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# X-ray Spectrometry

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### OVERVIEW

In this review, we focus on the most significant and essential progress in X-ray spectrometry (XRS) published during the period 2006–2007 covering the following topics: developments and improvements in the detection performance and instrumentation of X-ray techniques and X-ray optics, new quantification models in X-ray spectra and data evaluation, micro-X-ray fluorescence ( $\mu$ -XRF) including 3D-XRF, imaging techniques such as tomography and holography methods for 2D or 3D imaging of microstructures,

electron probe microanalysis (EPMA), total reflection X-ray fluorescence (TXRF), particle-induced X-ray emission (PIXE) analysis, and X-ray absorption spectrometry (XAS). Finally, different applications in each subfield of XRS are described. Since the previous review, the sections of  $\mu$ -XRF and 3D-XRF are newly introduced.

An international group of scientists published two overviews on XRS (1, 2) in the *Journal of Analytical Atomic Spectrometry* covering the period 2006–2007 in the principal field of XRS analytical spectroscopic methods and instruments. These review articles involve all the important sections of XRS in nine chapters: reviews, instrumentation, spectrum analysis, matrix correction and calibration, X-ray optics and microfluorescence, synchrotron radiation, TXRF, portable and mobile X-ray fluorescence (XRF), and online XRF and applications. In the present review, we use a different method of classifying the information published in the literature during the 2006–2007 period: detection, instrumentation (except detectors) and optics, quantification models and related fundamental data, tomography and holography methods as primary tools of X-ray imaging, TXRF, EPMA, PIXE, XAS, and a final chapter that reviews the application of these methods in geology, environmental research, industry, biology, and medicine.

Two practically useful books were published in 2006–2007. The handbook entitled *Practical X-ray Fluorescence Analysis* was edited by five famous German researchers (3). Following the historical progress of XRF, the basic and recent developments in X-ray sources, X-ray optics, and X-ray detectors are described. Quantification, specimen preparation, and special configurations, such as TXRF and micro-XRF, and their applications in environ-

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mental science, geology, metallurgy, archeology, and forensic investigations were introduced with 385 figures and 53 tables. Especially, the chapter "*Methodological Developments and Applications*" including many recent results with pictures, drawings, and more than 900 literature references is judged quite valuable to researchers in XRF field. Another useful book was written by Ide-Ektesabi (4). In the book entitled *Applications of Synchrotron Radiation, Microbeams in Cell Microbiology and Medicine*, the author describes the fundamentals and applications of synchrotron radiation (SR) in certain aspects of cell microbiology, specifically nondestructive elemental analyses, chemical-state analyses, and imaging of the elements within a cell. The high brilliance and energy variability of the SR X-ray beam are especially useful for XRF and X-ray absorption fine structure (XAFS) in the research areas of biology and medicine.

TXRF is now a well-established technique especially for applications in the field of semiconductors. Two excellent review articles were recently published. Wobrauschek (5) described the fundamentals of TXRF in the laboratory and the SR facility, concerning the theory of the total reflection phenomenon, applications in chemical analysis and wafer surface analysis, instrumentation, quantification, SR-TXRF, and X-ray absorption near-edge structure (XANES) measurement in TXRF geometry. In addition, he clearly discussed the drawbacks of TXRF concerning the preparation of clean sample carriers and quantification. Another TXRF review article, especially SR-TXRF, was written by Streltsov (6). Recent TXRF applications for environmental, medical, biological, polymer, and archeological samples were reviewed with over 80 references.

One of the research trends in XRF is micro-XRF analysis. To obtain detailed chemical information regarding advanced materials and environmental and biological samples, XRF analysis at localized regions has been required. Therefore, many papers on micro-XRF and synchrotron radiation-assisted X-ray fluorescence (SR-XRF) have been published. On the other hand, electron probes produce characteristic X-rays in a small region of only a few micrometers. Therefore, EPMA is a useful technique for micro-X-ray analysis of especially light elements, although the sample must be placed in a high vacuum. However, a strong continuum background is usually observed in the EPMA spectrum. Thus, Haschke et al. (7) attached micro-X-ray beam equipment to the vacuum chamber of a SEM, to utilize advantages provided by both micro-XRF and EPMA at the same time. In this system, excitations by both X-rays and electrons are possible. The authors discussed quantification for X-ray analysis in both excitation processes. Another recent trend in XRS research is medical applications and development of X-ray imaging techniques. The development of X-ray detectors is critically required for X-ray imaging. Hoheisel (8) authored an excellent review article on medical imaging with emphasis on X-ray detectors. After a historical introduction of classical radiography, the author discussed some new developments in X-ray detectors. These included energy-resolving methods for distinguishing different tissues in the patient, quanta-counting detection, phase contrast imaging, the charge-coupled devices (CCD) for very high spatial resolution with a large sensitive area of 49 mm × 86 mm and with 4 K × 7 K pixels, fast volume CT scanners, and organic semiconductors for a new generation of detection devices. 3D and functional imaging

will acquire more interest in the future. Besides X-ray imaging detectors such as CCD X-ray detectors, the development of microcalorimeters will also probably open a new phase for XRS. A joint mission (Suzaku) between NASA (U.S.A.) and ISAS/JAXA (Japan) (9) has planned the development of a high-resolution microcalorimeter array, which covers the energy band from 0.3 to 10 keV with a nearly constant energy resolution of 6 eV and a peak effective area of 200 cm<sup>2</sup> at 1.5 keV. Further developments will be required for practical use, not only for physical and astronomical studies but also for material and chemical studies.

High-gain free-electron lasers (FELs) are being developed as extremely bright sources. Huang and Kim (10) reviewed the basic theory of high-gain FELs. They discussed both shortening the X-ray pulse lengths and increasing the coherence of the source. The authors expected that the theoretical formula would progress in achieving X-ray FELs and improve their performance. Gaffney and Chapman (11) reviewed atomic-resolution images of materials with X-ray free electron lasers during chemical reactions. They discussed recent advances in ultrafast X-ray lasers, femtosecond X-ray scattering for the study of structural dynamics, and coherent X-ray imaging with atomic resolution. The same topic is reviewed in the section X-ray Imaging in the present review.

The number of papers concerned with biological and environmental applications of XRS is increasing. Thus, we will review only two such papers here, although they will also be reviewed in the section of Applications. Carvalho et al. (12) investigated the trace elements in cancerous tissues in healthy humans using several XRS techniques such as energy dispersive X-ray fluorescence (ED-XRF), TXRF, SR-XRF, and PIXE. They measured several tissue samples, including breast, lung, serum, intestine, prostate, and uterus. They mentioned that all XRS techniques showed good agreement, although some differences in detection limits or analytical performance were found. TXRF gave more sensitive results for light elements, while ED-XRF had advantages for the detection of heavier elements. Osan et al. (13) applied X-ray microanalytical methods, such as near edge X-ray absorption fine structure (NEXAFS), TXRF, and EPMA, for determination of nitrogen and sulfur compounds in Antarctic fine aerosol particles. It was possible to quantify the molar ratio of ammonium and nitrate based on linear combinations of standard reference spectra of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub>. Single-particle analytical results obtained by low-Z particle EPMA supported results obtained by TXRF-NEXAFS.

## DETECTION

Cryogenic detectors operating at very low temperature offer energy resolution with an order of magnitude higher than conventional, semiconductor-based, energy-dispersive detectors, such as Si or Ge detectors. The energy resolution of the cryogenic detector is currently 2–4 eV, which is comparable to that of the crystal spectrometer but much greater than the range of 120–200 eV achievable with the conventional Si or Ge detector. Compared with the crystal spectrometer, the advantage of the cryogenic detector is its high efficiency for the detection of photons. Since most crystal spectrometers choose only a single wavelength at any time, they must finely scan the analyzing crystals and detectors to obtain the X-ray spectra, resulting in long measuring time. For cryogenic detectors, the acceptance solid angle can be freely enlarged by placing the detecting surface close to the

sample position, as in the case of energy dispersive detectors. Therefore, cryogenic detectors are suitable for the measurement of very weak X-ray signals with high-energy resolution and were initially developed for astrophysics applications. Recently, they have increasingly been used in various analytical fields, for both detector characterization and high-resolution X-ray spectroscopy.

Of the two types of cryogenic detector, superconducting tunnel junction and transition edge sensors (TES), the latter is also called a "microcalorimeter". Mazin et al. (14) developed a microwave kinetic inductance detector, which can be adapted to X-rays as well as optical/UV, energy-resolved, single-photon detection by increasing the detector's responsivity. An energy-resolving detector for photon energies ranging between 0.1 and 10.0 keV can be fabricated by utilizing "strip-detector architecture", which comprises a long strip of a superconducting material with a quasiparticle sensor attached to each end. The quasiparticle sensor is a thin film, resonant circuit called a microwave kinetic inductance detector. When an X-ray is absorbed in a tantalum strip, a number of single electron excitations occur by breaking Cooper pairs, which is called a quasiparticle. The principle is similar to electron-hole generation by photons in semiconductor detectors, but the energy gap for excitation, which is only tenths of millielectronvolts, differs from the value of 1 eV or more for a semiconductor. This very low energy gap creates millions of quasiparticle excitations for each photon absorbed. The square of the number of the excitations is inversely proportional to the full width at high-maximum (fwhm) of the spectrum of the monochromatic X-rays. Moreover, by using two aluminum microwave kinetic inductance detectors on either side of a tantalum photon absorber strip, a position-sensitive X-ray detector can be made. Mazin et al. examined the diffusion constant, recombination time, and energy resolution and predicted that the energy resolution would be improved to  $\sim 12$  eV, although only 65 eV was achieved in their result. Zink et al. (15) reported a microcalorimeter  $\gamma$ -ray detector with a measured energy resolution of 42 eV fwhm for 103 keV photons. Generally, microcalorimeters based on superconducting TES exhibit high-energy resolution in the lower energy X-ray region such as 6 keV. For X-ray microanalysis and X-ray astronomy, researchers have realized the potential of TES microcalorimeters for measuring hard X-ray and  $\gamma$ -ray detectors, where a bulk absorber is required for sufficient absorption efficiency. This detector consists of a thermally isolated Mo/Cu TES and a superconducting bulk tin photon absorber. The  $\gamma$ -ray spectra show an energy resolution of 42 eV fwhm at 103 keV, which is more than an order of magnitude better than that for typical high-resolution  $\gamma$ -ray detectors, such as Ge detectors. The absorber is attached with a technique compatible with producing arrays of high-resolution  $\gamma$ -ray detectors. The authors made a 16 pixel, composite TES  $\gamma$ -ray detector array and evaluated the detailed characterization of the detector by testing the complex impedance, detector noise, and time-domain pulse response. They suggested that a deeper understanding and optimization of the thermal transport between the absorber and thermometer could significantly improve the energy resolution of future detectors.

Improvements of TES-based X-ray detector have been reported by a number of groups, and the construction of pixel arrays is still a major challenge. An alternative is to use a position-sensitive detector incorporating two or more TESs on a single absorber

and apply "heat division" as the position-sensitive principle. A group at the University of Leicester (16) developed a linearly distributed, read-out imaging device, consisting of two Ir TES at a linear Au or composite Au/Bi absorber. The sum of the TES signals gives the total energy of the absorbed photon, and the position is determined from the difference between the signals. The group also reported on a new optimal filtering algorithm for improved energy and position resolution, which takes account of the noise correlation between the detector outputs to minimize the variance on the estimated photon energy and position. The energy and position resolutions were significantly improved using the numerical method, compared to the previous version. Their simulations also revealed the trade-offs resulting from changes in the thermal conductances and heat capacities of the detector elements. Recently, microcalorimeters with thermometers based on dc superconducting quantum interference device (SQUID) measurements of the temperature-dependent magnetization of paramagnetic sensors have shown excellent resolution. These metallic magnetic calorimeters are predicted to surpass TES devices for certain applications, such as materials analysis and X-ray astronomy. Zink et al. (17) reviewed the principles of metal magnetic calorimeters and focused on Er-doped Au magnetic sensors fabricated by coevaporation and sputtering. In the basic principles of metallic magnetic calorimeters, an X-ray heats the microcalorimeter by  $\Delta T$ , causing a change in magnetization  $\Delta M$ . The  $\Delta M$  is measured by the SQUID measurements as a changing flux  $\Delta \Phi$ , which is proportional to the energy of the X-ray. Fabricating an array of the magnetic microcalorimeter requires a paramagnetic sensor fabricated with thin-film techniques. Zink et al. discussed two methods for depositing an Er-doped Au sensor film and presented magnetization measurements from 4 to 300 K in 5 T and near the detector's operating temperature and field. The properties of the deposited films they fabricated were poorer than the expected behavior of bulk materials at the present stage.

X-ray charge-coupled devices (CCDs), either of direct X-ray detection type or phosphor-coupled type, have become increasingly utilized in X-ray medical imaging, X-ray astronomy, protein crystallography, and two-dimensional XRF analyses. The direct detection CCD senses low energy X-rays (30 eV–10 keV), while the phosphor-coupled CCD is useful for high X-ray energy detection ( $>20$  keV). Matsuura et al. (18) developed an X-ray CCD for the next Japanese X-ray astronomical satellite mission, NeXT (new X-ray telescope/nonthermal energy exploration telescope). The detector for the hard X-ray telescope, using a special multilayer coating mirror, has spectroscopic imaging capability in the wide energy band of 0.3–80 keV. The CCD camera developed by Matsuura et al. can be used for X-rays below 20 keV. There are two types of CCD, n-channel and p-channel, which are fabricated on p- and n-type silicon wafers, respectively. Previously, the authors developed a p-channel CCD with a depletion layer of 70  $\mu\text{m}$ , which was relatively high at the time of development. Since the thickness of the depletion layer corresponds to the efficiency of X-ray detection, a thick depletion layer incurs the advantage of observing weak X-rays from space. The p-channel CCD fabricated on an n-type silicon wafer offered a thick depletion layer of approximately 300  $\mu\text{m}$  with a p-channel CCD because high resistivity was more easily obtained using the n-type silicon wafer in comparison with the p-type silicon wafer. The



fabricated CCD consisted of  $512 \times 512$  pixels with a pixel size of  $24 \times 24 \mu\text{m}^2$ . The horizontal charge transfer inefficiency of the CCD can be improved by reducing the operating temperature and increasing the readout frequency. The authors obtained the best horizontal charge transfer inefficiency of  $(0.98 \pm 0.09) \times 10^{-5}$  with an energy resolution of  $(202 \pm 6)$  eV fwhm for 5.9 keV X-rays and a readout noise of  $18 \text{ e}^-$  rms when the CCD was operated at a temperature of  $-110^\circ\text{C}$  and a readout frequency of 67 kHz.

X-ray crystallography is now an important method for determining the molecular structures of proteins at atomic resolution. This technique has benefited from the high flux of synchrotron radiation sources, software advances, and large-area detector. Although the large-area detector was mostly realized for the imaging plate and the phosphor coupled CCDs via optical fibers, a large-area CCD detector "PILATUS", which is a hybrid pixel array detector with over 1 000 000 pixels that operates in the single-photon counting mode, was recently developed. Broennimann et al. (19) reported on the performance of PILATUS. Since the detector was designed for macromolecular crystallography, it has the largest pixel array detector. A modular system consisting of 18 multichip modules covered an area of  $21 \text{ cm} \times 24 \text{ cm}$ . The components were designed, and the detector, including the bump-bonding, was manufactured at the Paul Scherrer Institute. The use of a single-photon counting detector for protein crystallography requires detailed studies of the charge collection properties of the silicon sensor. The 18 modules are read out in parallel, leading to a full frame readout-time of 6.7 ms, which allows the crystallographic data to be acquired in fine- $\varphi$ -slicing mode with continuous sample rotation. The detector was tested in several experiments at the protein crystallography beamline X06SA instrument at the Swiss Light Source in the Paul Scherrer Institute. Data were collected both in conventional oscillation mode using the shutter and in a fine- $\phi$ -slicing mode. After all the necessary corrections were applied to the data from a thaumatin crystal, satisfactory merging  $R$ -factors of the order of 8.5% were attained by conventional data processing. This allows, for the first time, a refined electron density map of a macromolecular biological crystal to be determined using a silicon pixel detector.

Phase contrast imaging is one application of the area detectors. The requirements of this technique are higher sensitivity and higher spatial resolution to reduce the radiation exposure to samples and to improve the image quality, because biological samples, such as brain tissues, are damaged by X-ray radiation. One of the most promising candidates for satisfying these requirements is a high-sensitivity, image pickup tube having a high gain avalanche rushing amorphous photoconductor (HARP) target. The HARP target is mainly composed of an amorphous photoconductive layer doped with impurities. The avalanche multiplication of photogenerated carriers occurs under an electric field higher than  $80 \text{ V}/\mu\text{m}$ . The HARP camera has been used for high-definition television and has even been used to capture star light images. Hirano et al. (20) developed a direct sensing X-ray HARP tube camera for X-ray phase imaging. They used a beryllium plate, rather than a glass plate, as the faceplate of the tube, in order to minimize the loss of X-rays due to absorption, and a  $15 \mu\text{m}$  thick HARP target was directly formed on it. The phase contrast images produced for a rat liver were observed with the direct-sensing X-ray HARP tube camera using synchrotron

X-rays ( $\lambda = 0.0766 \text{ nm}$ ). A phase-map image of the sample was successfully obtained using the fringe scanning method and phase unwrapping. A voltage of 1300 V was applied to the HARP target to give an output signal gain of 2. The camera was operated in 1125 scanning-line mode, and real-time images were stored on a workstation at a rate of 30 images/s with an image format of  $960 \times 1100$  pixels. The pixel size was  $15.4 \times 8.1 \text{ mm}^2$ , and the field of view was  $15 \times 9 \text{ mm}^2$ . For fast powder diffraction experiments, Basolo et al. (21) developed a hybrid pixel photon-counting detector, capable of working at room temperature, and its dynamic response ranged from 0.01 to  $10^6$  photons/s at each pixel. The pixel sizes were  $0.33 \text{ mm} \times 0.33 \text{ mm}$  for a total area of  $68 \text{ mm} \times 68 \text{ mm}$ . On recording high-resolution powder diffraction patterns, a reduction of the experimental time by more than a factor of 20 was obtained without loss of data quality. For the demonstration, measurements of the high-resolution Debye–Scherer data were carried out at the European Synchrotron Radiation Facility (ESRF). When the detector was located at 1 m from the sample, the total angular aperture was about  $4^\circ$  and the pixel size was  $0.02^\circ$ . An example conducted with X-zeolite demonstrated the capability of using such detectors for very demanding anomalous experiments. In situ experiments of quenching liquid oxides showed that frames of 0.01 s can be achieved for studying such processes. The authors demonstrated the possibilities of time-resolved experiments such as irreversible phase transitions or metastable phase characterization.

The conventional cascade model for the analysis of a scintillator-based X-ray imaging detector can be described by a number of elementary processes from the incident X-ray influence to the additional electronic noise during the electric processes. Kim (22) generalized the conventional cascade model to describe the direct X-ray-induced quantum noise. In his model, the direct X-rays that are unattenuated from a scintillator directly interact with photo-sensitive elements. The developed model provided a good accounting of the contribution of the unattended X-rays in the image quality. He claimed that it is better to incorporate scintillators as an X-ray converter for the design and assessment of X-ray imaging systems. Recent multilayer mirror technology can focus X-rays up to 80 keV, which necessitates a moderate spectral resolution for 0.3–100 keV X-rays for CCDs. Therefore, Tawa et al. (23) developed a new type of photon-counting device. The CsI(Tl) scintillator is directly coupled to the surface of the CCD. Soft X-rays are absorbed in the CCD, whereas hard X-rays are absorbed in the CsI(Tl) and generate visible photons that are also detected by the CCD. The CsI(Tl) was a needlelike structure with a diameter of about  $5 \mu\text{m}$  and thickness of  $300 \mu\text{m}$ , which reduced the lateral spread of visible photons. The spectral resolution was  $(68 \pm 4)\%$  at 59.5 keV, which was 2 or 3 times worse than that previously fabricated with  $100 \mu\text{m}$  thick CsI(Tl) needles. A Monte-Carlo simulation revealed that visible photons in the needlelike CsI(Tl) were reflected diffusely on the surface of the needle and that the number of visible photons detected varied according to the interaction point of X-ray, resulting in the degradation of spectral capability.

For macromolecular crystallography, detectors with large active areas are required. The active area of a CCD is several centimeters squared in general. In order to increase the active area, the use of fiber-optic taper (FOT) is convenient, which is

suitable for the CCD. X-rays are converted to visible light by a fluorescent screen, and this secondary radiation is then guided by FOT on a small CCD active area. Ito et al. (24) developed a  $3 \times 6$  arrayed CCD X-ray detector for the continuous-rotation method in macromolecular crystallography at the KEK Photon Factory, a synchrotron radiation facility in Japan. The detector has an area of  $235.9 \text{ mm} \times 235.9 \text{ mm}$  and a readout time of 1.9 s. Each module consists of a  $3 \times 6$  array of identical modules, a FOT, a CCD sensor, and a readout circuit. The outputs from 18 CCDs are read out in parallel and are then digitized by 16-bit analog-to-digital converters. The unique CCD readout scheme of fast frame transfer can record X-ray diffraction spots without interruption of the sample crystal rotation. The most significant characteristic is almost 100% duty cycle ratio of the X-ray exposure to the data collection time, attained by using the continuous rotation. A full data set of a lysozyme crystal was continuously collected within 360 s ( $180^\circ$  rotation, 3 s/ $1.5^\circ$  frame). The combination of this detector and synchrotron radiation is well suited to rapid and continuous data collection in macromolecular crystallography.

In the ESRF, an FOT-coupled CCD, called "FreLoN", was developed for medical imaging because of its fast-readout and low-noise characteristics. Coan et al. (25) assessed the imaging performance of an indirect conversion detector in terms of the modulation transfer function, normalized noise power spectrum, and detective quantum efficiency. Measurements were made with a synchrotron radiation laminar beam at monochromatic energies in the range of 20–51.5 keV for a gadolinium-based fluorescent screen with diverse thickness. Data acquisition and analysis were conducted by adapting beam geometry protocols used for conventional cone beams. At 33 keV and for the 40 (100)  $\mu\text{m}$  screen, the modulation of transfer function was 9.2 (8.6) line-pairs  $\text{mm}^{-1}$ . The normalized noise power spectrum of the systems was determined for a range of exposure levels by two-dimensional Fourier analysis of uniformly exposed radiographs. The detected quantum efficiencies were estimated from the measured modulation transfer function and normalized noise power spectrum. The highest detective quantum efficiency value (0.5) was found for the combination of a 100  $\mu\text{m}$  screen and 25 keV X-ray energy; however, it was still equal to 0.4 at 51.5 keV (above the gadolinium K-edge). Coan et al. concluded that the detective quantum efficiency is limited by the phosphor screen conversion yield and the CCD efficiency. By comparing the results of the FreLoN characterization with those from a selected number of detectors presented in studies published before 2004, they claimed good performance for the FreLoN camera.

Recently, micropattern gas detectors have emerged for X-ray radiography, cosmic X-ray polarimetry, cold neutron imaging, and cellular function analysis. A hole-type gaseous multiplier, as represented by a glass capillary plate (CP) and a gas electron multiplier, is an attractive gas detector. An interesting feature of hole-type gas detectors is that electron multiplication takes place in each of the highly granulated holes, making it possible to provide a true, two-dimensional imaging capability with high position resolution. The choice of a filling gas in the detector directly affects the signal-to-noise ratio and detection efficiency. Tokanai et al. (26) developed a real two-dimensional X-ray imaging system composed of an imaging plate and a CCD using Ar + CF<sub>4</sub>. The CP consists of a two-dimensional array of fine glass capillaries.

The electrode was made by fabricating Inconel onto the inner face of the capillaries for measuring charge signals. Gas gains of up to  $10^4$  can be achieved with a single CP. Scintillation light simultaneously emitted during the development of electron avalanches can be observed using a photomultiplier tube and optical imaging system, which consists of a CP gas detector and a cooled CCD camera coupled to lens optics. The energy resolutions obtained for the charge signal and the light signal were 22% and 24% for 10 keV X-rays, respectively. Clearer X-ray images of the emblem of Yamagata University and a conifer were successfully obtained using the optical imaging system. Moreover, a single photoelectron track image was clearly observed.

Measurement of X-ray polarization from space is one of the most exciting topics for gas pixel detectors. Many astronomical objects, such as active galactic nuclei or spinning bodies, emit polarized radiations at X-ray wavelengths. Knowledge about the polarization will offer information on the geometry and internal structure of these sources, which can indicate how matter in space behaves in extremely intense magnetic and gravitational fields. Conventional polarimeters based on Bragg diffraction or Thomson scattering require a high flux of X-rays due to poor sensitivity. To capture the polarization of a faint and weakly polarized source, a new instrument based on the photoelectric effect, which is sensitive to photon polarization, was introduced by Bellazzini et al. (27). An application-specific, integrated circuit built in deep submicrometer technology was developed to realize a monolithic device composed of a pixelized charge-collecting electrode and amplifying, shaping, and charge-measuring front-end electronics. CMOS chips have the top metal layer patterned in a matrix of 80  $\mu\text{m}$  pitch hexagonal pixels, where each pixel is connected to the underneath electronics chain realized in the remaining five layers of the 0.35  $\mu\text{m}$  VLSI technology. The degree and angle of the radiation polarization were derived by analyzing the photoelectron tracks recorded by the gas pixel detector. The experimental detector response to polarized X-ray radiation was successfully used to determine the polarization angles of the X-ray beam. Kanai et al. (28) developed a balloon-based, astronomical soft  $\gamma$ -ray polarimeter. The detector consists of a hexagonal, close-packed array of 217 well-type phoswich detector cells and a side antiscatter detector made of bismuth germanate oxide scintillators. Each phoswich detector cell is composed of a thin-walled tube (well) of a slow plastic scintillator (with a fluorescence decay time of 230 ns) at the upper part, a solid rod of a fast plastic scintillator (with a decay time of 2 ns) at the lower part, and a bismuth germanate oxide scintillator (300 ns) at the bottom. All photons created in each tube are viewed by one photomultiplier. The well and the bottom bismuth germanate oxide scintillator act as an active collimator and a lower active shield. The fast scintillator rod serves as a Compton scatter and active photon detector. The scintillation events occur at two locations: the Compton scattering site and the photoabsorption site. The beam test was conducted at KEK Photon Factory. The synchrotron beam was set at 30, 50, and 70 keV, and its polarization was clearly identified. The feasibility experiment showed that the flight PDC can detect recoil electrons and select valid Compton scattering events down to 30 keV from the background, which is promising.

Bamberger et al. (29) have used a Medipix2 CMOS readout chip, with amplifying, shaping, and charge discriminating front-

end electronics integrated on the pixel level. The CMOS readout concept offers the possibility of a pixel size small enough to observe individual primary electron clusters of minimum ionizing particle tracks and to provide real two-dimensional images of physical events. The Medipix2 chip serves as a highly segmented direct charge-collecting anode in a three-stage gas electron multiplier (GEM). Each GEM of  $10 \times 10 \text{ cm}^2$  has double conical holes and an arranged hexagonal pattern with a pitch of  $140 \mu\text{m}$  and a diameter of  $70 \mu\text{m}$ . To evaluate the GEM/ Medipix2 performance, the ionization from Fe-55 X-rays and electrons from Ru-106 were detected. The device allows moderate energy spectroscopy measurements (20% fwhm at 5.9 keV X-rays) to be performed using only digital readout and two discriminator thresholds. In 2007, Bellazzini et al. (30) developed a self-triggering CMOS analog chip with a large area ( $15 \times 15 \text{ mm}^2$ ) and high channel density ( $470 \text{ pixel/mm}^2$ ) as a pixelized charge-collecting electrode of a micropattern gas detector. The top metal layer of the CMOS pixel array is patterned in a matrix of 105 600 hexagonal pixels with a  $50 \mu\text{m}$  pitch. Each pixel is directly connected to the underlying full electronics chain, which is realized in the remaining five metal and single polysilicon layers of a  $0.18 \mu\text{m}$  VLSI technology. The chip has customizable self-triggering capabilities and includes a signal preprocessing function for the automatic localization of the event coordinates. These advances significantly reduce the read-out time and data volume by limiting the signal output to only those pixels belonging to the region of interest. In addition, the very small pixel area and the use of a deep submicrometer CMOS technology have reduced the noise to 50 electrons ENC.

