Atomic spectrometry update. Environmental analysis

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This is the twenty-sixth annual review published in JAAS of the application of atomic spectrometry to the chemical analysis of environmental samples. This Update refers to papers published approximately between September 2009 and August 2010 and continues the series of Atomic Spectrometry Updates in Environmental Analysis[1] that should be read in conjunction with other related reviews in the series [2-6]. In the analysis of air, work is ongoing in developing new and existing air sampler devices with an increasing focus on sampling nanoparticles. Determination of mercury in the atmosphere remains a focus for many research groups and this year has seen a renewed interest in sampling and analysis of respirable silica. There is a growing interest in measuring emissions from transport sources such as aviation and shipping. In the field of water analysis, as in previous years, the main areas of activity are the development of preconcentration and extraction procedures and elemental speciation protocols. In the field of soil, plant and related material analysis, the past year has seen a marked increase in publications featuring LIBS. The technique now appears well established for screening purposes but has not yet convinced detractors of its suitability for use in quantitative multi-element analysis. There is a growing body of literature examining species stability during sample pre-treatment and extraction. Slurry sampling has experienced renewed interest this year. In the field of geological analysis, as in previous years, considerable effort is being spent not only on the production, characterization and certification of new geological reference materials, but also on enhancing the certification of existing reference materials and the development of reference materials with assigned elemental isotopic ratios. Laser ablation continues to go from strength to strength in being adopted as a solid sampling

tool within the geochemical community with a growing interest in coupling laser ablation systems to multicollector ICP-MS systems for *in-situ* isotopic analysis. Feedback on this review is most welcome and the lead author can be contacted using the email address provided.

1   Air analysis

This section highlights noteworthy areas of research and development in the analysis of aerosols, particulates and inorganic gases by atomic spectrometric and complementary analytical techniques of interest to JAAS readership published since the last Update[1]. Initially, developments in air sampling and sample preparation are discussed. Advances in analytical instrumentation and methodologies are then reviewed. The Update then looks at specific applications that have caught the eye of this reviewer with respect to particular elemental species and to measurement activities in certain sectors.

1.1   Sampling techniques

Monitoring workers' exposure to airborne particles in the workplace through the use of *personal air samplers* is an ongoing activity in many countries as is the development and evaluation of sampler designs. French researchers have re-evaluated five, widely used sampler designs that conform to the ACGIH-EN-ISO inhalable sampling convention[7]: the IOM sampler, widely used in the UK; two versions of the CIP 10 sampler, widely used in France; the 37-mm closed face cassette sampler (CFC), widely used in the USA; a modified version of the 37-mm sampler employing an ACCU-CAP insert; and the Button sampler. The performance of such samplers is strongly dependent on particle size and ambient air velocity. The current focus is on evaluating their performance in near calm air conditions, i.e. low wind speeds of less than 1 ms⁻¹ that predominate in many workplaces. The IOM sampler and CIP 10 (version 2) sampler faired best when benchmarked against the inhalable sampling criterion. The Button sampler and the CIP 10 (version 1) showed lower sampling efficiencies. The 37-mm closed faced cassette sampler produced the poorest performance but this could be improved by using the modified version employing the ACCU-CAP, an insert that prevents particles losses to the internal walls of the sampler. Particles that enter samplers but fail to deposit on the filter can be considered to be transport loss according to Harper and co-workers[8]. Many measurement procedures only analyse the filter sample. These workers investigated the size

distribution of 0.5 – 20 μm Pb-containing particles collected from the walls and filters mounted in the CFC and IOM samplers, as part of ongoing work into investigating the extent of such transport losses. Problems can also arise in the analysis of filter samples by direct-on-filter methods such as X-ray techniques. As mentioned in previous Updates, X-ray techniques, because of their small beam size, generally do not interrogate the whole filter and hence the uniformity of particles on a filter becomes somewhat critical for unbiased results. Taiwanese researchers[9], in a very useful publication, studied the effects of uniformity of deposition on filters of respirable particles on the determination of their quartz content using XRD. In a foundry plant, they evaluated the performance of three respirable aerosol samplers: a 25-mm aluminium cyclone, a nylon cyclone and a cyclone developed by the Institute of Occupational Safety and Health in Taiwan. Filter samples were analysed for their crystalline silica content by the direct on-filter XRD approach and subsequently by the NIOSH 7500 method that involves an ashing or dissolution step in which recovered silica is re-filtered onto a silver filter for analysis. The three sampler designs gave fairly equivalent results when measured using the direct-on-filter approach. However, somewhat disconcertingly, this approach gave results that were 1.15 – 2.89 times higher than the refiltering procedure. Factors at play here can include variable particle deposition uniformity between air sampler designs, particle deposition uniformity effects arising from laboratory filtration procedures and actual sample loss during ashing or dissolution steps. This work compliments ongoing work in this reviewer's laboratory in evaluating sampling and analytical procedures for the determination of crystalline silica in air.

Increasing challenges in developing procedures to measure smaller concentrations of species in workplace air have led researchers to evaluate *sampler designs operating at higher flow rates* than those currently used. Anthony and co-workers[10] have developed a new inlet design for the above mentioned CFC sampler to meet the inhalable sample criterion at a revised flow rate of 10 L min^{-1} compared to the nominal 2 L min^{-1} currently used. Zhou and Cheng[11], on the other hand, simply investigated the performance of the IOM sampler running at an enhanced flow rate of 10.6 L min^{-1} and found that it performed fairly comparably when operated at its nominal 2 L min^{-1}, suggesting that with the advent of lighter more powerful sampling pumps, this widely used sampler could be operated at higher flow rates than previously thought. Lee and co-workers[12] have evaluated the performance of three

high flow rate samplers for respirable particle collection – the CIP 10R sampler, the GK.2.69 cyclone sampler and the FSP10 sampler – against the ACGIH-EN-ISO respirable sampling criterion.

Sampling nanoparticles, typically particles below 100 nm in size, is another fruitful area of research. Morawska and Australian coworkers[13] have reviewed instrumental methods for sampling and analysis of airborne nanoparticles (207 references). Methods to measure physical attributes such as particle number, concentration, size distribution and surface area are initially reviewed. This is followed by a review of methods to characterise the elemental composition of nanoparticles and concludes with a brief summary of sampling considerations related to nanoparticle monitoring. In all, a highly recommended paper for those wishing to learn more about airborne nanoparticle measurements! Wei *et al.*[14] evaluated the particle collection efficiency of a midget impinger sampler for nanoparticles in the range 3 – 100 nm and found that collection efficiency reached a minimum of 3 – 10% at a size range of 40 – 57 nm. Collection efficiency for nominal 10 nm particles was approximately 20%, increasing to 80% for smaller particles. Researchers at NIOSH [15] have developed a handheld electrostatic precipitator (ESP) for sampling airborne nanoparticles onto a grid, which can subsequently be examined using electron microscopic techniques. Gross sampler collection efficiencies were 76 – 94% for particles in the range 30 – 400 nm. The authors note that not all aerosols may be amenable to sampling with an ESP – explosive atmospheres for one! Semi-volatile and liquid aerosols droplets may undergo transformation during sampling and after collection on the sampling grid. Hence they suggest that prior knowledge of the source aerosol would be advantageous in the effective use of this new sampler. Plans are afoot to license this ESP sampler for commercial manufacture. Li and co-workers[16] report the development of a prototype of a miniature disk electrostatic aerosol classifer based on electric mobility and intended for personal exposure monitoring. Satisfactory performance was obtained for particles in the size range 10 – 120 nm.

Similar research is being carried out by researchers evaluating the *performance of ambient air sampler systems*. Swiss researchers[17] have evaluated the particle deposition uniformity and particle size distribution of ambient aerosol collected with a rotating drum impactor. Aerodynamic particle sizers in conjunction with micro-scanning SRXRF and TEM techniques were used in this evaluation.

Phares and Collier[18] have characterised the performance of an aerosol inlet that collects particles having a narrow range of electric mobility directly onto a heated filament for subsequent thermal desorption. Semi-volatile particles, such as ammonium nitrate, can be lost from filter samples thus introducing a sampling bias. The extent of such evaporative losses can depend significantly on the velocity of the incoming air arriving at the filter face. McDade and co-workers[19] have determined the effective filter face velocities for a number of sampler systems commonly used in ambient air studies in the United States.

