by XRF and XRD suggested that elephants select and eat soil not to supplement the mineral contents of their forage, but rather to detoxify unpalatable compounds from their diet. This conclusion was based on the observation that the preferred soils were richer in kaolin and illite than non-geophagic soils, which contained more smectite. The XRF and SEM techniques were used by Anda et al.[224] to investigate the red and black soil associations in the Monarto area of South Australia. This study was based on characterising zirconium and titanium bearing minerals resistant to chemical weathering. Whereas Zr was only associated with zircon, Ti was associated with a range of minerals, some of which (ilmenite, pseudorutile, biotite) were susceptible to chemical weathering. The overall conclusion of this work was that the presence of complex red and black soil associations in the landscape was attributed to different parent materials (mica schists and calcareous deposits, respectively). XRF contributed to a study of the soil biogeochemical properties of the Angren industrial area, Uzbekistan by Shukurov et al.[225] who assessed the impact of air pollution from a nearby heavy industry complex on soil health, based on microbiological activity. Not unexpectedly, they found less biomass formation and a higher metabolic quotient in heavy metal contaminated soils in a study designed to contribute to a national monitoring programme. Sphagnum peat is known to be capable of efficiently removing a wide range of pollutants from contaminated waters and a further study by Zaccone et al.[226] investigated variability in As, Ca, Cr, K, Mn, Sr and Ti concentrations by XRF in humic acids isolated from peat using NaOH, $Na_4P_2O_7$ and NaOH + $Na_4P_2O_7$ solution extraction. Results were related to the nature of each humic acid fraction and the physical and chemical form of each element supplied to the bog by atmospheric deposition.

XRF continues to contribute to a significant amount of work in the *analysis of sediments*, justifying the preparation of five new sediment reference materials from the China Sea and continental shelf, the particular feature of which was the use of a jet mill to achieve an ultra-fine particle size distribution.[227,228] Coastal dunes were the subject of two contributions from Turkey,[229,230] the first focusing on the classification of dune sands in a rapidly prograding delta environment on the East coast of the Saros Gulf (Northwest Turkey), the second using XRF to correlate a pumice layer with the plinian eruption of Thera (Santorini) in 1628 BC and associating some of the deposits with a tsunami event recorded in 1672. XRF with some ICP-MS data were used by Sheppard et al.[231] to undertake a stream sediment geochemical survey of an area of epithermal Au–Ag–Zn–Pb–Cu and

porphyry Cu deposits in the Coromandel Peninsula, New Zealand. Elemental anomalies were correlated with known mineral occurrences and compared with mining company records, although the latter had the advantage of a much higher sampling density. A combination of techniques, including XRF, EXAFS and XANES was used by Qafoku et al.[232] to characterise bio-reduced U-contaminated alluvial sediment in the Colorado River (Rifle, CO, USA) associated with a former uranium milling operation. Because of the association found between U and framboidal pyrite, the authors speculated that U may be sequestered in situ under conditions of microbially driven sulfate reduction and pyrite formation. Hong et al.[233] used WDXRF and XRD to characterise samples from a laterite in Hubei (South China) to link clay mineralogy in various beds with different degrees of weathering along the laterite profile and the formation and origin of laterites in the region. The Galician Continental Shelf was of interest to Correderia et al.,[234] using both INAA and EDXRF to identify the sedimentology and geochemistry, and noted that no significant heavy metal enrichment was detected, despite the current sediment contamination in the adjacent river Rias. Anthropogenic inputs of Cu, Pb and Zn originating from several decades ago were detected by Alvarez-Iglesias and Rubio[235] using XRF to analyse two sediment cores from the San Simn Bay (northwestern Spain) in which sediment accumulation rates had been established by ^{210}Pb and ^{137}Cs dating. Galman et al.[236] used XRF to measure Fe and S in unique core samples collected (1979–2004) from Lake Nylandssjon (northern Spain) to understand the formation of varves (annual laminations). Analytical data were used to model the formation of various chemical species, the conclusion of which was that either FeS or $Fe(OH)_3/FeOOH$ are the only solid phase species present and that there are redox ranges within which the two solid phases co-exist commensurate with the existence of blackish and grey-brown layers that formed in varves at the time of deposition. A problem associated with contaminated sediments, collected after dredging inland waterways, is their disposal, often on land. This topic was addressed by Piou et al.,[237] who studied the geochemical distribution of Cd, Fe, Mn and Zn in sediment dredged from the Scarpe canal (Nord Pas-de-Calais region, France). Analyses were undertaken 0, 12, 18 and 24 months after disposal and interpreted to reflect the initial oxidation of sulfides (after one year) followed by a reversible binding of metals to organic matter in Winter and iron oxihydroxides in Summer. Schwarzbauer et al.[238] used EDXRF to determine the major elements and ICP-AES, GF-AAS and ICP-MS to determine the heavy metals in surface sediments from Lake Bant and the Wadden Sea (Germany) to evaluate the effect of the disposal of ammunition after World War II. The main focus of this study was to assess the long-term behaviour of explosives in undamaged ammunition in an aquatic environment and the spectrum of organic substances that could be released by such ammunition residues. GC-MS contributed extensively to this study. These are just some of the examples of the plethora of applications of XRF to the study of sediments available for review this year. Other studies that involved XRF included sediments of the White Sea,[239] the mineralogy of lignites and intra-seam sediments from the Archlada Basin (northern Greece) and a multitechnique study of ferromanganese nodules in carbonate mud mounds from the Gulf of Cadiz (Spain).

XRF was also used in a large number of studies of sediment designed to *elucidate climate change over the geological record*, often in combination with other techniques. For example, Haberzetti et al.[240] presented a continuous palaeo-environmental record that extended over the last 55 ka derived from sediment cores from the Maar Lake Laguna Potrok Aike (southern Patagonia, Argentina) using high resolution XRF, magnetic susceptibility and grain size data. The outcome of this detailed work was to identify dust deposition in the Patagonian steppe in the Late Pleistocene and confirm the age of three tephra layers in the core. XRF core scanning was used by Westerhold and Rohl[241] on samples from the ocean drilling project, ODP Site 1258, to elucidate the origin of the Cenozoic cooling trend in the early Eocene. The element Fe, determined by XRF, was used by Abrantes et al.[242] as a proxy for river flow in the analysis of two high-sedimentation shallow water sedimentary sequences recovered off Lisbon (Portugal). In combination with other data, this work was designed to contribute to the reconstruction of past North Atlantic Oscillation conditions. EDXRF had a significant role in the analysis of sediment cores from the Bornholm Basin (Baltic Sea) to complement Pb/Cs dating. Results indicated that Cu and Zn showed an increase since the 1920s but a decline since the 1980s with trends in other elements associated with changes in salinity (Br) and the type of sedimentation. Sediment core from the Laguna Rabadilla de Vaca (southeastern Ecuadorian Andes) was analysed by XRF, magnetic susceptibility and pollen, spore and charcoal analysis in a study by Niemann et al.[243] to elucidate Holocene climate variability and vegetation dynamics over the last 11700 years. And finally in this section, Toucanne et al.[244] looked at marine sediment records in the Bay of Biscay (northeast Atlantic) using mass accumulation rates and XRF to determine the timing and amplitude of the 'Fleuve Manche' discharges during various glacial periods. This study gave a detailed insight into glaciation during the Middle and Late Pleistocene in Europe and the drainage network of the central and western European Rivers over the last 350 years. These are examples of the significant XRF literature in this area published over the current review period.

9.3 Environmental

9.3.1 Environmental forensics. *Rice* is the staple food for over half the world's population yet may represent a significant exposure route for toxins where crops are irrigated with contaminated water. Smith et al.[245] published their work on arsenic mobility from paddy water to the rice plant using XRF techniques. They found that As was present in all rice tissues and was correlated with the presence of Fe at the root surface and Cu in the rice leaf. Structural analysis using XANES showed that inorganic As was predominant and that arsenite became increasingly dominant in the aerial portion of the plant. In related studies, Carey and colleagues[246,247] used SRXRF mapping and fluorescence microtomography to investigate how different arsenic species were transported into the rice grains. Panicles were excised during grain filling and hydroponically pulsed with arsenite, arsenate, glutathione-complexed arsenic or dimethylarsinic acid (DMA). The results demonstrated that DMA was transported to the rice grain with an order of magnitude greater efficiency than the inorganic species and was

more mobile than arsenite in both the phloem and the xylem. Takahashi *et al.*[248] also used SRXRF to investigate the flow of metal nutrients (Cu, Fe, Mn and Zn) during rice seed germination. Micro-analysis showed different rates of metal transport during the germination process. The four analytes of interest were found to accumulate in the endosperm and embryos of the rice seeds with each analyte showing an individual pattern of mineral localisation during germination. Williams *et al.*[249] were concerned with the characterisation of Se in the global rice supply chain. Some one billion people on low protein diets rely on cereals as their main Se source. Crop Se content is known to be largely constrained by underlying geology with regional soil Se variations often mirrored by their locally grown staples. A total of 1092 samples of market sourced polished rice were obtained to reflect dominant rice producing and exporting countries. A combination of μ-XRF and μ-XANES showed that the majority of Se was located in the endosperm as organic species. Rice from India and the USA were found to be most enriched whilst Se levels were lowest in Egyptian rice. Similarly, Moore *et al.*[250] reported the sub-cellular localisation of As and Se in rice grains to find good quantitative agreement between high resolution secondary-ion mass spectrometry and SRXRF techniques. With so much rice consumed, attention now turns to the characterisation of ash from the combustion of rice husks. Angel *et al.*[251] used XRF, XRD and SEM to study rice husk combustion in a bubbling and atmospheric fluidised bed reactor. The potential of this type of reactor to process the husks was assessed in terms of speed, continuity and energy consumption. After combustion the rice husk ash was reported to contain 93% amorphous silica and <3% unburned char. Another group from the same Colombian institution[252] analysed rice husks and the flue gases (CO_x and NO_x) emitted as the reactor conditions were varied. In Nigeria, Omatola and Onojah[253] assessed rice husk ash from five different processes operating at two different temperatures, 500 °C and 1000 °C. Their XRF data showed the silica rich ash contained 90–98% silica after complete combustion. Hessien *et al.*[254] studied silica nanospheres from semi-burned rice straw for different electronic applications. Silica from the rice straw ash was dissolved by alkali leaching with sodium hydroxide and precipitated from the solution using sulfuric acid. Factors affecting the precipitation process were studied by XRD, XRF and TEM. The authors found that a particle of ~16 nm could be achieved at 30% Na_2SiO_3 and 4% H_2SO_4. The produced silica had 99.3% purity with a narrow size distribution and was suitable for use as a polishing slurry for the semiconductor industry.

The *presence and function of elements in other plants* also featured in the literature under review. Wellenreuther *et al.*[255] used μ-XRF to develop elemental maps of a cell monolayer to study the intravesicular coordination of Zn in isolated plant vesicles. The zinc was found to be present as a complexed form resembling regulatory or catalytic zinc sites in proteins. The authors considered that the coordination enabled reversible binding, acting as a "zinc sink". Studies such as these demonstrate the ability of μ-XRF techniques to generate elemental maps of discrete plant cells giving valuable data to researchers. Campos *et al.*[256] investigated the distribution of Nd, Pb, Th and U in 100 samples of 12 different species of common, edible and non-edible mushrooms collected from unpolluted areas in the province of Ciudad Real, Spain. The concentration of these elements was found to be related to factors such as mushroom species and habitat. Gardeners amongst the readership will be familiar with the benefits of feeding K, N and P to their plants to increase yield in the vegetable patch and blooms in their borders. Gunes *et al.*[257] used polarised EDXRF to investigate the response of wheat, sunflower, chickpea and lentil cultivars to P fertilisation. Their results showed that whilst the shoot growth of the plant species under investigation increased in response to P fertilisation, other analytes responded differently; notably Al, As, Ba, Br, Ca, Cl, Cu, Fe, Mg, Mn, Mo, Na, Ni, Rb, Si, Sr, Ti and Zn. Taspinar *et al.*[258] used WDXRF to measure chilling temperature effects on the composition of nutrient elements in cole (Brassica Oleracea L. Cv. Acephala). Seedlings of this hardy species were grown in soil for one month and then chilled under controlled conditions. The seedlings were subsequently cut into root tip, root middle part, root upper part, hypocotyls, epicotyl, petiole and leaf. The analytical data indicated that the distribution of some inorganic elements among the roots, stems and leaves of the cole plants was significantly altered by chilling stress. Ercisli *et al.*[259] also used WDXRF to measure 15 mineral and trace elements in the fresh green leaves of tea. Levels of Cl, K, Ni and P were highest in leaves collected during the first harvest and decreased continuously until the time for the third harvest. In contrast; Al, Ca, Fe, Mg, S and Sr concentrations were lowest in leaves from the first harvest and increased with successive collections. Grankina *et al.*[260] used SRXRF to measure the composition of trace elements in the roots, rhizomes, leaves, stems and reproductive (bean valves) organs of licorice (Glycyrrhiza uralensis Fisch). The data showed that the plant is an accumulator of Co, Cu, Fe and Mn.