The Si drift detector (SDD) with an integrated field effect transistor can detect X-ray photons at several hundred thousand counts per second, while keeping the energy resolution below 300 eV. This property has benefited X-ray spectroscopy. To improve the active area and detection rate, monolithic arrays of SDD cells have been developed and successfully tested. Since SDDs have a symmetric round shape and concentric drift rings, it is difficult to develop large monolithic matrixes. Castoldi et al. (31) proposed novel architectures of multianode SDDs with linear geometry (multilinear SDDs) which can image X-rays and Compton electrons with excellent time resolution and achieve energy resolution better than 200 eV fwhm at 5.9 keV. The prototype of the multilinear SDD has a small area of  $1.6 \times 1.7 \text{ mm}^2$  with 120  $\mu\text{m}$  pixels. However, the novel features are their imaging and spectroscopic capabilities. As an application example, fast 2D elemental mapping by means of K-edge subtraction imaging was demonstrated. Moreover, the charge deposited by Compton electrons irradiated by a  $^{22}\text{Na}$  source was measured, which demonstrated the possibility to clearly resolve the 2D projection of the ionization track and to estimate the specific energy loss per pixel. The reconstruction of Compton electron tracks within a Si detector layer can increase the sensitivity of Compton telescopes for nuclear medicine and  $\gamma$ -ray astronomy. A gas proportional counter can record X-ray photon intensity with only a very small amount of primary charge, which is a unique feature in the detector. The development of the multiwire gas proportional counter has enabled the detection of X-rays in multiple dimensions and has introduced further flexibility to the proportional counter. The advancement in CCD technology has resulted in multidimen-

sional representation of incident X-ray photons with improved resolution. The distinct disadvantages of CCD cameras are their incapability for single-photon counting over a wide X-ray energy range and their relatively poor real-time energy discrimination. The research team at University of Melbourne (32) developed a multiwire proportional counter based on a backgammon-type design for the detection of X-ray photons in two dimensions. The multiwire proportional counter was designed for operation in an experimental spectroscopy application requiring single-photon counting over a wide range of count rates, high photon detection efficiency and resolution, and a highly linear response function across the detector face. The team combined the multiwire proportional counter with a Johann curved crystal and made a working spectrometer for the energy range of 4–6 keV. The detector resolution of  $330 \mu\text{m}$  was extracted from the spectral profile of the V K $\alpha$  lines obtained by the aforementioned system. A plot of detector response as a function of position across the face of the detector showed good linearity, and its differential revealed that the nonlinearity appeared only in the region 2–3 mm from each end, thereby demonstrating that the 20 mm width of the detector was used for active measurements.

Because of their high sensitivity and fast response, avalanche photodiodes (APDs) are frequently used for optical communication applications. The performance of the large-area reach-through APD, manufactured by Hamamatsu Photonics, K.K., as a high-resolution X-ray detector was reported (33). The APD has an area of  $3 \text{ mm}^2$ , a fast time response for signal carrier collection and its thick depletion layer of 130  $\mu\text{m}$  confers the potential for use as an effective X-ray absorber below 20 keV. With a capacitance similar to 10 pF and a low dark current of 5 nA for a gain of 15 at room temperature, this APD has demonstrated one of the best energy resolutions of such devices: 6.4% (fwhm) for 5.9 keV photons with a minimum detectable energy of 0.3 keV, measured at  $-20^\circ\text{C}$ . The experiments for the timing property were made in a synchrotron beam facility using an 8 keV X-ray beam. The achieved count rate was above  $10^8$  counts/s, corresponding to a very short dead time of 4.5 ns/pulse. In order to test the radiation hardness of the APD, the device was irradiated with a 53.5 MeV proton beam. The total dose was 11.3 krad, and no fatal damage was found in the APD, although the dark current of the APD was increased by 1 order of magnitude. The reach-through APD has the potential to become an excellent X-ray detector, especially in the space mission application.

The CdZnTe (CZT) detector can be effectively utilized for the detection of hard X-ray and  $\gamma$ -ray radiations due to the high atomic number and density of this detector material. The role of Te inclusions and precipitates has attracted research attention since the introduction of the CZT detector. Te-rich droplets are trapped at the boundary layer of the interface as a consequence of morphological instability. Carini et al. (34) investigated the correlation between Te precipitates, which are visible in the IR image of CZT crystals, and the deterioration of device response for a 11 mm long Frisch-ring and a 1 mm thick planar detector. To study the local variation of device responses, X-ray scans were performed at Brookhaven National Synchrotron Light Source using 85 and 30 keV quasimonochromatic X-rays with a small beam size. Comparison between the IR and X-ray images showed the strong correlation between the Te precipitates and the



deterioration of the X-ray and  $\gamma$ -ray spectroscopic response of detectors by producing degraded localized zone within the device.

Tanaka et al. (35) focused on the astrophysical observation of the events due to Compton scattering of  $\gamma$ -rays. To realize their aim, they constructed a prototype Compton telescope consisting of six layers of double-sided Si strip detectors and CdTe pixel detectors to demonstrate the basic performance of this new technology. In the telescopes, Si detectors work mainly as scatterers and CdTe detectors mainly as absorbers. This combination is suitable for the  $\gamma$ -ray detection of sub-megaelectronvolts, because the probability of Compton scattering in Si is larger than that of photoabsorption, which is dominant in CdTe up to 300 keV. The detector has dimensions of  $18.55 \times 18.55 \text{ mm}^2$  and a thickness of  $500 \mu\text{m}$ . The pixel size is  $2 \times 2 \text{ mm}^2$ , and the gap between the pixels is  $50 \mu\text{m}$ . With the use of the Compton telescope, the Compton reconstruction of the images and spectra of  $\gamma$ -rays from the RI source was successfully obtained. The angular resolution is  $3.9^\circ$  (fwhm) at 511 keV, and the energy resolution is 14 keV (fwhm) at the same energy. Tanaka et al. also demonstrated a full reconstruction by tracking the Compton recoil electrons using the signals detected in successive Si layers. Moreover, by selection of the energy, an image of  $^{137}\text{Cs}$  662 keV line emission was successfully obtained with the Si/CdTe detector.

Owens et al. (36) fabricated a CZT ring-drift detector with a number of concentric ring electrodes that were designed with a bias so that a transverse electric field with potential gradient pushes the electrons toward the central anode. The device consists of a double ring electrode structure surrounding a central point anode with a guard plane surrounding the outer anode ring. By proper adjustment of the ring potential, the detector can be operated in two distinctively different modes of charge collection: pseudohemispherical and pseudodrift. Using a synchrotron X-ray beam, Owens et al. measured the detector response profiles obtained by scanning the focused X-ray beam over the whole detector area, in order to specifically include the variations in count rate, peak position, and energy resolution for X-rays from 10 to 100 keV. In addition, at 662 keV the energy resolution was 4.8 keV, more than twice as good as that for the CZT coplanar grid detectors. The experimental results confirmed the ability of the device to simultaneously provide excellent energy resolution and a wide dynamic range, in contrast to other detection schemes. This feature makes it particularly attractive in XRF, electron microprobe analysis systems, and nuclear medicine applications.

Onodera et al. (37) investigated the feasibility of a compound semiconductor, thallium bromide (TlBr), as an X- and  $\gamma$ -ray detector material due to its high atomic number (Tl, 81 and Br, 35) and high density ( $7.56 \text{ g/cm}^3$ ). TlBr has a wide band gap energy (2.68 eV), which enables TlBr radiation detectors to operate at and above room temperature. Onodera et al. fabricated the TlBr detectors with a simple planar structure from 0.4–0.5 mm thick crystals grown by the traveling molten zone method. The spectroscopic performance evaluated by measuring the  $\gamma$ -ray spectra ( $^{60}\text{Co}$ ) showed that the TlBr detector operating at  $-20^\circ\text{C}$  exhibited an fwhm energy resolution of 57 keV (4.3%) for 1.33 MeV  $\gamma$ -rays. One limitation suffered by TlBr detectors is degraded spectroscopic performance due to the polarization phenomena. Typically, peak shifts in measured spectra were observed. The influence of long-term operation on the spectral response of the

TlBr detectors was evaluated by acquiring energy spectra ( $^{137}\text{Cs}$ ) over a period of time at room temperature and at  $-20^\circ\text{C}$ . Although the TlBr detectors exhibited the polarization phenomena at room temperature, they exhibited no significant degradation in spectral response for 100 h at  $-20^\circ\text{C}$ . For applications with high-energy X-ray photons (30–120 keV), semiconductors with high  $Z$  such as CdTe and GaAs are required, because their absorption energy gap is higher than that of Si. The important advantages of GaAs with respect to Cd(Zn)Te are uniformity of material properties and availability of large wafers. Zwerger et al. (38) prepared GaAs wafers, which were bonded to the Medipix2 readout chip at the Freiburger Materialforschungszentrum, using a low-temperature process. They choose  $300 \mu\text{m}$  thick wafers for first measurements. The pixel and backside contacts were processed with Ti–Pt–Au to form Schottky contacts. The sample surfaces were passivated with BCB. The pixel pitch was  $55 \mu\text{m}$  (standard Medipix) and  $110 \mu\text{m}$ . The comparison study with  $700 \mu\text{m}$  thick Si assemblies revealed that the number of detected quanta in  $300 \mu\text{m}$  GaAs is 10 times higher than in  $700 \mu\text{m}$  Si for  $\gamma$ -rays at 44 and 60 keV.

Lithium fluoride (LiF) has a crystalline fcc structure and can host different types of color center (i.e., electronic point defects in the lattice matrix) under exposure to ionizing radiation such as X-rays, electrons, and ions. The primary F center comprises an electron which replaces an anion vacancy generated by the radiation.  $\text{F}_2$  and  $\text{F}_3^+$  color center defects are simply explained as aggregations of primary F centers, which essentially consist of two electrons bound to two and three close anion vacancies, respectively. The  $\text{F}_2$  and  $\text{F}_3^+$  color centers are optically active, with broad absorption and emission bands in the visible spectral range. Their photoluminescence bands, centered in the red and green, can be efficiently excited by a single pump of blue wavelength at around 450 nm. A relevant advantage of the LiF detector is its ability to be used in the form of both crystal and film deposited onto different substrates (e.g., Si or glass). Almaviva et al. (39) deposited  $1.4 \mu\text{m}$  thick LiF film on a glass substrate and recorded X-ray images of a Fresnel zone plate (FZP) on the LiF films in contact mode. The FZP for hard X-rays with a radius of 120 mm and a zone width of 203 nm was used to record the X-ray images. The microsource X-ray generator with Cu anode was operated at 20 W. After exposure to X-rays, the images stored in the LiF films were read with a confocal optical microscope (Nikon Eclipse C1-80i) equipped with a continuous wave coherent argon laser (INNOVA90), operating in the fluorescence mode. The estimated spatial resolution was about 250 nm, i.e., close to the resolution limit of the confocal microscope. Almaviva et al. summarized the advantages of the LiF detector as being high spatial resolution, large field of view, wide dynamic range, ease of use, and low cost, while the drawbacks were noted as relatively long exposure time and need for an external optical instrument to read the image. Calegari et al. (40) applied a LiF detector to soft X-ray contact imaging using a laser–plasma source. The  $\text{F}_2$  and  $\text{F}_3^+$  color centers are created efficiently by soft X-ray radiation. Expensive and delicate detectors such as X-ray CCD or zooming tube systems are not suitable for soft X-ray imaging with laser-produced plasma, due to the presence of debris. However, cheap and robust LiF detectors are very useful for this application. The experiment was carried out using a Ti:sapphire laser system, producing EUV and soft X-ray radiation ( $20 \text{ eV} < E < 1000 \text{ eV}$ ).



The sample was a damaged 150 nm thick aluminum filter. A 2 mm thick LiF crystal was placed in a vacuum chamber at 27 cm from the plasma source. The image was obtained by pumping the LiF crystal with 450 nm diode light and selecting the luminescence with a 590 nm interferential filter. The high colorization of the LiF crystal can clearly resolve thicknesses of a few tens of nanometers, even for low *Z* materials. Further, its high spatial resolution and very high sensitivity to X-ray radiation with detector energies higher than 1 keV can be useful for the characterization of thin foils with submicrometer spatial resolution.

## INSTRUMENTATION AND X-RAY OPTICS

First, we introduce three articles on X-ray generators that provide monochromatic X-rays. Parametric X-ray radiation (PXR) is a phenomenon that results from the polarization of crystalline media irradiated with charged particles. The radiation is quasi-monochromatic. The energy depends on the angle between the incoming direction of the charged particle and the crystal plane. Since the X-ray energy is tunable in a manner different from that of conventional X-ray tubes, PXR has been anticipated for use with XAFS, protein crystallography, and XRS as an alternative to SR. Moreover, the PXR shows the good directivity of the X-ray emission. The Laboratory for Electron Beam Research and Application at Nihon University (41) started to construct the PXR generator system in a dedicated beam line connected to the 125 MeV electron linac in 2001. This generator system consists of two perfect silicon crystal plates mounted on a precisely moving mechanical setup to vary X-ray energy from 6 to 20 keV. Experimental operation of the PXR generator started early in 2004. Several preliminary experiments were performed to demonstrate PXR applications, suggesting the possibility of applications to advanced X-ray imaging and to the measurement of XAFS. Sato et al. (42) developed plasma flash X-ray generators. In the plasma, the bremsstrahlung X-rays are effectively absorbed and are converted into fluorescent X-rays. Therefore, intense and pure characteristic X-ray lines were produced from the axial direction of weakly ionized linear plasma along the metal rod. For high-speed angiography, they made a tungsten plasma flash X-ray generator using cone beams because tungsten K lines were effectively absorbed by gadolinium-based contrast media. In the flash X-ray generator, a 150 nF condenser was charged up to 80 kV by a power supply, and flash X-rays were produced by discharge. The X-ray tube was a demountable diode, and the pressure inside the tube was kept at about 1 mPa. Since the electric circuit of the high-voltage pulse generator employed a cable transmission line, it produced twice the potential of the condenser charging voltage. At a charging voltage of 80 kV, the estimated maximum tube voltage and current were approximately 160 kV and 40 kA, respectively. When the charging voltage was increased, the characteristic X-ray intensities of the tungsten K $\alpha$  lines increased. The X-ray spectra observed using a transmission-type spectrometer with a lithium fluoride curved crystal showed pure tungsten K lines, and only a few bremsstrahlung X-rays were observed. The X-ray pulse widths were approximately 110 ns, and the time-integrated X-ray intensity had a value of approximately 0.35 mGy at 1.0 m from the X-ray source with a charging voltage of 80 kV. Demonstrations of angiography were performed with animal tissue, and fine blood vessels of approximately 100  $\mu$ m with high contrast were observed. Pokrovsky et al. (43) numeri-

cally showed that a periodic metal–metal multilayer nanostructure could serve as an efficient source of hard X-ray transition radiation. Their aim is to develop an X-ray source for medical applications, which is based on using low-energy relativistic electrons. They concluded that radiator–spacer couples for the generation of hard X-ray resonant transition radiation by a few megaelectronvolts electrons traversing solid multilayer structures for the energies of interest to medical applications (30–50 keV) require that the optimal spacer, as a rule, should have a higher atomic number than the radiator, whereas a light spacer and heavy radiator is good for the soft X-ray region. For a model pair of Mo (radiator) and Ag (spacer), they calculated the transition radiation efficiency, which showed a narrow line near the X-ray absorption edge of Mo of about 1% width, and pointed out that one of the most important factors in attaining an efficient source of resonant transition radiation based on atomic absorption edges is filtering out the bremsstrahlung radiation.

The following paragraphs introduce topics related to focusing optics. They are mostly classified into three categories: diffractive, refractive, and reflective optics. The diffractive lens is represented by the Fresnel zone plate, which has a number of zones with layers of different thicknesses to focus the monochromatic X-rays. A phase zone plate operating in the hard X-ray region requires a much larger thickness of the zone plate structures than that for the soft X-ray region to generate practical focusing efficiency because of the decrease in the refractive index with X-ray energy. The manufacture of a high-resolution zone plate with a small zone width operating in the hard X-ray region requires a much larger aspect ratio, which is defined as the ratio of zone thickness to zone width. High spatial resolution requires narrow widths in the outmost zones, which correspond to a larger diffraction angle and therefore a higher numerical aperture. However, such an ideal zone plate in hard X-rays is still hard to fabricate. Use of a higher order diffraction of a zone plate such as the third diffraction order can significantly increase the resolution of an X-ray microscope since the numerical aperture of the zone plate increases proportionally to the diffraction order used. Yin et al. (44) developed a hard X-ray transmission microscope with a spatial resolution of 30 nm using the third diffraction order of a zone plate objective. The microscope utilizes a capillary-type condenser with a suitable surface figure to generate a hollow cone illumination, which is matched in illumination range to the numerical aperture of the third order diffraction of a zone plate with an outmost zone width of 50 nm. Using a test sample of a 150 nm thick gold spoke pattern with a finest half-pitch of 30 nm, they obtained X-ray images with 30 nm resolution at 8 keV X-ray energy. Snigirev et al. (45) discussed two-step hard X-ray focusing combining a Fresnel zone plate and a single-bounce ellipsoidal capillary. Single-bounce capillaries show great potential in the development of nanofocusing techniques. However, owing to some unavoidable factors, e.g., surface slope errors of the original glass tube, temperature and density variations, and nonuniform mechanical movement, it is difficult to reliably achieve the elliptical shapes with the desired low-figure errors. To overcome these problems and to obtain the best performance of the ellipsoidal capillary, they used a Fresnel zone plate lens to generate a secondary source at the first ellipse focus. With 15 keV X-rays from the European Synchrotron Radiation Facility (ESRF) BM-5 bending magnet, the two-step

demagnification system produced a focus spot of about 250 nm with a gain of more than 1000. In their experiment, the use of an ellipsoidal capillary as a micromirror under off-axis illumination showed new possibilities in nanofocusing developments. Chang et al. (46) developed a method for soft X-ray differential interference contrast (DIC) imaging of nanoscale resolution using only a single-element objective lens. An overlaid binary grating and a zone plate were combined through a logical exclusive OR (XOR) pattern in order to act as an objective lens. The binary grating and zone plate are first pixelized, overlapped, and then compared pixel by pixel. At each pixel position, a logical XOR operation is performed, in which the corresponding pixel value of the resultant XOR pattern is 0 if the pixel values from the grating and zone plate are the same and 1 otherwise. The resultant XOR pattern effectively incorporates the function of a  $\pi$ -phase-shift grating into that of a zone plate. DIC images of the magnetic domains in a 59 nm thick amorphous Gd<sub>25</sub>Fe<sub>75</sub> layer were obtained using circularly polarized X-rays at the Advanced Light Source (ALS) at Berkeley Laboratory, demonstrating that magnetic phase contributions were directly imaged when the probing radiation was tuned about the  $L_3$  and  $L_2$  absorption edges of iron to image the local and element-specific magnetization.

Frontera et al. (47) reviewed a Laue lens telescope development project, named "HAXTEL," for hard X-ray (>60 keV) observation of the continuum spectra of celestial sources. The history of X-ray astronomy has shown that advancements in our knowledge of the X-ray sky are strictly correlated with increases in instrument sensitivity. Up to 60 keV, X-ray optics based on multilayer coatings are useful. Whereas, above 100 keV, the best candidate technique appears Bragg diffraction from mosaic crystals in transmission configuration, namely, a Laue lens. The intermediate band (60–100 keV) can be covered with lower efficiency by multilayer mirrors. However, the authors considered the use of Laue lenses as having a great advantage in sensitivity in this band. A feasibility study of the properties of the Laue lens based on mosaic crystals was theoretically estimated and successfully passed to establish the best lens design. Cu (111) was suggested as a good candidate material. The authors designed two types of Laue lenses for low X-ray energy (60–600 keV) and high X-ray energy (150–1000 keV), in which the outer radii are 496 and 198 mm, respectively. Since the sizes of the crystal tiles are  $10 \times 10 \times 2 \text{ mm}^3$ , the number of the tiles is over 100 000. The focal lengths are 50 m. Kang et al. (48) reported on a type of linear zone plate for nanometer-scale focusing of hard X-rays, a multilayer Laue lens, produced by sectioning a multilayer and illuminating it in Laue diffraction geometry. The diffraction limit for resolution given by the Rayleigh criterion is  $R_{\text{dl}} = 0.5\lambda/\text{NA}$ , where NA is the numerical (angular) aperture of the focusing optics. A higher NA can be achieved by using diffractive optics employing many interfaces, such as Fresnel zone plates. However, there are two main problems. (i) To date, it has been difficult to fabricate zone plates having a combination of nanometer-scale zone widths required for small focal sizes and millimeter-scale depths needed for high efficiency at hard-X-ray wavelengths. (ii) More fundamentally, the standard flat zone plate geometry has a low efficiency for nanometer-scale focusing of hard X-rays, owing to volume diffraction effects. The new type of linear zone plate, a multilayer lens, advanced the solutions to both of these problems.

For the calculations, the authors modeled three types of multilayer Laue lenses: the flat case, which is the analogue of a standard X-ray zone plate; (b) the ideal case with each layer satisfying its Bragg condition, which has the best performance but is difficult to fabricate; and (c) the "tilted" case, which is an approximation of the ideal case. Coupled wave theory calculations indicated that focusing to 5 nm or smaller with high efficiency should be possible in the ideal and tilted cases. Partial multilayer Laue lens structures (tilted case) with outmost zone widths as small as 10 nm were fabricated and tested with 19.5 keV synchrotron radiation. A focal size as small as 30 nm with efficiencies of up to 44% was measured.

Recently, single and polycapillary optics have been obtained, increasing attention on the potential of high efficiency devices for focusing high energy photons and thermal neutrons. Capillary optics use the principle of total external reflection on a smooth surface in capillary systems. Capillary optics has already found many applications and been used in new scientific and industrial instruments and methods. Hampai et al. (49) developed an original software package for polycapillary optics simulations, PolyCAD, which is based on ray tracing optics approximation in the ideal case of total reflection. For actually developed and future applications, it is important to obtain detailed knowledge of the optical characteristics of such devices. An exhaustive theoretical treatment of polycapillary properties is extremely complicated due both to the intrinsic complexity of the structure and the interaction between X-ray photon beams and mono- and polycapillary surfaces. PolyCAD, an original ray tracing package developed by their group, enables easy simulation of the propagation of X-ray beams inside capillary channels for the optics of various geometrical shapes using both point and extended sources. It also enables visualization of spot images formed on a screen at different positions with respect to the optics by calculating photon density distribution. The authors reported on the focusing properties of the cylindrical, conical, and curved mono- and polycapillaries. For different types of capillary optics, Bjeoumikhov et al. (50) discussed the main parameters, such as intensity gain, focal spot size, and beam divergence in their article. Elliptical and parabolic capillaries based on single reflections and polycapillary lenses based on multiple reflections were introduced as focusing lenses and parallelizing semilenses. They reported various applications in micro-X-ray fluorescence analysis for determining two-dimensional elemental distribution at the sample surface as well as depth profiling and examples for single crystal, polycrystal, and powder diffractometry with high spatial and time resolutions. Sun and Ding (51) reported on the properties of a polycapillary X-ray lens, namely, the energy dependence of the focal spot size, transmission efficiency, and output focal distance of a polycapillary X-ray lens. The experiments were performed using a low-current microfocus Mo source with a spot size of 50  $\mu\text{m}$  and SDD (XFlash) with 140 eV resolution at 6.4 keV. An axial scanning method using a knife-edge technique was devised to determine the output focal distance, which is changed by X-ray energy. In addition, the halo effect was studied by measuring the spatial distribution of X-rays with beams of various energies focused by a polycapillary X-ray lens.

Total reflection mirrors for microfocusing are still fundamental and necessary tools. Different from diffractive and refractive lenses, they have an advantage that the focusing point is not changed by the X-ray energy. This characteristic is useful for

combining X-ray microscopy and extended X-ray absorption fine structure (EXAFS) measurement. Suzuki et al. (52) at SPring-8 developed total reflection mirror optics for high-energy X-ray microfocusing. Tests were conducted in the energy range of 30–100 keV. The optical system consists of Kirkpatrick–Baez-type focusing optics with aspherical total reflection mirrors for reducing spherical aberrations. The mirror material was fused quartz with a thickness of 20 mm; the mirror surface was coated with Pt at a thickness of 1000 Å. A focused beam size of  $0.35 \times 0.4 \mu\text{m}^2$  was achieved at an X-ray energy of 80 keV; the measured spot size was less than  $1 \mu\text{m}$  in the X-ray energy region below 90 keV. Sun et al. (53) prepared a combined system of a polycapillary X-ray lens and a toroidal mirror for fine structure micro-X-ray absorption. A polycapillary X-ray lens is useful for focusing the SR when the source spot of the SR is smaller than the entrance of the polycapillary. However, when the SR has a source spot larger than the entrance of the polycapillary, loss of the SR is large. Moreover, another problem of the “escape halo” becomes serious with the decrease of the focal spot size of the polycapillary lens. A toroidal mirror can efficiently focus a larger SR beam; however, the focal spot size is larger than that of the polycapillary. To use the SR beam to full advantage, a larger SR beam can first be focused efficiently into a smaller beam by a toroidal mirror. Then the smaller beam was focused efficiently into a microfocal spot using the central part of the polycapillary lens. The SR at Beijing Synchrotron Radiation Facility is focused by using a combined system of the polycapillary lens and the toroidal mirror. At 8.0 keV, the SR beam with a  $2.3 \times 26 \text{ mm}^2$  area was first focused into a beam spot with an area of  $0.9 \times 0.3 \text{ mm}^2$  by a toroidal mirror. This beam was then focused into a focal spot with diameter of  $21.4 \mu\text{m}$  by using the polycapillary lens. The gain of the power flux density on the focal spot of the combined system and the focal distance of the monolithic half-focusing polycapillary X-ray lens (MHFPXRL) were reported to be 47 473 and 13.3 mm, respectively. With the use of this system, the transmitting EXAFS spectrum of Ni foil and the fluorescent EXAFS spectrum of zinc in a zinc hyperaccumulator were successfully measured. Matsuyama et al. (54) developed a high-spatial resolution scanning X-ray fluorescence microscope using Kirkpatrick–Baez mirrors. Their group fabricated X-ray total reflection mirrors with precisely flat surfaces using the techniques of plasma chemical vaporization machining and elastic emission machining. As a result of two-dimensional focusing tests at BL29XU of SPring-8, the full width at half-maximum measurement of the focused beam was  $50 \times 30 \text{ nm}^2$  under the best focusing conditions. With a change in the virtual source size determined with slits, the beam size was controllable within the wide range of 30–1400 nm. A scanning X-ray fluorescence microscope using the Kirkpatrick–Baez mirrors successfully visualized element distribution inside the SPring-8 logo in the test chart, which has a minimum line width of approximately 50–60 nm. The spatial resolution was better than 30 nm using the smallest focused X-ray beam. The group at SPring-8 (55) constructed a single-shot spectrometer for X-ray free-electron lasers (XFEL) by combining an ultraprecisely shaped mirror and a perfect crystal. The incident beam was diverged by the mirror and then dispersed by the analyzer crystal. A position-sensitive detector measures the energy spectrum as a spatial intensity distribution. The spectrometer could cover an energy

range from a few to a hundred electronvolts with high resolution. To study the fundamental properties of the spectrometer, a Si 555 channel-cut monochromator was set with a narrow bandpass of 13.8 meV. The profile observed by the spectrometer corresponds to  $19.0 \pm 2.7 \text{ meV}$ . The authors discussed application of the spectrometer to determine the XFEL pulse widths theoretically and experimentally and showed that the system can determine pulse widths from subfemtoseconds to picoseconds in a single shot.