Generation of stable atmospheres of particles in a laboratory setting is an ongoing requirement for testing the performance characteristics of new sampler designs and to produce near realistic test samples for proficiency testing schemes. Korean researchers[20] have designed and characterised an improved screw-assisted rotary feeding system for the precise aerosolization of ultra-small quantities of particle solids. Researchers at INRS in France have published results of a study into the homogeneity of replicate filters produced from two atmosphere generation systems[21]. The variability of material (asbestos fibres or silica-containing dusts) collected on filters, expressed as a coefficient of variation, was in the range 4 – 10%.

Passive air samplers, i.e. devices that collect gases from air by a diffusion process, are attractive given that they do not require costly pumping systems and hence can be easily deployed. Nash and Leith[22] present an overview of their use for sampling of some inorganic gases found in the atmosphere namely CO, H_2S and SO_2. Ambient NO_2 levels are a concern in many urban environments and where diffusive sampling is often deployed. Swedish researchers[23] have undertaken a field validation of the Ogawa diffusive sampler design in a cold climate. By using field-calculated diffusion uptake rates, estimated airborne concentrations compared favourably with results obtained with a real-time chemiluminescence monitor. Lin and co-workers[24], have field tested a new flow-through directional passive air sampler for NO_2. By means of a wind vane, this design is able to directionally discriminate between air pollutant signals. Fairly reasonable quantitative NO_2 data were obtained – usually within a factor of two of results obtained from a co-located real-time gas analyser. Garnett and Hartley[25] have developed a passive sampling method for the radiocarbon analysis of atmospheric CO_2 using a molecular sieve sorbent. The resultant ^{14}C measurements were within the measurement uncertainties obtained on samples collected with a pump-based sampling system. However, fractionation during the

passive sampling trapping meant that $\delta^{13}C$ values had to be adjusted as all passively collected molecular sieve samples were depleted in ^{13}C compared to pumped samples. American researchers[26] report the development of a passive sampler for collection of ambient concentrations of gaseous oxidised mercury. Results from field trials compared favourably with those from a co-located real time Hg analyser ($r^2 = 0.71$, p < 0.01, n = 100 for a one-week sampler deployment and $r^2 = 0.89$, p < 0.01, n = 22 for a two-week sampler deployment). Sampler uptake rate was not significantly affected by changes in temperature, humidity or ozone concentrations, but was somewhat dependent on wind speeds, which is not unusual for passive air samplers. The detection limit for a two-week sampler deployment was determined to be 5 pg m^{-3}.

Papers that consider *uncertainties in air sampling*, arising from spatial and temporal factors, have not received the same level of attention as that given to laboratory-based analysis. Therefore it is good to see work addressing such issues. Hyslop and White[27] examined sampling precision by assessing data from duplicate co-located air samplers. American[28] and Spanish[29] research groups describe their approaches to locating air samplers in order to optimise spatial distribution.

1.2   Reference materials

In a thought provoking paper, Epstein[30] examines two specific cases in the literature where analysts using spectroscopic instrumentation report elemental concentrations that agree with information values reported in *reference material* certificates that are subsequently found to be incorrect. One example involves the determination of Mn in NIST SRM 1648 Urban particulate matter, a widely used reference material in the air measurement field. Stone and co-workers[31] have reported on deliberations from a workshop organised by an EU funded network –NanoImpactNet – on how nanomaterials should be classified in discrete categories, what test materials should be developed as reference materials for use in studies such as ecotoxicological testing, and what physiochemical characterisation information is required on such materials for environmental impact testing. Reseachers at IAEA in Vienna[32] describe work undertaken to prepare and characterise a new set of reference air filter samples for use in their proficiency testing scheme. Target values and their standard deviations were established using INAA and PIXE techniques. A Japanese-Chinese consortium[33] has characterised the Pu concentration and its isotopic composition in a reference fallout material. It was prepared by the Japanese Meteorological Research Institute from

deposition samples collected at 14 air-monitoring stations throughout Japan between the period 1963 and 1979 and characterised by isotope dilution SF-ICP-MS. The Japanese Society for Analytical Chemistry[34] has announced the availability of two new coal fly ash CRMs, JSAC 0521 and JSAC 0522, certified for a wide range of elements.

1.3   Sample preparation

 The risk of *sample contamination* during air sampling, handling of filters and their subsequent analysis is a recurring theme. Researchers in Sweden[35] have published an informative overview on the sources of contamination and remedial strategies for laboratories undertaking multi-element trace analysis. This is particularly useful for researchers analysing ambient air particles where concentrations are often in the pg – ng m^{-3} range, equating to filter samples containing ng quantities of metallic species.

New, improved and quicker sample dissolution procedures are always welcome. American researchers[36] have evaluated sample dissolution procedures for the determination of metal impurities in single and multi-walled carbon nanotubes (CNT). They found that microwave-assisted digestion employing a nitric acid-hydrogen peroxide mixture, heated to 185 °C gave recoveries comparable to those obtained by INAA analysis, which was used to determine total metal values. Ultrasonic extraction using water or 1 % (v/v) nitric acid on the other hand released little, suggesting that the role of CNT metals in cytotoxicity may be limited owing to this suggested low bioavailability. The authors used both ICP-AES and ICP-MS techniques and, not surprisingly, encountered matrix intereferences from carbon. Hungarian researchers[37] have developed a rapid sample preparation for the determination by SF-ICP-MS of Pu and U and their isotopes in nuclear forensic swab samples. A microwave digestion procedure was found to be 2 – 3 times quicker than the commonly used ashing method.

Studies of airborne particles involving sequential extraction procedures continue to attract interest. French researchers[38] examined the speciation of Cd and Pb in dusts emitted from sinter plants. They concluded that highly soluble $CdCl_2$ and $PbCO_3$ species were generated. Supporting data were obtained by EXAFS. Workers at NIOSH[39] found that welding fumes from stainless steel gas metal arc processes contain multiple Mn species. In a review paper (94 references), French researchers[40] present an overview of methods for Cr speciation in solid matrices and their relevance

to legislative requirements. The NaOH-NaCO$_3$ leach procedure is widely used in an attempt to selectively leach Cr^{VI} from materials that may contain Cr^{III}, as is the case in welding fume and aerosol emissions from chrome-plating workshops. The authors suggest that species interconversion can occur during this leach step and that SIDMS protocols could be suitable for correcting these interconversions. Professor Furuta's group in Japan[41] has developed a procedure for the determination of S in size-classified airborne particulate matter. This involved a water leach, followed by an acid leach for the insoluble remainder. Using ion chromatography, they found that 99% of S in particles smaller than 2 μm was soluble ammonium sulfate. Brazilan researchers[42], in a study evaluating the occupational risk due to dust particle inhalation, determined the solubility of Ta, Th and U oxide species contained in pyrochlore (a niobium mineral) dust particles when subjected to a simulant lung fluid (Gamble solution). These experimentally derived dissolution factors were in broad agreement with calculated dissolution factors from worker exposure studies involving air monitoring and subsequent biomonitoring using faecal and urine samples.

Preparatory procedures continue to be developed to preconcentrate analytes, reduce interferences and to automate labour intensive steps. The determination of Pd in airborne particulate matter by ICP-MS remains challenging owing to isobaric interferences. Alsenz and co-workers[43] investigated the use of reductive co-precipitation involving either tellurium or mercury, in association with He collision gas and ID techniques, in an attempt to determine ultra-trace levels of Pd. Mercury co-precipitation was deemed to be better than tellurium co-precipitation in reducing interfering matrix constituents. Levels of Pd in air ranged from 0.5 pg m^{-3} at a rural site to 15 pg m^{-3} at urban sampling sites in the city of Frankfurt am Main. Canadian researchers[44] have developed a novel, rapid and automated procedure for the determination of ultra-trace long-lived actinides – Am, Pu and U – collected on air filters. Analytes were preconcentrated and separated using ion chromatography coupled to ICP-MS. Detection limits of 0.006 (^{238}U), 0.006 (^{239}Pu), 0.041 (^{240}Pu) and 0.062 (^{241}Am) μBq m^{-3} were obtained on filter samples from a total air volume of 3000 m^{-3}. Spike recoveries were typically better than 90% and the total analysis time was 18 minutes per sample.