Trees from the Burseraceae family exude a resin widely used in the manufacture of cosmetics and perfumes and in folk medicine for the treatment of diseases. Rudiger *et al.*[261] collected samples from five species grown in Brazil to measure the inorganic elements present in the resins and suggest patterns showing the different capacities for the transfer of analytes from tree to resin. Liodakis and Tsoukala[262] reported the chemical, mineralogical and leaching behaviour of three dominant Greek forest species of ash, before and after treatment with phosphate fire retardants. EDXRF was one of the techniques used to study the environmental effects on soil, water and underground streams from the chemical retardants released during forest fires. Unexpectedly, diammonium phosphate was found to prevent the leachability of Cr from the ash trees. Health awareness and concern for the environment have resulted in the voluntary removal of chromated copper arsenate (CCA) from wood preservatives in residential applications worldwide. Alternative copper-based preservatives, however, may not provide a permanent solution as Cu contamination has been reported in aquatic environments and corrosion of metal fasteners. Lin *et al.*[263] used XRF to study the Cu retention (before and after the leaching process) of five softwood specimens vacuum-treated with alkaline copper quaternary (ACQ) and copper azole (CA) at three retention levels. Metal corrosion and termite resistance were also studied under laboratory conditions. With the exception of Japanese larch wood, the copper retention levels of the other wood specimens were able to meet values specified in Chinese governmental legislation. Corrosion rates for both iron and zinc-galvanised nails also met the test standard. Both ACQ and CA treatments

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increased termite mortalities and significantly reduce mass losses in the timber after treatment.

A number of papers during this review period reported work on various plant species used as *bio-monitors*. Lichen, which lacks roots, is known to collect nutrients directly from precipitation, atmospheric gases and dry deposition of airborne particulates. Pabroa *et al.*[264] used XRF to measure Br, Co, Cu, Pb, S and Zn in lichen from four urban sites in Manila, Philippines and two sites near coal fired power plants. They showed that the lichen, Pyxine cocoes (Sw.) Nyl. may be used to differentiate levels of the cited elements in polluted and non-polluted sites. Calcutta, India is reputed to be one of the most polluted cities in the world, suffering an alarming increase in levels of air pollution as a consequence of rapid urbanisation and industrialisation. Majumdar *et al.*[265] used EDXRF to measure epiphytic lichens burdened with particulates from heavy vehicular load to show that seasonal variation also contributed to the pollution. In Havana City, Cuba, Montero *et al.*[266] used a combination of TXRF, FAAS and anode stripping voltammetry to determine trace analytes in lichen to assess the performance of the differing techniques for air quality assessment. Good agreement was reported between the three techniques. Tian *et al.*[267] used SRXRF to measure the stem and leaf sequestration of Zn at the cellular level in the hyper-accumulator, Sedum alfedii. They found that the proportion of Zn accumulated in stem epidermal layers, relative to other tissues, was much greater in some sedum sub-types. This study elegantly demonstrates the ability of SRXRF to measure elemental content in differing cells within a plant. Similarly Espinoza-Quinones and colleagues[268,269] used SRXRF to study the Pb phyto-accumulation by living free floating aquatic macrophytes, Salvinia auriculata. These plants were grown, under glass, in lead-doped hydroponic solutions forming, as a function of time, six collections of nutrient media, roots and leaves. The SRXRF data revealed a competition for plant growth between the phosphorus macro-nutrient and Pb. The authors suggest that the plant species be used in artificial wetlands to predict heavy metal removal dynamics from waste waters. Sabatini *et al.*[270] investigated oxidative stress and anti-oxidant defences in two green micro-algae exposed to copper. The Cu content was determined in both strains by TXRF to show that increased Cu in the environment evokes oxidative stress and an increase in the antioxidant defences of Scenedesmus vacuolatus whereas Chlorella kessleri did not show significant differences in these parameters.

It is always a concern to review papers that reveal hazardous levels of analytes in the food we enjoy, this time it is *seafood*. Crab (Cancer pagurus, Linnaeus 1758) is much appreciated in Southern Europe, especially during the summer months and in December. The elemental content of the crab's edible tissues were analysed by Barrento *et al.*[271] during the four seasons. Their results indicate that the content varied with tissue, season and crab gender. The hepatopanceas had more Br, Ca, Cd, Cl, Cu, Fe, Pb, S and Sr, the gonads had a higher concentration of Na whereas the muscle was richer in Zn. Autumn and winter corresponded to higher levels of Ca, Cl, Fe, K, Mg, S and Zn in both the muscle and hepatopancreas. Female gonads had more As, Fe, Se and Zn than males but less Br, Ca, Cl and Sr. The levels of As, Hg and Pb were reported to pose a minimal risk to consumers, however, Cd concentration in the hepatopancreas

was always measured above the action limit. Hence the authors recommend moderate hepatopancreas consumption. Mohapatra *et al.*[272] measured the elemental content in the pre-moult (hard shelled) and newly moulted (soft shelled) crab, Scylla serata by EDXRF. The study evaluated 10 elements from the body tissue and the exuvium of soft shelled and the carapace of pre-moulted hard shelled crabs in order to assess the food value from the nutritional and safety points of view. Ca, Cu, K and Mn were found to be reabsorbed from the carapace to the body tissue in order to meet further requirements in the soft shelled crabs and support the formation of new carapace. Lead was shown to be excreted during exuviations showing that freshly moulted soft shelled crabs are both safer and more nutricious than their hard shelled brethren. Two papers from Portugal[273,274] reported EDXRF studies on seafood consumed locally. The muscle from eight fish species, three cephalopods and one crustacean were measured for their arsenic content. The highest levels were found in Norway lobster followed by common octopus with fish species; sea bream, angler-fish and megrims offering lower As levels. The authors concluded that moderate consumption would not represent a dietary risk.

Other studies, noted in this section of the review, demonstrate the diversity of applications for XRF techniques. Mejia *et al.*[275] reported their XPS data on self-cleaning modified TiO_2 cotton fabric pre-treated by UVC-light and rf-plasma at atmospheric pressure. XPS data showed it was possible to monitor the decrease of C, N and S species on the textiles top-most layers during the discolouration kinetics of a wine stain. Peak shifts were observed indicating Ti^{4+}/Ti^{3+} oxido-reduction taking place during photo-catalysis. XRD showed the formation of anatase on the cotton. The TiO_2 layers on the fabric were reported to have no adverse affect on the touch or handling properties of the cotton, enabling the potential for commercial use of TiO_2 treated cotton fabrics. The powerful combination of SR based X-ray microscopic techniques (μ-XRF, μ-XANES and μ-XRD) featured in work by Lind *et al.*[276] on single particles of depleted uranium (DU) in soils collected from Kosovo and Kuwait. Oxidised U^{6+} was found in large, fragile and bright yellow DU particles released during a fire at a DU ammunition storage facility. Crystalline phases such as schoepite ($UO_3.2.25H_2O$) and dehydrated schoepite ($UO_3.0.75\ H_2O$) and metaschoepite ($UO_3.2H_2O$) were also identified indicating the bio-accessible nature of the DU. Strawn and Baker[277] studied the molecular characterisation of copper in soils using similar X-ray absorption spectroscopy. The μ-XRF results indicated that the majority of the Cu particles in the soils were not associated with calcium carbonates, iron oxides or copper sulfates. PCA analysis of the XANES and EXAFS data suggested that Cu adsorbed by humic acid was an acceptable match. Therefore, the authors concluded that Cu in all the soils under investigation was primarily associated with soil organic matter. Theoretical fitting of the molecular structure in the soil EXAFS spectra revealed that the Cu existed as Cu atoms bound in a bidentate complex to O and N function groups. Sussulini *et al.*[278] evaluated EDXRF and PCA for the qualitative analysis of artificial powdered fruit juice mixes. In particular X-ray scattering data, in the 18 to 24 keV region, were combined with PCA to distinguish the samples with and without sweeteners in their composition. Furthermore, two different artificial sweeteners (aspartame and cyclamate) were detected.

9.3.2 Aerosols and particles. The following five papers clearly demonstrate that significant advances have been achieved with XRF techniques enabling researchers to report work on the *elemental analysis of single particles*. Sun *et al.*[279] used μ-XRF based on a slightly focusing, polycapillary lens and X-ray tube excitation to produce a focal spot with a diameter of about 65 μm. Their configuration enabled them to report data from a single particle in which the elemental distribution was not uniform. A minimum detection limit of 15 μg g^{-1} was reported for Fe Kα. The origins of particulates collected at the exit of a subway station and a construction site were apportioned. Li *et al.*[280] used μ-SRXRF to analyse individual PM 2.5 particles collected from Shanghai air during the winter of 2007. Eight categories of emission sources were recognised with most derived from vehicle exhaust and metallurgical emissions. Another study by the Shanghai group[281] used the same sampling and analytical methods to report variations between day-time and night-time PM2.5 particles. Samples collected at night were approximately twice the mass of their day-time counterparts showing Cl, Cu, Mn and Zn enrichment. Czyzycki *et al.*[282] developed a Monte Carlo method to assess data from single particles analysed by a tube excited, μ-XRF system. The method was tested using glass micro-spheres of the certified reference material, NIST K3089 with diameters in the range 25–45 μm. Their results showed high dependence on particle size for low atomic number elements and that the root mean square of concentration uncertainty, for all elements present in the particle, increased with growing sample size. More accurate results were obtained for elements from Fe to Pb in the periodic table. Results obtained by the Monte Carlo method were compared with other analytical approaches. Day and colleagues[283] used an aircraft platform to collect single particles as part of the Intercontinental Chemical Transport Experiment-Phase B (INTEX-B) conducted over the eastern Pacific and western North America. Single particles were measured using NEXAFS and bulk sub-micrometre particles and organic functional groups and element concentrations were quantified by FTIR and XRF. The single particle spectra were classified and associated with different sources and atmospheric processing. Particles with spectra indicative of secondary organic aerosol and combustion sources were found at several locations and a range of altitudes. Particles from lower altitudes were found to resemble soil dust and biomass burning fingerprints. The single particle spectra provided evidence that condensation and surface-limited oxidation contributed to particle growth.

Coming back to Earth, children attending schools in the USA are exposed to *traffic-related air pollutants*, including health-related ultra-fine aerosols generated from school buses powered by diesel fuel. A study[284] was established in a mid-western (USA) metropolitan area to determine the concentration and elemental composition of aerosol in the vicinity of a school during the morning when bus traffic was especially intense. Simultaneous measurements were also performed at a control site. The ambient aerosol was first characterised in real time using a particle size selective aerosol spectrometer and then continuously monitored at each site with a real-time, non-size selective instrument that detected particles ranging from 20 nm to > 1 mm. In addition, air samples were collected with PM 2.5 Harvard Impactors and analysed for 38 elements by XRF and for carbon by thermal-optical transmission. Measurements were taken in March when

the ambient temperature was around 0 °C and in May when it ranged mostly between 10 and 20 °C. The data collected in this case study suggested that school buses significantly contribute to the exposure of children to aerosol pollutants in the vicinity of schools. In a second American study[285] daily exposure to traffic-related fine particulates and their sources were associated with an increased risk of symptoms and inhaler-use in children suffering from asthma. In the USA, national air quality particle standards consider total mass, not composition or sources and may not protect against health impacts related to specific components. The year-long study enrolled 149 children with asthma, aged 4–12 years. The particulate samples collected were analysed by XRF and by light reflectance for elemental carbon. Particle source apportionment, such as motor vehicle emissions, was identified using factor analysis and the children's symptoms and medication were recorded in a study diary. The results showed 42% of PM 2.5 was attributed to traffic-related sources and 12% to road dust. An increased likelihood of symptoms and inhaler use was largest when 3-day averaged exposures to traffic sources or their elemental constituents ranged from 10% expectation of wheeze for each 5 μg m^{-3} increase in particles from motor vehicles to a 28% likelihood of shortness of breath for increases in road dust. Clougherty *et al.*[286] examined the intra-urban variation in fine particle mass constituents using a geographic information system (GIS) and constrained factor analysis to derive latent source factors. They collected 3–4 day samples of NO$_3$ and PM 2.5 outside 44 homes in summer and winter from 2003 to 2005 in and around Boston, Massachusetts. Reflectance analysis, XRF and ICP-MS were used to measure particle filters for elemental carbon, inorganic analytes and water-soluble metal concentrations respectively. A five-factor model was reported to be optimal for the factor analysis, balancing statistical robustness and physical interpretability. The model produced loadings indicating long-range transport, brake wear/traffic exhaust, diesel exhaust, fuel oil combustion and suspended road dust. The authors offered their methodology for the evaluation of source contributions to outcomes in epidemiological studies. Buko-wiecki *et al.*[287] used a rotating drum impactor (RDI) to collect samples for analysis by SRXRF from an urban street and an inter-urban road in Switzerland. Their hourly measurements, enabling high temporal resolution, revealed that the effect of suspended road dust has to be taken into account for the calculation of vehicle exhaust factors. Individual values for light and heavy duty vehicles were obtained for stop-and-go traffic in the urban street. Mass based brake wear emissions were predominantly found in the coarse particle fraction. Antimony emissions on the inter-urban road, with free-flowing traffic, were significantly lower. It is interesting to note that the total aerosol mass of approximately 10 μg collected in such studies required an analytical approach with detection limits in the low ng range that was satisfied by SRXRF. Other work by this group[288] reported a modification to an RDI to obtain new midpoint cut-off diameters at 2.5 μm, 1 μm and 0.1 μm respectively. The analytical need was ably fulfilled with μ-SRXRF. Boman *et al.*[289] were interested in closed environments, such as a tunnel, where particulate matter is an important air pollutant. They determined mass, black carbon and elemental concentrations of particulates in two size fractions at an underground tram station in Gothenburg, Sweden. The samples were collected during June 2007

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using a dichotomous virtual impactor that separated the sampled particles into PM 2.5–10 and PM 2.5 fractions. The samples, collected on Teflon filters, were analysed by EDXRF, resulting in the identification of 14 elements in most samples. Possible sources were identified using PCA. On some days, the mass concentration was reported to exceed the Swedish daily ambient air quality standard of 50 μg m^{-3}, but was lower than the limits in the Environmental Work Act of 5 mg m^{-3}. In another study by Boman and colleagues,[290] PM 2.5 aerosols were collected to investigate the influence of winter thermal inversions on urban air pollution. The EDXRF data, local wind speed and direction and backward trajectories were used to investigate possible sources. The authors concluded that Br, Ni, Pb, S and V had their main sources outside the central collection area, since elevated concentrations of these elements were not observed during inversion episodes. Sea traffic and harbour activities were identified, primarily by the S and V content of the particles. Samek[291] presented results from a year long survey (2007–2008) on three particle size fractions collected in Krakow, Poland. The fine fraction consisted of particles below 2.5 μm, the medium between 2.5 and 8 μm, whilst the coarse particulates were above 8 μm. Ten analytes were correlated with meteorological parameters. During the winter months when the wind speed was low, the authors found that particulate matter remained in the air in higher concentrations but, nevertheless, was below permissible values specified by the EU.