Development of crystal spectrometers for observing X-ray emission lines from plasma is a hot topic because a time-resolved emission study leads us to understand the physical phenomena in the plasma. With the advent of short, intense laser pulses, new ways for hot, dense plasma generation are being investigated. Fundamental interests stimulate the characterization of the emitted X-rays, providing information on ionization or electric temperature and density. Further interest lies in characterizing such plasmas as potential sources of ultrashort X-rays. Picosecond and subpicosecond resolution streak cameras have been under development for a decade. Bonte et al. (56) developed a time-resolved X-ray spectrometer based on the coupling of a conical crystal with a subpicosecond X-ray streak camera. The conical crystal is used to disperse and focus the X-ray spectra along a line perpendicular to the detection axis. They used potassium acid phthalate with a  $50 \times 40 \text{ mm}^2$  conical crystal. The cone half angle is 0.3 rad with lower and upper radii of curvature of 88.65 and 103.42 mm, respectively. Spectra of the He  $\alpha$  line and its satellites (3.05–3.15 keV) from laser cluster interaction were observed. The width along the spatial resolution achieved  $300 \mu\text{m}$  fwhm. Focusing is adjusted along the entrance slit of the streak camera. The detector is designed to operate in accumulation mode at a high repetition rate (up to 1 kHz) producing a signal-to-noise ratio as high as  $10^4:1$ . Optical switches have been used to limit the jitter induced in the subpicosecond range, demonstrating the very long-term stability (a few hours) of the entire device. Using a conically bent crystal, Pikuz et al. (57) introduced a new configuration for a two-dimensional (2D) imaging X-ray spectrograph and called it an “extreme luminosity imaging conical spectrograph (ELICS).” X-ray imaging spectroscopy, which gives two-dimensional images of the distribution of each spectral line in the plasma, is a powerful tool for studying hot, dense plasma. The authors’ main goals of the new spectrograph are increasing the luminosity and achieving high spectral and spatial resolution. The ELICS configuration has important advantages over spectrographs that are based on cylindrically and spherically bent crystals. The main advantages are that a wide variety of large-aperture crystals can be used and any desired magnification in the spatial direction (the direction orthogonal to spectral dispersion) can be achieved by the use of different experimental arrangements. An ELICS can be set up so that the detector plane is almost perpendicular to the incident X-rays, a good configuration for time-resolved spectroscopy. The ELICS consists of a 100 mm thick  $50 \times 100 \text{ mm}^2$  mica crystal mounted on a massive conical aluminum block with a rectangular open aperture measuring  $90 \times 45 \text{ mm}^2$ . The radius of the central circle of the cone is  $R = 115 \text{ mm}$  and the apex angle is  $33^\circ$ . ELICS was used successfully for imaging on a pulsed power generator, yielding spectra with high spatial resolution.



Multilayers are now the standard optics of monochromators and analyzers especially for soft X-rays. Through control of the materials and layer thickness, the multilayer optics sometimes shows novel characteristics. Wang et al. (58) at ALS reported the development of the first dynamical sagittally focusing double-multilayer monochromator, which combines multilayer optics and the sagittally focusing concept to deliver a high-brightness, spatially extended X-ray beam whose size is dynamically adjustable. Multilayer monochromators have been widely used in applications such as XRS, X-ray radiography, and tomography where the energy resolution requirement is less stringent. However, most existing multilayer monochromators lack focusing capabilities. The developed monochromator consists of two W/B<sub>4</sub>C multilayers with a 25 Å period coated on Si single-crystal substrates. The second multilayer is mounted on a sagittally focusing bender, which can dynamically change the bending radius of the multilayer in order to condense and focus the beam on various points along the beamline. An X-ray focusing test showed that the smallest focal spot is 0.35 mm and 1.28 mm (fwhm) in the horizontal and vertical directions, respectively. With this new apparatus, the group will be able to adjust the X-ray beam size to best match the area detector size and the object size to facilitate more efficient data collection using ultrafast X-ray radiography and tomography. To study dense and warm plasmas, Champeaux et al. (59) designed and developed W/Si aperiodic multilayer mirrors at the Commissariat à l'Energie Atomique (CEA-DIF) in collaboration with the Laboratoire des Matériaux et de Microélectronique de Provence (L2MP). These "supermirrors," named MA151 and MA152, were designed to work at a 0.6° grazing incidence with a high reflectivity in a large photon energy range for X-ray energies above 5 keV. The MA151 multilayer, which consists of only 20 bilayers of W/Si, will be integrated into a high-resolution X-ray microscope. The thickness sequence of the W and Si layers has five zones. Basically, the thicknesses of the W and Si layers are the same at each zone. The average thicknesses for the Si and W layers are 31.85 and 38.8 Å, respectively. This prototype will be used for spatial and time-resolved imaging of dense and warm fusion plasmas produced during inertial confinement fusion (ICF) experiments at the future Laser Megajoule Facility. Experimental results obtained at the synchrotron radiation facility BESSY II in Berlin show that the average reflectivity of MA151 is above 40% in almost the entire energy range, 5–10 keV. On the other hand, the MA152 multilayer structure is a stack of 35 bilayers of W/Si. The thickness distribution of the W and Si layers is more complicated than that of MA151. The thickness of the layers varies between 12 and 42 Å, with an average thickness of 24.4 Å for Si and 23.74 Å for W. From the measurements on the MA152 mirror, a reflectivity above 15% can be expected in the energy range 7.2–14 keV. André et al. (60) fabricated a multilayer grating as components for soft X-ray wave dispersive monochromators and tunable radiation sources. The energy resolution  $E/\Delta E$  of the multilayers is approximately 100 in the soft X-ray region, which means that these structures are monochromators with poor resolution. This is due to the limited number of bilayers that participates effectively in the Bragg diffraction: because of the attenuation of the incident wave in the mirror, mostly due to absorption, the deepest layers cannot participate actively in the diffraction process. To circumvent this

problem, the authors proposed etching the multilayer to the profile of a lamellar grating. This operation enabled the deepest penetration of the incident beam. It was shown both theoretically and experimentally that these multilayer gratings with appropriate characteristics could be used as monochromators for soft X-rays, whose spectral resolving power was considerably improved with respect to mere interference mirrors. Moreover, they mentioned the possibility of tunable soft X-ray sources based on the interaction of medium-energy electron beams with periodic multilayer structures, which are presently being developed in several countries. Kessels et al. (61) investigated the use of hydrogen passivation of the silicon layers in Si/W soft X-ray reflective multilayer mirrors. High reflectivity of multilayers is critically dependent on the practical realization of an optically sharp interface. The use of H implantation into the Si layers of Si/W multilayer structures was shown experimentally to result in the formation of islandlike W structures and reduced multilayer reflectivity as compared to standard Si/W multilayers. The additional use of atomically thin Si adhesion layers corresponding to Si/H/Si/W led to improved growth and increased soft X-ray reflectivity. The effects taking place at the interfaces were analyzed by transmission electron microscope (TEM) and in situ X-ray reflectivity and were described in terms of interface and surface energies with quantitative analysis of intermixing, materials density, and geometrical optical effects. Eriksson et al. (62) discussed the interface engineering of short-period Ni/V multilayer X-ray mirrors in their article. Low-energy ion-assisted magnetron sputter deposition was used for the synthesis of highly reflective Ni/V multilayer soft X-ray mirrors. A low ion energy and a high ion-to-metal flux ratio were employed in order to stimulate adatom mobility while minimizing ion-induced intermixing at the interfaces. Simulation using binary collision approximation provided the best conditions of energy and flux of Ni and V for a series of Ni/V multilayer mirrors with periods of about 1.2 nm. However, it was also concluded that an interface mixing of about  $\pm 1$  atomic distance was unavoidable when a continuous flux of assisting ions was used. To overcome this limitation, the authors employed a sophisticated interface engineering technique in which the first 0.3 nm of each layer was grown with high-flux, low-energy ion assistance and the remaining part was grown with a slightly higher ion energy. This method was demonstrated to largely eliminate intermixing while maintaining the smoothing effect of ion assistance. Two Ni/V multilayer soft X-ray mirror structures, one with 500 periods designed for near-normal incidence and one with a 150 period reflecting polarizer at the Brewster angle, were grown utilizing the interface engineering concept. Both the near-normal incidence reflectivity as well as the polarizability were improved by a factor of 2 as compared to previously reported data for an X-ray energy of  $E = 511$  eV. Stollberg et al. (63) demonstrated large-diameter, normal-incidence spherical Cr/Sc multilayer condensers with high and uniform reflectivity. The normal-incidence multilayer condenser offers several advantages including high collection efficiency, well-defined spectral selectivity, and high numerical aperture. The compact X-ray microscope consists of a spherical multilayer mirror, microzone plate, and a CCD detector. The multilayer mirror matched the numerical aperture of the zone plate but required advanced processing for high total reflectivity. Direct current magnetron sputtering was



used to deposit 300 bilayers of Cr/Sc with a predetermined *d*-spacing of 3.374 nm operating wavelength on spherical substrates. The mirrors showed a uniform reflectivity similar to 3% over the full 58 mm diameter condenser area. With these mirrors, an improvement in exposure time by a factor of 10 was achieved in comparison with previous multilayer mirrors.

Waveguides, such as optical fibers, are materials that can propagate photons without loss. Although waveguides for X-rays exist, they have generally been developed as a tool for focusing 10–100 nm beams and as bandpass filters of X-rays different from optical fiber. The X-ray waveguide phenomena were first used for multilayers, where a low-density layer was sandwiched between high-density layers. In this case, the low-density and high-density layers act as the core and the cladding of the optical waveguide, respectively. Total reflections of X-rays at interfaces between the core and the cladding generate standing waves in the guiding layer. The character of the standing wave determines the finite number of guiding modes. Recently, two-dimensional X-ray waveguides have been achieved by e-beam lithography, and the possibility of fabricating a focusing tool with nanometer dimensions has been shown. Bukreeva et al. (64) investigated diffraction and refraction phenomena at the entrance of a hollow X-ray waveguide with weakly absorbing dielectric cladding layers using two independent approaches: (a) analytical and (b) numerical solutions of the wave equation in paraxial (parabolic) approximation. Previous approaches of theoretical calculations of X-ray waveguides did not take the interaction of the incoming beam with the cladding material at the entrance of the waveguide into proper account. The analysis by Bukreeva et al. showed that the wave penetrating through the cladding material substantially modified the wave field near the waveguide entrance. The result was a significant increase of the total energy flux inside the guiding layer and additional spatial modulation of the electromagnetic field. The two independent approaches of analytical and numerical solutions to the diffraction and refraction problems demonstrated very good qualitative and quantitative agreement. To obtain an accurate description of the field inside the waveguide, it is necessary to include the interaction of the incoming X-rays with the cladding layers. Pelliccia et al. (65) attempted to verify the predictions of computer simulations for mode transmission with experimental results of air-gap waveguides. The computer simulations were performed using a code based on finite difference scheme solutions of parabolic wave equations. Since both synchrotron sources and table-top laboratory sources were considered for incident radiation, they calculated the transmission through the waveguides in the case of an ideal plane wave and in the case of an incoherent source placed at a short distance from the waveguide as would be the case for a laboratory source. The simulation of the beam at the exit of the waveguide indicated an interesting focusing effect due to diffraction at the waveguide boundary. This can be a useful indication for the optimization of microprobe experiments. With the use of a fabricated air-gap waveguide by a simple procedure, SR measurements at the Elettra synchrotron source were performed. The results were in good agreement with theoretical expectations. Tiwari et al. (66) demonstrated that a thin marker layer, sandwiched in the guiding medium of a thin-film planar X-ray waveguide structure, could be used to determine X-ray compression efficiency for a particular

excitation mode. Usually, X-ray compression gain and transmission efficiency of a thin-film X-ray waveguide structure is realized by measuring the ratio of total intensity reaching the waveguide exit to that of the primary incident intensity. However, it is not feasible to directly measure the electromagnetic field intensity distribution inside a waveguide structure. By insertion of a thin marker layer at various depths in the guiding medium and with the performance of angle-dependent fluorescence measurements, the electromagnetic field distribution as well as the position of the marker layer can be unambiguously determined. This approach was applied for determining X-ray compression and transmission efficiency of a Mo/B<sub>4</sub>C/Mo-based X-ray waveguide structure by inserting a thin Fe marker layer and showed that the X-ray compression gain inside a thin-film waveguide was modulated in accordance with the primary beam spot size over its surface. Jarre et al. (67) fabricated two dimensionally confining X-ray channel waveguide structures for the delivery of nanoscopic X-ray beams. The waveguides are combined with a high gain Kirkpatrick–Baez-prefocusing mirror system yielding hard X-ray beams with a cross section down to 25 nm fwhm. The incoming synchrotron X-ray beam is coupled in from the front side of the waveguide. In their article, two fabrication methods using an e-beam lithography technique, direct and indirect structuring, were described both of which were provided with two-dimensionally confining X-ray waveguides, where direct and indirect structuring waveguide cores were polymer and air (or vacuum), respectively. Both kinds of waveguides were tested at the SR source providing the expected optical properties. The principal advantage in using the more elaborate, indirect structuring method is that air (or vacuum) is used as the guiding material, reducing absorption losses and increasing the difference of the refractive indices between the core and the cladding. The X-ray waveguides obtained by both methods can provide sufficiently intense hard X-ray nanobeams at highly brilliant sources, given an effective prefocusing optic.

## QUANTIFICATION AND FUNDAMENTAL DATA

In theoretical calculations for quantitative analysis using X-rays, accurate fundamental atomic data are essential, including data for mass attenuation coefficients. Cevik and Baltas (68) experimentally determined mass attenuation coefficients for Bi, Pb, Sr, Ca, and Cu metals; Bi<sub>2</sub>O<sub>3</sub>, PbO, SrCO<sub>3</sub>, CaO, and CuO compounds; and solid-state forms of a Bi<sub>1.7</sub>Pb<sub>0.3</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub> superconductor at 57.5, 65.2, 77.1, 87.3, 94.6, 122, and 136 keV energies from a <sup>57</sup>Co point source and X-ray secondary targets using a Si(Li) detector. The overall error for the measurements was estimated to be 3–5%. Ekinici and Astam (69) published experimental results for mass attenuation coefficients obtained from biological samples, such as cornea taken from keratitis patient; soft contact lens; leiomyomata uteri; and uterus, at 5.9 keV using a Si(Li) detector and <sup>55</sup>Fe radioactive source. With the use of their experimental setup, the observed relative standard error of the measured mass attenuation coefficients was 3.4%. Manohara and Hanagodimath (70) calculated effective atomic numbers, electron densities, and mass attenuation coefficients of several essential amino acids such as histidine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, and valine in the energy range of 1 keV–100 GeV using WinXCOM. The values of these parameters were found to change with energy and composition of the amino acids. Currently available experimental data of X-ray production cross sections,

especially for the L shell, in PIXE, are not satisfactorily accurate, e.g., the average uncertainty of the reported data of L X-ray intensity ratios for Au as a function of proton energy is  $\pm 8\%$ . Jones and Campbell (71) reported experimental X-ray intensity ratios,  $L_{\beta}/L_{\alpha}$  and  $L_{\gamma}/L_{\alpha}$  for W, Pt, Au, Pb, Th, and U atoms. Proton energies of 2.0 and 2.5 MeV were used to minimize united atom and intrashell effects and thus make feasible a test of the ECPSSR, together with the L subshell fluorescence and Coster–Kronig probabilities. They suggested that the most appropriate components of a PIXE database for the L subshells are the ECPSSR-DHS ionization cross sections and the fluorescence and Coster–Kronig yields from new vacancy decay parameters. This combination provides X-ray group intensity ratios that are within 1.5% of measured values. Accurate data for X-ray line intensities for a range of elements over a range of electron beam energies are critical in quantitative EPMA measurement; however, current experimental data for absolute X-ray yields are not accurate ( $\sim 5\%$ ). Hatzistergos and Lifshin (72) suggested the use of experimental data of the ratio of standard X-ray lines in quantitative analysis, which can be measured with 1% or better accuracy. They determined relative line intensities between elements ( $12 < Z < 32$ ) for incident beam energies between 5 and 20 keV and within spectral series for K, L, and M. By the use of relative line intensity data between elements, it is possible to perform quantitative X-ray microanalysis with the measurement of only a single standard rather than separate measurements of all element standards (with 2–4% accuracy). When the relative line intensity data between elements were employed in a standardless quantification procedure, accurate quantitative results (on average, within 1%) were obtained. Reliable modeling of electron transport in solids is important for quantification in EPMA. Jablonski et al. (73) introduced a new analytical expression for the electron stopping power (SP) for electron energies between 200 eV and 30 keV, given as the product of the SP and the inelastic mean free path (IMFP) and called the  $S\lambda_{in}$  expression, an empirical function of atomic number and electron energy. Parameters in the expression were obtained from fits to SPs and IMFPs calculated from optical data for a group of 27 elemental solids, resulting in fairly accurate mean deviation of 10.4%, which is less than the mean deviations found in similar fits with the empirical modifications of the Bethe SP equation. The new expression is considered suitable for Monte Carlo simulations of electron transport with the continuous slowing-down approximation relevant to EPMA.

The relative radiation intensity ( $R_i$ ), defined as fluorescent radiation intensity of analyte in specimen to fluorescent radiation intensity of pure standard element or compound, is used in the calculation of both fundamental parameter methods and theoretical influence coefficient algorithms for XRF quantification. Accuracy of calculated  $R_i$  is determined by uncertainties of fundamental atomic parameters, spectrometer geometry, and also by X-ray tube spectral distribution. Sitko (74) studied the differences between  $R_i$  calculated using experimental and theoretical X-ray tube spectra in order to investigate the effect of different X-ray tube distribution on the uncertainty of calculation of  $R_i$ . The X-ray tube spectra were obtained based on three different algorithms and for the most common targets such as Cr, Mo, Rh, and W. Calculated  $R_i$  was investigated when pure element standard, multielement standard similar to the analyzed material, and one pure element

standard for all analytes are used. When only one pure element standard is used, the differences of calculated  $R_i$  are significant, ranging from a few percent to more than 10%. Much lower differences are observed by the use of multielement standard similar to the analyzed material and for intermediate-thickness samples if sample thickness is small enough.

For thin-film analysis using XRF, the fundamental parameter (FP) method is popularly used because pure element or multielement bulk standards can be employed for calibration when film standards are not available. However, contribution of scattering effects to the fluorescence intensity for the coating specimen may be different from that of the bulk specimen, which was investigated by Han et al. (75). Theoretical equations to calculate fluorescence intensity enhanced by scattering effects for coating samples were developed based on FP models. The contributions of different scattering effects to fluorescence intensity were estimated for a hypothetical Zn coating on an infinite Fe substrate sample, which can be up to several percents of primary fluorescence intensity depending on the thickness of coating. The result implies that the fluorescence intensity enhanced by scattering effects should be included in the calculation when the FP method is employed for thin-film analysis, especially using bulk standard sample.

The quantitative analysis of precious metals requires more accurate determination than FP-based XRF methods can provide, whereas empirical calibration curve methods provide good results only when a large set of reference materials are used as calibration standards. Cernohorsky et al. (76) developed a quantitative method for EDXRF analysis of precious metallic alloys. The method combined a standardless FP method with a semiempirical calibration method utilizing a limited number of matrix specific standards. For the analysis of Ir–Pt, Rh–Pt, Rh–Pd–Pt, and Rh–Ir–Pt disk samples and Rh–Pt thermocouple wire, reference materials of Ir–Pt, Rh–Pt, Rh–Pd–Pt, and Rh–Ir–Pt alloys were used for the calibration of the combined FP XRF method. This new method provided the results accurate within 0.1%.

Correction of the self-absorption effect in particle analysis using  $\mu$ -XRF is difficult in a “standard” procedure which requires the measurements of the intensities of fluorescence peaks together with the peaks of coherently and incoherently scattered primary radiation. Bielewski et al. (77) developed a method of correction for the absorption effect where the absorptions of primary X-ray beams and characteristic fluorescence X-rays are separately treated using a SDD and a Si(Li) detector. The fast counting SDD and the Si(Li) detector are used to measure the primary X-ray beam transmitted through the sample and characteristic X-ray radiations, respectively. It was demonstrated that the method provided quantitative results better than the conventional absorption correction procedure provided when the method was applied to NIST K3089 glass microspheres of known composition.

Cauzid et al. (78) developed a new standardless quantification procedure for synchrotron radiation induced  $\mu$ -X-ray fluorescence ( $\mu$ -SR-XRF) analysis of fluid inclusions from the Brusson gold deposit, Italy. The procedure is based on an infinite homogeneous plane layer and a noniterative fundamental parameter method. Results showed a good agreement between the calculated concentrations obtained with the procedure and the corresponding crush-leach analysis. Cl, K, Ca, Fe, Cu, Zn, and As crush-leach

concentrations were within error bars of the  $\mu$ -SR-XRF concentration estimates. Br crush-leach content was above  $\mu$ -SR-XRF estimates and Ti, Cr, Mn, Ni, and Pb were detected with the  $\mu$ -SR-XRF technique only. In this standardless quantitative procedure of individual fluid inclusions, uncertainties on inclusion depths strongly affected calculated light element concentrations (Cl to Ca), whereas Mn and heavier elements concentration estimates are more sensitive to errors on fluid inclusion thickness, e.g., uncertainties of  $\pm 1\ \mu\text{m}$  or less on fluid inclusion depth and thickness yield statistical errors of  $\sim 50\%$  on Cl concentration estimates and lower than 20% on transition metals. Cauzid et al. claimed that this new standardless  $\mu$ -SR-XRF-based quantification procedure is more precise than those previously established and was efficiently applied to multielementary analysis (Cl to Pb) of diluted individual fluid inclusions.

X-ray emission and fluorescence spectra have been used to study chemical speciation, such as the dependence on the formal oxidation state. However, almost all studies have employed empirical methods to interpret the spectra, which require measurements of many reference materials and are applicable just to the specific system investigated. Ankudinov et al. (79) developed an ab initio code for the calculation of X-ray emission line shapes based on a self-consistent, real-space Green's function approach. Calculations were presented for the P K– $M_{2,3}$  and the Cr L-series emission lines for a selection of simple compounds. These lines exhibit changes depending on the oxidation state and on the neighboring atoms in the compounds that can be observed with instruments available in many XRF laboratories. The calculated spectra are in reasonable agreement with measured spectra, indicating that the approach has the potential to yield quantitative information about the chemical state.

Spatial inhomogeneity of sample thickness requires the correction of different X-ray yields due to thickness variation in  $\mu$ -PIXE. Because it is difficult to compensate for the variation of X-ray yields by  $\mu$ -PIXE analysis itself, the thickness distribution map of a sample with a spatial resolution of a few micrometers needs to be obtained by other means. Satoh et al. (80) employed the scanning transmission ion microscopy (STIM) technique for the purpose. A computer calculation code was developed to estimate the variation of X-ray yield due to thickness variation. For granulated powder samples of ion-exchange resin, the distribution of sodium concentration obtained from two-dimensional X-ray map was very much inhomogeneous, but after the correction for the thickness variation, the concentration distribution became homogeneous, indicating the feasibility of the correction procedure. In thick target PIXE analysis, the matrix effect is always a problem; in order to minimize the matrix effect, Aburaya et al. (81) used a matrix standardization method in which the powdered sample is diluted to a few percent in a known matrix made of "light" elements (graphite and boric acid) and applied a simple thick target correction factor to the known thin-target PIXE yields. The analysis of Marine Sediment SRM IAEA-356 diluted to 1% in boric acid showed that the deviations from certified values are all within one experimental standard deviation, except for Rb, which is still within  $\pm 2\sigma$ . However, detection limits were worse with matrix standardization.

Chemometrics is becoming used more in XRS, especially in the field of curve fitting, multivariate calibration, and pattern

recognition. The advantages of chemometrics include its nonlinear approach for the description of complex interactions, its fault tolerance in handling noisy and incomplete data, and its adaptive capability of learning from data by the training process. Luo (82) published a comprehensive review on recent developments in chemometrics and their application in XRS. In the review, relatively new algorithms, namely, genetic algorithms, neural networks, and support vector machines, are discussed. Together with the three algorithms, the performances of different algorithms are compared briefly, which mainly include principal component analysis (PCA), partial least-squares regression (PLS), factor analysis, cluster analysis, nearest neighbor methods, linear discriminant analysis, linear learning machine, and soft independent modeling of class analogy. It was claimed that the chemometric methods are generally superior to the conventional methods, such as Fourier transform and Marquardt–Levenberg algorithms. Chemometrics should also get much more successful applications to XRS than the current status. During this review period, several applications of chemometrics in XRS appeared. Goraieb et al. (83) published an application of chemometric techniques, such as PCA and PLS, for classifying Portland cements and quantifying some of its constituent elements. The samples were irradiated as powders for 200 s using conventional benchtop EDXRF equipment. The spectra were processed via The Unscrambler software, version 9.2. It was demonstrated that the classification of Portland cements, regarding their origins and calcium concentration, was feasible using the PLS. The PLS can easily quantify light elements, such as Al, Si, and Mg, a challenge in most X-ray analytical methods since their  $K_{\alpha}$  emission peaks are very close to each other. Nagata et al. (84) developed a multivariate calibration method for SR-TXRF data in order to determine Pb and As concentrations in aqueous samples. To overcome the serious spectral interference between the two species and the overlap of another interfering element (Br), a PLS method was used. The PLS calibration models were based on the X-ray fluorescence emission signals (9.550–13.663 keV) for a set of 26 different mixtures containing Pb, As, and Br. Root mean square errors of prediction are 0.03 and 0.24 mg/L for Pb and As, respectively, indicating that the proposed multivariate methodology overcomes the problems associated with spectral interferences and minimizes the influence of an interfering agent (Br). Antolak et al. (85) investigated the efficacy of a chemometric technique for locating and identifying specific particles-of-interest on a large area of collected samples using PIXE. Obtaining particulate compositional maps from scanned PIXE measurements is difficult due to the complexity of analyzing spectroscopic data collected with low signal-to-noise at each pixel. Samples consisting of particulates with known compositions and sizes were loaded onto Mylar and paper filter substrates and analyzed by scanned  $\mu$ -PIXE. The data sets were processed by PCA, and the associated principal component spectral data were quantified by converting the weighting images into concentration maps. The results indicate automated, nonbiased, multivariate statistical analysis is useful for converting very large amounts of data into a smaller, more manageable number of compositional components needed for locating individual particles of interest on large area of collection media. Correa et al. (86) applied an artificial neural network (ANN) to quantitative elemental analysis of organic materials using



PIXE. The ANN was trained with PIXE spectra of organic substances. Following the training stage, the ANN was applied to a subset of similar samples in order to obtain the elemental concentrations in muscle, liver, and gills of *Cyprinus carpio*. Concentrations obtained with the ANN method were in good agreement with results from the standard analytical procedure, showing the potential of ANN in PIXE quantitative analyses. Garcia et al. (87) published a work that applied Kohonen ANN for an exploratory analytical study of metalloproteins based on eight metallic descriptors (K, Ca, Cr, Mn, Fe, Co, Ni, and Zn). The metal ions were detected by SRXRF in 43 bands of proteins from sunflower leaves. The application of Kohonen ANN reduced the data dimensionality from eight to only two without information loss, making it possible to find a few protein bands that can represent all the sunflower proteins studied.

For fundamental parameter based quantification, detailed knowledge of characteristics of the detector, including efficiency, energy resolution, and the precise shape of response function, is essential. Plagnard et al. (88) published a work on the calibration of HP-Ge detector efficiency using complementary methods involving radioactive X-ray standards, reference synchrotron flux, and a monochromatic X-ray source, combined with Monte Carlo simulation. The monochromatic X-ray source was used to determine the thickness of detector components that create absorption sites in front of the active zone of the detector, such as the layers of Al (infrared shielding), Ni (electrical contact), and Ge (dead layer). The detector efficiency was calculated by Monte Carlo simulation. Differences between simulated data and experimental efficiency values were approximately 1–5% at energies above 1400 eV and reached 20% at lower energies, indicating that further improvement of this approach is needed. Pekoz and Can (89) investigated characteristics of the response function of an HPGe detector using a Monte Carlo program. They claimed that the possible escape of photoelectrons, created as a result of the photoelectric absorption of incident photons, plays an important role in the response function of an HPGe detector. The simulations always underestimated the measured escape of photoelectrons, indicating that the electron transport model needs significant improvement. Visňovezky et al. (90) studied the parameters related to characteristic X-ray peak asymmetry in a Si(Li) detector. The asymmetric X-ray peaks are mainly due to the presence of impurities and defects in the crystalline structure of Si in the detector. Spectra from mono- and multielement samples were collected for elements with atomic number between 7 and 20, using ED-EPMA for incidence energies between 5 and 25 keV. The area corresponding to the asymmetric correction exhibited an energy dependence similar to that of the mass absorption coefficient of the detector material. When two spectrometers with the same detector type and different pulse processors were compared, peaks were more asymmetric for lower peaking time values. When two different detectors were used, differences were even more important. Pile-up artifact in EDS spectra can lead to false element identifications, inaccurate correction for peak overlap, and losses of counts that give poor quantitative results. Statham (91) developed a correction procedure for sum peaks in acquired X-ray spectra using the fast Fourier transform. It was demonstrated that with the use of this correction procedure, sum peaks and pile-up continuums were removed and peaks were

restored to compensate for pile-up losses and accurate quantification was possible at count rates at least 4 times higher than without correction. Barradas and Reis (92) published another correction procedure for the pile-up in a Si (Li) detector. The procedure employs an analytic calculation based on first principles statistical analysis of incoming pulses for pile-up correction in PIXE spectra. No distinction between characteristic X-ray peak and continuum contributions is necessary, and the parameters required for the calculation are simply the collection time, the shaping time of the amplifier, and the resolving time of the pile-up rejection system. Calculations were performed for a series of experimental PIXE spectra, for different count rates and amplifier shaping times, and spectra collected with the pile-up rejection system on and off, showing that calculated and observed pile-ups are well in agreement.