1.4   Instrumental analysis

1.4.1. Atomic absorption, atomic emission and atomic fluorescence spectrometry

Atomic spectrometry techniques such as AAS, AFS, ICP-AES and ICP-MS are now well established for the determination of trace metal species in airborne particulate matter. Thus there is not a great deal to report in *instrumental developments*.

Mukhtar and Limbeck[45] report a method for the determination of Si in airborne particulates by *ETAAS*. Following a wet ashing step, the remaining in-soluble material is presented for analysis as a homogeneous suspension. A Zr-coated graphite tube was used to minimise the formation of stable SiC species. A cobalt matrix modifier was used in association with a low pyrolysis temperature to minimise the loss of volatile Si species and to minimise charring of residue organic material in the test aliquot. NIST SRM 2907, a soil standard, was used during method development and results obtained on split air filter samples compared favourably with those obtained following a total microwave assisted digestion.

There seems to be renewed interest in measuring *metalloid elements in the atmosphere* where hydride generation can be used to increase instrumental sensitivities. Savio and co-workers[46] have optimised a method for the determination of As, Bi, Sb and Se in airborne particulate matter by FI-HG-ICP-AES. Initially, filter samples were ultrasonically digested using an HCl/HF acid mixture. As reported in many previous hydride generation applications, a pre-reduction with KI was required to ensure that As and Sb were in optimal oxidation states for hydride formation. It was also noted that boric acid was required to complex free fluoride ions arising from the digestion step and which could form unwanted complexes with As and Sb. Quantitative recoveries were obtained for As, Sb and Se following analysis of NIST SRM 1648 urban particulate matter. In this SRM, where no data for Bi is included in the certification sheet, these researchers report a value of 34.1 ± 2.2 mg/kg. Assuming that an air volume of 1440 m^3 was used, the limits of detection (3 σ) were calculated to be 0.3 ng m^{-3} for As, 0.09 ng m^{-3} for Bi and 0.1 ng m^{-3} for Sb and Se. In a similar fashion but using a more sensitive ICP-MS detector, an American research group[47] used this HG approach thus enabling Se and Te to be determined in cloud droplets and aerosol particles at sub ng/L or pg/m^3 levels.

Researchers based in the UK[48] describe the origins of and present supporting validation data for the Dumaery equation which is used in *calibration systems for Hg analysers*. This equation is used to calculate the concentration of Hg vapour in the

headspace above a sealed pool of Hg held at a constant temperature. In an extension to this work, the same researchers[49] describe a new automated calibration system for Hg analyers. Here, diluent air, metered using mass flow controllers, is passed over a sealed pool of Hg held at constant temperature, to generate a known Hg in air concentration standard.

Instrumental reviews are welcome publications. In a wide ranging article (147 references), Stockwell and coworkers[50] extol the virtues of AFS as a suitable detection technique for the determination of As, Hg, Sb and Se in a range of environmental matrices, including air, biological material and food. They explain and comment on chromatographic and non-chromatographic separation protocols for speciation analysis, as well as considering sample preparation steps. Hahn[51], an exponent of LIBS, has reviewed (73 references) the current status of the technique for aerosol analysis and provides an useful insight into future research directions. Fiddler and coworkers[52] present an overview of laser techniques for atmospheric and environmental sensing (407 references).

1.4.2   Inductively coupled plasma mass spectrometry

ICP-MS remains at the forefront as a routine means of detemining trace levels of metals captured on air filter samples. Hence this section of the review now focusses on more 'exotic' applications of this technique.

Naoki Furuta's research group[53] in Japan has provided a progress report on the development of their ICP-MS based system for the determination of metals, particularly Pb, in single nanoparticles. Ambient air particles are directly aspirated into the plasma following selective particle sampling using a differential mobility analyser and an aerosol particle mass analyser. A recently developed gas exchange system allows the sampled air to be exchanged for argon. Instrument calibration was achieved by introducing desolvated Pb standards *via* an ultrasonic nebuliser. To determine the transport efficiency of this USN approach, the introduction of desolvated Cr standards was compared with the introduction of a Cr carbonyl gas standard. The concentration of the Cr gas standard had been previouslydetermined off-line by passing it at a set flow rate through three impinger samplers containing MIBK solutions for a set time period. The Cr content in these solutions was then determined by ICP-MS in order to derive a concentration value for the gas standard. It was then possible to convert Pb concentrations (pg ml^{-1}) in the standard solutions to

Pb mass flow rates (ag ms^{-1}). An instrumental detection limit of 2.8 ag ms^{-1} was calculated, allowing the Pb concentration in single nanoparticles with a nominal diameter of 90 nm and a mass of 0.46 fg to be determined! However, the authors suggest that increased instrumental sensitivities of a factor of 100 or more will be needed to enable elements such as Cd and Sb to determined in similar nanoparticles. Likewise a TOF instrument or a system employing a Mattauch-Herzog detector system would be required to undertake simultaneous multi-elemental analysis.

Brown and co-workers[54] used *LA-ICP-MS* as a means to examine the spatial distribution of metals in airborne particulate matter collected on air filters. Inhomogeneity in the distribution of dust on the filters was noted and thus sub-sampling of filters has to be carefully considered if, as often happens in air monitoring studies, assays are performed on separate test aliquots taken from a filter. A second aim of the study was to assess LA as a means of providing quantitative data from air filter samples. Whilst the absence of sample dissolution may be an attractive attribute of this approach, calibration issues and the lack of automation count against the use of LA for this particular analysis.

Feldmann and coworkers[55] studied the *atmospheric stability of arsines and their oxidative products in PM10 airborne particles.* The atmospheric half-life of the arsines ranged from 19 weeks for AsH$_3$ to two days for trimethylarsine for samples stored in the dark at 20 °C. Samples stored in simulated daylight were found to be much less stable. The total As content of airborne particles was below 1 ng m^{-3}. Arsenic species, namely MA, DMA and TMAO were determined using an HPLC-ICP-MS/ES-MS methodology and were detected in 90 % of the air samples collected. The predominant species was TMAO and was found at concentrations of between 4 and 60 pg m^{-3}. Maximum concentrations of DMA and MA determined were 16 and 6 pg m^{-3} respectively.

1.4.3   X-ray spectrometry

Characterisation of airborne particulate matter using *x-ray techniques* continues to be a fertile area for research. XRF instruments using polarised optics, reported in previous Updates, are now being used for routine air monitoring applications. Japanese researchers[56], undertaking measurements in Osaka, report calculated detection limits of 3.6, 3.5 and 1.0 ng cm^{-2} for S, Pb and Zn respectively. Calibrant filters were prepared by spiking mixed muiltielement standard solutions onto

polycarbonate filters. Determination of light elements in atmospheric particles, typical of a soil or geochemical origin, by x-ray techniques, can be problematic due to self-attenuation artefacts. Such effects and their magnitude have been studied by Formenti and coworkers[57]. Italian researchers[58] describe preliminary work using TXRF for the direct analysis of aerosol particles. Subsamples, ~ 5 mm square, were cut from air filters and fixed onto quartz sample carriers with a thin film of vacuum grease. The authors suggest that this simple approach is potentially very useful for source identification studies where simple elemental ratios and patterns can be effectively used. For quantification work, an internal standard would be required and, ideally, a sample dissolution step should be employed.

Solid-state speciation analysis of airborne particles using XAFS is a powerful tool. British researchers[59] describe the use of this technique to study the oxidation state of As in cigarette mainstream smoke, cut tobacco and cigarette ash. Results revealed that the cut tobacco powder and the cigarette ash contained almost exclusively As^V. On the other hand, the smoke particulate samples showed a mixture of both As^{III} and As^V species, this latter species however reduced upon aging to As^V. The study of nanoscale ferrite materials is an emerging field, given that such materials are being used in applications ranging from magnetic media and memory storage cores to catalysis and gas sensors. In an interesting and 'greening' article, US researchers[60] studied the growth of nanoscale nickel ferrite on a carbonaceous matrix isolated from particle emission byproducts arising from the combustion of residual oil. A selective leaching procedure involving water and dilute HCl was used to isolate the nickel ferrite material and the selectivity and the completeness of this procedure was evaluated using Fe, Ni and S K-edge XAFS.