Indoor dust was found to be an important route for human exposure to *brominated flame retardants* (BFRs) such as polybrominated diphenyl ethers (PBDEs) in two publications by Japanese workers. Suzuki *et al.*[292] used μ-XRF, digital optical microscopy and GC-MS to measure house dust collected from the interior of televisions. Bromine mapping was performed on dusts divided into particulates and fibres. Using a dwell time of 100 s, the resolution was sufficient to confirm the presence of Br in the dust coating. The authors suggested that Br was transferred from products to dust matrices not only through miniaturisation and subsequent direct migration into the dust as plastic and textile fragments but also *via* other pathways such as vaporisation and airborne transfer of micro-particulates. In the second paper, Takigami *et al.*[293] found high Br concentrations in dust on curtains and offered a preliminary estimation of the likely magnitude of inhabitants' exposure to polyhalogenated compounds *via* inhalation and dust ingestion.

In the United States, both the Environmental Protection Agency's (EPA's) Chemical Speciation Network (CSN) and the Interagency Monitoring of Protected Visual Environments (IMPROVE) network used XRF analysis to quantify trace elements in samples of fine particulates less than 2.5 μm in aerodynamic diameter (PM2.5). Reported *measurement uncertainty* values for the XRF data varied considerably amongst the participating laboratories reflecting instrument makes and models. Gutknecht *et al.*[294] developed a consensus model to harmonise these uncertainties and enable comparison within and between the monitoring programmes that was independent of the laboratories concerned and their XRF instrumentation. Factors such as variability in peak area, calibration, field sampling and attenuation of X-ray intensity for light elements were considered. The authors illustrated how the uncertainties reported by the CSN and IMPROVE network laboratories could be brought into good agreement. The proposed method should be applied at the time of data generation, but retrospective estimation of uncertainties in existing data sets was also possible. Niu *et al.*[295] considered measurement uncertainty in the evaluation of airborne particulate matter and metals data in personal, indoor and outdoor environments using EDXRF and ICP-MS. The assessment was made using co-located duplicate samples and showed good correlations between techniques for elements present in concentrations above their detection limits. Kellogg and Willis[296] considered problems associated with attempts to fit overlapping elemental spectral lines for many elements that may be undetectable in samples due to low concentrations. Fitting with many library reference spectra has the unwanted effect of raising the analytical uncertainty of the overlapping elements. The authors suggested that by carefully choosing the order of elemental processing, reference library spectra could be omitted for non-analyte lines of undetected elements without loss of information, thus lowering the number of library spectra needed for the fit and thereby reducing the uncertainty. This approach was demonstrated for blanks and a sample containing 64 elements. Formenti *et al.*[297] focused on the determination of aluminium in mineral dusts in their comparison between PIXE and particle induced gamma ray emission (PIGE) techniques. They found an under-estimation of the Al concentration determined by PIXE of up to 40% and compared it with results from a single calculation using basic physics and the size distribution of the collected aerosol. Similar attenuation was observed for Al, Mg and Si in samples analysed by EDXRF and WDXRF.

9.3.3 Consequences of industrial activity. Cement is an important component in repositories for low-level and intermediate-level *radioactive waste*. Mandaliev *et al.*[298] investigated neodinium uptake by hardened cement paste to develop an understanding of the immobilisation processes of trivalent lanthanides and actinides using μ-SRXRF, μ-XAS and SEM techniques. Samples were reacted over periods of time ranging from 15 min and 200 days. The μ-SRXRF and SEM data suggested preferential Nd accumulation in rims around "inner" calcium silicate hydrates. The data presented in this study has implications for an overall assessment of the safe disposal of trivalent actinides in cement-based repositories for radioactive waste. Ervanne *et al.*[299] determined ^{45}Ca and gamma-emitting radionuclides in cement from a nuclear power plant in order to estimate the activity of the long-lived ^{41}Ca isotope. Seven concrete samples, exposed to a varying neutron flux, were treated with HCl and HNO$_3$ for partial dissolution of calcium. Total stable calcium in the leachate was determined by XRF after separation using cycles of precipitation and ion exchange. In addition to ^{45}Ca, 17 gamma-emitting radionuclides were detected by gamma-spectroscopy. Two papers by Um and colleagues[300,301] characterised uranium phases in contaminated sediments below a nuclear waste storage tank in Hanford, Washington, USA. Sediments were collected from three boreholes after contamination, estimated to contain 7000 kg of dissolved U, that had seeped into the sub-surface after an accident that occurred whilst the storage tank was being filled. Again μ-XRF and μ-XANES were the techniques of choice to show that U was primarily associated with Ca and was predominantly U^{VI}.

The consequences of *mining activities* were studied by Guedron *et al.*[302] in their work on mercury speciation following mining for gold in French Guiana where Hg was used for amalgamation of the gold. A combination of XRD and μ-XRF were used to assess the soils and show that Au-amalgamated Hg and elemental Hg droplets could be differentiated. Degueldre *et al.*[303] also reported the benefits, in terms of precision and accuracy, of μ-XRF, μ-XRD and μ-XAS for an investigation of micro-crystalline and chemical structure of a radioactive zinc ferrite deposit phase formed on a zirconium dioxide substrate. Lattuada *et al.*[304] used TXRF for the determination of Cd, Fe, Mn, Ni, Pb and Zn concentrations in water and sediments impacted by coal mining in southern Brazil to show a clear relationship between the metal content and eco-toxicity.

Production of porous and light-weight bricks with reduced thermal conductivity and compression strength for the *construction industry* was reported by Sutcu and Akkurt.[305] Paper processing residues were used as an additive to an earthenware brick to enhance pore production. Mixtures containing brick raw materials and the paper waste were prepared in different proportions (up to 30% m/m). After compression and firing at 1100 °C, the bricks were characterised by SEM, XRF, XRD and TG-DTA. Preliminary brick production was then conducted on an industrial scale. Deposition, leaching and chemical transformation are processes that affect roofing tile and roof run-off water. Sulaiman *et al.*[306] used XRF to analyse exposed roof tile showing depletion of Al, K, Mg, P, Si and Ti at the surface of the tile and an enrichment of Fe and Mn, which hinted at a process akin to laterite formation. Wattanasiriwech *et al.*[307] presented the use of waste mud from ceramic tile production as a main component in paving blocks. The blocks were prepared by mixing the waste mud with Ordinary Portland Cement and water before compaction in a hydraulic press. The resultant blocks were characterised by XRF, XRD and SEM. Davis *et al.*[308] applied a commercial micro-beam X-ray fluorescence (μ-XRF) scanning spectrometer for performing large area elemental mapping of concrete samples. The aim of the work was to determine the penetration depth of ions from deicing salts into concrete. They determined the depth of ion infiltration over a distance of tens of millimetres. The research was part of a larger project on pavement durability. It is clear that during this review period the literature reflects the acceptance of complementary and efficient μ-X-ray techniques as powerful investigation methods for a variety of applications. Benard *et al.*[309] used μ-XRF, μ-XRD and μ-XAS to model the release of lead during weathering of Portland cement. Lead release was shown to be strongly related to its speciation. Molineux *et al.*[310] characterised four recycled materials that had been manufactured into useful substrates for use as green roof growing media. These were crushed red brick, used in the UK building industry as a standard substrate base and therefore used as a control and alternative pellets made from: waste clay, fly ash and sewage sludge, paper ash from recycled newspapers and carbonated limestone from quarry fines. Conifer bark compost was used as the organic content for plant nutrients. XRF and leachate analyses were used during the study which concluded that all the substrates have great potential in the green roof market. In Spain[311] XRF, XRD and SEM were used to characterise 53 raw materials containing phyllosilicates, from outcrops located between the provinces of Almeria and Granada, for possible use as waterproof layers under the floors of greenhouses. The WDXRF data generated 11 elements that were processed using a multivariate statistical approach and discriminating canon to isolate groups of phyllite samples with similar chemical profiles to assist in identifying potential waterproofing material.

Many industries are finding alternative and financially profitable uses for material that was previously considered as waste. Hu and Rem[312] reported such a *co-product* from municipal solid waste incineration bottom ash. With the increasing growth of incineration of household waste, more and more aluminium is retained in the bottom ash. Sampling and XRF analytical techniques were developed to determine which size fraction of the ash contained most aluminium for subsequent separation and reuse as an aluminium alloy. And finally in this section of the review, Abreu and Toffoli[313] reported their work on the characterisation of a chromium-rich tannery waste and its potential use in ceramics. XRF, XRD, TGA and DSC were all used to assess the waste which showed the tendency to produce some undesirable Cr^{VI}. However, after washing off the soluble salts and the elimination of organic matter by firing, the resultant material was successfully tested as a ceramic pigment for use in the production of conventional glazes.

9.4 Archaeological, cultural heritage and forensic

If the large number of papers available for review this year is anything to go by, quantitative scientific archaeology is really taking off with a sustaining contribution from XRF. Commencing then with the analysis of *paintings and pigments*. It has become common to use XRF, often complemented by Raman spectroscopy, to characterise the pallet of artists, and this year has seen further contributions in this field. Thus, Gautier *et al.*[314] characterised ready-mixed house paints used by artists such as Pablo Picasso in the first half of the twentieth century using FTIR, XRF and Raman. Measurements were made on historic paint sample cards from the collections of the Art Institute of Chicago and highlighted the dominance of zinc-based white pigments, consistent choice of particular pigments and the avoidance of others. However, the authors warned against use of a single chemical marker, but favoured identification of pigments based on a combination of parameters. Brostoff *et al.*[315] used XRF and μ-XRD to analyse the composition of pigments on a pastel drawing by the contemporary artist, Georgia O'Keefe and noted the use of lead and chromium-based pigments and calcium-based pastel fillers. Tanimoto and Verri[316] used XRF and Raman to examine 15th Century Italian metal point drawings that were found to be either silver or lead based in composition, images that were especially distinguished by the transparency of silver-based metal point drawings to IR radiation in the 800–1700 nm range. In combination with several other techniques, XRF was also used to characterise pigments used by the 15th Century French painter, Jean Bourdichon[317,318] and the 19th Century Brazilian painter, Rodolfo Amoedo.[319] Continuing to emphasise the importance of the multi-technique approach (often a combination of EDXRF, Raman and XRD), a number of studies were made of murals, to rediscover the pallet of earth pigments used in the Alentejo region of southern Portugal,[320] the origin and degradation of copper pigments found in

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Bohemian Gothic murals,[321] pigments and plasters used in Byzantine wall paintings from the Mani Peninsula, Greece[322] and mid 15th Century wall paintings from a chapel in the Aosta Valley, Italy.[323] In a more challenging application, de Viguerie et al.[324] investigated the use of XRF with fundamental parameters to reconstruct the composition and thickness of paint layers and found that on multilayer test samples, a maximum error in composition of 15% in thickness and 10% in composition was obtained. A slightly different object was studied by Kriznar et al.[325] in the examination of sculptures by Pietro Torrigiano, a well known Italian sculptor working in the first half of the sixteenth century. Two terracotta sculptures were analysed by XRF *in situ* and revealed modern restoration using Ti and Zn white to complement the original white lead (Pb), yellow and red ochre (Ca, Fe), cinnabar (Hg) and umbra (Mn, Fe), amongst others. These are a sample of the work in this area that has gone forward for publication in the present review period in which the use of XRF to detect elemental compositions has been accompanied by Raman or XRD to confirm the pigment type.