The most popular spectrum fitting program for EDXRF measurements has been commercial software based on the AXIL package which is robust and reliable. However, the commercial software has limited adaptability to users' needs and availability to the user community. Solé et al. (93) developed a user-friendly program for EDXRF analysis that allows interactive and batch processing of large data sets and is particularly well-suited for X-ray imaging. Its implementation of a complete description of the M shell is also helpful for analysis of data collected at low energies. The code is platform independent (Linux, Windows, MacOS X, Solaris), and it is freely available for noncommercial use.

## X-RAY IMAGING

X-ray imaging techniques are now rapidly advancing with third generation SR. The use of X-ray coherence has become important in the development of new analytical methods combined with 3D viewing of samples. In this section, we introduce 16 articles on X-ray imaging techniques including X-ray holography, X-ray fluorescence tomography, phase contrast tomography, and an oversampling method of coherent scattering.

X-ray holography techniques are primarily classified into two categories: traditional X-ray holography extracted from optical holography and atomic resolution holography using secondary emissions such as X-ray fluorescence. The latter method is called X-ray fluorescence holography (XFH), which provides three-dimensional atomic images around specified elements. XFH uses atoms as a wave source or monitoring of an interference field within a crystal sample. Therefore, it can record both the intensity and phase of scattered X-rays. Hayashi et al. (94) used X-ray excited optical luminescence (XEOL) for measurements using the X-ray standing wave method and atom-resolved X-ray holography instead of the use of X-ray fluorescence. They measured the incident beam angular dependence of the luminescence intensity from ZnO-coated  $\text{Al}_2\text{O}_3$  and found that it corresponded to the XSW/XH pattern of  $\text{Al}_2\text{O}_3$ . Furthermore, the Al and O atoms were successfully reconstructed using a fitting-based reconstruction algorithm (scattering pattern extraction algorithm using the maximum entropy method). It was demonstrated that hard X-ray XSW/XH studies for light elements, which have been difficult to accomplish by fluorescence detection, can easily be carried out by XEOL detection since the X-ray fluorescence of Al is hardly detectable in air due to absorption. Kopecky et al. (95) proposed X-ray diffuse scattering holography based on the measurement of the angular distribution of anomalous diffuse scattering. The



differences between diffuse scattering patterns of nondoped single crystals and doped single crystals produce a hologram providing information on local atomic structure around the doped atom. To confirm this theoretical assumption, they prepared  $\text{Ga}_{0.98}\text{Mn}_{0.02}\text{As}$  epitaxial film on a GaAs wafer. The experiment was carried out at the ESRF. X-rays of 30 keV were chosen in order to achieve good spatial resolution in the reconstructed image. Scattering patterns were recorded by an X-ray CCD. The experiment itself consisted of the collection of two high precision diffuse scattering patterns: the first from the  $\text{Ga}_{0.98}\text{Mn}_{0.02}\text{As}$  layer and the second from the GaAs substrate. A three-dimensional image of the local neighborhood of Mn atoms in a  $\text{Ga}_{0.98}\text{Mn}_{0.02}\text{As}$  layer was obtained by using X-ray diffuse scattering holography. The first and second nearest neighbors of the Mn atoms correspond to the local structure around the Ga atoms in a zinc blend GaAs structure. Accordingly, the Mn atoms are situated in substitutional positions. Kohmura et al. (96) introduced the determination of a transmitted X-ray wave field using X-ray in-line holograms and additional two-beam interferometry. Originally, they developed two-beam interferometry with an X-ray prism for two-beam off-axis holography, where refracted X-rays are used as a reference wave. Therefore, with the use of this interferometry, the phase of the X-rays transmitted through samples is quantitatively measured without an additional reference wave. Complex transmissivity of an object including several elements cannot be extracted from only a single in-line hologram, which is an interference of transmitted and scattered X-rays. However, by using the in-line hologram and additional two-beam interferometry, the complex transmissivity obtained from the phase information and the wave field at the detector plane can be completely determined. In their experiment, the sample–detector distance was fixed at both setups of the in-line holography and two-beam interferometry. A demonstration using beryllium foils and the brain of an ascidian larva was successfully performed. Scherz et al. (97) demonstrated phase imaging by means of resonant soft X-ray holography. Their technique is based on tuning the photon energy to an element-specific core–electron binding energy of the sample and utilizing the fact that the real part (phase) and the imaginary part (absorption) of the complex refractive index have resonant maxima at slightly different energies in the vicinity of an absorption resonance, providing enhanced image contrast. The general concept was shown by using a Co/Pd multilayer sample, which exhibits random nanosized magnetic domains. The sample has a higher perpendicular magnetic anisotropy. A 1 nm thick Au film, which is effectively opaque to soft X-rays, was sputter deposited onto the back of a membrane. The holographic structure was patterned into an Au film using focused ion beam milling. In their experimental setup, an aperture was used to make the source spatially coherent. The coherent beam illuminated the holographic mask having both the object of the Co/Pd multilayer sample and a small hole for making the reference wave. The far field diffraction pattern was recorded with a CCD. The real space images with nanometer resolution were obtained by Fourier transformation. By tuning below the Co L-edge resonance, the quantitative and spectroscopic phase method enabled high-contrast imaging on a nanoscale electronic and magnetic order. The complex refractive index was quantitatively obtained through the interference between the resonant and nonresonant scattering.

Chapman et al. (98) performed a new type of X-ray holography, named “femtosecond time-delay X-ray holography,” using extremely intense and ultrafast X-ray pulses from free-electron lasers. The ultrafast X-ray pulses offer unique opportunities to study fundamental aspects of complex transient phenomena in materials. Ultrafast time-resolved methods usually require highly synchronized pulses to initiate a transition and then probe it after a precisely defined time delay. In the X-ray regime, these methods are challenging because they require complex optical systems and diagnostics. Therefore, the authors proposed and applied a simple holographic measurement scheme inspired by Newton’s “dusty mirror” experiment to monitor an X-ray-induced explosion of microscopic objects. They placed 140 nm diameter spherical polystyrene particles on a 20 nm thick silicon nitride membrane that was mounted with a thin spacer in front of a multilayer mirror; this assembly resembles Newton’s dusty mirror. For recording the interference pattern, they used another plane mirror angled at 45° to reflect the backscattered X-rays onto a back-illuminated CCD detector. The experiment was performed using a focused 25 fs pulse of 32.5 nm wavelength light from the FLASH soft X-ray laser. The delay was encoded in the resulting diffraction pattern to an accuracy of 1 fs, and the structural change was holographically recorded with high resolution. The technique was applied to monitor the dynamics of polystyrene spheres in intense free-electron-laser pulses and to observe an explosion occurring well after the initial pulse. The results support the notion that X-ray flash imaging can be used to achieve high resolution beyond radiation damage limits for biological samples.

X-ray radiographic absorption imaging is an invaluable tool in medical diagnostics and materials science. For biological tissue samples, polymers, or fiber composites, however, the use of conventional X-ray radiography is limited due to their weak absorption. This is resolved by using phase-sensitive imaging methods to improve the contrast, and this has been realized with highly brilliant X-ray synchrotron or microfocus sources. However, the requirement of the illuminating radiation means that hard X-ray phase-sensitive imaging has until now been impractical with more readily available X-ray sources, such as X-ray tubes. Momose’s group (99) studied X-ray phase tomography based on X-ray Talbot interferometry. Their X-ray Talbot interferometry consists of a phase grating and an amplitude grating, which are positioned between the sample and a two-dimensional detector. The Talbot effect was originally discovered in the visible light region, which is known as a self-imaging effect by an object with a periodic structure under coherent illumination. While a transmission image becomes blurry with increasing distance from the object to an imaging plane under normal illumination, self-images are reconstructed at specific distances from a periodic object to an imaging plane by the Talbot effect, which is understood as a result of Fresnel or Fraunhofer diffraction. However, to extend this effect to the hard X-ray region, there is the difficulty of the fabrication of the grating, which needs a thick pattern and micrometer order period grating. Therefore, a high-aspect-ratio grating pattern was fabricated by X-ray lithography and gold electroplating. In their article, they introduced the imaging results obtained for a cancerous rabbit liver and a mouse tail with synchrotron radiation and mentioned an advantage in that the technique functions with polychromatic cone-beam X-rays and is

compatible with a compact X-ray source. Pfeiffer et al. (100) achieved phase-sensitive imaging with conventional X-ray tubes, and they reported how a setup consisting of three transmission gratings can efficiently yield quantitative differential phase-contrast images. In contrast with existing techniques, the method requires no spatial or temporal coherence, is mechanically robust, and can be scaled up to large fields of view. Like Momose's group, they used a Talbot–Lau type hard X-ray imaging interferometer. The source grating positioned in front of the X-ray tube creates an array of individually coherent, mutually incoherent sources. A phase object in the beam path causes a slight refraction for each coherent subset of X-rays, which is proportional to the local difference phase gradient of the object. This small angular deviation results in changes of the locally transmitted intensity through the combination of two gratings placed between the object and the detector. The phase contrast image of a small fish showed the fine structures of the tail fin and the region around the otoliths, which were not seen in conventional X-ray transmission images. Their method provides all the benefits of contrast-enhanced phase sensitive imaging but is also fully compatible with conventional absorption radiography. Friis et al. (101) applied phase contrast X-ray microtomography to explore cretaceous seeds with Gnetales and Bennettitales. Over the past 25 years, the discovery and study of Cretaceous plant mesofossils has yielded diverse and exquisitely preserved fossil flowers that have revolutionized our knowledge of early angiosperms, but the remains of other seed plants in the same mesofossil assemblages have so far received little attention. These fossils, typically only a few millimeters long, have often been charred in natural fires and both their three-dimensional morphology and cellular detail have been preserved. The authors used phase-contrast enhanced synchrotron radiation X-ray tomographic microscopy to clarify the structure of small, charcoallified gymnosperm seeds from the Early Cretaceous of Portugal and North America. For their samples, absorption-based SR X-ray tomography did not provide sufficient contrast because of the low absorption of the charcoallified cell wall, whereas phase contrast X-ray tomographic microscopy provided high resolution at the cellular level. The seeds were imaged on the X-ray microscope at the TOMCAT beamline of the Swiss Light Source of the Paul Scherrer Institute. The obtained information links these seeds to Gnetales (including Erdtmanithecales, a putatively closely related fossil group) and to Bennettitales, both important extinct Mesozoic seed plants with cycadlike leaves and flowerlike reproductive structures. The results suggested that the distinctive seed architecture of Gnetales, Erdtmanithecales, and Bennettitales defines a clade containing these taxa.

Koyama et al. (102) developed a hard X-ray nanointerferometer using two types of zone plates. One is an ordinary zone plate for a microscope objective and the other is a newly designed zone plate called an "annular zone plate" for configuring reference waves. The annular zone plate has no zone in the inner region with the same size as that of the outer diameter of the ordinary zone plate. These two zone plates are arranged coaxially on the optical axis in order for their focal points to coincide at the same point. The waves from the object zone plate and the annular zone plate overlap. The sample was positioned in front of the object zone plate. A slight phase shift caused by a sample is directly observable as image contrast. The authors obtained X-ray micro-

graphs of polystyrene microparticles at  $0$ ,  $\pi/2$ ,  $\pi$ , and  $3\pi/2$  phase shifts of the object waves, where phase shifts were caused by the phase plate positioned in front of the sample. A combination of these micrographs provided clear phase images of the sample. In addition, the authors reconstructed three-dimensional rendering images of polymer microfibers with the addition of titania nanoparticles. Spatial resolution was achieved to 60 nm. Baruchel et al. (103) reviewed SR microtomography from the viewpoint of materials science. The use of synchrotron radiation X-ray microtomography rests on the exploitation of beam coherence, high spatial (submicrometer) or temporal resolution (s), in situ and real-time experiments, and quantitative measurements. They presented selected original applications showing these capabilities, such as the phase contrast imaging of Si particles in Al alloys, the nucleation of fatigue cracks in structural materials, the visualization of hollow silica spheres within polymer foams, and the real-time observation of the semisolid state in Al–Cu alloys. In addition, future perspectives of SR microtomography were discussed. Feldkamp et al. (104) designed and built a compact X-ray microtomography system to perform element mapping and absorption imaging by utilizing scanning fluorescence tomography and full-field transmission microtomography, respectively. The system is based on a low power microfocus tube, an energy dispersive detector, and a PIN diode. Full-field transmission tomography and fluorescence microtomography provide the three-dimensional inner structure and the element distribution of an object, respectively. Since a small and intensive microbeam is required for fluorescence microtomography, polycapillary optics was used. By operating the microfocus tube with a molybdenum target at 12 W, a microbeam with a fwhm lateral extension of 16  $\mu\text{m}$  and a flux of about  $10^8$  photons/s was generated. To obtain a fluorescence tomogram, each projection was recorded by scanning the sample horizontally through the microbeam and recording the fluorescence and transmitted radiation at each position in the scan with the fluorescence detector and the PIN diode, respectively. The authors demonstrated images of element distribution inside dried plant samples. For full-field scanning tomography, the X-ray optics was removed and the sample was imaged in magnifying projection onto a two-dimensional position-sensitive detector. Depending on sample size, a spatial resolution down to about 10  $\mu\text{m}$  was possible in this mode. The method was demonstrated by three-dimensional imaging of a rat humerus. Aoki's group (105) at the University of Tsukuba constructed a full-field X-ray fluorescence imaging microscope using a Wolter mirror at the Photon Factory BL3C2 at KEK (High Energy Accelerator Research Organization, Tsukuba, Japan). White X-rays from a bending magnet were used to emit strong X-ray fluorescence from samples. The imaging optical system was constructed normal to the incident X-ray beam to reduce the effect of elastic scattering. A Wolter type-I mirror made of Pyrex glass was used to image the elementary distributions of samples on the detector plane. The effective field of view was approximately 600  $\mu\text{m}$ , assuming the spatial resolution to be 10  $\mu\text{m}$ . A photon-counting method using a charge-coupled device was applied to obtain an X-ray fluorescence spectrum at the image plane. The spatial distributions of some specific atoms such as Fe and Zn were obtained from photon-counting calculations. An energy resolution of 220 eV at the Fe K $\alpha$  line was obtained from the X-ray

fluorescence spectrum by the photon-counting method. Three-dimensional element analysis of a plant seed (alfalfa) was demonstrated by a reconstruction technique using computed tomography. Alderden et al. (106) showed that X-ray fluorescence microtomography is a suitable technique for imaging the distribution of Pt drugs within multicellular tumor spheroids, models of solid tumors. The limited penetration of cytotoxic drugs into tumors is a significant contributing factor to the limited effectiveness of cancer chemotherapy. Pt(IV) complexes are substantially more inert and therefore have the potential to penetrate further into the tumors while remaining largely intact. The authors presented the results of the first microtomographic study of the distribution of cisplatin and three Pt(IV) complexes in spheroids. The spheroids were analyzed using a 13.45 keV monochromatic X-ray beam focused on a 4–5  $\mu\text{m}$  spot to give elemental images in micrograms per centimeter squared at the advanced photon source (APS). Images in element weight fraction were computed by dividing the micrograms per centimeter squared value in each pixel by beam height and assuming the density was that of water. The detection limit for Pt was determined to be near 10 ppm. Radial distribution profiles for each tomogram were produced by determining the concentration profile through the center of the spheroid at 1° intervals. The resulting tomographic images revealed that there is no significant difference between the distributions of the ranges of the Pt(II) and Pt(IV) complexes investigated, suggesting that complexes that are more resistant to cellular uptake may be needed to ensure more complete distribution throughout a tumor.

X-ray scattering using a highly coherent X-ray beam provides not only average periodical structural information of the sample but also the shape of the sample. Miao et al. (107) demonstrated for the first time that a combination of coherent X-ray scattering with a method of direct phase recovery called oversampling accomplishes lensless microscopy (i.e., X-ray diffraction microscopy). They applied a novel tomographic reconstruction algorithm to direct phase retrieval of coherent X-ray diffraction patterns and reconstructed quantitative 3D imaging of a heat-treated GaN particle with each vortex corresponding to  $17 \times 17 \times 17 \text{ nm}^3$ . In their experiment, an undulator SR beam at SPring-8 of 5 keV was used. The temporal coherence of the beamline was  $\sim 1.86 \mu\text{m}$ , and the vertical and horizontal spatial coherent lengths were  $\sim 110$  and  $\sim 30 \mu\text{m}$ , respectively, at the sample position. The sample of GaN particles was suspended in ethanol and deposited on a 30 nm thick  $\text{Si}_3\text{N}_4$  membrane. The well-isolated and micrometer-sized particles were selected for coherent X-ray diffraction. The coherent X-ray diffraction patterns were recorded on a CCD detector. From 27 coherent X-ray diffraction patterns with a tilt range of  $-69.4^\circ$  to  $+69.4^\circ$ , the authors reconstructed the platelet structure of GaN and the formation of small islands on the surface of the platelets, successfully capturing the internal GaN-Ga<sub>2</sub>O<sub>3</sub> core-shell structure in three dimensions. Using a FLASH soft X-ray free-electron laser, Chapman et al. (108) performed femtosecond X-ray diffraction microscopy at the FLASH facility (formerly known as the VUV-FEL) at the Deutsches Elektronen-Synchrotron in Hamburg. Theory predicts that, with ultrashort and extremely bright coherent X-ray pulses, a single diffraction pattern may be recorded from a large macromolecule, a virus, or a cell before the sample explodes and turns into a plasma. The aim of their work was

confirmation of this theoretical prediction. An X-ray free-electron laser beam was focused on a 20  $\mu\text{m}$  spot on the sample, which was a 20 nm thick transmissive silicon nitride membrane with a picture milled through its entire thickness. The direct beam passed through the sample window and exited the camera through a hole in a graded multilayer planar mirror. The diffracted X-rays from the sample were reflected from this mirror onto a CCD detector. With an intense 25 fs,  $4 \times 10^{13} \text{ W cm}^{-2}$  pulse containing  $10^{12}$  photons at a wavelength of 32 nm, a coherent diffraction pattern from a nanostructured nonperiodic object was successfully observed before it was destroyed at 60 000 K. A novel X-ray camera assumed single-photon detection sensitivity by filtering out parasitic scattering and plasma radiation. The reconstructed image, which was obtained directly from the coherent pattern by phase retrieval, showed no measurable damages, although the pattern was acquired with the diffraction-limited resolution. The authors verified that measurements of the coherent X-ray scattering before sample explosion is possible, revealing that a three-dimensional data set may be assumed from such images when copies of a reproducible sample are exposed to the beam one by one. Two of the reviews mentioned above concerning X-ray diffraction microscopy described the coherent “small angle” scattering technique, which provides full three-dimensional images of the interior density of the samples. The “coherent Bragg diffraction” from crystalline materials introduces the additional possibility of imaging the strain fields in the crystal lattice. Pfeifer et al. (109) presented a method of obtaining three-dimensional mapping of a deformation field inside a lead nanocrystal. A lead nanocrystal was crystallized in an ultrahigh vacuum from a droplet on a silica substrate and equilibrated close to its melting point. Undulator X-rays from the APS were monochromatized to be 1.38 Å and collimated by narrow slits to illuminate a few hundred crystals of the sample. A direct-reading CCD X-ray detector, at a distance of 1.32 m, was centered on the (111) Bragg peak of the crystals to give the diffraction patterns. The sample was rotated at steps of  $0.01^\circ$ , and 50 diffraction patterns were collected. A three-dimensional image of the density, obtained by inversion of the coherent X-ray diffraction, showed the expected faceted morphology but, in addition, revealed a real-space phase that is a field arising from the interfacial contact forces. They claimed that quantitative three-dimensional imaging of lattice strain on the nanometer scale would have profound consequences for our fundamental understanding of grain interactions and defects in crystalline materials.

## TOTAL REFLECTION X-RAY FLUORESCENCE ANALYSIS

A review article entitled “Challenges of TXRF for Surface- and Thin-Layer Analysis” was written by Klockenkemper (110). TXRF has essential advantages in surface- and thin-layer analysis, especially for flat substrates such as wafers. Actually, TXRF has become a major technique for contamination control in the semiconductor industry. Furthermore, it is capable of a nondestructive analysis of thin near-surface layers deposited on flat substrates. Recent advances in TXRF analysis were introduced in this article. Depth profiling by repeating both sputter etching and TXRF analysis is a new approach, which has a depth resolution of a few nanometers. In addition, recent sweeping TXRF and VPD (vapor-phase decomposition) TXRF were also reviewed.



Hellin et al. (111) also reviewed some recent developments in TXRF used for metallic contamination control on Si wafers. They discussed expansion of the elemental range and the dynamic range. Three methodologies (microdroplet, film, and bulk type standards) were critically reviewed. In addition, a recent development of sweeping TXRF, suitable for fast screening of large surface areas, was discussed. Finally, the performance of TXRF was assessed with respect to competitive analytical techniques. These two excellent review articles on TXRF show that TXRF is an established method for the analysis of contamination on Si wafers.

We can find new developments of TXRF using recent advanced technology, such as high-performance X-ray detectors and small X-ray tubes. Pahlke et al. (112) reported an application of a new-generation SDD to a TXRF system. Since SDD operates with an electric cooling device, it is suitable for use in a cleanroom. Recently developed SDD has a large sensitive area of up to 100 mm<sup>2</sup>. The authors applied an SDD (KETEK, sensitive area, 10 mm<sup>2</sup>) to a commercial TXRF instrument (ATOMIKA 8030W). The adapted system was tested and compared with the original setup using a conventional Si(Li) detector (sensitive area, 80 mm<sup>2</sup>). Multielement droplet samples on silicon wafers were analyzed and the results showed 2 times better detection limits for the Si(Li) detector for 1000 pg of Ni in comparison to that of the SDD. Waldschlaeger (113) reported on low-power TXRF spectroscopy by using the SDD and an air-cooled X-ray tube in a tube power range lower than 50 W. They proposed the use of a microfocus X-ray tube, because the power density is increased to 4000 W/mm<sup>2</sup>, leading to a 60% increase in X-ray fluorescence intensity. In addition, the recent development of a new generation of SDD increased the active detector area by a factor of 3, enhancing the peak-to-background ratio by a factor of 2. The author concluded that the detection limit for nickel could be decreased to 1 pg. Furthermore, the application of a low-power X-ray tube and a small SDD enables the development of a portable TXRF instrument. Kunimura and Kawai (114) developed a portable TXRF instrument with an air-cooled glass X-ray tube, operated at 9.5 kV and 150  $\mu$ m, and a Si PIN photodiode detector (X-123, Amptek Inc.). Since control of the incident angle is very important in TXRF, a collimator for the primary X-rays is necessary. They used a waveguide-type slit for this purpose. The developed TXRF instrument had a size of 23 cm (height), 30 cm (width), and 9 cm (depth). Since no monochromator was applied in their TXRF instrument, continuum X-rays were used for excitation of the X-ray fluorescence. They reported detection limits of 6 ng for Cr and Fe with this portable instrument. Since the total reflection phenomenon depends on the energy of the X-rays, excitation of X-ray fluorescence with monochromatic X-rays are preferable for reducing the detection limits of TXRF. An exchangeable secondary target was applied to TXRF by Vasin et al. (115). A high voltage power source with a voltage of up to 75 kV and X-ray tubes with a power of up to 2.5 kW were used in the spectrometer to generate the primary X-ray radiation. The exchangeable secondary targets made it possible to obtain monochromatic radiation. The use of tubes with different anode materials (chromium, tungsten, and rhodium) and different secondary targets provides efficient performance for the analysis of elements with atomic numbers 13 < Z < 92. In this case, it was possible to optimize the TXRF analysis with detection limits of 10  $\mu$ g/g in aqueous solutions.

A new method of sample preparation especially for TXRF analysis was proposed. Sparks et al. (116) investigated a BioDot BioJet dispensing system (AD 3050, Irving, CA) for this purpose. The BioDot system was programmed to dispense arrays of 20 nL droplets of sample solution on Si wafers. Each 20 nL droplet was approximately 100  $\mu$ m in diameter. A 10  $\times$  10 array (100 droplets) was deposited and dried in less than 2 min at room temperature. A satisfactory calibration curve was obtained for Ni deposited on a wafer with a Ru film substrate. The research activity of a European group on the same subject will be reviewed in the Applications section in this review article.

In the conventional TXRF, a considerably large area of the sample surface is analyzed because the primary X-rays irradiate a large surface area. In some TXRF analyses, the residue of a sample droplet on a flat sample carrier is measured. Therefore, the X-ray fluorescence emitted from areas other than the residue area produces background peaks. Thus, micro-TXRF was proposed to measure only residue from a small droplet under total reflection conditions (117). The authors used a simple pinhole to detect the X-ray fluorescence from a localized region. Single pinholes with different diameters of 1, 0.5, and 0.1 mm each were attached to the top of an EDX detector. X-ray elemental maps of the droplet residue were also obtained by scanning the sample. The same Japanese group (118) investigated the feasibility of combining TXRF with a chemical microchip. The chemical microchip has a flat region on its surface, which was used for TXRF analysis. A sample solution was introduced through an inlet of the chemical microchip with a microsyringe and flowed into a microchannel. The solution overflowed from the well-type microchannel on the flat surface of the chemical microchip. After the sample solution dried on the surface, it was measured by TXRF, showing an excellent spectrum with a low background level. Since various chemical processes including extraction and speciation can be performed on chemical microchips, a system of total analysis is expected by combining TXRF with chemical microchips. The research group of Zaray (119) presented a combination of off-line thin-layer chromatography (TLC) and TXRF analysis. They applied this method to arsenic speciation and analysis of root extracts of cucumber plants grown in As(III) containing modified Hoagland nutrient solution. After development and drying the TLC plate, the sheets were divided into 0.8  $\times$  0.8 cm segments and digested. The solution (25  $\mu$ L) including the sample and the standard solution was dropped on a quartz carrier. TXRF measurements were performed using a commercial TXRF instrument (EXTRA IIA, Atomika Instruments, Germany). As a result, both As(III) and As(V) were successfully detected.

The analytical performance of TXRF analysis has been improved by the development of X-ray optics to enhance the intensity of the primary X-rays. Egorov et al. (120) studied a planar X-ray waveguide resonator composed of two polished planar reflectors, where the uniform X-ray standing wave interference field is created. They applied this resonator with an output hole to TXRF analysis. The recent development of a TXRF instrument at the Physikalisch-Technische Bundesanstalt (PTB, Berlin, Germany) was reported by Bechkoff et al. (121). This TXRF instrument was especially designed for analyzing contaminations including light elements on 200 and 300 mm Si wafers. The entire surface of a 200 or 300 mm wafer could be scanned by monochromatized



radiation provided by a plane grating monochromator beamline for undulator radiation at the electron storage ring BESSY II. The authors presented the calculation formula for TXRF quantification using fundamental parameters, leading to completely reference-free quantitation in TXRF analysis. Since the preparation of reference materials for TXRF quantification of ultratrace contaminations is often difficult, it is expected that reference-free quantitation of TXRF analysis will be applied to various types of TXRF instruments, although further modifications of the calculation procedures are required. Another numerical approach for grazing exit X-ray fluorescence (GE-XRF) analysis was performed by Okhrimovskyy and Tsuji (122). The atomic percentage of implanted particles on the sample surface was estimated from the peak position of angle dependency of the experimental GE-XRF intensity profile. An algorithm for constructing Gaussian-type depth profiles of atoms implanted in a substrate was developed. The model was applied to the intensity profile of the As K $\alpha$  line emitted from As atoms implanted in a Si wafer. The least-squares method was used to minimize the overall difference between experimental and calculated GE-XRF intensities. Optimum parameters of particle distribution were determined in this procedure, resulting in a depth profile for As.