Data interrogation and processing with x-ray techniques can be challenging. Kellogg and Willis[61] have published an optimised protocol for the spectral deconvolution of overlapping elemental spectral lines typically found in the analysis of air filter samples. They state that fitting with many library reference spectra has an unwanted effect of raising the analytical uncertainty. By carefully choosing the order of elemental processing, one can reduce the number of reference spectra required for spectrum fitting, hence reducing this analytical uncertainty. Ceccato[62] describes developments with the MAPPIX software, a package for the off-line analysis of data obtained from the analysis of single airborne particles using a μ-PIXE technique. American researchers[63] describe a standardised approach to estimating analytical

uncertainities for the XRF analysis of $PM_{2.5}$ filter samples and which has been successful applied to data generated by three laboratories involved in analysing filters samples from US air monitoring programs.

Readers are directed to our companion Update for further information on X-ray developments and applications[5].

1.4.4 Intercomparison studies

Papers that compare the *performance of different methods and techniques or different laboratories* are always most welcome. Ayrault and co-workers[64] have evaluated ICP-MS, INAA, PIXE and SEM-EDXRF for air pollution biomonitoring studies, highlighting the complementary nature of these techniques. Ashley and co-workers[65] report data from an interlaboratory comparison exercise conducted to generate method precision data for a new ASTM ICP-MS method for the determination of Be in air filter samples. Canadian researchers[66] evaluated the quality of elemental data obtained following analysis of air filter samples. Duplicate filter samples were initially analysed by ED-XRF, then digested and the resultant solutions analysed at one of two laboratories employing ICP-MS. The authors conclude that rigorous filter handling operations are required to minimise possible metallic contamination. They also note that inter-laboratory and inter-method comparisons using duplicate sampling protocols can help to evaluate the reliability of elemental data and assist in the identification and quantification of possible sources of variation during sampling, handling and processing. An international consortium[67] has published the findings of a field inter-comparison exercise in which eleven instruments, involving eight different methods of measurement, were evaluated for the continuous determination of atmospheric ammonia gas. Good agreement between the instruments was found where the airborne ammonia levels were above 10 ppbv but below this value it was worse. The authors conclude that, despite recent instrumental advances, continuous measurement of atmospheric NH_3 remains a challenging and costly exercise.

1.5 Applications

1.5.1 Specific elements

Mercury is recognised as a global pollutant and remains the focus of much research. Pirrone *et al.*[68] present an informative overview of global mercury emissions to the

atmosphere from both anthropogenic and natural sources. These emission budgets can be subject to errors arising from variability in feedstock and uncertainties in sampling and measurements. Papers studying such uncertainties are therefore welcome, such as that by Wu *et al.*[69] on the uncertainties in estimating mercury emissions from Chinese coal-fired power plants. Papers that present new emission data from point sources are also most welcome. Japanese researchers have undertaken a study of emissions from crematoria[70]. Chinese researchers have studied emissions of Hg from five municipal solid waste landfills[71] where they found that the total gaseous mercury in landfill gas ranged from 2 – 1400 ng m^{-3}, that organic forms accounted for less than 2 %, and that total yearly emissions ranged from 17 – 3300 g yr^{-1}. In two informative papers, Dommergue and co-workers[72] and Sprovieri and coworkers[73] present overviews of mercury measurements carried out in the prestine Antarctic troposphere and in the wider world.

Respirable crystalline silica is classified as a human carcinogen and has been studied in the working environment. However, few measurements have been reported from the wider ambient environment. Richards and co-workers[74] report emission factors and ambient air concentrations at three sand and gravel plants. They estimate that the emission factor could be up to 0.00011 lbs of silica per ton of processed stone and that the resultant silica release made up 3 – 8 % of the measured PM$_{10}$ release. Ambient respirable concentrations of crystalline silica in air, measured upwind and downwind, at such facilities ranged from 0.3 – 2.8 ug m^{-3}. British researchers questioned whether crystalline slica can be formed and released from sugarcane burning [75]. The limited data they collected suggested that no crystalline silica was detected in airborne smoke particles but that the sugarcane trash ash formed after pre-harvest burning contained between 10 and 25 % (m/m) SiO$_2$, mostly in an amorphous form, but containing up to 3.5 % (m/m) quartz. Likewise, both quartz and cristobalite were identified at levels of 5 – 15 % (m/m) and 1 – 3 % (m/m) respectively in the sugarcane bagasse ash formed in the processing factory. The authors recommend that adequate protection should be given to workers exposed to such dusts and that appropriate disposal routes for the ash material should be sought in order to prevent secondary exposure.

Carbonaceous particles from combustion sources are of continuing interest owing to their impact on health and atmospheric chemistry. Current understanding of their sources, their variability and their subsequent fate in the atmosphere remains

incomplete and requires further measurement and data interrogation. A European research consortium has determined the particulate carbon content in precipitation samples collected at five background sites over a west-east European transect, from the Azores to Hungary[76]. Tumolva and co-workers[77] used TEM/EDS to examine the morphological and elemental properties of soot particles generated in a laboratory setting using a variety of fuel stocks. They subsequently used this information to classify the sources of carbonaceous particles collected at three sampling sites – urban, industrial and coastal – and to apportion their relative contributions.

1.5.2   Specific research topics

Advanced materials made from *engineered nanoparticles* continue to be developed. However, quantitative risk assessments on the impacts of such particles, if released into the atmosphere, on workers, end users and the wider environment are currently lacking, in part because of limited published emission data and exposure studies. Guidance is most welcome in this emerging field and here NIOSH[78] have published a useful survey strategy for assessing nanoparticle emissions within workplaces. Similar blueprints are being developed in other countries.

Emissions from traffic sources continue to attract attention with *emerging focus on particle emissions from aviation and shipping*. Kinsey and researchers from the US EPA[79] report findings from the US Aircraft Particle Emissions Experiment (APEX) in which emissions from the exhaust plumes of nine models of commercial aircraft engine were monitored carefully on a ground test bed. Measurements were made for particle mass and numbers, particle size distributions and total volatile matter using both time-integrated and continuous sampling techniques. Winnes and Fridell[80] have studied the particle emissions from ships in relation to fuel type. Irish researchers[81] have characterised single particles from in-port ship emissions using ATOFMS, in association with other air quality monitoring equipment, as a means of determining the relative contribution of shipping traffic to air quality in port cities.

Emissions from road transport sources continue to be researched. A US group compared different measurement strategies for emissions from modern diesel engines that emit low levels of particulate matter[82]. They evaluated two gravimetric methods, a chemically reconstructed mass measurement method that measured the chemical constituents of particles, and an integrated particle size distribution (IPSD) method where the measured particle number data were converted to mass data using a particle

density function. They concluded that, whilst gravimetric methods are traceable to primary standards, the alternative chemical speciation and the IPSD approaches might better characterise ultra low emissions typical from modern engines.

Despite greater efforts to recycle, much waste is still sent to *landfill* and research continues in evaluating the releases of particles and gases to the atmosphere from such sites. Fowler and fellow UK researchers[83] have undertaken a quantitative assessment of dust propagation at a hazardous waste landfill where solid residues from incineration are dumped. In summary, they investigated the use of low cost wind directional passive sampling onto sticky pads to obtain airborne samples. Elemental fingerprinting analysis employing ICP-AES was then carried out in association with chemometric analysis to quantify the extent of these fugitive dust emissions from this waste site.

Studies into *emissions from agricultural activities and composting* have been reported, in particular, where there is a need to derive industry or sector specific emission rates. Spanish researchers have developed a methodology for the determination of ammonia and total VOC in a composting plant. The novel part was to devise a normalisation function relating such emissions to efficiency of the composting process using a biological respiration index[84]. It is hoped that, by using such an approach, emissions from differing composting plants can be presented in a more comparative format.

Source apportionment studies attempt to elucidate the origins of airborne pollutants and ascertain the relative contributions from source emitters. Chemical markers are commonly used in such studies, but often these markers are not unique to any one specific emission source. Korean researchers have determined the Nd and Sr isotopic composition of airborne particles and were able to trace dust events back to specific arid locations in China[85]. Weinbruch and co-workers[86], using SEM and EDAX microanalysis, characterised the size, morphology and chemical composition of airborne particles collected on moss samples, a substrate often used as a dust deposition sampler. Their study suggests that analysis of individual particles can provide source-specific information that cannot be derived from bulk chemical analysis. In particular, fly ash particles from combustion sources can sometimes be incorrectly adjudged to be derived from geochemical weathering process, given that particles can have similar bulk chemical compositions but where there are differences at an individual particle level.