The *analysis of paper and manuscripts* was also an area of interest, including the development of a method by Alcalde-Molina et al.[326] for the determination of As and Hg in extracts from ancient papers by combining solid-phase extraction with EDXRF. Limits of detection were claimed to be 0.007 µg g^{-1} As and 0.006 µg g^{-1} Hg. A group from the University of Lisbon described the quantification of Hg in the ink used to colour some eighteenth century books by EDXRF,[327] highlighting for the first time, it was claimed, the hazard to restorers, conservators and collectors. The group extended this work to include a SRXRF microprobe and portable XRF study of the pigment vermillion in books from the eighteenth and nineteenth centuries and although high concentrations of Hg were found in the coloured borders of the books, no diffusion was observed to the inner parts of the paper.[328] XRF was also a contributing technique to other studies including air-induced paper discolouration in an eighteenth century book,[329] foxing stains in eighteenth and nineteenth century drawings[330] and as a subsidiary technique of the degradation of red lead in a medieval Portuguese manuscript.[331]

The *characterisation of glass* is another classical archaeological application and the current review period has seen a number of contributions in this area. Revenko[332] reviewed a number of relevant analytical issues including sample preparation, heterogeneity effects, matrix effects and the importance of characterising raw materials related to production. Schalm et al.[333] were interested in causes of degradation in stained glass windows incorporating blue and purple enamel paint layers using µ-XRF, EPMA and TEM. The authors concluded that some compositions appeared to be unstable, including those with high concentrations of K_2O and low CaO and PbO with deterioration of some paint layers caused by less than optimal vitrification of the enamel during the firing process. Alonso et al.[334] used a multi-technique approach to characterise 13th-14th century stained-glass windows of the Huelgas Monastery (Spain) and a multi-technique approach was also used by Sokaras et al.[335] to analyse an Archaic glass bead collection recently excavated from the city of Thebes (Greece) to identify raw materials and manufacturing technologies. A newly developed portable XRF spectrometer was used by Tantrakarn et al.[336] to analyse Roman glass artifacts on site. The particular feature of this instrument

was an enlargeable vacuum sampling chamber to facilitate the determination of the light elements Na and Mg and results from a Roman cemetery in Zadar, Croatia showed the use of natron as fluxing agent and differences in Mn and/or Sb as the decolourising agent. Smit et al.[337] distinguished two types of glass from artefacts excavated from the city of Lezha (Albania) based on the higher chemical purity of one glass and the use of As_2O_3 as decolorant, using data obtained by PIXE/PIGE and XRF. Portable XRF was the instrument of choice by Kato et al.[338] who studied 8th to 11th century Islamic glass vessels from the historically important trading port of Raya on the Sinai Peninsula, Egypt. The authors found variations in glass content between centuries but concluded that a fixed recipe was used in the production of glass from the 9th century.

Lithic artefacts especially in an archaeological context are also a commonly characterised medium, an application typified by the work of Gluhak and Hofmeister[339] who used major and trace element determinations by XRF to obtain geochemical signals from Roman millstones assumed to be from the Eifel region to elucidate trade patterns in Roman times. Geochemical discrimination and cluster and discriminant analysis was used to distinguish 13 well-known Roman basaltic lava quarries in the East and West Eifel volcanic fields and so to provenance millstones to a specific quarry with a specified degree of confidence. Linthout et al.[340] used petrographic and XRF analysis and $^{40}Ar/^{39}Ar$ dating to provenance basaltic blocks from Roman sites at Vleuten-De Meern, The Netherlands. The origin was deduced to be sites in Germany with transport facilitated by a now sanded up branch of the Rhine. Phillips and Speakman[341] were interested in the prehistoric mobility, exchange and social networking in the Kuril Islands, North Pacific Ocean based on evidence gathered from the portable XRF analysis of obsidian artefacts from 18 archaeological sites on the islands and speculated that the obsidian may have originated from sources on Hokkaido (Japan) or Kamchatka (Russia). Other obsidian artefact studies using XRF include those of Khalidi et al.[342] from sites in Northeast Syria and Niknami et al.[343] in Northwest Iran. IR and Raman spectroscopies and XRF were used by Olivares et al.[344] to characterise chert from the Basque Country to evaluate the way lithic artefacts could be used to trace the transport of chert artefacts from sources to final settlements.

Soil can preserve evidence of human habitation as shown by Oonk et al.,[345,346] who used XRF and ICP-OES to analyse a grid of samples from three archaeological house plans embedded in sandy clays from a site in The Netherlands. Geochemical signatures of human occupation were indicated by enrichments of Cr, Cu, Nd and Sn (all elements with no or weak relation to the lithology) and depletions in Fe and Mn. Geochemical patterns revealed the presence of an in-house barn at two sites. Interestingly, ICP-OES based on an HCl extraction of elements was not considered to give reliable data for this study. A comprehensive study of past human-climate-environment interactions in southern Morocco over the last 2000 years was undertaken by McGregor et al.[347] using XRF, particle size analysis and pollen analysis from two marine sediment cores. Detailed analysis of the results by the authors suggested that land degradation might have taken place over a longer period than previously thought and might be particularly sensitive to changes in land use. By contrast, Niemann and Behling[348] used XRF,

magnetic susceptibility scanning, and pollen, spore and charcoal analysis to evaluate environmental change in the Late Holocene period in the southeastern Ecuadorian Andes and documented human influence from the impact of past fires, and the relatively high occurrences of grasses and some plantations.

Bone provides incontrovertible archaeological evidence of human activity and Piga *et al.*[349] published an interesting study based mainly on XRD but with XRF contributions on human and animal fossil bones that date from the Middle Triassic (245 Ma) to the present. This study showed that the unit cell volume of monoclinic apatite varied over geological time due to substitution of fluorine for the hydroxyl group providing an alternative way of dating the fossil, although stratigraphic observations were recognised as the main reliable source of dating, because of various uncertainties in the proposed method. The SRXRF microprobe was one of a range of techniques used by Kuczumow *et al.*[350] to investigate chemical changes in bone material from South African fossil hominid deposits. Their aim was to establish the degree of preservation and the possibilities of inferring the life conditions from them.

Studies of pottery, ceramics and building materials are one of the longest applications of XRF and the power of combining results from portable XRF and XRD instrumentation was illustrated by the work of Abe *et al.*[351] who analysed pigments from blue-painted pottery and plasters produced in the New Kingdom, Egypt. These were identified as Egyptian blue and cobalt blue and results were interpreted to assess compositional transitions of the cobalt blue pigment with time. XRF and XRD combined with ED-SEM were used by Marghussian *et al.*[352] to analyse pottery samples from the fifth to the forth centuries BC from Rahmatabad, Iran and showed that high firing temperatures confirmed the adoption of specialised pottery making techniques. Adan-Bayewitz *et al.*[353] used several statistical techniques to evaluate INAA and high precision XRF data plus morphological data for cooking pots and bowls from two production locations in Roman Galilee, showing that samples from the two sites could be distinguished. Several other contributions similarly evaluated the source of pottery materials or aimed to elucidate some aspect of firing technology using XRF in combination with other techniques. Such studies included Neolithic painted pottery fragments from the Lumea Noua (fifth millennium BC) and other cultures in Romania,[354,355] potsherd samples from the archaeological site of Aiani, northern Greece,[356] Middle to Late Bronze/Early Iron Age ceramics from Didi Gora and Udabno I, eastern Georgia,[357] Late Cypriot Bronze Age plain white ware ceramics,[358] the glazes on sixteenth to nineteenth century ceramics from Coimbra, Portugal and ceramic fragments uncovered in excavations of a workshop in Tirana, near Seville.[359] The paper by Xenogiannopoulou *et al.*[360] indicated that the key role of XRF may not last for ever; these authors used LIBS for the qualitative and quantitative elemental analysis of black glazes and the main body of an ancient Attic black ceramic. Results showed that the glaze originated from the same clay, but processed differently, with LIBS data compared with results from more conventional techniques, including XRF. LIBS was also used by Brai *et al.*[361] with XRF as the reference technique to characterise building materials (bricks and mortar) sampled in the ancient Greek-Roman Theatre of Taormina. Combined results distinguished chemical features and the state of

degradation of these building materials. Bricks were also the subject of the study by De Francesco *et al.*[362] using XRD, XRF and optical microscopy to study 26 bricks from two buildings in the ancient city of Kaulon in Calabria, Southern Italy; results showed that the raw materials for all bricks were probably quarried locally. A rather more exotic range of techniques was used by Nakano and Tsuji[363] by combining grazing exit XRF and confocal 3D XRF to study Japanese lacquer-ware ('Tamamushi-nuri'). The 3D instrument used two independent polycapillary X-ray lenses and two X-ray sources (Cr and Mo anode tubes) to show the elemental distribution with depth, so demonstrating the layered structure of this lacquer-ware.

The *characterisation of metals* by XRF and increasingly in combination with other techniques can make significant contributions in a number of fields of archaeology. Thus, Harrison *et al.*[364] offered a new perspective on certain Iron Age and Archaic (1000–480 BC) Etruscan industrial and habitation sites and to investigate the problem of heavy metal poisoning, reported the first use of handheld XRF for the analysis of Etruscan hair. Their conclusions recognised the complex political and social reasons for the abandonment of several flourishing Etruscan settlements but suggested heavy metal contamination as an additional stimulus, based on their results which showed a strong likelihood of heavy metal poisoning in areas of metallurgical activity. In a contrasting study, Danevich *et al.*[365] used XRF and ICP-MS to support the study of archaeological lead from the wreck of a first century BC Greek ship found in the Black Sea – the principle aim of this study was to assess the radiopurity of this material. Iron production technologies were the interest of Iles and Martinon-Torres[366] in a study of furnace and production refuse sites on the Laikipia Plateau, Kenya, dating from the second half of the second millennium. This work investigated the consistency in technological style between the smelting sites in a broad socio-cultural sense based on the analysis of slag residues by ED-SEM and EDXRF. Each year, coins attract XRF interest, as represented this year by the contribution of Constantinescu *et al.*,[367] who examined medieval silver coins of Moldavian origin by PIXE and EDXRF and Xia *et al.*[368] who employed XRD as well as XRF to characterise several brass coins of the Qing dynasty. Compositions indicated a high degree of competence in brass technology. The significant degrees of corrosion were attributed to the high chlorine content in the local environment. Additional studies included the characterisation by SRXRF and laboratory XRF of Spanish baroque and modern organ pipes,[369] copper-based finds known as the 'Fucino bronzes', which were discovered during the drainage of Lake Fucino at the end of the XIX century[370] and portable XRF analysis of bronze objects from the hoard of San Francesco found near Bologna, Central Italy. Preliminary measurements did not identify a clear correlation between composition and destination of use.[371]

As well as the identification of materials and techniques and provenancing studies, XRF has an important role to play in *characterising the deterioration and conservation of cultural objects*. Thus, Herrera and Videla[372] review the use of a wide range of techniques, including XRF, available to assess weathering and biodeterioration of stone buildings, metallic artefacts, pigments, *etc.*, including the use of molecular biology techniques to identify the microbial components of biofilms. XRF was used

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to support a study by Varvara et al.,[373] who evaluated the effectiveness of some amino acids in solution as corrosion inhibitors. Mircea et al.[374] used the SEM technique, supported by XRF to investigate the impression on textiles caused by the corrosion crust on metallic fragments discovered in cremation and inhumation graves from the second and third centuries AD. Restoration of paint and drawings on ancient Chinese architectural structures was of interest to Wang et al.[375] These authors undertook a detailed investigation of the green pigments using XRD, XRF and ED-SEM and found the presence of both emerald green and modern organic pigments, but not malachite or atacamite, green pigments known to have been used in ancient times. This observation was associated with the need to repaint these architectural structures at least every 50 years because of the detrimental effects of sunlight and rain. The analysis of paints and pigments has attracted interest in a significantly wider range of applications, including a PXRF investigation of painting techniques on early Meissen stoneware,[376] identifying the broad range of pigments used on polychrome prints representing famous painters such as Albert Durer,[377] the use of EDXRF and other techniques in the conservation of a German house altar with seven reverse paintings of oil on glass[378] and an EDXRF study[379] of imperial porcelain from the Chenghua period (1465–1487) where damaged colour ('chazi') effects were originally attributed to defects associated with the original firing process, but were shown by this study to have been caused by a fire at the Jianfu Palace in the Forbidden City in 1923. In addition, Van der Snickt et al.[380] characterised the degradation of cadmium yellow pigment on oil paintings of James Ensor (1860–1949) by μ-XANES and μ-XRD (and other techniques) and demonstrated the oxidation of cadmium sulfide to hydrates cadmium sulfate and ammonium cadmium sulfate. This oxidation and secondary reaction with ammonium was found to have penetrated into the yellow paint down to a depth of 1 to 2 μm leading to a fading of the originally bright yellow areas. Of relevance to all these studies is a contribution from Namowicz et al.[381] in promoting standard working practice in the application of XRF to works of art and cultural heritage materials. The authors reported results from the most recent (2008) round robin evaluation of 25 laboratories participating in the analysis of 13 modern and traditional pigments on canvas and results were evaluated in terms of the challenges associated with peak overlap and sum peak effects, layering/shielding effects, the detection of low-Z elements and modern pigments.

The *analysis of wood* is an interesting and novel application and is illustrated by the work of Nagyvary et al.,[382] who used a combination of techniques (SEM, WDXRF, EDXRF, EPMA) to answer the question whether or not the wood of Stradivari and Guarneri antique violins were treated with wood preservative materials. Unmistakeable signs of chemical treatment were identified from the presence of $BaSO_4$, CaF_2, borate and $ZrSiO_4$ contributing to an understanding of why all attempts to recreate a Stradivarius from natural wood have failed. An SR X-ray microprobe, ICP-OES and ICP-MS were used by Pearson et al.[383] to investigate why the most serious anomaly in the Aegean dendrochronological record over the last 9000 years occurs in the mid 17th century BC and has been speculatively linked to the impact of the volcanic eruption of Thera (Santorini). Results from the analysis of growth rings demonstrated the increased presence of Ca, REE and S following the onset of altered growth with Hf and Zn spikes in the affected growth ring. Although these data were interpreted as supporting a volcanic association, they were not sufficient to confirm a link to a specific event.