## ELECTRON PROBE MICROANALYSIS

With the advent of fast computers and affordable memory storage, the utilization of Monte Carlo (MC) simulations in quantitative EPMA becomes a more practical tool. MC-based quantification methods can provide the most versatile approach for quantification, especially for samples with complex geometries or for unconventional measurement conditions. Salvat et al. (123) reviewed practical aspects of MC simulation of EPMA experiments and described a MC code system, called PENELOPE, which includes geometry tools and variance reduction methods that allow the simulation of X-ray spectra for samples with complex geometries in moderate computing times. The influence of different interaction models and simulation algorithms employed in MC calculation on the simulated X-ray spectra was investigated, revealing that the ionization cross section is the parameter that can limit the capability of MC simulation for standardless quantification methods. Gauvin et al. (124) developed a new MC program, Win X-ray, which simulates the X-ray spectrum of a given material of homogeneous composition measured with SEM-EDX, operating between 10 and 40 keV. Underlying equations of the MC simulation model were introduced in details. By simulating the X-ray spectra, it is possible to establish the optimum conditions to perform a specific analysis as well as establish detection limits or explore possible peak overlaps. However, it was claimed that further improvement of simulation models is needed to achieve 5% relative accuracy for true standardless quantification; currently, the relative accuracies are approximately 10% when simulated X-ray spectra for Au/Cu, Ti/Al/V, and Au/Ag alloys were compared with measured spectra. Gauvin (125) published a study on quantitative EPMA of heterogeneous specimens in an effort to extend the capability of the MC program. The heterogeneous specimens included a vertical layer embedded in a homogeneous matrix and a spherical particulate deposited onto a substrate. The simulations showed that a 10 nm layer of boron in a steel matrix can be imaged using backscattered electrons and detected using X-ray microanalysis with a field emission SEM (FESEM), even

with an electron beam energy equaling 20 keV. It was also demonstrated that these simulations could be useful to estimate the optimum acceleration voltage for performing such analyses. For a carbon spherical particulate located on the top of a gold substrate, Gauvin showed that X-ray emission and electron backscattering are a strong function of the diameter of the particulate and also of the electron beam energy. A new method to determine the thickness of a thin film deposited on a substrate is proposed, based on the ratio of intensities of elements of the thin film and the substrate obtained from the same X-ray spectrum, eliminating the measurement of the specimen current.

EPMA of stratified specimens has been intensely developed during the last few decades. Most methods require an accurate description of the analyzed sample as they are all based on the fundamental assumption that each layer of the sample is uniform in structure and composition. Dumelie et al. (126) developed a new quantification procedure that allows a simultaneous determination of both concentration and thickness from X-ray intensities of the coating on the heterogeneous substrate. The proposed procedure is an extension of their previous work that allows the determination of chemical compositions of thin films on heterogeneous substrates but requires a priori knowledge of the film thickness. The new procedure is based on the measurement of the backscattering coefficient during X-ray microanalysis and the determination of film thickness employing an iteration scheme. Through application of the procedure on two experimental examples, they obtained thickness and concentration maps free of artifacts associated with compositional changes in the substrate. Figueroa et al. (127) published a standardless quantification procedure for thin-film characterization based on invariance principles. Experimental quantities such as the detected X-ray intensities and electron fluxes in the boundaries of a solid system were formulated by an invariant embedding method. In the invariant embedding, any individual process is considered a member of a family of related processes and a mathematical model of the physical processes focused on the boundary fluxes is formulated. The procedure was applied to two thin-film systems such as a Cu film on a Pb substrate and Ti on Si. Despite its potential advantage as a standardless method for thin-film analysis, substantial improvement is still needed for addressing more realistic situations in microanalysis.

Quantitative EPMA of highly insulating materials is a complicated problem due to the buildup of strong electric fields in irradiated volumes that seriously enhances scattering and energy losses of primary electrons, known as the charging effect. Lulla et al. (128) investigated this effect on quantitative EPMA using thin-film systems, such as HfO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub>, and TiO<sub>2</sub>, grown onto both semiconductive Si and insulating quartz substrates. No clear correlation among band offsets, charging of the film surface, and dependence of charging effect on the primary electron beam energy was observed. Further, determination of mass thickness of an insulating layer is a much greater problem than the measurement of local elemental concentration of impurities in insulating materials, meaning that further advancement of calculation models is evidently needed for reliable determination of the thin-film mass thicknesses in insulating samples from EPMA data.

Electron-excited X-ray mapping is a key operational mode of SEM-EDX. The popularity of X-ray mapping persists despite the

significant time penalty due to the relatively low output count rates, typically less than 25 kHz that can be processed with the conventional EDX. The SDD uses the same measurement physics, but modifications to the detector structure permit operation at a factor of 5–10 times higher than conventional EDX for the same resolution. With an output count rate much higher than that of the conventional Si(Li) detector, versus input count rate of SDD, it can be advantageous in X-ray mapping, as demonstrated well by Newbury (129). Output count rates as high as 500 kHz can be achieved with 217 eV energy resolution. Such high count rates make possible X-ray mapping through the method of X-ray spectrum imaging, in which a complete spectrum is captured at each pixel of the scan. Useful compositional data can be captured in less than 200 s with a pixel density of  $160 \times 120$ . This high-speed X-ray mapping with the SDD was applied to alloy and rock microstructures, ultrapure materials with rare inclusions, and aggregate particles, demonstrating its practical capability of the new approach.

In recent years, electron backscattering diffraction (EBSD) techniques have been getting more and more popular because of their capability for crystallographic information of the specimen. In these techniques, the specimen needs to be tilted away from the perpendicular incidence by over  $70^\circ$  in order to acquire good Kikuchi patterns. Bastin et al. (130) developed a double-Gaussian  $\varphi(\rho z)$  procedure (PROZA96TILT) for handling cases of nonperpendicular incidence of the electron beam onto the specimen and investigated its feasibility by comparing the experimental data and the results of MC simulations with the calculations of the PROZA96TILT program. It was found that up to a  $50^\circ$  tilt, the predictions of their software were satisfactory, but further refinement of the program is required for the approach to be applicable at larger tilt angles.

The focused ion beam (FIB) technique has been a very efficient and site-specific method for fabricating TEM samples. However, FIB can also be useful in SEM-EDX applications. Kaegi and Gasser (131) developed an interesting methodology for characterizing airborne particles in great detail, eventually enabling a detailed source apportionment of specific particles, by the combined use of computer-controlled SEM, FIB, and TEM. The FIB technique was used to fabricate TEM lamellas of selected, micrometer-sized airborne particles. First, a large number of particles between 0.6 and  $10 \mu\text{m}$  in diameter were analyzed using computer-controlled SEM-EDX. Two individual particles were then selected, and the particle-loaded filter was transferred from SEM to FIB, where lamellas of the selected particles were fabricated. The lamellas were finally analyzed with TEM. With the use of this technique, the particle of interest can be selected from a large data set (based on chemistry and/or morphology) and then investigated in greater detail later. FIB also can be applied to obtain three-dimensional (3D) tomographic spectral imaging. Kotula et al. (132) developed a 3D microanalysis procedure using a combined SEM/FIB system equipped with an EDX. The FIB system is used first to prepare a site-specific region for X-ray microanalysis followed by the acquisition of an electron-beam generated X-ray spectral image. A small section of material is then removed by the FIB, followed by the acquisition of another X-ray spectral image. This serial sectioning procedure is repeated in order to sample a volume of material. This resultant four-

dimensional (three real space and one spectral dimension) spectral image data is so big in size that efficient multivariate statistical analysis (MSA) is required for data interpretation. The site-specific comprehensive analysis capability of tomographic spectral imaging combined with MSA was demonstrated for two specific real samples.

Simulation of X-ray spectra is commonly performed by MC calculation approach. Eggert (133) introduced another approach for the simulation of EDX spectra. The procedure, which is the inverse of the standardless spectra evaluation procedure, is based on the absolute calculation of P/B ratios using a fundamental parameter method and a computation of bremsstrahlung over the entire distribution of energies. One advantage of this approach is its easiness for the estimate of minimum detection limits (MDL) as MDL is always based on P/B ratios. The expected MDL can be calculated in advance, so it is possible to optimize the excitation and absorption conditions before a time-consuming measurement. Still, further refinement is needed for reliable spectra simulation in an energy region below 1 keV.

Standardless quantitative analysis in EPMA requires accurate data on physical parameters as well as accurate spectrometer efficiency. When spectrometer efficiency is calculated from assumed data for the detector design, considerable errors can be involved. Alvisi et al. (134) developed a calibration procedure for the detection efficiency of EDX in SEM based on the comparison of X-ray spectra from a reference material (RM), measured with the EDX to be calibrated and with a reference EDX. The calibration of the reference EDX is performed using synchrotron radiation. Measurement of RM spectra and comparison of the specified line intensities enable a rapid efficiency calibration on most SEMs with a minimum of operator assistance. The efficiency calibration was performed for an unknown EDX system with about 5% RSD.

EPMA is a powerful tool for quantitative elemental analysis. However, if molecular speciation of the specimen, in addition to elemental concentrations, can be performed, rich information on the specimen can be obtained. Godoi et al. (135) developed a sequential EPMA technique using thin-window EDX detection and micro-Raman spectrometry (MRS) on the same atmospheric particles using nanomanipulation. The advantageous combination of these two techniques allows the acquisition of information on the morphology, size, elemental and molecular composition, as well as the molecular structure of the same individual particle with a diameter as small as 500 nm. Particle relocation was achieved by manipulative transfer onto TEM grids, in an environmental SEM, using 100 nm glass tips. A moderate correlation between the elemental composition obtained by thin-window EPMA and the molecular fingerprint obtained by MRS is observed. It was demonstrated that the obtained information using the sequential EPMA technique is useful in the interpretation of indoor air quality.

## PARTICLE-INDUCED X-RAY EMISSION

Micro-PIXE analysis is one of the trends in PIXE analysis. To produce microion beams, Nebiki et al. (136) used glass capillary optics. A slightly tapered glass capillary optic device was applied for a differential pumping orifice as well as a focusing lens, enabling in-air PIXE measurements. The flux intensity was enhanced by at least 1 order of magnitude due to the focusing effect. Using capillaries of 10–20  $\mu\text{m}$  outlet diameters, the authors

obtained a  $\text{He}^{2+}$  ion beam at several hundred picoamps of 4 MeV and applied it to PIXE analysis without any sample treatment. This simple glass capillary optics device is expected to be used for micro-PIXE analysis of many types of samples, including solids, liquids, and gases.

Another topic in PIXE is the development of three-dimensional micro-PIXE (3D-PIXE). Kanngiesser et al. (137) proposed and developed confocal geometry in an external micro-PIXE setup. This geometry is closely related to the geometry of 3D micro-XRF, which her research group has also studied. The experiment was performed with the external microproton beam facility at the AGLAE particle accelerator. Characteristic X-rays were detected by a Si(Li) detector through a polycapillary X-ray half-lens, which was placed in front of the detector. The position of the X-ray optics and its proper alignment with respect to the proton microbeam focus provided the possibility of carrying out 3D micro-PIXE analysis. As the first application, depth profiling of layered material was performed. Simulated curves showed good agreement with the experimental results. A simulation approach of the 3D micro-PIXE data produced elemental concentration profiles rather in good agreement with the corresponding results obtained by electron probe microanalysis for a cross-sectioned patina sample. The authors considered that 3D micro-PIXE seems especially well suited for investigations in the field of cultural heritage. The same group (138) reported on depth-resolved elemental analysis by 3D-PIXE. The confocal micro-PIXE setup was characterized with respect to its spatial and depth resolution. The spatial resolution of this technique in the 1–10 keV energy range varied from about 34  $\mu\text{m}$  at 10 keV to about 120  $\mu\text{m}$  at 1 keV X-ray energy. The authors reported on an information depth up to 40–50  $\mu\text{m}$ . As an example of application for this new nondestructive analytical technique, an archeological ceramic fragment was examined. The potential of 3D micro-PIXE to provide advanced qualitative information on the elemental distribution in the sample was discussed. Ishii et al. (139) also developed a 3D imaging system using characteristic X-rays produced from a Ti target by proton microbeam bombardment. The 3D imaging system consists of a microbeam and a 1 megapixel X-ray CCD camera (Hamamatsu Photonics C8800X) and has a spatial resolution of 4  $\mu\text{m}$  for Ti K-X-rays (4.558 keV) produced by 3 MeV protons of a beam spot size of  $1.1 \times 1.41 \mu\text{m}^2$ . The authors applied this system, namely, a micrometer-CT, to observe the inside of a small, living ant's head about 1 mm in diameter. Three-dimensional images of the ant's head were obtained with a spatial resolution of 4  $\mu\text{m}$  by rotating and scanning the sample.

Another approach to obtain depth profiles of elements is by changing the detection angles in PIXE geometry. Miranda et al. (140) changed the detection angle to obtain depth profiling for a Au-implanted Ti thick target and a Cu film on a Ti target. The sample was placed on a goniometer in a vacuum chamber. The detection angle was varied from 30 to 80°. This measurement gave good results regarding the range of implanted ions and film thickness. However, the authors concluded that there was no complete information about the width of the distribution of the implanted ions, emphasizing the need to develop a full mathematical algorithm to obtain a general depth profile. Broadhurst et al. (141) presented a new generic method of directly determining experimental spectra arising from specific depths beneath a

surface by transforming experimental angle-dependent data. The method was applied to PIXE spectra from a thin CdS film deposited on soda lime silicate glass. The PIXE spectra from a range of incident beam angles were transformed into PIXE spectra from a range of depths using an algorithm that was previously applied to X-ray diffraction. The authors concluded that the transformation algorithm had two limitations, poor depth resolution and the production of a negative X-ray yield. Another PIXE data analysis was performed to determine variations in sample thickness.

## MICRO X-RAY FLUORESCENCE ANALYSIS

Micro-XRF is a useful technique to obtain two-dimensional imaging of elemental distribution in inhomogeneous samples, such as geological, biological, and archeological samples. The main advantages of micro-XRF are that it is a nondestructive analysis and does not require a vacuum condition like EPMA. Furthermore, recent superior X-ray focusing optics such as mono- and polycapillary X-ray lenses and low-power X-ray tubes enable downsizing to a benchtop or portable micro-XRF spectrometer. Buzanich et al. (142) developed a portable micro-XRF spectrometer equipped with a compact vacuum chamber to effectively detect low-Z elements. A compact vacuum chamber was attached to the X-ray tube and pumped down to 0.1 mbar. An X-ray microbeam was produced by a polycapillary X-ray lens equipped with a low-power Pd-anode tube. A polycapillary X-ray lens with a spot size of about 160  $\mu\text{m}$  or a collimator with a 1 mm inner diameter was used alternatively either for focusing or collimating the primary X-ray beam. The concentrations of the analytes were calculated using the fundamental parameter method. The authors analyzed a bronze horse by using the proposed XRF spectrometer. Papadopoulou et al. (143) studied the development and optimization of a portable micro-XRF instrument for in situ multielemental analysis of ancient ceramics focused by a monocapillary X-ray lens. The X-ray microbeam was 126  $\mu\text{m}$  as evaluated by scanning a 50  $\mu\text{m}$  thick Ni wire. The detection limits that were calculated as  $3\sigma$  values for ceramic and glass standard materials were on the order of 7–62 mg/kg, for elements with atomic numbers 19–30. Quantitative analyses of several standard materials were performed using the fundamental parameter method and a single standard. The quantitative results showed good agreement between the certified and experimental values. In many cases, the relative error of the micro-XRF analysis was <10%.

Recent approaches in micro-XRF for the analysis of depth-sensitive elemental distributions, eventually leading to a three-dimensional analysis, are remarkable. In particular, confocal 3D micro-XRF analysis combined with a polycapillary X-ray lens becomes a powerful tool for nondestructive depth-sensitive elemental analysis at ambient pressure.

A research group at Cornell University (144) built a confocal X-ray fluorescence microscope at the Cornell High Energy Synchrotron Source (CHESS) to obtain compositional depth profiles of historic paintings. The composition of buried layers in a painting can often answer questions regarding the work's authenticity, the extent of previous restorations, the working methods of the artist, and the piece's condition. The microscope consists of a single-bounce, borosilicate monocapillary optic to focus the incident beam onto the painting and a commercial borosilicate polycapillary lens to collect the fluorescent X-rays. The



former single-bounce monocapillary, developed at CHESS, focuses an incident beam of approximately 20  $\mu\text{m}$  in diameter. The resolution of the microscope was measured by scanning a variety of thin metal films through this confocal volume while monitoring the fluorescence signal. They successfully demonstrated the confocal X-ray fluorescence microscope using test paint microstructures with up to four distinct layers, each having a thickness in the range of 10–80  $\mu\text{m}$ .

For other 3D micro-XRF approaches, Yang et al. (145) demonstrated a depth-sensitive film analysis using grazing exit-micro-XRF (GE- $\mu$ -XRF) combined with a polycapillary X-ray lens. The three types of thin-layer samples, which were 500 nm thick Ti, 50 nm thick ferric film, and Fe/Ti layers (50 nm thick Fe/50 nm thick Ti), were deposited by a vacuum evaporation method on a Si substrate. The primary X-ray beam emitted from a Mo X-ray tube was focused into a polycapillary X-ray lens. A silicon drift detector with a slit was adjusted at a specific low takeoff angle. Applying this method to the film analysis, the authors were able to obtain information on the film thickness, composition, and density. Tsuji et al. (146) proposed a unique micro-XRF method for soft materials by using commercially available injection needles. One injection needle, which was connected directly to an X-ray tube, was used as an X-ray guide to irradiate the sample with the X-rays. Another needle, which was inserted into the sample, was used to detect fluorescent X-rays emitted inside the sample. The ends of both needles were covered with a thin polyimide film to avoid penetration of the sample material into the needles. The analyzing volume estimated from the beam size was evaluated to be 0.24 mm<sup>3</sup>. The detection limit of Zn in a gelatin sample was 28 ppm when operated at 40 kV and 30 mA with a measuring time of 300 s. Bjeoumikhov et al. (147) reported a new depth-sensitive micro-XRF method by using the "knife-edge" method for determining the distribution of the fluorescence radiation yield. In the proposed configuration, a microfocusing X-ray beam irradiated the sample. Then, a knife-edge was put between the sample and the detector. The sizes of the focal spots focused by a polycapillary X-ray lens were 56  $\mu\text{m}$  at 3–10 keV, 47  $\mu\text{m}$  at 10–15 keV, 33  $\mu\text{m}$  at 15–20 keV, and 29  $\mu\text{m}$  at 20–30 keV. By the analysis of the relationship between the Ni K $\alpha$  intensities and the scanned distances of the Ni film (4  $\mu\text{m}$  thick), the obtained depth resolution was 23  $\mu\text{m}$ . The proposed method was applied to a Ti–Ni–Mo layer and a brass sample.

## X-RAY ABSORPTION SPECTROMETRY

XAS is a widely used tool for obtaining local structural information including chemical bonding, charge distribution, and oxidation–reduction of atoms and molecules because the information obtained by X-ray absorption is limited to the local environment of a particular atom.

On the basis of the development of laser-driven X-ray sources, time-resolved XAS probing the transient chemical and structure changes in solids and liquids can be performed using tabletop X-ray spectrometers. In the review period, Seres and Spielmann (148) were able to generate sub-20 fs X-ray probe pulses in an energy range up to several 100 eV by high harmonic generation of intense femtosecond laser pulses at a repetition rate of 1 kHz. In a proof of principle experiment, they found an oscillatory motion of the atoms, which can be explained by the excitation of coherent phonons. By irradiating He and Ne atoms with near-infrared laser

pulses from a tabletop laser system, Seres' group (149) also generated spatially and temporally coherent X-rays up to a photon energy of 3.5 keV. They were able to clearly resolve the L absorption edges of titanium and copper and the K edges of aluminum and silicon and to estimate the interatomic distances from the fine structure of the X-ray absorption spectra. Okano et al. (150) developed an imaging system for time-resolved (soft) X-ray absorption spectroscopy. The system consists of a femtosecond-laser-plasma X-ray source and an X-ray microscope with critical illumination. The temporal and spatial resolutions were 23 ps and better than 12.5  $\mu\text{m}$ , respectively. The authors applied their system for the measurement of an aluminum ablation plume induced by irradiation with a 120 fs laser pulse. The shift of the L-shell photoabsorption edge in the expanding plume was observed in the spatiotemporally resolved absorbance spectrum.

Now, through the use of synchrotron radiation sources, picosecond (hard) X-ray absorption spectroscopy is also possible. This technique is often employed for observing photochemical processes with a laser pump/X-ray probe setup. In the review period, Pham et al. (151) reported the observation of the solvation shell rearrangement after abstraction of the electron from aqueous I<sup>−</sup> in a laser pump/X-ray probe experiment by recording the X-ray absorption L<sub>1</sub>- and L<sub>3</sub>-edge spectra for 50 ps after laser excitation. The L<sub>1</sub>-edge spectra clearly identified the I<sup>0</sup> neutral species after excitation and suggested a substantial amount of back transfer of charge from the solvent species. Both edge spectra revealed a significant rearrangement of the solvation shell around I<sup>0</sup>. Bartelt et al. (152) investigated the role of orbital magnetism in the laser-induced demagnetization of Fe/Gd multilayers by using 2 ps X-ray magnetic circular dichroism (XMCD) given by an X-ray streak camera. An ultrafast transfer of angular momentum from the spin via the orbital momentum to the lattice was observed, which was characterized by rapidly thermalizing spin and orbital momenta. Strong interlayer exchange coupling between Fe and Gd led to a simultaneous demagnetization of both layers.

Millisecond XAS can be routinely measured in several synchrotron radiation sources and is a promising tool in material science and structural biology. Dau and Haumann (153) demonstrated that millisecond-resolved XAS spectroscopy leads to an extension of the classical S-state cycle model of photosynthetic oxygen evolution. In oxygenic photosynthesis, a complete water oxidation cycle requires absorption of four photons by the chlorophylls of photosystem II (PSII). The photons can be provided successively by applying short flashes of light. In a basic model to explain the flash-number dependence of O<sub>2</sub> formation, the third flash applied to dark-adapted PSII induces the S<sub>3</sub> → S<sub>4</sub> → S<sub>0</sub> transition, which is coupled to dioxygen formation at a protein-bound Mn<sub>4</sub>Ca complex. The sequence of events leading to dioxygen formation and the role of the S<sub>4</sub> state are, however, only partly understood. The authors showed by millisecond-resolved XAS that in the S<sub>3</sub> → S<sub>0</sub> transition an interesting intermediate is formed prior to the onset of the O–O bond formation. The identity of the reaction intermediate was considered, and the question was addressed as to how the novel intermediate is related to the S<sub>4</sub> state.

There are many applications of millisecond-resolved XAS to catalysts. Several examples will be considered in the section on Applications.



Technical improvements of XAS measurement for heterogeneous systems were reported during the review period. One possibility for surface-sensitive structural analysis is grazing incidence XAS. For obtaining V K-XAS spectra for a series of anisotropic single crystals of  $(\text{Cr}_x\text{V}_{1-x})_2\text{O}_3$ , Frenkel et al. (154) employed the glancing-emergent-angle (GEA) method in order to minimize fluorescence distortion. The reliability of the GEA technique was tested by comparing the polarization-weighted single-crystal XAS data with experimental powder data. These data were found to be in excellent agreement throughout the entire energy range. Thus, it was demonstrated that GEA is a prime method for nondestructive high-photon-count in situ studies of local structure in bulk single crystals.

Micro-XAS can be a useful analytical tool for investigating the composition of particulate matter (PM) in the atmosphere. While PM can lead to a wide array of adverse health effects, the cause of its toxicity is largely unknown. One aspect of PM that likely affects health is its chemical composition, in particular the transition metals within the particles. Chromium is one transition metal of interest due to its two major oxidation states, with Cr(III) being much less toxic than Cr(VI). Werner et al. (155) analyzed the Cr speciation in fine particles (diameters  $< 2.5 \mu\text{m}$ ) collected at three sites in the Sacramento Valley of Northern California, using micro-XAS with a resolution of typically  $5\text{--}7 \mu\text{m}$ . With XAS, the authors were able not only to distinguish between Cr(VI) and Cr(III) but also to identify different types of Cr(III) and more reduced Cr species.

Lifetime-broadening-suppressed (LBS) selective XAS spectra can be deduced by analyzing resonant inelastic X-ray scattering (RIXS) spectra in terms of a formula derived from the Kramers–Heisenberg (KH) equation. With the combination of a third-generation synchrotron source and a spectrometer equipped with large acceptance as well as high-resolution crystals, Hayashi (156) was able to collect high quality RIXS data to warrant extraction of LBS-XAS spectra of CuO nanoparticles on ZnO with various Cu concentrations as low as 1 mol %. The obtained spectra showed marked concentration dependence, including the pre-edge region. Szlachetko et al. (157) extended the RIXS-XAS method to Al,  $\text{Al}_2\text{O}_3$ , Si, and  $\text{SiO}_2$ . They found that by using the KH approach, the oscillator strengths that are similar to those deduced from X-ray absorption measurements could also be extracted from the RIXS of light elements. For elemental silicon, weak  $1s\text{--}3p$  excitation was observed and found to be consistent with the results of density of states calculations.

In recent years, the ability to interpret and analyze XAS data has progressed dramatically. Advances of data treatment techniques aiming at quantitative structural analysis using XAS were also reported during the review period. Witkowska et al. (158) presented detailed results of a multiple scattering (MS) EXAFS data analysis of crystalline and nanocrystalline ( $1\text{--}7 \text{ nm}$ ) platinum. The advanced MS EXAFS analysis was applied to raw X-ray absorption data including the background, using the expansion of the absorption cross section in terms of local two-body and three-body configurations up to the fifth neighbors. The importance of a correct account of the reduction of the number of neighbors for calculating MS contributions was emphasized in their analysis. The authors estimated that, using their methods, EXAFS could be used to study cluster shapes only for sizes below

2 nm. Soldatov et al. (159) used full MS XAS calculations for metallothioneins (proteins containing seven Cd atoms in tetrahedral arrangement of S atoms) as a tool for verification of structural models generated using molecular dynamics. They tested the method for a  $\text{Cd}(\text{SPh})_4$  model compound in order to determine the sensitivity of the spectrum to different structural parameters and to check that the best-fit XANES spectrum corresponds to the correct structure of the complex.

## APPLICATIONS

**Sample Preparation.** The nano- or picodroplet technique has become a recent trend in the preparation of standard solutions in micro-XRF analysis. A European group (160) proposed the use of picodroplets generated by inkjet printers for sample preparation of TXRF analysis. They generated droplets of picoliter volume ( $5\text{--}130 \text{ pL}$ ) by using a commercially available and slightly modified inkjet printer operated with popular image processing software. The diameter of the dried droplets was between 50 and  $200 \mu\text{m}$  (corresponding to volumes of  $5\text{--}130 \text{ pL}$ ) depending on the cartridge type. The group performed SR-TXRF analysis of the droplets at the beamline L at HASYLAB, Hamburg, Germany. The precision of the printing of a certain amount of a single element standard solution was found to be comparable to aliquoting with micropipets in TXRF, where relative standard deviations of 12% were found for 2.5 ng of cobalt. The authors emphasized the possibility of the printing of simple patterns, which is important when structured samples have to be analyzed. Miller et al. (161) studied the automated printing technology (APT) as a means of dried spot sample preparation for the micro-XRF. APT was used to dispense 20 and 50 nL volumes of multielemental standard solutions onto a film substrate. The multiple dried spots could be accurately and reproducibly deposited at the same precise location on the film substrate surface, allowing increased sample loading within the micro-XRF analysis area for higher elemental sensitivity. A laboratory micro-XRF spectrometer equipped with a Rh-anode X-ray tube and polycapillary X-ray lens was used for analyzing the dried spots. The lower limits of detection were obtained on the order of  $1.3\text{--}5.3 \text{ pg}$  for a 20 nL dried spot when measured by micro-XRF analysis.