Numerous *atmospheric pollutant surveys* continue to be published and, for brevity, it is probably useful just to mention one important paper. A pan-European group[87] has distilled data on the physical and chemical characteristics of aerosols obtained over the past decade in research and monitoring programmes conducted at more than 60 locations in Europe, ranging from natural background sampling sites to kerbside sites in urban environments.

Estimating future atmospheric concentrations using projections based upon current data occupies a number of researchers. In an interesting paper, Brown[88] compared the estimated UK annual emissions of metals with the measured average ambient air concentrations for the same metals over the period 1980-2007 using a generalised least squares regression technique. Elemental sensitivity factors were calculated, as were 'predicted' elemental airborne concentrations in the absence of any future emission sources. For example, it was calculated that ambient airborne levels of Pb could drop to ~ 10 ng m^{-3} in the absence of any future anthropogenic emissions. This value is broadly in agreement with current airborne measurements made at a remote Scotish sampling location deemed to be free from current man-made emission sources.

2 Water Analysis

This section highlights new developments and improved analytical methods that use atomic spectrometry for the determination of trace metal(loids) and their associated elemental species in environmental water samples since the last Update [1].

2.1 Sample preparation

For laboratories about to embark on multi-elemental trace and ultra trace analysis for the first time two papers highlight the importance of sample preparation. That by Rodushkin and co-workers[35] is full of useful information and sound advice on how to handle samples and reagents to reduce contamination sources. Particularly important

in this author's opinion is their advice that, "the targeted purity levels should be fit for purpose to be cost-efficient", the analyst "should limit the number of steps and general manipulations of the sample" as well as "make sure that available reagents are of sufficient purity". The determination of Pu isotopes in waters and environmental solids has been reviewed[89] (135 references) and includes a summary of related sample preparation procedures such as filtration, acidification, and valence adjustment prior to the preconcentration and analysis of environmental water samples

2.2 Preconcentration, extraction and separation procedures

A driver for the development of analytical methods for water analysis continues to be the preconcentration of the analytes to above the limit of detection of the instrumental techniques to be used. The methodologies are mostly based upon solid phase extraction, liquid-liquid extraction or co-precipitation. Variations on these themes are fertile ground for publications, and the novelty of some of the articles push the definition of analytical novelty to its limit. The aim of this Update is to highlight some of the more interesting papers and new methods for problematic elements.

Amongst the truly novel stationary phases for solid phase extraction and specific affinity chromatography that have emerged are *imprinted polymers*. These are "bio-inspired" materials capable of recognizing a family of compounds. Their production and evaluation for the determination of organotin compounds in seawater has been described by Gallego-Gallegos and co-workers[90], who reported that when used for the SPE of TBT, a breakthrough volume of over 1 L was found for seawater spiked with 50 ng L^{-1} of TBT resulting in a preconcentration factor of 150, with a spike recovery of 93 ± 12%. Another Spanish research group has reported the use of polymers imprinted with 8-hydroxyquinoline for the on-line SPE of Ni and Pb from seawater with subsequent ICP-AES detection[91]. The static adsorption capacities for the metals were found to be 0.023 mmol g^{-1} for Ni and 0.0015 mmol g^{-1} for Pb. Standard solutions (50 μg L^{-1}) adjusted to pH 8.5 and passed through a 300 mg bed of molecularly imprinted polymer (MIP), were found to have breakthrough volumes in excess of 200 mL resulting in enrichment factors of 14.8 for Ni and 5 for Pb.

Dispersive liquid-liquid micro-extraction (DLLME) together with homogeneous liquid- liquid extraction in the determination of inorganic elements has been reviewed[92] (65 references) covering 1970 to 2009, although the majority of

articles are from after 2000. In DLLME a ternary component solvent system is used, which consists of an appropriate mixture of an extractor solvent, such as tetrachloroethene, and a disperser solvent such as acetone that must be highly miscible in the aqueous sample and the extraction solvent. On addition of this mixture, a cloudy solution is produced by the dispersion of the organic solvent in the aqueous phase. The analytes are subsequently extracted into the organic phase after complex formation, and the two phases are separated by centrifugation. The advantages of this method are that it uses micro-volumes of organic solvents, and the extraction surface is extremely large, so that vigorous mixing or shaking is not required. A disadvantage is that the analytes are extracted into an organic solvent making the technique more suitable for FAAS or ETAAS than for ICP-AES or ICP-MS. Another review of DLLME that includes a section on inorganic analysis was published in 2009[93] (129 references). This will be of interest to researchers who do not just carry out inorganic analysis. Moreover, the widespread use of DLLME in organic analysis suggests that it may well work for organometallic compounds. Ligandless DLLME has also been proposed using 1,2-dichlorobenzene as the extraction solvent and ethanol as the dispersive solvent for the micro-extraction of Cu^{II} ions[94], although this has opened the door for a series of "novel" methods where the same authors change the extraction solvent to extract another ion, in this case $Ag^{I[95]}$. We are curious to see what other elements they manage to extract next year.

Another growing technique is the use of *ionic liquids* (IL) to carry out liquid-liquid extractions. In the extraction of $Cd^{[96]}$ the IL is the hydrophobic liquid, 1-hexyl-3-methylimidazolium hexafluorophosphate, that can be used to carry out DLLME without the need for a disperser solvent, as the IL is dispersed using ultrasound. The analyte is complexed with DDTC and extracted into the IL, which is then separated from the aqueous phase by centrifugation. The authors report an enrichment factor of 67 and a LOD of 7.4 ng L^{-1} with ETAAS determination. These IL lend themselves to the various micro-extraction methods such as SDME[97] that already exist in the literature.

Liquid phase micro-extraction for the determination of trace elements has been reviewed[98] (104 references), covering the methodologies of SDME, HF-LPME, DLLME and SFODME. The last of these proved popular this year for the determination of Co and Ni[99], Hg[100], Pd[101] as well as Pb and Cd[102].

The use of *cloud point extraction* (CPE) with atomic spectrometric methods has been reviewed[103] (91 references, in Slovak with an English abstract). An interesting application was the use of CPE followed by ICP-MS detection of radionuclides in aqueous samples[104]. The trivalent lanthanides are complexed with APDC and then extracted into Triton X-114®. Extraction efficiencies of up to 90% were achieved with corresponding concentration factors of up to 6.3 for Eu. Meeravali and Jiang[105] used CPE for the selective preconcentration of Cr species prior to ICP-MS detection in DRC mode. Hexavalent Cr was selectively extracted from the sample using Aliquat-336® while total Cr (after conversion to Cr^{III}) was extracted using APDC. In both cases the cloud point surfactant was Triton X-114®. The Cr^{III} concentration was estimated by difference. Preconcentration factors of 10 resulted in LODs of 0.01 ng mL^{-1} for Cr^{VI} and 0.025 ng mL^{-1} for Cr^{III}. A Chinese group has reported the development of an online flow injection CPE method that does not require a chelating agent for the determination of trace metals in sea water by ICP-AES[106].

The use of *nanoparticles* as adsorbents for the solid phase extraction of environmental pollutants including metal ions has been reviewed[107] (176 references). Unmodified TiO_2 nanoparticles have been employed to extract dissolved Fe from seawater[108] and it has been demonstrated that the same material, modified with a calixarene compound, is capable of preconcentrating Cr, Cu, Pb and V from environmental water samples[109].

Thanks to a special issue of the Journal of Chromatography A, volume 1217 (16), there have been a large number of review articles recently, including one on *carbon nanotubes*[110](180 references). Their use has been extensively reported over the last few years and this year is no exception. In their oxidized form they are able to extract Cu, Co and Pb[111] and Cu, Mn, Pb and Zn[112]. They have also been shown to retain complexes of Rh[113] and selectively retain Cr^{III} for speciation studies[114], as well as quantitatively adsorb Au and Pd from solutions in the pH range from 2.0 to 5.0[115]. The precious metals retained were eluted with a 3% *m/v* thiourea solution in 0.5 M HCl with a recovery of up to 103%. The LODs were 0.23 ng mL^{-1} for Au and 0.06 ng mL^{-1} for Pd, when using ICP-MS.

2.3   Speciation

Feldmann and co-workers[116] critically reviewed (91 references) *elemental speciation analysis*, covering three main analytical methodologies: electrochemical, X-ray absorption spectroscopy and chromatography coupled to mass spectrometric detection.   Researchers from the University of Vienna provided a more specific review (141 references) of the environmental applications of HPLC or GC coupled to ICP-MS[117].