XRF has also an important role to play in *forensic analysis*, as reviewed by Bell,[384] who emphasised the role of forensic chemistry to satisfy the needs of the scientific and legal communities. One popular forensic application is in the detection of forgeries, an area illustrated by the report of Burgio et al.[385] into five miniatures by the so-called 'Spanish Forger', which were believed to be authentic medieval miniatures until the mid-twentieth century. A comprehensive analysis of pigments by Raman microscopy and XRF showed the presence of traditional pigments (vermillion, carbon black, red lead, lead white and indigo), but also more modern chrome yellow, Scheele's green, emerald green and ultramarine blue providing a scientific basis for confirming them as forgeries. Authentification of Dacian gold bracelets was achieved by Constantinescu et al.[386] by using μ-PIXE and μ-SRXRF to determine Cu, Hg, Pb, PGE, Sb, Te in placer and primary Transylvanian gold. The detection of counterfeit bank notes was of interest to Rusanov et al.[387] on the basis of Moessbauer and XRF spectroscopies, studies that indicated many banknotes are printed with pigments containing significant amounts of iron. The discrimination of multipurpose office paper was of interest to van Es et al.,[388] who investigated the discriminating powers of XRF, LA-ICP-MS and isotope ratio MS. Turning now to the more criminal end of forensic applications, Sano and Suzuki[389] described an unusual case where μ-XRF was one of a group of techniques (with micro-spectrometry for colour analysis and μ-FTIR) used to link artificial leather fragments from a hit and run victim's bag with fibres recovered from the bumper of the suspect's automobile. This combination of techniques offered a high degree of discrimination when evaluated across a wide range of artificial leather samples from different manufacturers. Scheid et al.[390] evaluated the use of LA-ICP-MS, INAA and XRF to demonstrate the value of these techniques in the forensic analysis of brick stones based on principal component analysis and cluster analysis of elemental data. In a different type of forensic application, portable XRF was used by Imm et al.[391] to measure Br in upholstered furnishings, bedding, vehicle interiors and electronic devices in a study of human exposure pathways to polybrominated diphenyl ethers (PBDE) in 38 households in Wisconsin, USA. Data was complemented by GC measurements on air samples, vacuum cleaner contents and blood serum and the overall conclusion reached by the authors was that sleeping pillows and primary vehicle cushions were the strongest predictors of blood serum PBDE contamination.

9.5 Industrial

The frequent use of the XRF technique, combined with other analytical methods, for the characterisation of *ceramic building products*, *catalysts*, *alloy analysis and cements* is reaffirmed in this year's review. A broad range of these applications can be consulted in our companion ASU review on Industrial analysis: metals, chemical and advanced materials.[5] Nevertheless, a number of prominent papers are discussed in this review.

In a Chinese contribution,[392] the growing demand for a fast quantitative determination method for Fe and P in *co-catalysts* for maximum propylene production was addressed by the implementation of an XRF method using powder pellets. Calibration samples were manually synthesised and the matrix effects were corrected by the empirical coefficient method. With concentration ranges of 0.01% m/m up to 2.5% m/m for both Fe and P, and a measurement time of only 5 min, a relative deviation of 0.59% for Fe and 0.34% for P, respectively, was obtained. Satisfactory accuracy and high precision, less interferences, easy sample handling and efficiency, underlined the benefits of the XRF method compared to other analytical techniques.

The XRF technique is frequently used for the determination of the elemental composition of *fly ash*. Zhao et al.[393] used XRF in combination with field scanning electron microscopy-energy dispersive X-ray analysis and XRD to gain insight into the formation mechanism of high-calcium fly ashes from a coal-fired power plant. The occurrence of Ca in coal was determined using sequential extraction tests. These results demonstrated that CaO and $CaSO_4$ were mainly derived from the original calcium-bearing minerals in coal, whereas the observed Ca–Al–Si and Ca–S–X (X: Al, Fe, Mg, Si, *etc*) compounds were formed by the secondary reaction of CaO and $CaSO_4$. Provis et al.[394] investigated the nanoscale distribution within fly ash and the aluminosilicate gels products of its alkaline activation by means of SRXRF using a hard X-ray nanoprobe instrument. The distribution of Ca within a hydroxide-activated (fly ash/KOH solution) geopolymer gel was seen to be highly heteregeneous, with these data providing, for the first time, direct evidence of the formation of discrete high-calcium particles within the binding structure of a geopolymer synthesized from a low-calcium (<2 m/m% as oxide) fly ash. The silicate-activated (fly ash/potassium silicate solution) sample, by contrast, showed a much more homogeneous geopolymer gel binder structure surrounding the unreacted fly ash particles. Additionally, Cr and Fe were seen to be very closely correlated within the structures of both fly ash and the geopolymer product and remained within the regions of the geopolymer that could be identified as unreacted fly ash particles. Given that the potential for Cr release had been one of the issues surrounding the widespread utilisation of construction materials derived from fly ash, the observation that this element appeared to be localised within the fly ash rather than dispersed throughout the gel binder, indicated that it is unlikely to be released into the environment.

Micro-XRF analyses in combination with XRD and X-ray absorption fine structure (XAFS) were used by a French research group[309] to determine Pb and, thereby the development of a model for the molecular release of Pb within Portland *cement* leaching. As Pb release is strongly related to its speciation (*i.e.*, atomic environment and the nature of bearing phases), the evolution of Pb retention sites together with the evolution of the cement mineralogy during leaching was investigated. Combined results indicated that in both the unaltered core and the altered layer of the leached cement, Pb^{II} would be retained through C–S–H nano-structure. Moreover in the altered layer, the presence of Fe atoms in the atomic environment of Pb was highly probable. Modelling results were consistent with Pb retention through C–S–H in layers and also in an additional, possibly Fe-containing, Pb-retention phase in the altered layer.

The application of the XRF technique within the framework of *Restriction of Hazardous Substances* (*RoHS*) *and Waste of Electric and Electronic Equipment* (*WEEE*) *regulation* is a recurrent issue in this yearly review. Ma et al.[395] presented the results of an international comparison study for the determination of the mass fraction of Cd, Cr, Hg and Pb in polypropylene using a broad range of analytical techniques (IDMS, ICP-MS, ICP-OES, INAA and also XRF). The median values of Cd, Cr, Hg and Pb, calculated from the results of 21 laboratories, were 26.1 ± 0.5 mg kg^{-1}, 253 ± 3 mg kg^{-1}, 387 ± 10 mg kg^{-1} and 466 ± 9 mg kg^{-1}, respectively. Comparing the results of all methods, those of IDMS showed the less spread amongst the laboratories and had a smaller uncertainty, moreover the results of XRF and INAA reflected a satisfactory agreement with the median values. Dimitrakakis et al.[396] investigated the presence of hazardous substances in plastics from electric and electronic waste using both handheld XRF and AAS. At first, a broad range of samples (n = 161) was screened using the handheld XRF in order to obtain a representative overview of the range and concentration of the additives in small WEEE plastics. As would be expected, the mass fraction of these additives can vary over a wide range. Based on the XRF results, 51 samples with measurable concentrations of the 4 RoHS restricted heavy metals were selected for further AAS measurements. These results showed a mean value of 17.4 mg kg^{-1} for Pb, 5.7 mg kg^{-1} for Cd and 8.4 mg kg^{-1} for Cr over all the samples which was significant lower as the prescribed limits. Moreover, the authors pointed out the lack of suitable reference materials for calibrating the handheld XRF for screening EEE plastics or complex electr(on)ic components. The reviewers can confirm that the development of new reference materials for such applications is indeed a challenge and an opportunity for the analytical community. In a complementary study, Hua et al.[397] demonstrated that the EDXRF technique was a very useful screening tool to verify the presence (or absence) of the element Cr with regards to the RoHS regulation. To further identify the valent state of the measured Cr (*i.e.*, Cr^{VI} or Cr^{III}) a spot test was applied and, subsequently, an alkali digestion was performed followed by UV-VIS spectrophotometric analysis to determine the Cr^{VI} content quantitatively.

The implementation of XRF in the *characterisation of waste* is a growing market as reflected in a number of interesting contributions. Gonzalez-Fernandez et al.[398] used EDXRF with tri-axial geometry for *in situ* checking of the Pb content in various fractions of automotive shredder residues to comply with the legislation for end of life vehicles. Matrix effects were compensated using incoherent (Compton) scattering radiation. With a measurement time of 1000 s, a limit of detection of 1.1 mg kg^{-1} was obtained. The fast and easy-to-handle XRF measurements revealed that the Pb content was the highest (11600 mg kg^{-1}) in the finest fraction (less than 125 μm) compared to the coarse fraction (between 2 and 6 mm) with a Pb content of 4600 mg kg^{-1}. Khezri and Bloorchian[399] determined the TiO_2 content in paint sludge from the automotive industry using XRF combined with XRD and differential thermal analysis. Recovery of this compound would provide an economic benefit and, therefore, the authors developed an extraction method. The results showed that the sludge contained about 34% m/m TiO_2 which could be extracted with 89.8% purity. In a simulated (inactive) nuclear waste glass the microscopic distribution and

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speciation of Cs, Mg, Na and Ni were studied by Curti et al.[400] using μ-XRF and μ-XAS, after aqueous leaching over 12 years at 90 °C (definitely a long-term study!). The Na–Mg μ-XRF maps revealed that the core regions of the glass fragments were apparently unaltered and compositionally homogeneous, whereas rims and interstitial spaces were enriched with Mg-rich smectite formed during the leaching process. Micro-EXAFS and μ-XANES analyses at the Ni K-edge revealed three distinct Ni(II) species: (a) Ni uniformly distributed in the glass matrix, representing the original coordinative environment of Ni in the glass; (b) micro-inclusions with high Ni concentrations, reflecting structural Ni in trevorite ($NiFe_2O_4$) and (c) Ni associated with the Mg-clay, assumed to correspond to the specific adsorption or incorporation of Ni into the lattice of tri-octahedral Mg-clay minerals. Further aqueous concentration data were used to calculate the speciation of the leachate.

Vanadium (V) *speciation* analysis in lead or scales associated with lead-line pipe corrosion of drinking water distributions systems was performed by Gerke et al.[401] A range of synchrotron-based techniques, including bulk XANES, μ-XANES, μ-XRD and μ-XRF mapping were employed along with traditional powder XRD, ED-SEM and ICP-OES to evaluate vanadium speciation and distribution in these deposits. Vanadinite ($Pb_5(VO_4)_3Cl$) was positively identified, and occurred most frequently in the surface layers (in contact with water). A low total content of V in these waters was thought to be the limiting factor in the abundance of vanadinite in the pipe scales, along with the existence of divalent Pb. The occurrence of V in these samples as a discrete mineral is important because it is formed in the presence of very low concentrations of V in the water, and provides a mechanism to concentrate μg L^{-1} amounts of V in the water to near-percent levels in the pipe scales.

A preconcentration methodology was applied by Teixeira et al.[402] to determine indirectly chloride and sulfate ions in *ethanol fuel* by EDXRF. The analytes were precipitated as silver chloride and barium sulfate and collected on a paper filter. Subsequently, XRF analysis was performed directly on the filter by measuring the Ag and Ba spectral lines to determine the concentration of chloride and sulfate ions. The precisions calculated from 20 consecutive measurements and defined as the coefficient of variation of standard solutions containing 1.0 μg mL^{-1} of Cl^- and SO_4^{2-} were 7.3% and 5.9%, respectively. The limits of detection defined as three times the standard deviation of a blank (n = 10), were found to be 25 μg L^{-1} and 30 μg L^{-1} for Cl^- and SO_4^{2-}, respectively.

Seifert et al.[403] reported a *synchrotron-based investigation* of Fe precipitation in multicrystalline silicon using X-ray beam induced current, μ-SRXRF and μ-XAS. The samples were intentionally contaminated with Fe and annealed at temperatures between 850 and 1050 °C. Annealing at 950 °C resulted in detectable Fe precipitation inside the grains and at the grain boundaries. Only small Fe clusters were detected when annealing at 850 °C while no Fe clusters were found after the 1050 °C treatment. XANES analysis of the Fe clusters revealed mostly iron silicide and in one case iron oxide. Under the given condition at the beamline, the detection sensitivity for Fe was estimated to be 4×10^7 atoms, corresponding to a spherical $FeSi_2$ particle of 40 nm radius. The characterisation of a carbon nanotube fibre using synchrotron radiation microbeam small- and wide-angle

X-ray scattering in combination with micro-fluorescence was published by Davies et al.[404] The results revealed that a fibre consisted of highly oriented nanotube bundles and non-oriented carbonaceous material. Within the oriented component there was variable orientation distribution and evidence of differences within the nanotube packing. From their wide-angle X-ray scattering signal and the particulate distribution image, single catalyst crystallites were located within the fibre. Simultaneous combination of Raman with XAS was applied by Vantelon et al.[405] to provide complementary chemical and structural information for the discrimination and characterisation of chemical phases in heterogeneous materials at the micrometer scale.

In the research related to *nuclear fusion* Patterson et al.[406] applied X-ray microtomography (μ-CT) and confocal microbeam X-ray fluorescence (μ-XRF) to render three-dimensional (3D) density profiles and elemental distributions of fusion targets prepared in the form of a beryllium ablator capsule sputtered and graded doped with copper and argon.

Finally, the WDXRF technique was applied by Perez and Leon[407] to determine bromine as an indication of pre-baking bromate-addition in *bread*. Measurements were performed directly on the solid sample. After calibration, results showed a low detection limit and a high sensitivity to distinguish precise Br concentrations that exceeded natural Br levels.

9.6 Clinical and biological

Metallomics is an emerging field featured in a number of scientific contributions during this review period. Two reviews[408,409] were presented focussing on metallomic analytical techniques including XRF. The first review discussed the so-called hyphenated techniques which combine a high-resolution separation technique (gel electrophoresis/laser ablation, chromatography or capillary electrophoresis) with a highly sensitive detection method such as elemental (inductively coupled plasma) or molecular (electron spray ionisation or matrix-assisted laser desorption/ionisation) mass spectrometry, or nuclear X-ray fluorescence/absorption spectrometry. The second contribution made a particular emphasis on the role of Cu in vascular diseases. Kehr et al.[410] used X-ray fluorescence microscopy to visualise and quantify the tissue, cellular, and subcellular topography of Se to reveal the role of Se in spermatogenesis. A dramatic Se enrichment specifically in late spermatids was identified, due to elevated levels of the mitochondrial form of glutathione peroxidase 4, which was completely dependent on the supplies of Se by selenoprotein P. High-resolution scans revealed that Se concentrated near the lumen side of elongating spermatids, where structural components of sperm are formed. During spermatogenesis, maximum Se concentrations were associated with decreased phosphorus, whereas Zn did not change. In sperm, Se was primarily in the mid-piece and co-located with Cu and Fe. XRF microscopy allowed quantification of Se in the mid-piece (0.8 fg) and head (0.2 fg) of individual sperm cells, revealing the ability of sperm cells to tollerate amounts of this element well above its toxic levels.