Miller et al. (162) developed the preparation of a sample substrate containing a gold grid pattern on its surface for synchrotron-based-IR and micro-XRF imaging. The sample substrate consisted of a low trace element glass slide with a gold grid patterned on its surface; the major and minor parts of the grid contained 25 and 12 nm of gold, respectively. The pattern could be imaged with SR-XRF because the intensity of the Au fluorescence changed with the thickness of the gold. The results demonstrated that IR and X-ray images could be correlated precisely, with a spatial resolution of less than one pixel (i.e.,  $2\text{--}3 \mu\text{m}$ ). The proposed substrate was successfully used for the characterization of paraffin-embedded metalloprotein crystals, the tissue of Alzheimer's disease, and hair composition.

Quantitative analysis of liquid samples by XRF usually requires preconcentration of the analytes through accepted sample pretreatments because the abundance of effective amounts of analytes in the irradiated volume is insufficient for the determination of trace metals in natural water. Abe et al. (163) studied a convenient preconcentration procedure for trace amounts of metals in environmental water by using an iminodiacetate extraction disk.

The iminodiacetate extraction disk was coated with a laminating film to avoid damage by exposure to X-ray irradiation. Detection limits of the subppb level were obtained when 1–2 L of a water sample were analyzed.

**ED-XRF.** EDS has an advantage as the size of the spectrometer can be considerably smaller when compared to that for wavelength dispersive X-ray spectrometry (WDS). Therefore, several projects on the development of portable EDS and its applications in various fields were underway in 2006–2007. Cesareo et al. (164) investigated the detection limits of different portable EDS systems. These portable EDSs consisted of different types of X-ray detectors, such as Si-PIN, SDD, and HP-Ge detectors, and different X-ray tubes with anodes of Pd and W. In many cases, the total weights of the benchtop EDS systems were 10–20 kg, but the weights of the mobile parts were only 3 or 4 kg. The authors evaluated the detection limits by measuring the standard sample of a 50 euro cent coin, whose alloy is made of 89% Cu, 5% Al, 5% Zn, and 1% Sn. The experimental data showed that the use of different X-ray tubes and detectors resulted in detection limits different from each other by a factor of 6 for Zn and almost 100 for Sn. They mentioned that the high voltage of the X-ray tube was the most important parameter involved in improving detection limits. Desnica and Schreiner (165) developed a software package based on National Instruments LabVIEW to monitor and control all hardware components of a portable XRF analyzer that was based on energy-dispersive XRF using an Oxford XTF5011 50-W X-ray tube, an SDD (Röntec XFlash 1000), and two lasers as locating devices. This software allowed efficient and convenient spectral presentation and preliminary analysis. Another unique portable X-ray analysis system was developed by Pappalardo et al. (166), which enables simultaneous PIXE and XRF analyses. This EDS system has a  $^{244}\text{Cm}$  radioactive source as an  $\alpha$ -particle and X-ray emitter coupled to a Si drift detector. Light elements were detected mainly by PIXE, while medium atomic number elements were measured mainly by XRF.

One of the worst pollutants for stone monuments is associated with sulfur compounds, especially with gypsum. Diana et al. (167) performed in situ investigations of sulfur in stone monuments by using a portable EDXRF system, consisting of a miniaturized low-power, air-cooled tungsten X-ray tube and an SDD. After the interference problem of the silicon escape peak of calcium on the sulfur peak was resolved, the authors obtained quantitative data of the sulfur in several stone monuments. EDXRS was applied to study the influence of biomass burning on air quality in Swedish cities by Lindgren et al. (168).  $\text{PM}_{2.5}$  and  $\text{PM}_{2.5-10}$  fractions in aerosol particles were sampled to determine the contribution of biomass burning to particulate air pollution. They used an EDXRF spectrometer specially designed at the Royal Veterinary and Agricultural University of Denmark. X-rays from a high-power Mo target were monochromatized by a highly oriented pyrolytic graphite (HOPG) crystal, and X-ray fluorescence was measured by a Si(Li) detector. In order to identify typical indicators for biomass burning, principal component analysis was performed on data of the elemental contents and black carbon. The authors concluded that the K/Zn ratio would be useful as an indicator of biomass incineration.

Tsutsumimoto and Tsuji (169) applied time-resolved EDXRS for studying living plants. The intake of mineral nutrients in a

living plant such as stevia was observed. The time dependence of the X-ray fluorescence intensity of K, Ca, Mn, Fe, Cu, and Zn in the mineral nutrient solution showed specific intake processes. The experimental results suggested differences in the translocation of each element in the stevia stem. The sensitivity and detection limits in EDXRS were improved by applying a special polarized geometry. Margui et al. (170) reported the recent improvement of instrumental sensitivity and detection limits for determining several trace elements (Cd, Pb, As, Cu, Fe, and Zn) in vegetation species by using new instrumentation based on high-energy polarized-beam EDXRS (Epsilon 5, PANalytical, The Netherlands). The instrumental background was reduced by applying an  $\text{Al}_2\text{O}_3$  Barkla target and filters. Cd was determined by using its  $\text{K}\alpha$  line, while the mutual interference of As and Pb was resolved by employing selective excitation conditions with targets of different materials. As a result, the detection limit of Cd was on the level of 1 mg/kg. The obtained analytical performance showed that high-energy polarized-beam EDXRS can be applied for determining these toxic elements in vegetation matrixes with levels of accuracy and precision fulfilling the requirements of environmental studies.

**Micro-XRF.** Micro-XRF is an essential tool for confirming homogeneity or heterogeneity in a microregion of a sample. The micro- or submicrometer ultrabright X-ray beam produced at SR facilities redounded to numerous and novel applications in biological, archeological, and waste studies. Perés et al. (171) studied the toxic effects of trace elements, especially chronic arsenic poisoning in rat kidneys, by using SR-micro-XRF analysis. The animals received drinking water containing 100 ppm of sodium arsenite ad libitum for 30 and 60 days. Lyophilized kidneys sectioned from normal and treated rats were scanned with a collimated white synchrotron X-ray beam ( $300\text{ }\mu\text{m} \times 300\text{ }\mu\text{m}$ ). While Cu was restricted to the renal cortex, As showed changes in its spatial distribution suggesting nephrotoxicity. A correlation between the spatial distributions of Zn and As was observed, which appeared to be caused by the antioxidant properties of Zn. Cl and P also changed their spatial distributions under As exposure, probably to maintain electrical neutrality. Hokura et al. (172) observed the As distributions in the As hyperaccumulating fern (*Pteris vittata* L.) using SR-micro-XRF and micro-XANES analysis. The focused micro X-ray beam ( $3.5 \times 5.5\text{ }\mu\text{m}^2$ ) produced by K-B optics at SPring-8 was applied to the fern in order to determine elemental distribution in the plant tissue and cell levels. Fronds of various ages were subjected to XRF imaging analysis, and it was found that the As distribution in the pinnae of the fronds changed according to their stage of growth. The results indicated that As of high concentration accumulates at the base of sporangium with lamina of pinnae. The authors reported that As exists as the As(III) form in pinnae and as a mixture of As(III) and As(V) in rachis, while As(V) is present in cultivated soil. These findings indicate that the fern takes up As as As(V) from the soil, the As(V) is then partially reduced to As(III) within the plant, and the As finally accumulates as As(III) in a specific area of the pinna. The same research group also reported on the Cd distributions in another hyperaccumulating plant (*Arabidopsis halleri* ssp. *gemmifera*) using a similar method (173).

Martin and coauthors (174) studied the elemental distributions of Br, Zn, and Pb in archeological human tooth and bone samples

from an ancient burial site located on the north coast of Peru by SR-XRF analysis. Micro-XRF maps were collected in two SR facilities, the PNC/XOR (Pacific Northwest Consortium) facility at the APS and the Brookhaven National Laboratory at NSLS. The authors reported that the elemental mapping results of Zn and Pb seemed to be confined to similar regions (cementum and periosteum). Br showed a novel distribution with enrichment close to the Haversian canals and/or in regions that appear to be Ca deficient. Worley et al. (175) studied the fingerprint detection using a micro-XRF method to be applied in forensic science. The fingerprints were prepared on polypropylene using a 4 mm thick film. After being contaminated by sebum, perspiration, lotion, saliva, banana, and sunscreen, the fingerprint samples were measured by two commercially available micro-XRF instruments equipped with a polycapillary X-ray lens. The XRF intensities of the samples were collected for the analyzed elements: Na, Mg, Si, S, Cl, K, Ca, Ti, Mn, Fe, Cu, and Rh (X-ray source scatter). Clear X-ray 2D-mapping images of the fingerprint samples were easily obtained.

Camerani et al. (176) studied the Cd-bearing phases of municipal solid waste (MSW) and biomass single fly ash particles using SR-micro-XRF spectrometry in order to determine the distribution of Cd. In their report, the authors described that Cd was more evenly distributed throughout all particle sizes. For MSW fly ashes, the results indicated the presence of Cd mainly as  $\text{CdBr}_2$  hot spots, whereas for biomass fly ashes, which exhibited a lower  $\text{CdX}_2$  concentration, a thin Cd layer on/in the particles was reported. For both types of ash, Ca-containing matrixes were found to be the main Cd-bearing phases.

Recently, three-dimensional micro-XRF analysis has induced interest in applications of micro-XRF. Patterson and Havrilla (177) demonstrated 3D elemental imaging by using a confocal 3D-XRF microscope in a laboratory setup. The X-ray source and detector optics consisted of a pair of monolithic polycapillary lenses with a focal spot size of approximately  $35\text{ }\mu\text{m}$ . The confocal volume determined by the fwhm value of XRF depth profiling of a Ta thin foil (10 mm thick) was  $40\text{ }\mu\text{m}$ . The 3D elemental imaging was performed on a paint chip, which was composed of a pigment made of Ca, Ti, Fe, Zn, and Pb. 3D mapping images of the sample in different orientations were obtained. Tsuji and Nakano (178) built a laboratory-made confocal 3D-XRF spectrometer that had two different X-ray sources (Cr and Mo) to enhance the primary X-ray intensity. A micro-X-ray beam was produced by two polycapillary X-ray lenses. The depth resolution that was evaluated by the use of a  $10\text{ }\mu\text{m}$  thick Au foil was approximately  $90\text{ }\mu\text{m}$  for an X-ray energy of  $\text{Au L}\alpha$ . The 3D elemental mapping images of the major elements (K, Ca, and Fe) in a single amaranth seed were created nondestructively at atmospheric pressure. Each element in the seed showed different mapping images at the different layers. Kanngiesser et al. (179) demonstrated the capabilities of 3D micro-XRF under cryogenic conditions for investigations of biological specimens. A 3D micro-XRF setup at the new synchrotron microfocus beamline at BESSY II was equipped with a nitrogen cryogenic stream. A rootlet of common duckweed (*Lemna minor*) was measured as an example of a water-rich biological sample emphasizing the importance of the investigation of heavy metal metabolism in plants and the interaction of roots and the environment. In a virtual cross section, the

distribution of Ca, Fe, Zn, and Cu revealed structural features of the lemna root, especially the central cylinder with xylem and phloem structures and the root rhizodermis with a lateral resolution of about  $10\text{--}20\text{ }\mu\text{m}$ .

**TXRF.** TXRF has been applied to biological and environmental samples because of its excellent analytical performance in the analysis of trace elements. Magalhaes et al. (180) studied the elemental distributions of several elements such as K, Ca, Fe, Cu, Zn, Se, Br, and Pb in normal and cancerous tissues of the same person along several contiguous thin sections (up to  $10\text{ }\mu\text{m}$  thick) of each tissue. Samples were analyzed directly by TXRF. The tissues were also analyzed by normal EDXRF. The authors concluded that a similar pattern was obtained for almost all the analyzed tissue samples: increased or constant levels of P, S, K, Ca, Fe, and Cu, and decreased levels of Zn and Br were found in carcinoma tissues, when compared with corresponding healthy tissues. They explained this result by considering that the analyzed samples were not exactly the same and the differences could be explained by the lack of homogeneity of the samples. The research group of Pajek (181) also studied trace element concentrations in malignant and benign human breast neoplasm tissues taken from women who were patients of Holycross Cancer Center in Kielce, Poland. They investigated the possibilities of using TXRF for cancer diagnosis and monitoring therapy. They measured 26 samples of malignant and 68 samples of benign breast neoplasm tissues. Concentrations were determined for 13 elements (from P to Pb) and were in the range from a few ppb to 0.1%. For comparison of the concentrations in the two populations, a log-rank test was applied, which enabled comparison of the collected TXRF data. The comparative studies of the malignant and benign neoplasm tissues indicated statistically significant elevated levels of some trace elements in the cancerous tumors.

SR-TXRF analyses of the brains of Wistar rats were performed at the Synchrotron Light Brazilian Laboratory, Campinas, Sao Paulo, Brazil, by Serpa et al. (182). It is important to know the spatial distribution and the local concentration of trace elements in tissues because trace elements are involved in a number of metabolic and physiological processes in the living organisms, and their deficiency and/or excess might lead to different metabolic disorders. In the temporal cortex, Ca, Fe, and Br concentration levels increased with age; in contrast, P, S, Cl, K, and Rb levels decreased with age. In the visual cortex, the levels of almost all the elements decreased with age: Cl, Ca, Fe, Ni, and Zn. In the hippocampus, the levels of most elements increased with age. The authors mentioned that the increase of Fe with age in the hippocampus is important, because it is involved in oxidative stress. The authors believe that oxidative stress is one of the principal causes responsible for neuronal death in Parkinson's disease.

Khuder et al. (183) applied TXRF to multielement determination of trace elements in whole blood and human hair samples in nonoccupational exposed population living in the city of Damascus. Direct analysis by TXRF was used for the determination of Rb and Sr in digested blood and human hair samples, respectively, while the coprecipitation method was applied for the TXRF determination of Ni, Cu, Zn, and Pb elements in both matrixes. The mean concentrations of analyzed elements in both matrixes were within the reported range values for nonoccupational



populations in other countries. The mineral elements (P, S, K, Ca) and essential trace elements (Fe, Cu, Zn, Se, Rb, Sr) in the blood of seals in the North Sea were measured by TXRF (184). Samples from 81 free-ranging harbor seals from the North Sea and two captive seals were collected during 2003–2005. Simultaneous measurements of several elements in only 500  $\mu\text{L}$  volumes of whole blood provided the possibility of obtaining information both on the electrolyte balance and the hydration status of the seals. The authors concluded that the method could serve as an additional biomonitoring tool for health assessment.

The elemental analysis of environmental samples is also an important application of TXRF. A European research group (185) has studied TXRF analysis of low-Z elements and applied it to biofilms living on all subaqueous surfaces consisting of bacteria, algae, and fungi embedded in extracellular polymeric substances (EPS). The authors used the Atominsitute's TXRF vacuum chamber, equipped with a Cr-anode X-ray tube, a multilayer monochromator, and a Si(Li) detector with a 30 mm<sup>2</sup> active area and with an ultrathin entrance window. They concluded that the biofilm was a useful indicator for polluting elements. To have homogeneous biofilms, it was recommended the biofilms be cultivated no longer than 6 or 7 days. TXRF was applied for the analysis of aerosols by Samek et al. (186). Samples were collected on filters in two churches, one situated at a rural area and the other at an urban area. A five-stage sequential leaching scheme for the speciation of K, Ca, Fe, Zn, and Pb was applied. The authors found that, for the samples collected in the church at the urban area, much of the K, Fe, and Zn appeared as mobile elements (exchangeable fraction), whereas for the church at the rural area, all elements were observed in all stages. A single-particle transfer technique was developed and applied to TXRF by Esaka et al. (187). A glass needle coated with gold was used for particle transfer. A particle with a diameter between 3.9 and 13.2  $\mu\text{m}$  was picked up and transferred onto the center of a Si sample carrier in a SEM. After that, the sample carrier with the transferred Cu particle was removed from the SEM and introduced into the TXRF instrument. With consideration of the absorption effects, the amount of Cu in an individual particle was determined with a deviation within 10.5%. Environmental pollution was monitored by trace analysis of tree rings using SR-TXRF (188). Trace metals were deposited in the rings and accumulated in the wood. Sample collection was performed in the city of Piracicaba, Sao Paulo State, Brazil, and where a high level of environmental contamination in the water, soil, and air is well documented. The species *Caesalpinia peltophoroides* ("Sibipiruna") was selected because it is widely used for urban forestation. SR-TXRF analysis was performed in the Brazilian Synchrotron Light Source Laboratory. In several samples, P, K, Ca, Ti, Fe, Sr, Ba, and Ph were quantified. The K/Ca, K/P, and Pb/Ca ratios were found to decrease toward the bark, indicating a reduction in air pollutants in the last several years, primarily after 1990. TXRF was compared with instrumental Neutron Activation Analysis in order to test its potential application for the study of archeological ceramics in the archaeometric field (189). The influence of the particle sizes was checked by TXRF sample angle scans. Anomalous behaviors were found for three additional detected elements: As, Sr, and Zn, which could be attributed to the effects of interference of the sizes of the mineral grains in their associated chemical phases in

the total-reflection X-ray fluorescence interference region. The authors concluded that the solid chemical homogenization procedure in the sample preparation was useful for archeological interpretation.

**EPMA.** EPMA is a powerful technique for nondestructive chemical analysis of ancient artifacts. Hung et al. (190) examined Southeast Asian nephrite (jade) artifacts, many archeologically excavated, dating from 3000 B.C. through the first millennium A.D. On the basis of a series of mineral analyses for several nephrite deposits from Asian regions as well as museum jade antiquities, this sourcing study revealed a pattern of prehistoric sea-based trade networks across a vast area of mainland and island Southeast Asia. Schalm et al. (191) studied a set of approximately 500 window glass fragments originating from different historical sites in Belgium and covering the period of the 12th–18th century using EPMA. Most samples are archeological finds deriving from nonfigurative windows in secular buildings. However, the analyzed set also contains glass sampled from still existing nonfigurative windows in secular buildings and stained-glass windows in religious buildings. A sudden compositional change at the end of the 14th century can be noticed among the series of glass compositions that were obtained. These changes could be related to the use of different glassmaker recipes and to the introduction of new raw materials for glass making. Kraft et al. (192) applied WD-EPMA to map elemental distributions of entire coin surfaces. Their study was about ancient Roman coin silvering techniques. Roman coins, especially forgeries, contain various amounts of silver on the surfaces, and the measurement of the silver distribution on the entire surfaces of coins is needed for uncovering the manufacturing techniques. Element mapping by EPMA with increasing step size to survey the complete coin surface was applied to coins having a dark optical appearance and unknown minting technique.

Study of major and trace elements in source rocks is useful as it provides information on paleoenvironmental sedimentation conditions. An EPMA X-ray mapping study on distributions of major and trace elements in Venezuelan source rocks for stylolites, framboids, and kerogen was performed by Monaco et al. (193). In the stylolites, an association of S with Fe, Cu, Zn, and Ni was observed, suggesting the presence of authigenic sulfides, whereas V and Ni are associated with organic matter. In the framboids, it was found that Ni and Zn coprecipitate with pyrite. In these samples Ni is associated both with the sulfide phase and the organic matter, but V is only associated with the latter. In kerogen, elemental mapping showed that V is associated with kerogen. In this study, its capability of EPMA for providing information on elemental associations with mineral or organic phases of the rock was demonstrated, which is valuable for interpretation related to paleoenvironmental conditions or primary migration.

Biomined structures are often used as indicators of environmental conditions in which they have grown. The avian eggshell is a simple system for the study of biomineralizing processes due to the speed of crystal growth and the common mechanism of formation among avian species. Dalbeck and Cusack (194) used EBSD together with EPMA for the examination of the eggshell structure in order to establish possible relationships between the crystallographic structures and the trace element distribution within each specimen, as well as between

species. Mg and Na vary across the eggshell profile in a carbonate system produced in a constant temperature environment. It was found that variability in trace element distribution in such systems is more closely related to variation in organic distribution than merely environmental and physical crystallographic factors.

Quantitative light element analysis of individual particles using thin-window EPMA (TW-EPMA) was applied for the characterization of various types of environmental and soil samples. Hwang and Ro (195) demonstrated that quantitative single particle analysis using TW-EPMA is a practical and useful tool for the study of heterogeneous reactions of mineral dust and sea salts. The technique does not require a special treatment of sample to identify particles reacted in the air. Also, quantitative chemical speciation of reacted particles can provide concrete information on what chemical reactions, if any, occurred for individual particles. When the technique was applied to a sample collected during an Asian dust storm event, it was found that heterogeneous chemical reactions mostly occurred on  $\text{CaCO}_3$  mineral dust and sea salts. Worobiec et al. (196) applied conventional EPMA and TW-EPMA techniques combined with principal component analysis (PCA) to characterize aerosol samples collected at the Amazon Basin. Intensive transport of soil dust particles from the Sahara was observed at the end of March and beginning of April. Reactions of the Saharan dust, agglomeration with sea salt above the Atlantic Ocean and with local particulate matter, were observed. A significant contribution of natural biogenic particles and the chemical transformation of airborne marine particles in the abundant presence of gaseous pollutants originating from biomass burning and biogenic emissions were observed as well. These two articles show that TW-EPMA is a useful technique for the study on chemical modification of Asian and Saharan dust particles during long-range transport. The single-particle TW-EPMA technique was applied to characterize municipal solid waste fly- and bottom-ash particle samples collected at two municipal incinerators (197). According to their chemical compositions, many distinctive particle types were identified. For the fly-ash sample collected at one incinerator,  $\text{CaCO}_3$  particles are the most abundantly encountered, followed by carbonaceous,  $\text{SiO}_2$ , NaCl, and iron-containing particles. For the fly-ash sample collected at the other incinerator, NaCl particles are the most abundantly encountered, followed by iron-containing, carbonaceous,  $\text{CaCO}_3$ , and  $\text{SiO}_2$  particles. Chemical compositions of two bottom-ash samples were not much different compared to those of the two fly-ash samples. The authors claimed that the technique has advantages over conventional analytical techniques in that both crystalline- and glasslike ash particles can be analyzed at the same time. Semenov et al. (198) studied soils of the Pereemnaya river catchment, Russia, characterized by a high percentage of particles under  $10\text{ }\mu\text{m}$  size and the almost total absence of clay minerals using TW-EPMA. Three subfractions, 10–5, 1–5, and  $<1\text{ }\mu\text{m}$  were distinguished within the  $<10\text{ }\mu\text{m}$  fraction on the basis of mineralogical composition and chemical peculiarities. It was shown that concentrations of alkali and alkaline-earth metals within the  $<10\text{ }\mu\text{m}$  fraction increased in the row  $(5\text{--}10\text{ }\mu\text{m}) < (1\text{--}5\text{ }\mu\text{m}) < (<1\text{ }\mu\text{m})$ . Compared with the soil bulk chemistry, the data obtained for the fraction  $<10\text{ }\mu\text{m}$  showed that this fraction is the major source of alkali and alkaline-earth metals and consequently the main contributor to element release due to weathering.

As a forensic application, Steffen et al. (199) used ED-EPMA data for chemometric classification of gunshot residues in order to assign a detected particle to a particular ammunition brand. A gunshot residue sample that was collected from an object or a suspected person is automatically searched for gunshot residue relevant particles. According to particle morphological data, as well as the corresponding X-ray spectra, particles are classified into different groups by the analysis software. The data obtained as X-ray spectra for a number of particles (3000 per ammunition brand) were reduced by fast Fourier transformation and subjected to a chemometric evaluation by means of regularized discriminant analysis.

In the steel industry, the carbon content measurements are important to find optimal carburization process conditions. The carbon contents in carburized steels were investigated by EPMA for a range of carbon levels in the solid solution less than 1 wt % (200). In their work, they used an analytical procedure based on a calibration curve method after discussing the difficulties encountered with the classical analytical procedure using the  $k$  ratio of X-ray intensities and the  $\varphi(\rho z)$  model. It is emphasized that the metallographic study of standard specimens and the carbon decontamination of samples are necessary for the successful application of the procedure to carbon determination in steels.

**PIXE.** Many applications of PIXE analysis have been reported for biological and environmental samples. Although the micro-PIXE method competes with micro-XRF, applications of micro-PIXE with a spatial resolution of a few micrometers, which is better than the resolution of laboratory micro-XRF, are reviewed. Mrak et al. (201) applied micro-PIXE to the study of arsenate metabolism in the lichen *Hypogymnia physodes* (L.) Nyl. Lichen thalli were exposed to a solution of an inorganic arsenic compound arsenate. Perpendicular sections that revealed the morphological properties of the lichen thallus were subjected to micro-PIXE measurements to obtain data on the localization of the arsenic and its influence on the distribution and concentrations of the selected elements (P, S, K, Ca, Cl, Mn, Fe, and Zn). In high-current mode, a proton beam with a diameter of  $2 \times 2\text{ }\mu\text{m}^2$  and energy of 3 keV at a beam current of 300 pA was used. The authors distinguished five groups of elements regarding losses and redistribution due to arsenic exposure. Tylko et al. (202) at iThemba Laboratories in South Africa applied in-vacuum micro-PIXE for analysis of biological samples in a frozen-hydrated state. A commercially available cryotransfer system used in electron microscopy was adapted for this purpose. The analyzed material was frozen in propane cooled by liquid nitrogen, fractured, carbon coated, and transferred onto a cold stage (100 K) in a nuclear microprobe chamber. Micro-PIXE and simultaneous proton backscattering were performed using a 3 MeV proton beam. Monitoring of the water vapor composition during the proton bombardment showed good stability of the analyzed material. Quantitative results were reported by the standardless method and tested using 20% gelatin standards with added  $\text{PbCl}_2$ . Leaf tissue of *Senecio anomalochrous* and larvae of *Chysolina pardalina* were measured as examples of plant and animal tissue. Quantitative elemental mapping of the frozen-hydrated specimens compared with subsequent analysis of the same areas after freeze-drying revealed the same distribution pattern in both cases. The authors concluded that micro-PIXE

had the potential to be a quantitative analytical method of frozen-hydrated material with low detection limits down to  $1 \mu\text{g g}^{-1}$ .

Other important applications of micro-PIXE are for the characterization of airborne particles and soils in environmental science. It is well-known that metal-containing elements in airborne particles are harmful. It is important to clarify their sources. Micro-PIXE with an excellent spatial resolution of  $1\text{--}2 \mu\text{m}$  was applied to study the sources of Cr, Mn, Ni, and Zn in aerosol  $\text{PM}_{10}$  particles (203).  $\text{PM}_{10}$  samples were collected on a nitrocellulose filter using an air sampler in the north of Shanghai, China, where several power plants and steel plants are located. Micro-PIXE spectra of single particles were treated as fingerprints since each particle was characterized by its micro-PIXE spectrum. The sources of the metal-containing particles were identified using the fingerprints of the single particles. The study showed that the major sources of the four kinds of metals in the air were metallurgic emission, vehicle exhaust, coal combustion, and soil dust. A Japanese group (204) determined the major and trace elements in soils by the acid digestion method combined with PIXE. The digestion of the soils was achieved by using nitric acid ( $\text{HNO}_3$ ), hydrochloric acid (HCl), and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) with repeated additions. A  $20 \mu\text{L}$  aliquot from the digested samples was evaporated on a Nuclepore Track-Etch Membrane and irradiated with a 2.5 MeV proton beam from a single-end type Van de Graaff accelerator. The accuracy of this method was estimated based on a series of measurements on a reference material of soil CRM 023-050. The corresponding limits of detection for several elements (Na, Mg, As, and Cd) were estimated in the range of  $0.1\text{--}2 \text{ ppm}$ . The reproducibility of the lower ( $< \text{Mn K}\alpha$ ) and higher ( $> \text{Mn K}\alpha$ ) values ranged between  $5.7\text{--}16.5\%$  and  $3.6\text{--}19.5\%$ , respectively.