Non-chromatographic speciation methods continue to dominate the literature. Reviews by Vieira *et al.*[118] (176 references) and Gonzalvez *et al.*[119] (43 references) both note that, although atomic spectroscopy coupled to chromatographic separation gives the most complete information, non-chromatographic techniques are competitive as they are less time consuming and more cost effective.

The *fractionation* of trace elements in water samples is now being studied more closely. Puls and Limbeck[120] have described a flow injection system for the identification of the neutral, anionic and cationic fractions of Al, Ca, Cd, Co, Cr, Cu, Mg, Mn, Pb and Zn in urban snow samples. Three different SPE cartridges were employed in sequence, followed by ICP-AES detection. Turkish researchers[121] determined the distribution of P in seawater between Al-bound, Fe-bound, Ca-bound and loosely bound P forms with ICP-AES detection. Studies of this kind are important for understanding the bioavailability of this marine nutrient.

Chromatographic and non-chromatographic methods for arsenic speciation continue to be investigated. The use of the SFODME preconcentration technique to obtain a 1000-fold enhancement factor, followed by ETAAS detection of the As species (As^{III} and total As after reduction of As^V to As^{III}) has been reported by Iranian researchers[122]. They achieved a LOD of 9.2 pg mL^{-1} with an RSD of < 8.6%. A method for the speciation analysis of arsenic and antimony using DLLME and ETAAS has been developed in a Spanish laboratory[123]. Samples were acidified to pH 1, the As^{III} and Sb^{III} complexes with APDC were extracted into carbon tetrachloride and determined by ETAAS. Total As and Sb were obtained after the reduction of the sample with sodium thiosulfate and the As^V and Sb^V concentrations obtained by difference. A narrow bore HPLC SF-ICP-MS method for the determination of As^{III}, As^V, MMA, DMA and AsB has been developed[124]. A NH_4NO_3 buffer allowed high salt gradients to be run. Separation was achieved in less than 9 minutes using the Dionex AS11 and AS7 columns. Column deposits that could cause reversible

adsorption of As^V were eliminated by having the samples in an excess of phosphate buffer that prevented artefacts in the As^{III} to As^V ratios. Retention times were stable and LODs were in the low ng L^{-1} range.

A *multi-elemental speciation* method for the determination of As^{III}, As^V, MMA, Cr^{III}, Cr^{VI}, Se^{IV} and Se^{VI} has been reported[125]. Chromatographic separation was achieved within 11 minutes using a Hamilton PRP-X100 column and a binary mobile phase mixture of 0.5 mM $NH_4H_2PO_4$ / 10 mM NH_4NO_3 at pH 6 and 30 mM NH_4NO_3 at pH 6. An ICP-MS instrument equipped with a dynamic reaction cell was used to detect the analytes, resulting in LODs of between 0.12 to 0.44 µg L^{-1} for the individual species. A method for the analysis of waste waters for As^{III}, MMA, DMA, As^V, Se^{IV}, Se^{VI} and $SeCN^-$ has been developed by a Brazilian research team[126] using a binary gradient elution of H_2O and 100mM NH_4NO_3 at pH 8.5 and a Metrosep A Supp10 (250×4.0 mm) analytical separation column. Using ICP-MS detection, LODs of between 56 and 81 ng L^{-1} were reported for the Se species and 16 to 25 ng L^{-1} for the As species.

The speciation of chromium continues to be of interest. Brazilian researchers[127] have developed a non-chromatographic method based on CPE and preconcentration to determine Cr^{III} and Cr^{VI} species ,by difference, in river waters contaminated with leather effluents. Trivalent Cr is complexed and trapped in a TritonX-114® surfactant solution after being brought to the cloud point temperature by microwave-assisted heating. Under optimized conditions, an enrichment factor of 48 was achieved for a 50 mL sample. Detection of Cr was by ETAAS calibrated over a linear range of 2.5 to 80 µg L^{-1}, giving a LOD of 0.7 µg L^{-1}. Method repeatability was 2.0% for 10 replicates of a 50 µg L^{-1} Cr^{III} solution. Micro-extraction techniques seem to be much in vogue in Iran, so it was no surprise that Iranian workers had developed a method for the speciation analysis of chromium based on DLLME followed by FAAS detection[128]. Enrichment factors of up to 275 were achieved resulting in a LOD of 0.07 µg L^{-1} for Cr^{VI}, a linear working range of 0.3 to 20 µg L^{-1} and precision of 2.0% (n=7)]. These figures of merit are comparable to those achieved by ETAAS[127]. Xing and Beauchemin[129] have described an HPLC-ICP-MS method for chromium speciation at trace levels in potable water using cell-based ICP-MS for interference elimination. Chromium species were separated on an IonPac AG-7 column using a gradient elution of 0.1 M NH_4NO_3 and 0.8 M HNO_3. Accuracy was

verified against the NRCC river water CRM SLRS-2 and detection limits of 0.02 µg L^{-1} for Cr^{VI} and 0.04 µg L^{-1} for Cr^{III} were attained.

Methods for the determination and speciation of mercury in natural waters have been reviewed[130] (120 references). The ability of sodium diethyldithiocarbamate (NaDDC) to form complexes with mercury species has been exploited, either by immobilizing it on polyurethane foam[131] or by extracting the complexes using CPE[132]. Alternatively, the use of a dithiazone functionalized C$_{18}$ column for SPE of Hg^{2+}, MeHg$^+$ and EtHg$^+$ has been reported[133].

Inorganic selenium speciation in environmental samples has been carried out using selective electrodeposition coupled to ETAAS[134]. In this technique, Se^{IV} and selenocystine are selectively electrodeposited onto a mercury electrode before removal and detection by ETAAS. Spike recoveries of between 91 and 99% are achieved with a selenium LOD of 1.0 µg L^{-1} and an RSD of 3.5 % (n=6) at a level of 100 µg L^{-1}.

A method for the speciation analysis of tellurium by electrodeposition followed by ETAAS detection has been described[135]. Trace amounts of Te^{IV} were preconcentrated using DLLME prior to detection. The Te^{VI} concentration was found by difference after reduction to Te^{IV}[136]. The enrichment factor of 125 meant that a LOD of 0.004 ng mL^{-1} and a precision of 3.6 % RSD (n=6) for a 0.5 ng mL^{-1} standard were achieved.

A Dowex Monosphere 550A (OH) anion exchange resin has been used to successfully *retain and separate thallium species in waters*[137]. The species Tl^{I} and Tl^{III} were eluted using thiourea followed by ICP-MS detection. The use of the column resulted in a 100-fold enrichment factor for the analytes.

Given their toxicity, even at low concentrations, *the analysis of water for organotin compounds* continues to attract research interest. A liquid-liquid extraction followed by HPLC separation and ICP-MS detection was used by Chinese researchers[138] to quantify organotin compounds in seawater; LODs were better than 3 ng L^{-1}. They found that the only compound present was TPhT at a concentration of 53 ng L^{-1}. Although an atomic spectrometric detector has not been used in the following methods, it will of interest that two research groups from Spain have demonstrated that HS-SPME after *in situ* ethylation improved method sensitivity with GC-FID[139] with LODs (n=9) of 0.17 µg L^{-1} for MBT, 0.012 µg L^{-1} for DBT and 0.009 µg L^{-1} for TBT. Using a more sensitive GC-MS technique[140], the same researchers obtained

LODs between 0.025 and 1 ng L^{-1} for the target tin species. A Japanese research group has succeeded in quantifying TPhT and TBT using HILIC-ESI-MS[141]. Following preconcentration of a 500 mL water sample using mixed mode reversed phase and weak anion-exchange SPE cartridges, they determined a method LOD of 3 ng L^{-1} for TBT and 6 ng L^{-1} for TPhT.

The speciation of vanadium in water samples has been studied by Chinese researchers[142] using on-line separation and preconcentration. A silica column modified with CTAB retains V^V in a pH range between 2.0 and 7.0, while V^{IV} is retained between pH 5.0 and 7.0. Hence, V^V was retained at pH 2.5 and total V at pH 6.0 and the V^{IV} concentration was obtained by difference. With ICP-AES detection, the LOD of 0.03 µg L^{-1} for V^v was obtained after preconcentration of a 3 mL sample with an enrichment factor of 27.9; the RSD for a 5 µg L^{-1} standard (n=9) was 4.3%.