Synchrotron-based methods were compared to ion beam and mass spectrometry for direct analysis of *metalloproteins* in electrophoresis gels. XAS techniques and genetic methodologies

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were integrated to explore Cs-tolerance in Arabidopsis.[411] The authors characterised the genetic and phenotype of a T-DNA insertion mutant line of *A. thaliana* (*L.*) *Heynh* selected for Cs resistance when germinated and grown on Cs concentrations up to 600 μM that is lethal for the wild type. In order to investigate the Cs speciation and to measure the Cs content of living plants, the determination of the concentration and the localisation of Ca, Cs, and K was conducted on plants grown *in vivo* utilising μ-SRXRF and μ-XANES. A comparison between wild type and mutant plants led to the conclusion that a single gene mutation impaired the Cs uptake and translocation, and produced Ca and K homeostasis in the plant biomass. Ortega *et al.*[412] discovered Co distribution in keratinocyte cells indicating nuclear and per-inuclear accumulation and interaction with Mg and Zn homeostasis. Contact dermatitis and occupational skin damage within the nuclear industry is induced by Co at high concentrations. The authors reported their investigation of the intracellular distribution of Co in human adult low calcium temperature (HaCaT) keratinocytes as a model of skin cells, and its interaction with endogenous trace elements. For the first time μ-SRXRF in tomography mode was performed on a single cell to determine the 3D intracellular distribution of Co. Results obtained with these micro-chemical techniques were compared to a more classical method based on cellular fractionation followed by ICP-OES measurements. Cobalt was found to accumulate in the cell nucleus and in perinuclear structures indicating the possible direct interaction with genomic DNA and nuclear proteins. The perinuclear accumulation in the cytosol suggested that Co could be stored in the endoplasmic reticulum or the Golgi apparatus. The multi-elemental analysis revealed that Co exposure significantly decreased Mg and Zn content, with a likely competition of Co for Mg and Zn binding sites in proteins. Overall, these data suggested a multiform toxicity of Co related to interactions with genomic DNA and nuclear proteins, and to the alteration of Mg and Zn homeostasis. In another contribution, Ortega *et al.*[413] reported bio-metals imaging and speciation in cells using proton and μ-SRXRF. The potential for these methods in biomedical investigations was illustrated with examples of application in the fields of cellular toxicology, and pharmacology, bio-metals and metal-based nano-particles.

Trace element concentrations and their distribution in healthy and neoplastic breast *cancer tissue* samples were investigated by da Silva *et al.* in two contributions. The first[414] described the use of mono-energetic SRXRF to determine the concentration of Ca, Cu, Fe and Zn in 26 neoplastics and 26 adjacent normal tissues, using the scattered radiation from each sample as the internal standard to construct calibration curves for the elements of interest. Elevated concentrations of these elements were observed in neoplastic breast tissue, of which Cu and Fe as well as Ca and Zn levels were correlated in malignant breast tissue. These findings confirmed the hypothesis of their connection with the formation of neoplasies in breast tissue. In the second contribution,[415] TXRF was used to determine Ca, Cu, Fe, Ti and Zn in normal, normal adjacent, benign and malignant breast tissues. Except for Ti, elevated concentrations were observed in both benign and malignant tissues, with a higher Fe content in malignant tissues compared to benign neoplastic tissues, and with an opposite behaviour for Ca, Cu and Zn. Multivariate discriminant analysis was able to successfully identify differences

between trace element distributions in normal and malignant tissues with an overall accuracy of 80% and 65% for independent and paired breast samples respectively, and of 87% for benign and malignant tissues. Moreover, Pereira *et al.*[416] used X-ray fluorescence and transmission microtomography to determine the elemental distribution map of breast tissue samples to verify their concentration levels with pathology. Zinc was the element of interest for Podgorczyk *et al.*,[417,418] who studied its presence in native tissues and cultured cell lines of human prostate by SRXRF and XANES. To understand the aetiology of prostate cancer on molecular level, attention was paid to the unique capability of prostate epithelial cells to accumulate zinc. The latter plays a role in a wide range of cellular processes such as the function of the immune system, angiogenesis or apoptosis. The authors reported Zn concentration and oxidation level in the samples of human colon cancer tissues and cultured human prostate cell lines aided by X-ray bioimaging. The dependence of the Zn concentration upon histological status of tissue (healthy, hyperplastic or cancerous) was discussed. Trunova and Zver-eva[419] studied the distribution of macro and micro-elements in myocardium and vessel samples from cardiosurgery patients. Studies of the imbalance of chemical elements in myocardium of patients with all ischemic heart disease and aortic aneurysm are very important as predictors of irreversible changes in damaged tissues. SRXRF was used to analyse tissue samples up to 1 mg taken during surgery (biopsy).

The XRF technique was often implemented in the framework of *osteoporotic studies* to determine the Ca and P content. Hubler *et al.*[420] evaluated the effect of low-level laser therapy on the biomodulation of newly formed bone after distraction osteogenesis performed on rabbits. XRF determination of Ca and P revealed greater mineralisation in the treated group. Rabionet *et al.*[421] evaluated the use of synthetic hydroxyapatite, a bone growth stimulator, on porous stainless steel substrates as a biocompatible medical implant. By employing SRXRF, the intracellular distribution and concentration of osteoblast-like cells on the fabricated implant could be determined, showing a significant increase in the total Ca content. The SRXRF microprobe was also applied by Yang *et al.*,[422] who evaluated anti-osteoporosis in ovariectomised Wistar rats treated with antler blood. These experiments showed that loss of the elements Ca, P, Sr and Zn was closely related to the bone mineral density reduction in ovariectomised rats; moreover, the relative contents of Ca, P and Zn could only be normalised by antler blood treatment.

Moroz *et al.*[423] investigated micro-elemental and mineral compositions of pathogenic biomineral concrements by SRXRF, SRXRD, infrared and Raman spectroscopy to determine the composition of kidney stones, gallstones and salivalities from natives of Novosibirsk and Novosibirsk region, Russia. The relationship between mineral, organic and micro-elemental composition of pathogenic calculus was shown.

Nicolis *et al.*[424] presented a mini-review of the medical use of arsenite to treat leukaemia, its mammalian metabolism, its elimination and pharmacokinetics and the application of *hair analysis* as a biomonitoring tool. Additionally, the authors presented their own results by SRXRF to determine the arsenic content in hair samples of patients treated with arsenic trioxide, μ-XRF cartography on thin hair slices to obtain distribution

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maps of As, and μ-XANES to verify that inorganic As was incorporated in the hair samples in its trivalent oxidation state. Asian researchers[425] analysed hair samples of patients with dementia using XANES and WDXRF. Elevated amounts of Ca, Cl and P were detected in dementia patients relative to normal persons, but XANES analysis revealed that in both groups the same chemical from was present namely $CaCl_2$ and PO_4^{3-}. Sulfur, on the other hand, was always present at the same concentration level, but in hair from dementia patients the sulfate form was accumulated in significantly higher levels. Kempson et al.[426] determined As in taxidermy specimens to aid in discriminating its use as a preservative from that incorporated by ingestion and hence indicate poisoning. The presence of As was verified using TOF-SIMS and quantified by INAA to be 176 mg g^{-1} in one particular sample. Micro-SRXRF of hair cross sections proved that As had significantly penetrated all hair samples, whereas XANES measurements identified predominantly arsenate species. These findings suggested that only longitudinal distributions of hair samples and chemical speciation might allow differentiation.

The synchrotron rapid-scanning XRF (RS-XRF) technique confirmed the ability of this technique to be used for the localisation and quantification of *heavy metals in brain slices*. Popescu et al.[427] applied this technique to map Cu, Fe and Zn in spinal cord and brain tissue in a patient suffering from spinocerebellar ataxia. Abnormal metal distributions were measured compared to a control. The authors recognised the need for further research and indicated that if these findings were confirmed, Cu, Fe and Zn should be considered as possible therapeutic targets. In another contribution by the same group,[428] simultaneous mapping of Cu, Fe and Zn in the normal cerebellum was performed using RS-XRF to gain insight in the natural metal distribution, which could be seen as a first step towards understanding how multiple metals could play a role in the neurodegenerative process. The results showed that cerebellar white and grey matter could be clearly defined, based upon the unique metal content of each region. The dentate nucleus was particularly metal-rich with Cu localised at the periphery and the Fe and Zn abundance central.

The analysis of *trace elements relevant to nutrition* in human blood and serum was performed by TXRF, whereby the authors[429] focused on the development of less time-consuming sample preparation techniques. Whole blood and serum samples were diluted with ultrapure water and 10 μL of internally standardised sample was transferred to an unsiliconised quartz glass sample carrier with subsequent drying in a laboratory oven. Using this preparation method, the optimal TXRF analysis could be performed for the determination of Cu, Fe, Se and Zn with a measurement time of 600 s. Enhanced sample preparation using microwave or open digestion improved the detection limits, but for routine analysis the dilution preparation method was found to be suitable. Kaulich et al.[13] demonstrated, in two pilot experiments, new opportunities for low-energy fluorescence microscopy in bio-related research. The structural and compositional enrichment, distribution and correlation of essential trace elements in the lorica of *Tintinnopsis radix*, and the lateral distribution of trace nutrients in the seeds of wheat *Triticum aestivum* was investigated. Gothankar et al.[430] estimated the daily intake of Mn at a proposed uranium mining area (India), to act

as a biokinetic parameter for the local population and to be used as a baseline to monitor the conditions during proposed uranium mining. EDXRF analysis of different types of local foodstuff for the determination of the Mn concentration level revealed that cereal is a major source (86.2%) of the supply of Mn through diet. Garlic chives showed the highest concentration of Mn followed by French beans and cereals. The dietary intake of Mn was found to be 3.83 ± 0.25 mg day^{-1}, which is in the range of Recommended Dietary Allowances of 2 to 5 mg day^{-1}.

For the monitoring of the metals Cr, Fe, Ni and Zn in *active pharmaceutical ingredients* (API) a simple and rapid method based on the direct analysis of the solid sample by WDXRF spectrometry was developed and validated.[431] Results showed that the matrix of these APIs (*i.e.*, neutral organic compound or sodium salt) significantly influenced the determination of metals by WDXRF spectrometry and had to be taken into consideration when preparing the synthetic calibrants. The validated method proved to be sufficiently specific, selective and sensitive to fulfill the rigorous limit requirements of the current European legislation. Novikova et al.[432] published their results from an investigation into the molecular mechanisms for interaction of chelating drugs on protein-lipid model membranes by SRXRF. State-of-the-art X-ray techniques were used to develop new methods for the *in vitro* evaluation of the efficiency of drugs, providing differential data on their actions.

A Brazilian research group used μ-XRF to investigate the effects of laser irradiation on *dental components*. Soares et al.[433] performed the μ-XRF mapping of Ca and P in bovine incisor specimens in which the dentin surface was stored and treated in a number of different ways. The mapped data covering an area of 80×60 points with steps of 20 μm supported the hypothesis that etching with phosphoric acid on dentin produced a more chemically homogeneous surface than Er:YAG laser etching and thus a more favourable surface for the diffusion of adhesive monomers. De Sant'Anna et al.[434] irradiated dental enamels with a low-level infrared diode laser and photo-absorbing cream as a simple and non-invasive caries preventative treatment. The μ-XRF mapping of Ca and P demonstrated compositional changes in mineral phases of laser treated enamel designed to prevent caries. The results suggested that with a combined treatment involving laser and a photo-absorbing agent, it was possible to disorganise the organic content in the tooth enamel due to hydroxyapatite crystal reordering and reorganisation. Matsunaga et al.[435] determined *in situ* the Zn concentration in remineralised enamel as a consequence of gum chewing. The incorporation of Zn into an enamel crystal was measured using the Zn K-edge EXAFS in fluorescence mode at the SPring-8, Japan, and was shown to accelerate the remineralisation. Moreover, the Zn substitution probably occurred at the calcium position in enamel hydroxyapatite. Martin et al.[436] explored a possible correlation between the metal status in human cementum and periodontal disease using SRXRF imaging on cross sections of diseased and healthy teeth. The results showed elevated levels of Cu, Ni and Zn in diseased teeth in contrast to healthy teeth suggesting that metals might play a role in the progress of periodontitis.

It is thought that exposure to *nano-sized particles* can induce more severe health effects than that from larger particles. Matsui et al.[437] tracked the pathway of diesel exhaust particles,

consisting predominantly of Ca, Cu, Fe, Ni and Zn, from the nose to the brain using SRXRF at SPring-8, Japan. The study revealed an increase in the amount of nano-sized particles in the glomerular layer with higher levels of Fe as well as in the neurons in the olfactory epithelium, with elevated Ni and Zn concentrations in the olfactory epithelium's lamina propria mucosae in comparison to that in the control group. Physicochemical properties and potential health effects of nanoparticles from pulverized coal combustion were studied by Yu et al.[438] using high-resolution field emission scanning electron microscopy and XRF. Nanoparticles from the same coal-fired boiler had a similar composition and were predominantly composed of sulfur, refractory elements and alkali/alkaline earth elements together with some transition and heavy metals. For different boilers, greater variations were observed as well as in the formation as in the composition of the nanoparticles. Readers should refer to section 9.3.2 for more interesting contributions on this topic.