The final application of PIXE is for investigation of cultural heritage. In the field of cultural heritage,  $^4\text{He}$  particle beams are often used to perform Rutherford backscattering spectroscopy (RBS) analysis. In most cases, the simultaneously produced X-rays were not considered for PIXE analysis. Rohrs et al. (205) explored the potentials of  $^4\text{He}$ -induced X-ray emission ( $\alpha$ -PIXE) using 4, 5, and 6 MeV  $^4\text{He}$  beams and compared its performance with that of conventional PIXE with 3 MeV protons. The  $\alpha$ -PIXE and  $\alpha$ -RBS spectra were collected at the same time in a vacuum chamber. For elements with atomic numbers below 25, the X-ray yields produced by a 6 MeV  $^4\text{He}$  beam for K-lines were found to be superior to those by protons. An additional advantage of  $\alpha$ -PIXE is the lower bremsstrahlung background, which leads to an improved peak-to-noise ratio for certain elements and is useful for trace analysis. von Bohlen et al. (206) applied external micro-PIXE for the characterization of small samples of varnish from historic violins and pieces of varnished wood from historic and modern stringed instruments. To obtain spatially resolved information on the distribution of elements across the varnish layers, single-spot analysis, line scans, and area mapping were performed. Micro-PIXE analysis was performed at the AGLAE facility at the Centre de Recherche et de Restauration des Musées de France (C2RMF), situated in the Louvre Museum, Paris. Local resolution of approximately  $20 \mu\text{m}$  was obtained from the 3 MeV, 1 nA proton microprobe. Two Si(Li) detectors were applied especially for detection of light elements and heavier elements. Since PIXE has an advantage of elemental analysis of light elements compared to

other X-ray methods, the authors were able to show good results for Na, Mg, Al, Si, P, S, K, and Ca.

**XAS.** An interesting application of XAS was reported by Pagès-Camagna et al. (207) for the study of the local chemical environment of  $\text{Cu}^{2+}$  in archeological Egyptian blue and green. The information is essential for the understanding of the coloring mechanisms in both pigments. Using XAS data at the Cu K-edge, the authors could obtain new insights into the origin of the coloring mechanisms of both pigments. In Egyptian blue,  $\text{Cu}^{2+}$  is mainly allocated in a square-planar site in a crystalline cuprovaite phase, whereas in Egyptian green,  $\text{Cu}^{2+}$  is basically situated in a distorted octahedral site in an amorphous phase. Gaudry et al. (208) reported that the colors of the  $\text{Cr}_x\text{Al}_{2-x}\text{O}_3$  series (e.g., red in ruby ( $\alpha\text{-Al}_2\text{O}_3/\text{Cr}^{3+}$ ) and green in eskolaite ( $\alpha\text{-Cr}_2\text{O}_3$ )) were connected with the structural and electronic local environment around Cr, using XAS methods. Their study indicated that the colors of the red ruby and the green eskolaite are partially due to both the crystal field and covalence of the Cr–O bonding.

Material science is one of the major application fields of XAS. Vedrinskii et al. (209) measured temperature-dependent pre-edge and EXAFS at the Zr K-edge for perovskite-type zirconates,  $\text{PbZr}_{0.515}\text{Ti}_{0.485}\text{O}_3$  (PZT),  $\text{PbZrO}_3$  (PZ), and  $\text{BaZrO}_3$ . It was shown that neither the displacive nor the order–disorder model could correctly describe the changes of local atomic structure during phase transitions in PZ and PZT. Arçon et al. (210) examined a new material for solid-oxide fuel cells,  $\text{La}_2\text{RuO}_5$ , by XANES and EXAFS. From XANES, the average Ru valence state was found to be  $\sim 4.0$ . EXAFS showed that the crystal structure of this compound contained no systematic defects in the vicinity of the Ru atoms. With these results, the stoichiometry of  $\text{La}_2\text{RuO}_5$  was fully established. Stone et al. (211) measured the XMCD at the Mn  $L_{2,3}$ -edges in ferromagnetic  $\text{Ga}_{1-x}\text{Mn}_x\text{P}$  films for  $0.018 < x < 0.042$ . Large XMCD asymmetries at the  $L_3$ -edge indicate significant spin polarization of the density of states at the Fermi energy. The spectral shapes of the X-ray absorption and XMCD are nearly identical with those for  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  indicating that the hybridization of the Mn d states and anion p states is similar in the two materials.

During the review period, the O K-edge XAS of water attracted the attention of many researchers. For example, Prendergast and Galli (212) presented a series of ab initio calculations of the XAS of ice and liquid water at ambient conditions. Their results showed that all available experimental data and theoretical results are consistent with the standard model of the liquid as consisting of molecules with approximately four hydrogen bonds. Thus, the authors proposed that the standard, quasi-tetrahedral model of water, although approximate, represents a reasonably accurate description of the local structure of the liquid. Cappa et al. (213) found that the O K-XAS of aqueous HCl and NaCl solutions revealed distinct perturbations of the local water molecules by the respective solutes. While the addition of NaCl led to large spectral changes, the effect of HCl on the observed XAS spectrum was surprisingly small. Density functional theory calculations suggested that this difference primarily reflects a strong blue shift of the hydrated proton (in either the Eigen ( $\text{H}_9\text{O}_4^+$ ) or Zundel ( $\text{H}_2\text{O}_5^+$ ) forms) spectrum relative to that of  $\text{H}_2\text{O}$ , indicating the tighter binding of electrons in  $\text{H}_3\text{O}^+$ . This spectral shift counteracts the spectral changes that arise from direct electrostatic perturbation of water molecules in the first solvation shell of  $\text{Cl}^-$ .



Thus, it was concluded that the observed spectral changes affected by HCl addition were minimal compared to those engendered by NaCl.

In situ XAS measurements have been actively performed in the field of catalysis. The elucidation of the structure of the catalytically active sites in supported metal catalysts is a long sought goal. For the purpose, Bus et al. (214) employed the in situ XAS method. Ethene-induced changes in the XAS spectra of Pt and related supported catalysts as a function of temperature and pressure were correlated to changes in the adsorption mode of the hydrocarbon. At low temperature, ethene was adsorbed at on-top ( $\pi$ ) and bridged (di- $\sigma$ ) sites on small Pt clusters. Below room temperature, the adsorbed ethene was dehydrogenated to an ethylidyne species, which was adsorbed at 3-fold Pt sites. On larger clusters, dehydrogenation proceeded at a higher temperature indicating a different reactivity. Their EXAFS results showed that changes in the geometrical structures were primarily due to (co)adsorbed hydrogen. Becker et al. (215) measured in situ millisecond Pt-XAS spectra of a similar system in order to correlate changes in catalyst surface composition with catalytic activity for methane oxidation. Changes in the surface O/Pt ratio were monitored by the introduction of a new analysis method of the white line area corresponding to the Pt  $L_3$ -edge XANES. Their results showed that during the gas-phase transients, the surface O/Pt ratio changes, which, in turn, affects the methane oxidation rate. Activity maxima were observed for an intermediate surface O/Pt ratio. An oxygen-rich surface seemed to hinder the dissociative adsorption of methane, leading to low methane oxidation activity at an oxygen excess. Suzuki et al. (216) studied the structural changes during the supporting process of a rhodium cluster  $[\text{Rh}_6(\text{CO})_{16}]$  on  $\text{Al}_2\text{O}_3$  by millisecond XAS. They found that with an increase of temperature the bridging CO desorbed continuously at first and almost completely desorbed until 460 K. However, less than 20% terminal CO desorbed until 420 K. About 60% terminal CO desorbed between 420 and 500 K, and the remaining terminal CO desorbed above 500 K. The Rh–Rh distance decreased suddenly from 0.277 to 0.268 nm between 470 and 490 K, then gradually decreased to 0.264 nm.

The increased importance of the chemical characterization of hazardous elements produced several XAS applications in life and environmental sciences. Meirer et al. (217) employed a synchrotron-radiation-induced total reflection X-ray fluorescence (SR-TXRF) technique for XANES measurements for the speciation of arsenic in cucumber xylem sap. Their experiments were performed by growing cucumber plants in hydroponic media containing arsenite  $[\text{As}(\text{III})]$  or arsenate  $[\text{As}(\text{V})]$  in order to identify the arsenic species of the collected xylem saps by K-edge SR-TXRF XANES. Cucumber xylem saps, as well as nutrient solutions containing arsenic in the two above-mentioned species, were analyzed and compared with arsenate and arsenite standard solutions. Arsenic speciation in xylem sap was achieved down to 30 ppb. From the TXRF-XANES analysis, the authors found that As(V) taken up from the nutrient solution was reduced to the more toxic As(III) in the xylem saps. Pinakidou et al. (218) applied SR-XRF mapping as well as micro- and conventional XAFS spectroscopies in order to study the bonding environment of Fe and Zn in vitrified samples that contained electric arc furnace dust from metal processing industries. The samples were studied in the as-cast state as well

as after annealing at 900 °C. Their SR-XRF results demonstrated that annealing did not induce any significant changes in the distribution of either Fe or Zn both in the as-cast and annealed glasses. The XAFS spectra at the Fe–K and Zn–K edges revealed that the structural role of both Fe and Zn remains unaffected by the annealing process and that Fe acts as an intermediate oxide while Zn occupies tetrahedral sites.

Micro-XAFS has also been applied for the study of  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (LNAO) cathode material for lithium ion batteries (219). Nonaka et al. investigated the change in the oxidation state and local structure of Ni and Co during charge. The Ni K-edge micro-XANES showed that the oxidation of Ni proceeds homogeneously in a grain of LNAO within a special resolution similar to 2  $\mu\text{m}$  and proceeds independently of grain size. The considerable stability of LNAO was also demonstrated.

**Standards.** The certified reference materials (CRMs) are essential for confirming the accuracy and precision of analytical procedures and analytical results. The Japan Society for Analytical Chemistry (JSAC; Japan) prepared and certified three types of plastic CRMs by using XRF analysis for the RoHS (Restrictions on Hazardous Substance) directive as set out in Directive 2002/95/EC. For Hg, five CRMs (JSAC 0621 to 0625) were certified for XRF analysis (220). These plastic CRMs were prepared by filling Al-cylindrical molds with liquid polyester resin mixed with hardener and organometallic compounds. The new CRM (NIST SRM 695) was prepared from 160 kg of floury fertilizer. Certified values for 17 elements (As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Ni, Pb, Na, V, and Zn) were reported. Reference values for Al, B, N, P, and Se, and information values for Cl and Ti were also provided (221). The National Geophysical Research Institute (NGRI, India) prepared one high-grade gold geochemical CRM (BND 3401.01) from 350 kg of a sulfide-bearing quartz vein located in sheared acid volcanic rock. The certified value of Au evaluated by an interlaboratory comparison study was  $12.1 \pm 0.7$  mg/kg (222).

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## LITERATURE CITED

### OVERVIEW

- (1) Potts, P. J.; Ellis, A. T.; Kregsamer, P.; Strel, C.; Vanhoof, C.; West, M.; Wobrauschek, P. *J. Anal. At. Spectrom.* **2006**, *21*, 1076–1107.
- (2) West, M.; Ellis, A. T.; Kregsamer, P.; Potts, P. J.; Strel, C.; Vanhoof, C.; Wobrauschek, P. *J. Anal. At. Spectrom.* **2007**, *10*, 1304–1332.
- (3) Beckhoff, B.; Kanngiesser, B.; Langhoff, N.; Wedell, R.; Wolff, H., Eds *Handbook of Practical X-ray Fluorescence Analysis*; Springer: Berlin, Germany, 2006.
- (4) Ide-Ektessabi, A. *Applications of Synchrotron Radiation*; Springer: Berlin, Germany, 2007.
- (5) Wobrauschek, P. *X-ray Spectrom.* **2007**, *36*, 289–300.
- (6) Strel, C. *Appl. Spectrosc. Rev.* **2006**, *41*, 473–489.
- (7) Haschke, M.; Eggert, F.; Elam, W. T. *X-ray Spectrom.* **2007**, *36*, 254–259.
- (8) Hoheisel, M. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2006**, *563*, 215–224.
- (9) Cottam, J.; Boyce, K. R.; Brown, G. V.; Fujimoto, R.; Furusho, T.; Ishisaki, Y.; Kelley, R. L.; Kilbourne, C. A.; McCammon, D.; Mitsuda, K.; Morita, U.; Ota, N.; Porter, F. S.; Saab, T.; Takei, Y.; Yamamoto, M. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2006**, *559*, 617–619.
- (10) Huang, Z.; Kim, K.-J. *Phys. Rev. Spec. Top.-Accel. Beams* **2007**, *10*, 034801/1–034801/25.
- (11) Gaffney, K. J.; Chapman, H. N. *Science* **2007**, *316*, 1444–1448.
- (12) Carvalho, M. L.; Magalhaes, T.; Becker, M.; von Bohlen, A. *Spectrochim. Acta, Part B* **2007**, *62*, 1004–1011.
- (13) Osan, J.; Torok, S.; Beckhoff, B.; Ulm, G.; Hwang, H.; Ro, C. U.; Abete, C.; Fuoco, R. *Atmos. Environ.* **2006**, *40*, 4691–4702.

### DETECTION

- (14) Mazin, B. A.; Bumble, B.; Day, P. K.; Eckart, M. E.; Golwala, S.; Zmuidzinas, J.; Harrison, F. A. *Appl. Phys. Lett.* **2006**, *89*, 222507.
- (15) Zink, B. L.; Ullom, J. N.; Beall, J. A.; Irwin, K. D.; Dorries, W. B.; Duncan, W. D.; Ferreira, L.; Hilton, G. C.; Horansky, R. D.; Reintsema, C. D.; Vale, L. R. *Appl. Phys. Lett.* **2006**, *89*, 124101.
- (16) Smith, S. J.; Whitford, C. H.; Fraser, G. W. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2006**, *556*, 237–245.
- (17) Zink, B. L.; Irwin, K. D.; Hilton, G. C.; Ullom, J. N.; Pappas, D. P. *J. Appl. Phys.* **2006**, *99*, 08B303.
- (18) Matsuura, D.; Ozawa, H.; Tohiguchi, M.; Uchino, M.; Miyata, E.; Tsunemi, H.; Inui, T.; Tsuru, T. G.; Kamata, Y.; Nakaya, H.; Miyazaki, S.; Miyaguchi, K.; Muramatsu, M.; Suzuki, H.; Takagi, S. *Jpn. J. Appl. Phys.* **2006**, *45*, 8904–8909.
- (19) Broennimann, C.; Eikenberry, E. F.; Henrich, B.; Horisberger, R.; Huelsen, G.; Pohl, E.; Schmitt, B.; Schulze-Briesse, C.; Suzuki, M.; Tomizaki, T.; Toyokawa, H.; Wagner, A. *J. Synchrotron Rad.* **2006**, *13*, 120–130.
- (20) Hirano, K.; Tiyoishi, K.; Igarashi, N.; Takeda, T.; Wu, J.; Lwin, T. T.; Kubota, M.; Egami, N.; Tanioka, K.; Kawai, T.; Wakatsuki, S. *Phys. Med. Biol.* **2007**, *52*, 2545–2552.
- (21) Basolo, S.; Berar, J. F.; Boudet, N.; Breugnot, P.; Caillot, B.; Clemens, J. C.; Delpierre, P.; Dinkespiller, B.; Hustache, S.; Koudobine, I.; Meessen, C.; Menouni, M.; Mouget, C.; Palancher, H.; Pangaud, P.; Potheau, R.; Vigeolas, E. *J. Synchrotron Rad.* **2007**, *14*, 151–157.
- (22) Kim, H. K. *Appl. Phys. Lett.* **2006**, *89*, 233504.
- (23) Tawa, N.; Ikegami, K.; Aono, M.; Miyata, E.; Tsunemi, H. *Jpn. J. Appl. Phys.* **2007**, *46*, 873–879.
- (24) Ito, K.; Gaponov, Y.; Sakabe, N.; Amemiya, Y. *J. Synchrotron Radiat.* **2007**, *14*, 144–150.
- (25) Coan, P.; Peterzol, A.; Fiedler, S.; Ponchut, C.; Labiche, J. C.; Bravin, A. *J. Synchrotron Rad.* **2006**, *13*, 260–270.

- (26) Tokanai, F.; Atsumi, T.; Endo, T.; Fujita, Y.; Ohishi, Y.; Okada, T.; Sakurai, H.; Gunji, S.; Kishimoto, S. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2006**, *567*, 376–380.
- (27) Bellazzini, R.; Angelini, F.; Baldini, L.; Bitti, F.; Brez, A.; Cavalca, F.; Del Prete, M.; Kuss, M.; Latronico, L.; Omodei, N.; Pinchera, M.; Massai, M. M.; Minuti, M.; Razzano, M.; Sgro, C.; Spandre, G.; Tenze, A.; Costa, E.; Soffitta, P. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2006**, *560*, 425–434.
- (28) Kanai, Y.; Ueno, M.; Kataoka, J.; Arimoto, M.; Kawai, N.; Yamamoto, K.; Mizuno, T.; Fukazawa, Y.; Kiss, M.; Ylinen, T.; Bettolo, C. M.; Carlson, P.; Klamra, W.; Pearce, M.; Chen, P.; Craig, B.; Kamae, T.; Madejski, G.; Ng, J. S. T.; Rogers, R.; Tajima, H.; Thurston, T. S.; Saito, Y.; Takahashi, T.; Gunji, S.; Bjornsson, C. I.; Larsson, S.; Ryde, F.; Bogaert, G.; Kishimoto, S. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2007**, *570*, 61–71.
- (29) Bamberger, A.; Desch, K.; Renz, U.; Titov, M.; Vlasov, N.; Wienemann, P.; Zwerger, A. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2007**, *573*, 361–370.
- (30) Bellazzini, R.; Spandre, G.; Minuti, M.; Baldini, L.; Brez, A.; Cavalca, F.; Latronico, L.; Omodei, N.; Massai, M. M.; Sgro, C.; Costa, E.; Soffitta, P.; Krummenacher, F.; de Oliveira, R. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2007**, *566*, 552–562.
- (31) Castoldi, A.; Galimberti, A.; Guazzoni, C.; Rehak, P.; Hartmann, R.; Struder, L. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2006**, *568*, 89–95.
- (32) Kimpton, J. A.; Kinnane, M. N.; Chantler, C. T. *Rev. Sci. Instrum.* **2006**, *77*, 083102.
- (33) Yatsu, Y.; Kuramoto, Y.; Kataoka, J.; Kotoku, J.; Saito, T.; Ikagawa, T.; Sato, R.; Kawai, N.; Kishimoto, S.; Mori, K.; Kamae, T.; Ishikawa, Y.; Kawabata, N. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2006**, *568*, 375–381.
- (34) Carini, G. A.; Bolotnikov, A. E.; Camarda, G. S.; Wright, G. W.; James, R. B.; Li, L. *Appl. Phys. Lett.* **2006**, *88*, 143515.
- (35) Tanaka, T.; Watanabe, S.; Takeda, S.; Onouki, K.; Mitani, T.; Nakazawa, K.; Takashima, T.; Takahashi, T.; Tajima, H.; Sawamoto, N.; Fukazawa, Y.; Nomachi, M. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2006**, *568*, 375–381.
- (36) Owens, A.; den Hartog, R.; Quarati, F.; Gostilo, V.; Kondratjev, V.; Loupilov, A.; Kozorezov, A. G.; Wigmore, J. K.; Webb, A.; Welter, E. *J. Appl. Phys.* **2007**, *102*, 054505.
- (37) Onodera, T.; Hitomi, K.; Shoji, T. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2006**, *568*, 433–436.
- (38) Zwerger, A.; Fauler, A.; Fiederle, M.; Jakobs, K. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2007**, *576*, 23–26.
- (39) Almagiva, S.; Bonfigli, F.; Franzini, I.; Lai, A.; Montareali, R. M.; Pelliccia, D.; Cedola, A.; Lagomarsino, S. *Appl. Phys. Lett.* **2006**, *89*, 054102.
- (40) Calegari, F.; Stagira, S.; D'Andrea, C.; Valentini, G.; Vozzi, C.; Nisoli, M.; De Silvestri, S.; Poletto, L.; Villoresi, P.; Faenov, A.; Pikuz, T. *Appl. Phys. Lett.* **2006**, *89*, 111122.

### INSTRUMENTATION AND X-RAY OPTICS

- (41) Hayakawa, Y.; Sato, I.; Hayakawa, K.; Tanaka, T.; Mori, A.; Kuwada, T.; Sakai, T.; Nogami, K.; Nakao, K.; Sakae, T. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2006**, *252*, 102–110.
- (42) Sato, E.; Hayasi, Y.; Tanaka, E.; Mori, H.; Kawai, T.; Inoue, T.; Ogawa, A.; Sato, S.; Takayama, K.; Onagawa, J.; Ido, H. *Radiat. Phys. Chem.* **2006**, *75*, 1841–1849.
- (43) Pokrovsky, A. L.; Kaplan, A. E.; Shkolnikov, P. L. *J. Appl. Phys.* **2006**, *100*, 044328.
- (44) Yin, G. C.; Song, Y. F.; Tang, M. T.; Chen, F. R.; Liang, K. S.; Duewer, F. W.; Feser, M.; Yun, W. B.; Shieh, H. P. D. *Appl. Phys. Lett.* **2006**, *89*, 221122.
- (45) Snigirev, A.; Bjeoumikhov, A.; Erko, A.; Snigireva, I.; Grigoriev, M.; Yunkin, V.; Erko, M.; Bjeoumikhova, S. *J. Synchrotron Radiat.* **2007**, *14*, 326–330.
- (46) Chang, C.; Sakdinawat, A.; Fischer, P.; Anderson, E.; Attwood, D. *Opt. Lett.* **2006**, *31*, 1564–1566.
- (47) Frontera, F.; Pisa, A.; Loffredo, G.; Pellicciotta, D.; Carassiti, V.; Evangelisti, F.; Andersen, K.; Courtois, P.; Amati, L.; Caroli, E.; Franceschini, T.; Landini, G.; Silvestri, S.; Stephen, J. *Exp. Astr.* **2005**, *35*, 241–251.
- (48) Kang, H. C.; Master, J.; Stephenson, G. B.; Liu, C.; Conley, R.; Macrander, A. T.; Vogt, S. *Phys. Rev. Lett.* **2006**, *31*, 127401.
- (49) Hampai, D.; Dabagov, S. B.; Cappuccio, G.; Cibin, G. *Spectrochim. Acta, Part B* **2007**, *62*, 608–614.
- (50) Bjeoumikhov, A.; Bjeoumikhova, S.; Wedell, R. *Part. Syst. Character.* **2005**, *22*, 384–390.
- (51) Sun, T. X.; Ding, X. L. *X-ray Spectrom.* **2006**, *35*, 120–124.
- (52) Suzuki, Y.; Takeuchi, A.; Terada, Y. *Rev. Sci. Instrum.* **2007**, *78*, 053713.
- (53) Sun, T. X.; Xie, Y. N.; Liu, Z. G.; Liu, T.; Hu, T. D.; Ding, X. L. *J. Appl. Phys.* **2006**, *99*, 094907.



- (54) Matsuyama, S.; Mimura, H.; Yumoto, H.; Sano, Y.; Yamamura, K.; Yabashi, M.; Nishino, Y.; Tamasaku, K.; Ishikawa, T.; Yamauchi, K. *Rev. Sci. Instrum.* **2006**, *77*, 103102.
- (55) Yabashi, M.; Hastings, J. B.; Zolotorev, M. S.; Mimura, H.; Yumoto, H.; Matsuyama, S.; Yamauchi, K.; Ishikawa, T. *Phys. Rev. Lett.* **2006**, *97*, 084802.
- (56) Bonte, C.; Harmand, M.; Dorchie, F.; Magnan, S.; Pitre, V.; Kieffer, J. C.; Audebert, P.; Geindre, J. P. *Rev. Sci. Instrum.* **2007**, *78*, 043503.
- (57) Pikuz, S. A.; Shelkovenko, T. A.; Mitchell, M. D.; Chandler, K. M.; Douglass, J. D.; McBride, R. D.; Jackson, D. P.; Hammer, D. A. *Rev. Sci. Instrum.* **2006**, *77*, 10F309.
- (58) Wang, Y. J.; Narayanan, S.; Liu, J. Y.; Shu, D. M.; Mashayekhi, A.; Qian, J.; Wang, J. *J. Synchrotron Radiat.* **2007**, *14*, 138–143.
- (59) Champeaux, J. P.; Troussel, P.; Villier, B.; Vidal, V.; Khachroum, T.; Vidal, B.; Krumrey, M. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2007**, *581*, 687–694.
- (60) Andre, J. M.; Jonnard, P.; Benbalagh, R. *X-ray Spectrom.* **2007**, *36*, 62–65.
- (61) Kessels, M. J. H.; Verhoeven, J.; Tichelaar, F. D.; Bijkerk, F. *Surf. Sci.* **2006**, *600*, 1405–1408.
- (62) Eriksson, F.; Ghafoor, N.; Schafers, F.; Gullikson, E. M.; Birch, J. *Thin Solid Films* **2006**, *500*, 84–95.
- (63) Stollberg, H.; Yulin, S.; Takman, P. A. C.; Hertz, H. M. *Rev. Sci. Instrum.* **2006**, *77*, 123101.
- (64) Bukreeva, I.; Popov, A.; Pelliccia, D.; Cedola, A.; Dabagov, S. B.; Lagomarsino, S. *Phys. Rev. Lett.* **2006**, *97*, 184801.
- (65) Pelliccia, D.; Bukreeva, I.; Ilie, M.; Jark, W.; Cedola, A.; Scarinci, F.; Lagomarsino, S. *Spectrochim. Acta, Part B* **2007**, *62*, 615–621.
- (66) Tiwari, M. K.; Nayak, M.; Lodha, G. S.; Nandedkar, R. V. *Spectrochim. Acta, Part B* **2007**, *62*, 137–144.
- (67) Jarre, A.; Seeger, J.; Ollinger, C.; Fuhse, C.; David, C.; Salditt, T. *J. Appl. Phys.* **2007**, *101*, 054306.
- (92) Barradas, N. P.; Reis, M. A. *X-ray Spectrom.* **2006**, *35*, 232–237.
- (93) Solé, V. A.; Papillon, E.; Cotte, M.; Walter, P.; Susini, J. *Spectrochim. Acta, Part B* **2007**, *62*, 63–68.