2.4   Instrumental analysis

2.4.1   Atomic absorption spectrometry

Russian researchers[143] have developed an *ETAAS instrument with two vaporization zones* for the simultaneous determination of Cd, Hg and Pb in sea and river waters. Silver nanoparticles, prepared by the reduction of silver nitrate with sodium citrate, have been proposed as a new modifier for the elimination of interferences when determining As and Sb in seawater[144]. Pyrolysis temperatures of at least 1100 °C for As and 900 °C for Sb were achievable, reducing interferences. Detection limits were 0.022 ng for As and 0.046 ng for Sb. Blank values were negligible and this modifier is said to be cheaper than alternatives.

2.4.2   Atomic emission and fluorescence spectrometry

In this review period papers advocating the use of *tungsten coil atomic emission spectrometry* have been published. Donati and co-workers[145] developed a double coil instrument to improve the detection of refractory elements in water. They report improvements of 40-fold for V and 5-fold for Ti. The use of two coils and the consequent extra energy added to the system facilitated the detection of elements with

transition energies higher than 350 kJ mol^{-1} such as Ag, Cu and Sn. The same research group also report the simultaneous detection of Cr, Ga, In and V in water and soils using a single coil instrument[146], and the indirect determination of I[147].

Chinese researchers[148] have instead used *tungsten coil electrothermal vaporization atomic fluorescence spectrometry* to detect trace Cd in water after CPE. They report an enrichment factor of 152 and a LOD of 0.01 µg L^{-1}.

An ICP-AES method[149] for the *indirect determination of F$^-$* in aqueous samples following precipitation of CeF$_3$ has been reported. The excess Ce^{III} remaining after precipitation is used indirectly to determine the F$^-$ concentration. The method has been shown to work well for F$^-$ in the range 0 – 20 mg L^{-1} in solution giving a LOD of 1.4 mg L^{-1}.

A review of atomic fluorescence spectrometry as a suitable detection technique in speciation studies for As, Hg, Sb, Se[50] (147 references) has been published.

2.4.3 Vapour generation methods

Vapour generation remains an important method for boosting the sensitivity of atomic spectrometric methods for the hydride forming elements. However, it suffers from a number of interferences. To address these an Australian research group[150] developed an *in-line anion-exchange separation* for the removal of Co^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} in the determination of Cd. Under optimum conditions, with a sample loading of 9.6 mL, a LOD of 3 ng L^{-1} was achieved.

Mercury in river water[151] was detected using a FAPES low power atmospheric pressure He plasma source directly coupled to either a conventional vapour generation system, using Sn^{II}Cl$_2$ as a reductant, or a UV photochemical system for the generation of elemental mercury vapour. The concentration of mercury was monitored using the characteristic 253.7 nm resonance line, and the 70 W plasma was found to be tolerant of the water vapour generated by the gas-liquid separator. With the furnace at 400 °C, a measurement precision of 2.4 % RSD at the 1 ng mL^{-1} concentration level was achieved. With chemical reduction a LOD of 240 pg mL^{-1} was obtained, and with photochemical reduction the LOD was 250 pg mL^{-1}. The addition of a gold amalgamation system improved the LODs 5-fold. Chemical vapour generation using NaBH$_4$ cannot be coupled to this emission source since the large quantity of H$_2$ generated extinguishes the He FAPES source!

The *determination of Bi by tungsten trap hydride generation AAS* has been extensively investigated[152]. Bismuth hydride is generated and trapped on a tungsten coil held at 289 °C. After preconcentration, the coil is heated to 1348 °C to release the trapped Bi species, which are subsequently transported to a flame heated quartz atom cell for detection. Interferences from As, Au, Ca, Cd, Cu, Fe, Mg, Mn, Na, Ni, Pb, Se and Zn, as well as Cl$^-$, SO$_4^{2-}$, and PO$_4^{2-}$ were examined. The calibration was found to be linear between 0.1 and 10.0 μg L^{-1} for an 8 mL sample giving a LOD of 25 ng L^{-1}. The tungsten trap gave an enhancement factor of 21.

Work on the *development of vapour generation methods for non-traditional elements* continues. Sturgeon and co-workers[153] have developed a UV photochemical vapour generation method for Ni with ETAAS detection. This is based on the photochemical generation of highly toxic Ni(CO)$_4$ and its trapping on the surface of a graphite furnace. With a Ni^{II} solution containing formic acid, the vapour generation efficiency was 35%. A 2 mL sample gave a LOD of 8 pg mL^{-1} and the measurement precision was better than 3% RSD at the 1 ng mL^{-1} level. The method was validated using the NRCC CRM SLRS-4 River water. The same researchers[154] have developed a high yield photochemical vapour generation method for Fe with ICP-AES detection. In this approach, Fe^{2+} and Fe^{3+} in solutions containing low molecular weight acids such as formic, acetic or propionic acids are exposed for 250 s to a UV source, in this case a 17 W low pressure mercury lamp. Optimum vapour generation efficiency (60 ± 2%) was obtained when the sample solution contained 50% *v/v* formic acid at pH 2.5. Compared to conventional solution nebulisation, the sensitivity was improved 80-fold and the LOD 100-fold when monitoring the 238.204 nm Fe line. An analytical precision of 0.75 % RSD was obtained at the 100 ng mL^{-1} level and the method was validated against the NRCC CRM SLRS-5 River water. This research team[155] also developed a thin film HG method with ETAAS detection for the determination of trace Cu. Using tetrahydroborate as the reductant, the overall efficiency was 8-12%. A solution LOD of 100 pg mL^{-1} was achieved with a measurement precision of 4% RSD for a 1 mL sample spiked at 1 ng mL^{-1}. A Czech research group[156] has developed a method for the determination of sulfide in water samples by vapour generation ICP-AES. Hydrogen sulfide and acid volatile sulfides are transformed into a vapour by acidification. The method gave results comparable to those from iodometric titration over a linear range of 0.06 to 22.0 mg L^{-1} and a LOD of 0.03 mg L^{-1} for H$_2$S.

2.4.4   X-ray fluorescence spectrometry

Total reflection X-ray fluorescence is of growing interest for the determination of trace elements in waters. Selenium has been determined in waters, including seawater, following reduction of Se^{IV} with ascorbic acid and collection of colloidal Se on TXRF reflectors[157]; the LOD was 0.8 ng mL^{-1}. Juvonen *et al.*[158] have evaluated TXRF for the determination of As, Co, Cr, Cu, Mn, Ni, Pb, V and Zn in waters affected by acid mine tailings. They compared results with those obtained by accredited ICP-AES methods and found differences varying from 12 to 20%. They concluded that TXRF could only be recommended as a preliminary screening technique. Carbon in natural fresh water biofilms has been determined[159] using a TXRF instrument fitted with a Cr-anode X-ray tube, a multilayer monochromator, a vacuum chamber and a Si(Li) detector with an ultra thin window. The accuracy was checked against total C measurements carried out with a combustion carbon analyzer. A bench top TXRF instrument has been evaluated[160] for the determination of As, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sn and Zn in industrial waste water. Data obtained by direct TXRF compared favourably with values from ICP-AES and ICP-MS detection after microwave digestion.

Tolokonnikov *et al.*[161] considered *the application of EDXRF to the analysis of potable water*. They discuss the use of thin layer samples and X-ray optics with total internal reflection. They report that, when compared to thick layer optic geometries, LODs can be lowered 1000-fold, making the instrument suitable for the analysis of potable waters.

Preconcentration methods for the analysis of liquid samples by XRF techniques have been reviewed[162] (118 references) with emphasis on new efficient variations that extend the possibilities of XRF for liquid sample analysis. To the same end, powdered silica[163] has been used to preconcentrate trace elements before WDXRF detection, and the ion-exchange resin Amberlite IRC748 to preconcentrate Cu, Fe, Ni, Pb and Zn from surface waters before detection with transportable EDXRF [164].

2.4.5   Inductively coupled plasma mass spectrometry

The application of collision/reaction cell instruments continues to increase. The quantification of major and trace elements in water samples by ICP-MS using a collision cell to attenuate interferences derived from Ar and Cl has been described[165].