Fayard et al.[439] investigated practical limits set by radiation damage induced in hydrated and unfixed cells at room temperature during XRF imaging. They found that the maximum dose tolerated by ascidian blood cells was 10^5 Gy. They proposed a simple model for predicting radiation damage and reported high-Z trace elements in cryo-preserved cells, the relative detection limit set by radiation damage is below 0.1 mg/kg at a spatial resolution of 100 nm. Donovan et al.[440] presented a detailed evaluation of steps leading to optimal determination of the modulation transfer function (MTF) applicable to X-ray imaging. The MTF is used in X-ray digital radiography and medical imaging to render the object's details. The authors investigated new procedures and combinations of procedures used in various steps of the MTF algorithm to determine a set producing superior results as compared to the existing methods.

A recurrent issue in this yearly review is the measurement of trace elements in bone. Bellis et al.[441] successfully investigated the application of a prototype bench top μ-XRF system for the measurement of Pb and Sr at physiological levels in bone. An experimental set-up based on focused monochromatic microbeam X-ray fluorescence instrumentation with a low power source (45 W Mo tube) coupled to doubly curved crystal (DCC) optics was developed. A cross-section of bone measuring about 5 mm × 8 mm size was mapped with 80 μm resolution showing heterogeneous distribution of Pb and Sr. Compared to alternative methods such as conventional SR-based XRF and LA-ICP-MS, this low cost and simple, automated μ-XRF system demonstrated excellent detection capability and stability for determination of trace elements with micrometer-scale resolution in bone. Finally, several contributions used the K-X-ray fluorescence technology for Pb in bone measurements and discussed the long-term consequences of exposure to Pb. The first contribution[442] presented a review in this research field, while the others described the results of studies related to cumulative Pb exposure and its influence on health aspects.[443–448]

9.7 Thin films, coatings and nano-materials

Literature during this review period abounds with papers using XRF in combination with a number of other analytical techniques for the *characterisation of thin films*. Hence, in recent years, researchers, having appreciated the non-destructive nature and capabilities of X-ray methods, have concentrated on the production and uses of their films with the inevitable consequence that the analytical methods adopted have become routine. Therefore, the following papers caught the attention of your reviewer because the X-ray techniques adopted played a significant and/or novel role in the work. De Wael et al.[449] presented work to characterise a cross-linked horse heart cytochrome c (HHC) film on cysteamine-modified gold electrodes. Quantitative data and information on the heterogeneity of the film were obtained by means of μ-SRXRF to understand the effect of immobilisation strategies on protein conformations, leading to the development and optimisation of biosensors. Chandril et al.[450] recognised the angular dependence of XRF measurements from Mn and Y inner K shell ionisation induced by a grazing incidence electron beam during their studies on Mn/Y structures. Estimates of the structural parameters, thickness and interfacial roughness were obtained using TXRF and compared with *ex situ* X-ray reflectivity data. Thickness values for both single and buried layers were in good agreement with the reflectivity data. Ghosh et al.[451] published the synthesis and characterisation of a series of Ge,Al-ZSM-5 samples made in hydroxide media. XRF and XPS indicated there was a germanium-rich over-layer on the crystals. XAS showed that the germanium was tetrahedrally coordinated in the zeolite framework and that GeO_2 was not present in the samples after ion exchange with sodium nitrate solutions. This work highlights some of the complexities involved in characterising zeolite crystals and verified that the materials were phase pure. Novotortsev et al.[452] used XRF to determine Mn solubility at temperatures near the melting point of $ZnGeAs_2$ to assist in the understanding of the ferromagnetic semiconductor. The hydrothermal synthesis of $CuO–SnO_2$ and $CuO–SnO_2–Fe_2O_3$ mixed oxides was studied by Jayalakshmi and Balasubramaniam.[453] Their powders were characterised by XRD, XRF and XPS to show a decrease in electrochemical capacitances on cycling attributed to the passive film formation on the surface of the mixed oxide electrode surfaces. Hernandez et al.[454] synthesized a series of $Ce_{1-x}Eu_xO_{2-x/2}$ mixed oxides by co-precipitation. The Eu content was measured as Eu_2O_3 by XRF and the existence of oxygen vacancies in the solids with Eu_2O_3 between 3 and 17% m/m was demonstrated by the presence of bands at 532 and 1275 cm^{-1} in their Raman spectra. The catalytic performance of the solids correlated with the amount of defects in the solid solution. Berzina et al.[455] applied SR-GIXRF for time-resolved characterisation of an organic memristor conductivity variation mechanism. They observed correlation between XRF intensity of rubidium and the ionic charge transferred between the conducting polymer and the solid electrolyte. Yang et al.[456] used GE-XRF spectrometry to characterise Ti and Fe layers deposited on GaAs single crystal by metal vapour vacuum arc ion sources. They concluded that GE-XRF spectrometry can be used for complete layer characterisation and control of the deposition process. Caridi et al.[457] employed EDXRF, XPS, and profilometry to characterise thin films produced by pulsed laser deposition technique. The goal of the research was to characterise plasma produced during laser irradiation of Al_2O_3 targets in order to measure the parameters governing the growth of the thin films.

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Further developments in the manufacture of Cu(In,Ga)Se$_2$ (CIGS) *thin film solar cells* have been reported. Luo *et al.*[458] prepared polycrystalline ZnS films by pulsed laser deposition on quartz glass substrates at temperatures of 20, 200, 400 and 600 °C as a buffer layer in CIGS solar cells. XRF measurements confirmed the composition of the ZnS films showing they were near stoichiometric. The energy band gaps at different temperatures were measured by absorption spectroscopy, increasing from 3.2 eV to 3.7 eV with increasing deposition temperature. This wider energy band gap, compared with CdS at 2.4 eV, enhanced the blue response of the photovoltaic cells. These results show the benefits of the ZnS buffer layer materials, prepared with an all-dry technology, for the manufacture of CIGS thin film solar cells. Liu *et al.*[459] were concerned with the selenisation process of CIGS thin films, the relationship between the element loss rate and the precursor depositions. They described a novel *in situ* resistance measurement, by which the formation of compound semiconductors could be observed directly and simultaneously. The structures, phase evolutions and element losses were measured by XRD and XRF. This work provided an effective method for the fabrication of high quality CIGS thin films with low element losses. Shi *et al.*[460] deposited ZnO layers as diffusion barriers by dc magnetron sputtering from a pure Zn target on stainless steel substrates. They found that the insertion layer of ZnO between a Mo film and stainless steel substrate had no influence on the orientation and composition of the CIGS films, as identified by XRD and XRF, respectively. Kang and colleagues published three studies on the preparation and properties of CIGS thin films. Absorbers grown from Ga-rich electrodeposited precursors followed by selenisation[461] used XRF and SEM data to show that the deposition potential of −0.7 V was suitable for the production of precursor films with Ga enrichment. Their second paper[462] concentrated on different levels of selenium in the electrodeposited precursors. Comparing results obtained by XRF, XRD, SEM and illuminated current–voltage measurements, they found that absorber layers processed from Se-poor precursors showed better crystallinity and increased Ga incorporation, thus improving cell performance, compared with the layers grown using Se-rich precursors. Their third study[463] used pulse-reverse electrodeposition with the selenisation process and was characterised by XRF, XRD, SEM and atomic force microscopy. These films adhered to the substrate and showed a smooth surface finish with fine grains. The chalcopyrite structure demonstrated enhanced crystallinity after treatment in a Se vapour for use as absorber layers within a soda-lime glass structure. Nickel diffusion in CuInSe$_2$ thin films was reported by Celik *et al.*[464] in the temperature range 430–520 °C. EDXRF was used to monitor the Ni concentration with the measurements fitted to a complementary error function solution to evaluate the diffusion coefficients at four different temperatures within the temperature range of interest.

Dakhel published four papers during this review period on *CdO films doped with differing elements*. The studies used XRF, XRD, UV-VIS-NIR absorption spectroscopy and dc-electrical measurements to characterise the resultant thin films. In the first paper[465] CdO films were lightly doped with dysprosium (molar 0.5%, 1%, 2% and 2.5% m/m) and evaporated on glass and Si wafer substrates. The second paper[466] reported europium doping (0.4%, 0.5%, 0.8% and 1.1% m/m) and band gap narrowing. In

the third publication[467] samarium was doped at 0.4%, 1.1%, 3%, 7.5% and 9.3% m/m by vacuum evaporation again on glass and Si wafer substrates. The Sm^{3+} doping created a slight compressive stress that changed the optical and electrical properties. In the final paper reviewed in this series[468] the influence of annealing in nitrogen at different temperatures (200 °C, 250 °C and 300 °C) on films doped with 1.5% m/m samarium was reported. The lower temperature nitridation produced a better transparent conducting oxide. All these doped films produced degenerate semiconductors.

We now consider analytical investigations on samples with thicker *coatings*. Wang and Yang[469] were interested in the influences of binder on the fire protection and anti-corrosion properties of intumescent, fire resistive coatings for steel structures. A combination of epoxy emulsion and self-cross-linked silicone acrylate emulsion (SSA) was used as a mixed binder for preparing a series of water-borne coatings. The influence of binders on the properties and char formation of the coatings was investigated using TGA, SEM, XRD and XRF in addition to a number of physical tests. Fire protection and the foam structure of the coating were found to significantly improve with the addition of 14% m/m SSA. The XRF measurements showed that the antioxidation of the coatings improved with increasing SSA into the binder mix. Pereira and Bueno[470] used EDXRF and PCA to evaluate 17 varnishes and 10 paints. The samples were analysed following accelerated laboratory tests and atmospheric environmental exposures. The data enabled the authors to classify the coatings into groups of weatherproofing products thereby avoiding subjective interpretations. It is always reassuring to read that analytical data overrides opinion. Sakata *et al.*[471] discussed the influence of laser surface texturing on the micro-structure and mechanical properties of adhesive bonded steel sheets that were subsequently zinc coated. XRF measurements of the thickness of the Zn coating were correlated as a function of process parameters. Both XRF and XRD analyses demonstrated that the protective coating remained on the surface and that the underlying steel structure was not adversely affected by the laser treatment. Alfonso *et al.*[472] used μ-XRF for thickness determinations of a thin gold layer deposited as a liner on the interior of a uranium hohlraum to protect the uranium from oxidation. The work then progressed to measure the thickness of an alternative boron-doped gold coating. Ma and colleagues[473] reported a method for the quantitative analysis of elements in a bromine-doped micro-shell coating used in an inertial confinement fusion experiment. The measurement error was calculated to be ~5% for coatings with a 10 μm thickness. Weber *et al.*[474] measured the loss of tin from films on Cu–Zn–Sn–S material and the sub-systems Cu–Sn–S and Sn–S. A combination of SRXRF and SRXRD was used to identify phases that tended to decompose and evaporate under high vacuum. The XRF quantification of the Sn loss during annealing experiments was reported as the evaporation rate from the different phases decreased in the order SnS → Cu$_2$SnS$_3$ → Cu$_4$SnS$_4$ → Cu$_2$ZnSnS$_4$.

The relative intensity of analyte lines in the X-ray spectrum may be measured as a means to assess *the thickness of thin films and multilayers*. Karimi *et al.*[475] used the relative intensities of Cu and Ni K lines to measure a Ni layer on brass. The Kα/Kβ ratios of the two analytes increased as a function of the Ni layer

thickness on a brass plate sample in the range of fractions of one to several micrometers. Cesareo et al.[476] measured Kα/Kβ, or Lα/Lβ and Lα/Lγ X-ray ratios for an element in a multilayered material to show that the ratios depend on the composition and thickness of the layer in which the element is situated and on the composition and thickness of the superimposed layer or layers. This technique was used by the authors to study pigment layers on paintings and gilded or silvered alloys. Readers interested in similar archaeological and cultural heritage applications are referred to section 9.4 of this review. Pacella et al.[477] proposed a method for detecting layers of dust accumulation on tokamak surfaces based on the differential absorption of the L-shell and K-shell emissions from molybdenum that has been chosen as the material for the substrate of present-day tokamaks. Section 9.8 of this review explores other ways in which the measurement of the relative intensities of analyte lines in the X-ray spectrum may be used to assess the valence state and speciation of elements in a sample.