## X-RAY IMAGING

- (94) Hayashi, K.; Hayashi, T.; Shishido, T.; Matsubara, E.; Makino, H.; Yao, T.; Matsushita, T. *Phys. Rev. B* **2007**, *76*, 014119.
- (95) Kopecky, M.; Kub, J.; Busetto, E.; Lausi, A.; Cukr, M.; Novak, V.; Olejnik, K.; Wright, J. P.; Fabry, J. J. *Appl. Crystallogr.* **2006**, *39*, 735–738.
- (96) Kohmura, Y.; Sakurai, T.; Ishikawa, T.; Takeuchi, A.; Suzuki, Y.; Goto, S. *J. Appl. Phys.* **2007**, *102*, 023101.
- (97) Scherz, A.; Schlotter, W. F.; Chen, K.; Rick, R.; Stohr, J.; Luning, J.; McNulty, I.; Gunther, C.; Radu, F.; Eberhardt, W.; Hellwig, O.; Eisebitt, S. *Phys. Rev. B* **2007**, *76*, 214410.
- (98) Chapman, H. N.; Hau-Riege, S. P.; Bogan, M. J.; Bajt, S.; Barty, A.; Boutet, S.; Marchesini, S.; Frank, M.; Woods, B. W.; Benner, W. H.; London, R. A.; Rohner, U.; Szoke, A.; Spiller, E.; Moller, T.; Bostedt, C.; Shapiro, D. A.; Kuhlmann, M.; Treusch, R.; Plonjes, E.; Burmeister, F.; Bergh, M.; Caleman, C.; Huidt, G.; Seibert, M. M.; Hajdu, J. *Nature (London)* **2007**, *448*, 676–679.
- (99) Momose, A.; Yashiro, W.; Takeda, Y.; Suzuki, Y.; Hattori, T. *Jpn. J. Appl. Phys.* **2006**, *45*, 5254–5262.
- (100) Pfeiffer, F.; Weitkamp, T.; Bunk, O.; David, C. *Nat. Phys.* **2006**, *2*, 258–261.
- (101) Friis, E. M.; Crane, P. R.; Pedersen, K. R.; Bengtson, S.; Donoghue, P. C. J.; Grimm, G. W.; Stampanton, M. *Nature (London)* **2007**, *450*, 549–551.
- (102) Koyama, T.; Tsuji, T.; Yoshida, K.; Takano, H.; Tsusaka, Y.; Kagoshima, Y. *Jpn. J. Appl. Phys.* **2006**, *45*, L1159–L1161.
- (103) Baruchel, J.; Buffiere, J. Y.; Cloetens, P.; Di Michiel, M.; Ferrie, E.; Ludwig, W.; Maire, E.; Salvo, L. *Scripta Mater.* **2006**, *55*, 41–46.
- (104) Feldkamp, J. M.; Schroer, C. G.; Patommel, J.; Lengeler, B.; Gunzler, T. F.; Schweitzer, M.; Stenzel, C.; Dieckmann, M.; Schroeder, W. H. *Rev. Sci. Instrum.* **2007**, *78*, 073702.
- (105) Hoshino, M.; Ishino, T.; Namiki, T.; Yamada, N.; Watanabe, N.; Aoki, S. *Rev. Sci. Instrum.* **2007**, *78*, 073706.
- (106) Alderden, R. A.; Mellor, H. R.; Modok, S.; Hall, M. D.; Sutton, S. R.; Newville, M. G.; Callaghan, R.; Hambley, T. W. *J. Am. Chem. Soc.* **2007**, *129*, 13400–13401.
- (107) Miao, J.; Chen, C.; Song, C.; Nishino, Y.; Kohmura, Y.; Ishikawa, T.; Ramunno-Johnson, D.; Lee, T.; Risbud, S. H. *Phys. Rev. Lett.* **2006**, *97*, 215503.
- (108) Chapman, H. N.; Barty, A.; Borgan, M. J.; Boutet, S.; Frank, M.; Hau-Riege, S. P.; Marchesini, S.; Woods, B. W.; A. Bajt, S.; Benner, W. H.; London, R. A.; Plönejes, E.; Kuhlmann, M.; Treusch R.; Düsterer, S.; Tschentscher, T.; Schneider, J. R.; Spiller, E.; Möller, T.; Bostedt, C.; Hoener, M.; Shariro, D. A.; Hodgson, K. O.; van der Spoel, D.; Burmeister, F.; Bergph, M.; Calemann, C.; Stahuld, G.; Seibert, M. M.; Maia, F. R. N. C.; Lee, R. W.; Szöke, A.; Timneanu, N.; Hadju, J. *Nat. Phys.* **2006**, *2*, 838–843.
- (109) Pfeifer, M. A.; Williams, G. J.; Vartanyants, I. A.; Harder, R.; Robinson, I. K. *Nature (London)* **2006**, *442*, 63–66.

## TOTAL REFLECTION X-RAY FLUORESCENCE ANALYSIS

- (110) Klockenkemper, R. *Spectrochim. Acta, Part B* **2006**, *61*, 1082–1090.
- (111) Hellin, D.; De Gendt, S.; Valckx, N.; Mertens, P. W.; Vinckier, C. *Spectrochim. Acta, Part B* **2006**, *61*, 496–514.
- (112) Pahlke, S.; Meirer, F.; Wobrauschek, P.; Strel, C.; Westphal, G. P.; Mantler, C. *Spectrochim. Acta, Part B* **2006**, *61*, 1110–1114.
- (113) Waldschlaeger, U. *Spectrochim. Acta, Part B* **2006**, *61*, 1115–1118.
- (114) Kunimura, S.; Kawai, J. *Anal. Chem.* **2007**, *79*, 2593–2595.
- (115) Vasin, M. G.; Ignatyev, Y. V.; Lakhitkov, A. E.; Morozov, A. P.; Nazarov, V. V.; Trakhtenberg, L. I. *X-ray Spectrom.* **2007**, *36*, 270–274.
- (116) Sparks, C. M.; Gondran, C. H.; Havrilla, G. J.; Hastings, E. P. *Spectrochim. Acta, Part B* **2006**, *61*, 1091–1097.
- (117) Tsuji, K.; Kawamata, M.; Nishida, Y.; Nakano, K.; Sasaki, K. *X-ray Spectrom.* **2006**, *35*, 375–378.
- (118) Tsuji, K.; Hanaoka, Y.; Hibara, A.; Tokeshi, M.; Kitamori, T. *Spectrochim. Acta, Part B* **2006**, *61*, 389–392.
- (119) Mihucz, V. G.; Moricz, A. M.; Kropf, K.; Szikora, S.; Tatar, E.; Parra, L. M. M.; Zaray, G. *Spectrochim. Acta, Part B* **2006**, *61*, 1124–1128.
- (120) Egorov, V. K.; Egorov, E. V. *Appl. Surf. Sci.* **2006**, *253*, 138–144.
- (121) Beckhoff, B.; Fliegau, R.; Kolbe, M.; Mueller, M.; Weser, J.; Ulm, G. *Anal. Chem.* **2007**, *79*, 7873–7882.
- (122) Okhrimovskyy, A.; Tsuji, K. *X-ray Spectrom.* **2006**, *35*, 305–311.

## QUANTIFICATION AND FUNDAMENTAL DATA

- (68) Cevik, U.; Baltas, H. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2007**, *256*, 619–625.
- (69) Ekinci, N.; Astam, N. *Radiat. Meas.* **2007**, *42*, 428–430.
- (70) Manohara, S. R.; Hanagodimath, S. M. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2007**, *258*, 321–328.
- (71) Jones, B. N.; Campbell, J. L. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2007**, *258*, 299–307.
- (72) Hatzistergos, M. S.; Lifshin, E. *J. Appl. Phys.* **2006**, *100*, 124312/1–124312/9.
- (73) Jablonski, A.; Tanuma, S.; Powell, C. J. *Surf. Interface Anal.* **2006**, *38*, 76–83.
- (74) Sitko, R. *Spectrochim. Acta, Part B* **2007**, *62*, 777–786.
- (75) Han, X. Y.; Zhuo, S. J.; Shen, R. X.; Wang, P. L.; Tao, G. Y.; Ji, A. *Spectrochim. Acta, Part B* **2006**, *61*, 113–119.
- (76) Cernohorsky, T.; Pouzar, M.; Jakubec, K. *Talanta* **2006**, *69*, 538–541.
- (77) Bielewski, M.; Wegrzynek, D.; Lankosz, M.; Markowicz, A.; Chinea-Cano, E.; Akoto Bamford, S. *X-ray Spectrom.* **2006**, *35*, 238–242.
- (78) Cauzid, J.; Philippot, P.; Somogyi, A.; Menez, B.; Simionovici, A.; Bleuet, P. *Chem. Geol.* **2006**, *227*, 165–183.
- (79) Ankudinov, A. L.; Elam, W. T.; Sieber, J. R.; Rehr, J. J. *X-ray Spectrom.* **2006**, *35*, 312–318.
- (80) Satoh, T.; Sakai, T.; Oikawa, M. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2006**, *249*, 234–237.
- (81) Aburaya, J. H.; Added, N.; Tabacniks, M. H.; de Almeida Rizzutto, M.; Barbosa, M. D. L. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2006**, *249*, 792–795.
- (82) Luo, L. *X-ray Spectrom.* **2006**, *35*, 215–225.
- (83) Goraieb, K.; Lopes, A. S.; Sato, C. A.; Segatelli, M. G.; Pacheco e Silva, V.; Verzoto, J. C.; Bueno, M. I. M. *S. J. Chemom.* **2007**, *20*, 455–463.
- (84) Nagata, N.; Peralta-Zamora, P. G.; Poppi, R. J.; Perez, C. A.; Bueno, M. I. M. *S. X-ray Spectrom.* **2006**, *35*, 79–84.
- (85) Antolak, A. J.; Morse, D. H.; Grant, P. G.; Kotula, P. G.; Doyle, B. L.; Richardson, C. B. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2007**, *261*, 470–474.
- (86) Correa, R.; Chesta, M. A.; Morales, J. R.; Dinator, M. I.; Requena, I.; Vila, I. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2006**, *248*, 324–328.
- (87) Garcia, J. S.; da Silva, G. A.; Arruda, M. A. Z.; Poppi, R. J. *X-ray Spectrom.* **2007**, *36*, 122–129.
- (88) Plagnard, J.; Bobin, C.; Lépy, M. C. *X-ray Spectrom.* **2007**, *36*, 191–198.
- (89) Pekoz, R.; Can, C. *X-ray Spectrom.* **2006**, *35*, 347–351.
- (90) Visnovezky, C.; Limandri, S.; Canafoglia, M. E.; Bonetto, R.; Trincavelli, J. *Spectrochim. Acta, Part B* **2007**, *62*, 492–498.
- (91) Satham, P. J. *Microchim. Acta* **2006**, *155*, 289–294.



## ELECTRON PROBE MICROANALYSIS

- (123) Salvat, F.; Llovet, X.; Fernandez-Varea, J. M.; Sempau, J. *Microchim. Acta* **2006**, *155*, 67–74.
- (124) Gauvin, R.; Lifshin, E.; Demers, H.; Horny, P.; Campbell, H. *Microsc. Microanal.* **2006**, *12*, 49–64.
- (125) Gauvin, R. *Microchim. Acta* **2006**, *155*, 75–81.
- (126) Dumelie, N.; Benhayoune, H.; Balossier, G. *J. Phys. D: Appl. Phys.* **2007**, *40*, 2124–2131.
- (127) Figueroa, C.; Brizuela, H.; Heluani, S. P. *J. Appl. Phys.* **2006**, *99*, 044909/1–044909/5.
- (128) Lulla, M.; Asari, J.; Aarik, J.; Kukli, K.; Rammula, R. *Microchim. Acta* **2006**, *155*, 195–198.
- (129) Newbury, D. E. *Microsc. Microanal.* **2006**, *12*, 26–35.
- (130) Bastin, G. F.; Oberndorff, P. J. T. L.; Heijligers, H. J. M.; Dijkstra, J. M. J. *Microsc.* **2006**, *224*, 52–57.
- (131) Kaegi, R.; Gasser, P. *J. Microsc.* **2006**, *224*, 140–145.
- (132) Kotula, P. G.; Keenan, M. R.; Michael, J. R. *Microsc. Microanal.* **2006**, *12*, 36–48.
- (133) Eggert, F. *Microchim. Acta* **2006**, *155*, 129–136.
- (134) Alvisi, M.; Blome, M.; Griepentrog, M.; Hodoroaba, V.-D.; Karduck, P.; Mostert, M.; Nacucchi, M.; Procop, M.; Rohde, M.; Scholze, F.; Statham, P.; Terborg, R.; Thiot, J.-F. *Microsc. Microanal.* **2006**, *12*, 406–415.
- (135) Godoi, R. H. M.; Potgieter-Vermaak, S.; De Hoog, J.; Kaegi, R.; Van Grieken, R. *Spectrochim. Acta, Part B* **2006**, *61*, 375–388.

## PARTICLE INDUCED X-RAY EMISSION

- (136) Nebiki, T.; Kabir, M. H.; Narusawa, T. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2006**, *249*, 226–229.
- (137) Kanngiesser, B.; Karydas, A. G.; Schütza, R.; Sokaras, D.; Reichel, I.; Röhrsch, S.; Pichon, L.; Salomonic, J. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2007**, *264*, 383–388.
- (138) Karydas, A. G.; Sokaras, D.; Zarkadas, C.; Grlj, N.; Pelicon, P.; žitnik, M.; Schütz, R.; Malzer, W.; Kanngiesser, B. *J. Anal. At. Spectrom.* **2007**, *22*, 1260–1265.
- (139) Ishii, K.; Matsuyama, S.; Watanabe, Y.; Kawamura, Y.; Yamaguchi, T.; Oyama, R.; Momose, G.; Ishizaki, A.; Yamazaki, H.; Kikuchi, Y. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2007**, *571*, 64–68.
- (140) Miranda, J.; Rickards, J.; Trejo-Luna, R. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2006**, *249*, 394–396.
- (141) Broadhurst, A.; Lane, D. W.; Rogers, K. D.; Lowe, T. W. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2006**, *249*, 808–811.

## MICRO-XRF

- (142) Buzanich, G.; Wobrauschek, P.; Strel, C.; Markowicz, A.; Wegrzynel, D.; China-Cano, E.; Bamford, S. *Spectrochim. Acta, Part B* **2007**, *62*, 1252–1256.
- (143) Papadopoulou, D. N.; Zachariadis, G. A.; Anthemidis, A. N.; Tsiroliganis, N. C.; Stratis, J. A. *Talanta* **2006**, *68*, 1692–1699.
- (144) Woll, A. R.; Mass, J.; Bisulca, C.; Huang, R.; Bilderback, D. H.; Gruner, S.; Gao, N. *Appl. Phys.* **2006**, *A83*, 235–238.
- (145) Yang, J.; Ding, X.; Liang, C. *Appl. Surf. Sci.* **2007**, *253*, 8352–8355.
- (146) Tsuji, K.; Matsuda, A.; Nakano, K.; Okhrimovskyy, A. *Spectrochim. Acta, Part B* **2006**, *61*, 460–464.
- (147) Bjeoumikhov, A.; Bjeoumikhova, S.; Wedell, R.; Gubzhokov, R.; Margushev, Z. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2006**, *248*, 142–149.

## X-RAY ABSORPTION SPECTROMETRY

- (148) Seres, E.; Spielmann, C. *Appl. Phys. Lett.* **2007**, *91*, 121919.
- (149) Seres, E.; Seres, J.; Spielmann, C. *Appl. Phys. Lett.* **2006**, *89*, 181919–181921.
- (150) Okano, Y.; Oguri, K.; Nishikawa, T.; Nakano, H. *Rev. Sci. Instrum.* **2006**, *77*, 046105.
- (151) Pham, V.-T.; Gawelda, W.; Zaushtsyn, Y.; Kaiser, M.; Grolimund, D.; Johnson, S. L.; Abela, R.; Bressler, C.; Chergui, M. *J. Am. Chem. Soc.* **2007**, *129*, 1530–1531.
- (152) Bartelt, A. F.; Comin, A.; Feng, J.; Nasiatka, J. R.; Eimüller, T.; Ludescher, B.; Schütz, G.; Padmore, H. A.; Young, A. T.; Scholl, A. *Appl. Phys. Lett.* **2007**, *90*, 162503.
- (153) Dau, H.; Haumann, M. *Photosynth. Res.* **2007**, *92*, 327–343.
- (154) Frenkel, A. I.; Pease, D. M.; Budnick, J. I.; Shanthakumar, P.; Huang, T. *J. Synchrotron Radiat.* **2007**, *14*, 272–275.
- (155) Werner, M. L.; Nico, P. S.; Marcus, M. A.; Anastasio, C. *Environ. Sci. Technol.* **2007**, *41*, 4919–4924.
- (156) Hayashi, H. *AIP Conf. Proc.* **2007**, *882*, 833–837.
- (157) Szlachetko, J.; Dousse, J.-C.; Berset, M.; Fennane, K.; Szlachetko, M.; Hoszowska, J.; Barrett, R.; Pajek, M.; Kubala-Kukus, A. *Phys. Rev. A* **2007**, *75*, 022512.

- (158) Witkowska, A.; Di Cicco, A.; Principi, E. *Phys. Rev. B* **2007**, *76*, 104110.
- (159) Soldatov, A. V.; Smolentsev, G.; Yalovega, G.; Chan, J.; Stillman, M. *Radiat. Phys. Chem.* **2006**, *75*, 1901–1904.

## APPLICATIONS

- (160) Fittschen, T. E. A.; Hauschild, S.; Amberger, M. A.; Lammel, G.; Strel, C.; Förster, S.; Wobrauschek, P.; Jokubonis, C.; Pepponi, G.; Falkenberg, G.; Broekaert, J. A. C. *Spectrochim. Acta, Part B* **2006**, *61*, 1098–1104.
- (161) Miller, T. C.; Hastings, E. P.; Havrilla, G. J. *X-ray Spectrom.* **2006**, *35*, 131–136.
- (162) Miller, L. M.; Wang, Q.; Smith, R. J.; Zhong, H.; Elliott, D.; Warren, J. *Anal. Bioanal. Chem.* **2007**, *387*, 1705–1715.
- (163) Abe, W.; Isaka, S.; Koike, Y.; Nakano, K.; Fujita, K.; Nakamura, T. *X-ray Spectrom.* **2006**, *35*, 184–189.
- (164) Cesareo, R.; Ferretti, M.; Gigante, G. E.; Guida, G.; Moiola, P.; Ridolfi, S.; Roldan Garcia, C. *X-ray Spectrom.* **2007**, *36*, 167–172.
- (165) Desnica, V.; Schreiner, M. *X-ray Spectrom.* **2006**, *35*, 280–286.
- (166) Pappalardo, L.; de Sanoit, J.; Marchetta, C.; Pappalardo, G.; Romano, F. P.; Rizzo, F. *X-ray Spectrom.* **2007**, *36*, 310–315.
- (167) Diana, M.; Gabrielli, N.; Ridolfi, S. *X-ray Spectrom.* **2007**, *36*, 424–428.
- (168) Lindgren, E. S.; Henriksson, D.; Lundin, M.; Therning, P.; Laursen, J.; Pind, N. *X-ray Spectrom.* **2006**, *35*, 19–26.
- (169) Tsutsumimoto, K.; Tsuji, K. *X-ray Spectrom.* **2007**, *36*, 324–327.
- (170) Margui, E.; Padilla, R.; Hidelgo, M.; Queralt, I.; Van Grieken, R. *X-ray Spectrom.* **2006**, *35*, 169–177.
- (171) Perés, R. D.; Marcelo, R.; Perés, C. A.; Eynard, A. D.; Bongiovanni, G. A. *X-ray Spectrom.* **2006**, *35*, 352–358.
- (172) Hokura, A.; Omura, R.; Terada, Y.; Kitajima, N.; Abe, T.; Saito, H.; Yoshida, S.; Nakai, I. *J. Anal. At. Spectrom.* **2006**, *21*, 321–328.
- (173) Hokura, A.; Omura, R.; Kitajima, N.; Terada, Y.; Saito, H.; Abe, T.; Yoshida, S.; Nakai, I. *Chem. Lett.* **2006**, *35*, 1246–1247.
- (174) Martin, R. R.; Naftel, S. J.; Nelson, A. J.; Sapp, W. D., III. *Can. J. Chem.* **2007**, *85*, 831–836.
- (175) Worley, C. G.; Wiltshire, S. S.; Miller, T. C.; Havrilla, G. J.; Majidi, V. J. *Forensic Sci.* **2006**, *51*, 57–63.
- (176) Camerani, M. C.; Somogyi, A.; Vekemeans, B.; Ansell, S.; Simionovici, A. S.; Steenari, B. M.; Panas, I. *Anal. Chem.* **2007**, *79*, 6496–6506.
- (177) Patterson, B. M.; Havrilla, G. J. *Am. Lab.* **2006**, *38*, 15–19.
- (178) Tsuji, K.; Nakano, K. *X-ray Spectrom.* **2007**, *36*, 145–149.
- (179) Kanngiesser, B.; Malzer, W.; Pagels, M.; Lühl, L.; Weseloh, G. *Anal. Bioanal. Chem.* **2007**, *389*, 1171–1176.
- (180) Magalhaes, T.; von Bohlen, A.; Carvalho, M. L.; Becker, M. *Spectrochim. Acta, Part B* **2006**, *61*, 1185–1193.
- (181) Kubala-Kukus, A.; Banas, D.; Braziewicz, J.; Gozdz, S.; Majewska, U.; Pajek, M. *Spectrochim. Acta, Part B* **2007**, *62*, 695–701.
- (182) Serpa, R. F. B.; de Jesus, E. F. O.; Anjos, M. J.; do Carmo, M. G. T.; Moreira, S.; Rocha, M. S.; Martinez, A. M. B.; Lopes, R. T. *Spectrochim. Acta, Part B* **2006**, *61*, 1205–1209.
- (183) Khuder, A.; Bakir, M. A.; Karjou, J.; Sawan, M. K. *J. Radioanal. Nucl. Chem.* **2007**, *273*, 435–442.
- (184) Griesel, S.; Mundry, R.; Kakuschke, A.; Fonfara, S.; Siebert, U.; Prange, A. *Spectrochim. Acta, Part B* **2006**, *61*, 1158–1165.
- (185) Hoefler, H.; Strel, C.; Wobrauschek, P.; Ovari, M.; Zaray, G. *Spectrochim. Acta, Part B* **2006**, *61*, 1135–1140.
- (186) Samek, L.; Ostachowicz, B.; Worobiec, A.; Spolnik, Z.; Van Grieken, R. *X-ray Spectrom.* **2006**, *35*, 226–231.
- (187) Esaka, F.; Esaka, K. T.; Magara, M.; Sakurai, S.; Usuda, S.; Watanabe, K. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2006**, *251*, 218–222.
- (188) de Vives, A. E. S.; Moreira, S.; Brienza, S. M. B.; Medeiros, J. G. S.; Tomazello, M.; Zucchi, O. L. A. D.; do Nascimento, V. F. *Spectrochim. Acta, Part B* **2006**, *61*, 1170–1174.
- (189) Fernandez-Ruiz, R.; Garcia-Heras, M. *Spectrochim. Acta, Part B* **2007**, *62*, 1123–1129.
- (190) Hung, H.-C.; Lizuka, Y.; Bellwood, P.; Nguyen, K. D.; Bellina, B.; Silapanth, P.; Dizon, E.; Santiago, R.; Datan, I.; Manton, J. H. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 19745–19750.
- (191) Schalm, O.; Janssens, K.; Wouters, H.; Caluwe, D. *Spectrochim. Acta, Part B* **2007**, *62*, 663–668.
- (192) Kraft, G.; Flege, S.; Reiff, F.; Ortnor, H. M.; Ensinger, W. *Microchim. Acta* **2006**, *155*, 179–182.
- (193) Lo Monaco, S.; Lopez, L.; Rojas, H.; Lugo, P.; Garcia, D.; Gastiel, J. *Fuel* **2007**, *86*, 641–648.
- (194) Dalbeck, P.; Cusack, M. *Cryst. Growth Des.* **2006**, *6*, 2558–2562.
- (195) Hwang, H.; Ro, C.-U. *Atmos. Environ.* **2006**, *40*, 3869–3880.
- (196) Worobiec, A.; Szaloki, I.; Osan, J.; Maenhaut, W.; Stefaniak, E. A.; Van Grieken, R. *Atmos. Environ.* **2007**, *41*, 9217–9230.
- (197) Hwang, H.; Ro, C.-U. *Atmos. Environ.* **2006**, *40*, 2873–2881.

- (198) Semenov, M. Y.; Spolnik, Z.; Van Grieken, R. *Microchim. Acta* **2007**, *157*, 121–126.
- (199) Steffen, S.; Otto, M.; Niewoehner, L.; Barth, M.; Broëk-Mucha, Z.; Biegstraaten, J.; Horvath, R. *Spectrochim. Acta, Part B* **2007**, *62*, 1028–1036.
- (200) Robaut, F.; Crisci, A.; Durand-Charre, M.; Jouanne, D. *Microsc. Microanal.* **2006**, *12*, 331–334.
- (201) Mrak, T.; Simcic, J.; Pelicon, P.; Jeran, Z.; Reis, M. A.; Pinheiro, T. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2007**, *260*, 245–253.
- (202) Tylko, G.; Mesjasz-Przybyłowicz, J.; Przybyłowicz, W. J. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2007**, *260*, 141–148.
- (203) Yue, W. S.; Li, X. L.; Liu, J. F.; Li, Y. L.; Zhang, G. L.; Li, Y. J. *Radioanal. Nucl. Chem.* **2007**, *274*, 115–121.
- (204) Bolormaa, O.; Baasansuren, J.; Kawasaki, K.; Watanabe, M.; Hattori, T. *Nucl. Instrum. Methods Phys. Res., Part B* **2007**, *262*, 385–390.
- (205) Rohrs, S.; Calligaro, T.; Mathis, F.; Ortega-Feliu, I.; Salomon, J.; Walter, P. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2006**, *249*, 604–607.
- (206) von Bohlen, A.; Rohrs, S.; Salomon, J. *Anal. Bioanal. Chem.* **2007**, *387*, 781–790.
- (207) Pagès-Camagna, S.; Reiche, I.; Brouder, C.; Cabaret, D.; Rossano, S.; Kanngiesser, B.; Erko, A. *X-ray Spectrom.* **2006**, *35*, 141–145.
- (208) Gaudry, É.; Saintavit, P.; Juillot, F.; Bondioli, F.; Ohresser, P.; Letard, I. *Phys. Chem. Miner.* **2006**, *32*, 710–720.
- (209) Vedrinskii, R. V.; Nazarenko, E. S.; Lemesko, M. P.; Nassif, V.; Proux, O.; Novakovich, A. A.; Joly, Y. *Phys. Rev. B* **2006**, *73*, 134109.
- (210) Arçon, I.; Benčan, A.; Kodre, A.; Kosec, M. *X-ray Spectrom.* **2007**, *36*, 301–304.
- (211) Stone, P. R.; Scarpulla, M. A.; Farshchi, R.; Sharp, I. D.; Haller, E. E.; Dubon, O. D.; Yu, K. M.; Beeman, J. W.; Arenholz, E.; Denlinger, J. D.; Ohldag, H. *Appl. Phys. Lett.* **2006**, *89*, 012504–012506.
- (212) Prendergast, D.; Galli, G. *Phys. Rev. Lett.* **2006**, *96*, 215502.
- (213) Cappa, C. D.; Smith, J. D.; Messer, B. M.; Cohen, R. C.; Saykally, R. J. *J. Phys. Chem. B* **2006**, *110*, 1166–1171.
- (214) Bus, E.; Ramaker, D. E.; van Bokhoven, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 8094–8102.
- (215) Becker, E.; Carlsson, P.-A.; Grönbeck, H.; Skoglundh, M. *J. Catal.* **2007**, *252*, 11–17.
- (216) Suzuki, A.; Inada, Y.; Nomura, M. *Catal. Today* **2006**, *111*, 343–348.
- (217) Meirer, F.; Pepponi, G.; Strel, C.; Wobbrauschek, P.; Mihucz, V. G.; Záray, G.; Czech, V.; Broekaert, J. A. C.; Fittschen, U. E. A.; Falkenberg, G. *X-ray Spectrom.* **2007**, *36*, 408–412.
- (218) Pinakidou, F.; Katsikini, M.; Paloura, E. C.; Kavouras, P.; Kehagias, T.; Komninou, P.; Karakostas, T.; Erko, A. *J. Hazard. Mater.* **2007**, *142*, 297–304.
- (219) Nonaka, T.; Okuda, C.; Seno, Y.; Nakano, H.; Koumoto, K.; Ukyo, Y. *J. Power Sources* **2006**, *162*, 1329–1335.
- (220) Nakano, K.; Nakamura, T.; Nakai, I.; Kawase, A.; Imai, M.; Hasegawa, M.; Ishibashi, Y.; Inamoto, I.; Sudou, K.; Kozaki, M.; Turuta, S.; Ono, A.; Kakita, K.; Sakata, M. *Anal. Sci.* **2006**, *22*, 1265–1268.
- (221) Mackey, E. A.; Cronise, M. P.; Fales, C. N.; Grrenberg, R. R.; Leigh, S. D.; Long, S. E.; Marlow, A. F.; Murphy, K. E.; Ofiaz, R.; Sieber, J. R.; Rearick, M. S.; Wood, L. J.; Yu, L. L.; Wilson, S. A.; Briggs, P. H.; Brown, Z. A.; Budahn, J.; Kane, P. F., Jr. *Anal. Bioanal. Chem.* **2007**, *387*, 2401–2409.
- (222) Balaram, V.; Patil, M. L.; Agrawal, A. K.; Subba Rao, D. V.; Charan, S. N.; Satanarayanan Ramavati Mathur, M.; Sarma, D. S.; Sankara Gowda, M.; Ramesh, S. L.; Sangurmath, P.; Anjaiah, K. V.; Dasaram, B.; Saxena Zahida Begum, R. K. *Accredit. Qual. Assur* **2006**, *11*, 329–335.

AC800678S