Papers continue to feature in the literature on the contribution that XRF techniques make towards the understanding of *nano-materials*. Baer et al.[478] confirmed the important role that methods for surface chemical analysis play in the characterisation of nano-particles. Valuable information may be gained from Auger electron spectroscopy, X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry, low-energy ion scattering plus various X-ray and microscopy techniques. Analytical considerations and issues associated with surface-analysis were discussed, including, shape instability, environmentally induced changes, deliberate and accidental coating *etc.* Kumar et al.[479] used EDXRF to measure the formation of gold nano-particles in a matrix of a plasticized anion-exchange membrane to assist in the understanding of the formation process. Silver nano-particles are used as an antimicrobial agent in wound dressings and as surface coatings on catheters. Askari et al.[480] deposited silver nano-particles on silica sub-micrometre-spheres using ultrasound. XRF measurements showed that the amount of silver deposited on the silica was proportional to the ultrasound power. Zin and colleagues[481] also used ultrasound for the preparation of Fe/Co nano-particles and EDXRF measurements to relate their chemical composition to the influence of the metal salt anions used. El-Hilo et al.[482] used EDXRF for the determination of the atomic ratio of Ni:Zn to monitor the synthesization of Ni doped ZnO powder. Takesada et al.[483] compared $MgGa_2O_4$:Mn^{2+} nano-phosphors with those made from $ZnGa_2O_4$:Mn^{2+} to show that Mn^{2+} was more homogeneously distributed within the Mg based nano-phosphur. Erdelyi et al.[484] reported their depth profiling methods of a-Si/Co/a-Si layers to give nano-resolution for the monitoring of Co/Si inter-metallic phases. A combination of GIXRF and EXAFS with XSW enabled the authors to offer sufficient sensitivity and accuracy to monitor the production of the waveguide structures. The morphology of metal nano-particles supported on oxide substrates plays an important role in heterogeneous catalysis and in the nucleation of thin films. Christensen et al.[485] evaporated platinum onto $SrTiO_3$ (001) followed by vacuum annealing to find an unexpected growth formation of Pt nano-particles that aggregated into clusters without coalescence. This hierarchical nano-particle morphology with enhanced surface to volume ratio for Pt was analysed by grazing incidence small angle X-ray scattering, XRF, AFM and SEM. The nano-particle constituents in the clusters measured 2–4 nm in size and were nearly continuously spaced where the edge to edge spacing was less than 1 nm. The clusters were 10–50 nm in diameter and were spaced some 100 nm apart.

9.8 Chemical state and speciation

The effects of the *absorption edge structure* in XRF can be seen as a strong attenuation of an analyte line in XANES studies. Borkhodoev[486] demonstrated this effect on Ce Lβ1 line attenuated by the L3 Ba absorption edge. These effects are also considered in fundamental parameter models for quantitative XRF analysis. Bielewski et al.[487] reported a fast XANES data collection method suitable for mapping oxidation states of actinides in environmental samples. This is a welcome improvement since the time required for conventional XANES data collection is unacceptably long. The authors showed the effectiveness of their model by measuring the distribution of Pu oxidation states in a "hot" particle from a nuclear weapons test site. The morphology and composition of uranium alpha sources with co-deposited platinum was investigated by XAFS, XPS and a number of other techniques. The XPS analysis suggested that the presence of platinum initially increased the concentration of hydroxyl species, which then acted as centres for subsequent preferential uranium precipitation. XPS and XAFS data also showed for the first time, an indication of oxidation states of uranium present in sources prepared by the Hallstadius method. Chrysochoou et al.[488] used μ-SRXRF at the Advanced Light Source in Berkeley, USA to build elemental maps of Cr^{VI} in chromite ore processing residues. Borovoy[489] was interested in the structure and relative intensity of Mα and Mβ XRF spectra of Au atoms at the energies of absorbed photons both below and above the ionisation thresholds of L sub-shells of Cr, Cu and Mo. A model was proposed for L to M transitions that agreed with theoretical values. The photo energy region above the ionisation threshold of the L3 sub-shell did however generate data that was not in agreement with calculated data reported by other authors. Possible reasons for these discrepancies were discussed. It will be interesting to see if the literature reviewed next year responds to this paper. Bu and Vaknin[490] collected XRF spectra from Ba^{2+} and Cs^+ ions from vapour/water interfaces that formed near a charged Langmuir monolayer. The fluorescent spectra collected as a function of incident energy near to the L(III) edge and was compared to recent independent data. Yilmaz et al.[491] measured the L spectra of Lu, Os, Pt and Yb at energies in the range 9.572–14.384 keV to calculate absolute values of L X-ray cross-sections that incorporated the enhancement due to the Coster-Kronig effect. The experimental enhancement factors tended to be smaller than those predicted by theory. Kumar and Puri[492] measured L(I) and L(II) sub-shell fluorescence yields for Dy at 22.6 keV using 7.4 × 10⁸ Bq, ¹⁰⁹Cd sealed point source and a Peltier cooled X-ray detector arranged in reflection geometry. Their data were compared with theoretical and semi-empirical values as well as those recommended by Campbell.

Chemical shift and full width at half maximum (FWHM) intensities of Cr Kα and Kβ₁,₃ lines were measured by Baydas and Oz[493] to show the *oxidation state* of chromium in twelve Cr-containing materials. The authors found that the chemical shifts

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for compounds containing fluorine were higher than those containing chlorine. Knowledge and control of redox in commercial glass production are important in order to optimise the glass melting process and properties of the end product. In particular, the solubility of sulfur in the glass melt and the Fe^{2+}/Fe^{total} ratio are strongly dependent on the relative amounts of reducing and oxidising raw materials in the batch. A constant redox state is required for the production of reduced coloured glass containers, such as amber, yellow-green UV absorbing glass and the "dead leaf" colour often used to contain wine and other beverages. Daneo et al.[494] used XRF and visible-near infra-red spectrophotometry for the detection of Fe_2O_3 (total), FeO, SO_3 (total), S^{2-} and Cr_2O_3 to define the different chromatic stability fields for different glass container colours to support quality control. The root uptake and reduction of Cr^{VI} by aquatic macrophytes was assessed by Espinoza-Quinones et al.[495] using high resolution X-ray emission. Cr Kβ spectra from dried root tissues and Cr reference materials (100% Cr, Cr_2O_3 and CrO_3) were compared. All the species of aquatic, floating plants treated with Cr^{VI} showed that the energy of the Cr $K\beta_{2,5}$ shifted around 8 eV below the same spectral line from the Cr^{VI} reference, but it was also near to the Cr^{III} reference line. There is more work to be done and we wait the results with interest. A group of workers in Turkey[496] reported the influence of alloying effects on XRF intensity ratios of Co and Cu K and L spectra in CoCuAg alloy films. The changes were attributed to the rearrangement of valence state electrons and the charge transfer process between the 3d elements (Co and Cu) and Ag. Similarly, in a second paper[497] the intensity rations of Co and Zn were measured in Zn_xCo_{1-x} alloys. A third contribution[498] was concerned with Fe and Zn in Fe_xZn_{1-x} thin film alloys.

10. Abbreviations

AAS	Atomic absorption spectrometry
ac	Alternating current
ACQ	Alkaline copper quaternary
ADR	Adiabatic demagnetization refrigerator
AFM	Atomic force microscopy
ALD	Atomic layer deposition
API	Active pharmaceutical ingredients
APS	Advanced Photon Source
APXS	Alpha Particle X-ray Spectrometer
ASU	Atomic Spectrometry Updates
ASV	Anodic stripping voltammetry
BC	Before Christ
BFR	Brominated flame retardants
BMD	Bone mineral density
BP	Before present
CA	Copper azole
CAMAC	Computer automated measurement and control
CCA	Chromated copper arsenate
CCD	Charge coupled device
CDD	Controlled drift detector
CIGS	Copper indium gallium selenide
CRM	Certified reference material
CSN	Chemical Speciation Network
CT	Computer tomography
CZT	Cadmium zinc telluride
2D/3D	2 Dimensional/3 Dimensional
dc	Direct current
DCC	Double curved crystal
DEPFET	Depleted P-channel field effect transistor
DIN	Deutches Institut für Normung
DFT	Density function theory
DMA	Dimethylarsinic acid
DNA	Deoxyribonucleic acid
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
DU	Depleted uranium
EC	Elementary carbon
ED-SEM	Energy dispersive-scanning electron microscopy
EDTA	Ethylenediaminetetraacetic acid
EDXRF	Energy dispersive X-ray fluorescence
EF	Enrichment factors
EPA	Environmental Protection Agency
EPMA	Electron probe microanalysis
ERDA	Elastic recoil detection analysis
ESA	European Space Agency
ESRF	European Synchrotron Radiation Facility
ETV-AAS	Electrothermal vaporisation atomic absorption spectrometry
EU	European Union
EXAFS	Extended X-ray absorption fine structure
FAAS	Flame Atomic absorption spectrometry
FP	Fundamental parameter
FPGA	Field programmable gate array
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width at half maximum
GC	Gas chromatography
GC-MS	Gas chromatographic-mass spectrometry
GF-AAS	Graphite furnace-atomic absorption spectrometry
GEXRF	Grazing exit X-ray fluorescence
GIS	Geographic information system
GIXRF	Grazing incidence X-ray fluorescence
HA	Hydroxyapatite
HaCaT	Human adult low calcium temperature
HEX	High Energy X-ray spectrometer
HHC	Horse heart cytochrome
HPAA	Hydroxyphosphonoacetatis acid
HPLC	High performance liquid chromatography
IAEA	International Atomic Energy Agency
ICF	Inertial confinement fusion
ICP-MS	Inductively coupled plasma – mass spectrometry
ICP-AES	Inductively coupled plasma – atomic emission spectrometry
ICP-OES	Inductively coupled plasma – optical emission spectrometry
IDMS	Isotope dilution mass spectrometry
IMPROVE	Interagency Monitoring of Protected Visual Environments
INAA	Instrumental neutron activation analysis

IR	Infrared	RBS	Rutherford backscattering
INTEX-B	Intercontinental Chemical Transport Experiment – Phase B	RDA	Regularised discriminant analysis
		RDI	Rotating drum impactor
IRLS	Iteratively reweighted least-squares	rf	Radiofrequency
IUPAC	International Union of Pure and Applied Chemistry	REE	Rare earth elements
		ROI	Region of interest
JSAC	Japanese Society of Analytical Chemistry	RS-XRF	Rapid scanning – X-ray fluorescence
KXRF	K-line X-ray fluorescence	RoHS	Restriction of Hazardous Substances
LA-ICP-MS	Laser ablation - inductively coupled plasma – mass spectrometry	SCD	Swept charge device
		SDD	Silicon drift detectors
LCSM	laser confocal scanning microscopy	SEM	Scanning electron microscope
LEXRF	Low-energy X-ray fluorescence	Si(Li)	Lithium-drifted silicon
LIBS	Laser induced breakdown spectroscopy	SIMS	Secondary ion mass spectrometry
LINAC	Linear accelarator	Si-PIN	Silicon 'PIN' detector device
LNF	Laboratory Nazionali di Frascati	SLNL	Synchrotron Light National Laboratory
LNLS	Laboratorio Nacional de Luz Sincroton	SOM	Self organising maps
LREE	Light rare earth elements	SPF	Sun protection factor
MC	Monte Carlo	SRM	Standard reference material
MCLLS	MC library least-squares	SR	Synchrotron radiation
MFA	Micro-fibril angle	SR-GEXRF	Synchrotron radiation - grazing exit X-ray fluorescence
MGAU	Multi-group gamma-ray analysis method for uranium		
		SR-GIXRF	Synchrotron radiation - grazing incidence X-ray fluorescence
MIXS	Mercury imaging X-ray spectrometer		
MLX	Motionless laminography system	SR-TXRF	Synchrotron radiation - total reflection X-ray fluorescence
MRI	Magnetic resonance imaging		
MS	Mass spectrometry	SR-XAS	Synchrotron radiation- X-ray absorption spectroscopy
MTF	Modulation transfer function		
MWPC	Multi-wire gas proportional counter	SR-XSW	Synchrotron radiation X-ray standing waves
NASA	National Aeronautics and Space Administration	SRXRD	Synchrotron radiation X-ray diffraction
		SRXRF	Synchrotron radiation X-ray fluorescence
NEXAFS	Near-edge X-ray absorption fine structure	SSA	Self-crosslinked silicone acrylate
NIST	National Institute of Standards and Technology	STEM	Scanning transmission electron microscope
		STJ	Superconducting tunnel junction
NRA	Nuclear reaction analysis	STXM	Scanning transmission X-ray microspectroscopy
NREL	National Renewable Energy Laboratory		
NSLS	National Synchrotron Light Source	TEM	Transmission electron microscope
OC	Organic carbon	TES	Transition edge sensor
ODP	Ocean drilling project	TES-EDS	Transition edge sensor energy dispersive spectrometer
OLS	Ordinary least-squares		
ODXAS	Optically detected X-ray absorption spectroscopy	TG	Thermo-gravimetry
		TGA	Thermo-gravimetric analysis
PBDE	Polybrominated diphenyl ethers	TG-DTA	Thermo-gravimetric-differential thermal analysis
PBD/F	Polybrominated dioxins and furans		
PCA	Principle component analysis	TOF-SIMS	Time-of-flight-secondary ion mass spectrometry
PCB	Printed circuit board		
PEI	Polyethylenimine	TXRF	Total reflection X-ray fluorescence
PGAA	Prompt gamma activation analysis	TWQR	Target Water Quality Range
PGE	Platinum group elements	US	United States
PIGE	Particle induced gamma ray emission	USA	United States of America
PIXE	Particle-induced X-ray emission	USB	Universal serial bus
PLS	Partial least square	US-EPA	United States-Environmental Protection Agency
PMF	Positive matrix factorization		
PM	Particulate matter	UV	Ultraviolet
PT	Proficiency testing	UVC	Ultraviolet C
PUREX	Platinum, uranium refining by extraction	UV-VIS	Ultraviolet-visible spectrophotometry
PXD/F	Polyhalogenated dioxins and furans	UV-VIS-NIR	Ultraviolet-visible spectroscopy-near infrared
PXRF	Portable X-ray fluorescence	VNIR	Visible and near-infrared reflectance
QDs	Quantum dots	WDXRF	Wavelength dispersive X-ray fluorescence

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WEEE	Waste of electric and electronic equipment
XAFS	X-ray absorption fine structure
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectroscopy
XPS	X-ray photon spectroscopy
XRBIC	X-ray beam induced current
XRD	X-ray diffraction
XRF	X-ray fluorescence
XRF-CT	X-ray fluorescence-Computer tomography
XRMD	X-ray magnetic diffraction
XRR	X-ray reflectivity
XSW	X-ray standing waves
YAG	Yttrium aluminium garnet

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