A collision cell pressurized with a mixture of 7 % H_2 in He can improve the background equivalent concentrations for As, Cr, Cu, Fe, Se and V by two orders of magnitude. A ICP-MS instrument fitted with a collision/reaction interface was capable of measuring elevated levels of ^{129}I in environmental samples[166]. However, interferences from ^{127}I were so high that their quadrupole ICP-MS instrument was unsuitable for the measurement of the $^{129}I/$ ^{127}I ratio in uncontaminated environments.

Although cell-based instruments eliminate many of the inherent interference problems in ICP-MS, *chromatographic separations for interference removal* are sometimes necessary. An in-line chromatographic separation of Ba from Cs for the measurement of ^{135}Cs and ^{137}Cs at trace levels in ground waters has been reported[167]. A Dionex CG3 IonPac guard column is used to reduce the blank Ba levels and preconcentrate Cs. To improve instrument sensitivity, the in-line chromatographic system was used in conjunction with a high efficiency desolvating nebulizer. Detection limits were 2 fg mL^{-1} for ^{135}Cs and 0.9 fg mL^{-1} for ^{137}Cs.

Sector field high resolution ICP-MS is sometimes the only alternative to matrix separation/removal techniques. When measuring trace element profiles in high altitude ice cores[168], sample manipulation can be reduced to a minimum, thus reducing any contamination risk. A Lithuanian research group[169] determined As in seawater by SF-ICP-MS at medium resolution where ^{75}As is resolved from $^{40}Ar^{35}Cl$. In contrast, where interferences are less of an issue, a low-resolution mode is often used to maximize ion transmission and take advantage of the low background signals. To further boost sensitivities, microconcentric nebulizers and high efficiency nebulization/ desolvation units can be used. Two such sample introduction systems have been compared for the determination of REE in surface and subsurface waters[170]. The authors report that, for spiked (1 µg L^{-1}) NRCC water CRMs, REE recoveries were about 100% and that, overall, LODs were of the order of 0.05 - 0.2 ng L^{-1} and not significantly different between either system.

Isotope dilution as a calibration strategy has been investigated for the determination of total Cr in seawater[171]. All the Cr present was reduced to Cr^{III} with hydroxylamine hydrochloride, before the sample pH was adjusted to 9.3. The Cr^{III} was retained on silica immobilized diphenylcarbazone and subsequently eluted with 1.5 M HNO_3. A throughput of ten 7.5 mL samples per hour and a LOD of 0.005 ng g^{-1} were obtained. Results were in agreement with the certified values for the NRCC seawater CRMs NASS-5 and CASS-4. The validated method provided results of 0.1132 ±

0.0047 ng g^{-1} for the candidate CRM NASS-6 and 0.0942 ± 0.0040 ng g^{-1} for the candidate CRM CASS-5. The same research group reported the use of ID-ICP-MS for the determination of Mo in seawater[172] after matrix separation on an immobilized 8-hydroxyquinoline microcolumn. A concentration of 9.42 ± 0.22 ng g^{-1} was obtained for the NRCC NASS-5 CRM, which was in good agreement with the certified value of 9.4 ± 1.0 ng g^{-1}. Milne *et al.*[173] determined Co, Cd, Cu, Fe, Mn, Ni, Pb and Zn in seawater using ID-SF-ICP-MS and applying standard additions after a preconcentration step on a microcolumn containing Toyopearl AF-Chelate-650M resin. The samples were irradiated with a UV lamp to destroy any organic ligands before preconcentration and extraction. The results were in good agreement with those of the NASS-5 CRM and consensus values from inter-comparison exercises. The method was used to produce vertical profiles of the target elements at the Bermuda Atlantic Time Series station. Tagami and Uchida[174] have used ID-ICP-MS to survey Re concentrations in 45 Japanese rivers. After a 20-fold preconcentration, ID-ICP-MS gave a recovery of almost 100%. A geometric mean Re value of 0.81 ng L^{-1} was found and the values had a high correlation with SO_4^{2-} concentrations. Isotope dilution ICP-MS has also been used to determine the vertical profile of dissolved Pb in Lake Baikal[175]. The results were validated against the river water reference material JSAC 0302. Concentrations in the profile ranged from 6.39 to 14.5 pg mL^{-1} with the exception of surface water, which had a value of 194 pg mL^{-1}. This was attributed to a surface input source. The mean concentration was approximately 9.6 pg mL^{-1}, which was much lower than the results found by other researchers.

Isotope ratio measurements are becoming more important for identifying sources of pollutants. Lead concentrations and isotope ratios have been measured on rainfall collected in Central Tokyo[176]. A sequential rain sampler was used to collect 1 mm precipitation intervals. Lead concentrations decreased rapidly during a rainfall event and the isotope ratios clearly changed. This was explained with an atmospheric mixing model that involved four possible sources: diesel vehicle emissions, natural soil components, airborne particulate matter and fly ash from a local incinerator. Lithium isotope ratios in seawater and natural carbonates have been determined by quadrupole ICP-MS[177]. A single step ion chromatographic method was used to recover and separate Li from matrix elements, involving on a 2 mL column packed with AG 50W-X8 resin. High column yields (> 99.98%) were obtained with low procedural blanks (< 500 fg mL^{-1}). The precision was < ± 0.8‰ (2 σ) for L-SVEC Li

standards and better than ± 1.5‰ (2 σ) for natural samples. Seawater δ^7Li values of 30.75 ± 0.41‰ (2 σ) were similar to those reported by other workers (31 ± 0.5‰). Lithium isotope ratios have also been determined using a MC-ICP-MS coupled with a low memory APEX IR high efficiency nebuliser[178]. A simple one-step column separation was used to isolate Li from the matrix elements. The long-term precision of δ^7Li values was ± 0.12‰ (2 σ, n=46). Using this method, δ^7Li values for the following seawater RMs were determined: IAPSO, 30.84‰, NASS-5, 30.72‰, CASS-4, 30.69‰ and SLEW-3, 30.45‰. A value of 9.36‰ was found for NIST SRM 1640 River water. Results are also reported for two silicate rock standards.

2.4.6   Thermal Ionisation-Mass Spectrometry

Thermal Ionisation-Mass Spectrometry is recognized as the most precise instrumental technique for isotope ratio analyses. *High precision measurements of Os concentration and isotopic compositions in seawater* have been made[179]. Water samples of 50 mL were spiked with ^{190}Os as a tracer, then heated to 300 °C at a pressure of 128 bar in quartz Carius tubes. The new procedure was applied to seawater profiles from the Atlantic, Pacific and Southern Oceans. The authors found that their results were between 25-35% higher than those of other studies, that Os did not behave conservatively and that surface seawater has lower ^{187}Os/ ^{188}Os values than deep water.

2.4.7   Laser-based spectrometry

The performance of *laser induced breakdown spectrometry for the detection of aqueous ions* has been improved by the use of laser induced fluorescence[180]. This combination was found to improve the LOD for Fe and Pb in liquid water. The LIBS plasma was produced with a 266 nm frequency quadrupled Q-switched Nd:YAG laser and the target analytes were re-excited using a nanosecond optical parametric oscillator laser tuned to the strong absorption lines of Fe and Pb. A LOD of 39 μg L^{-1} was obtained for Pb and 65 μg L^{-1} for Fe and RSDs as low as 6.7% were found for 100 shots at a repetition rate of 0.7 Hz. The sensitivity increase was estimated to be 500 times better than LIBS alone. A thin wood substrate has been shown to be a suitable liquid absorber for LIBS determination of trace elements in water[181]. The

authors demonstrated that detection limits as low as 30 μg L^{-1} can be achieved using low energy pulses and 1000 shot accumulations.

Continuous flow hydride generation laser induced fluorescence spectrometry has been investigated for the determination of Pb in water and sediment samples. The Pb hydride generated was excited with a laser at 283.306 nm, and fluorescence was detected at 365 and 405.8 nm. Method repeatability was 3.5 % RSD at the 10 ng mL^{-1} level[182].

Laser induced thermal lens spectrometry has been used in combination with CPE for the detection of Pd in water samples[183]. After extraction, the sample was transferred into a quartz microcell and probed with a single laser thermal lens spectrometry instrument. Under optimum conditions the calibration was found to be linear between 0.3 to 60 ng mL^{-1}, with a LOD of 0.04 ng mL^{-1}.

2.5   Data quality and method intercomparison

Kumar and Riyazuddin[184] made a detailed study of *the effect of Fe in ground waters on the determination of total Cr* . They found that digestion with HNO_3 or hydroxylamine was not enough to release organically bound Cr or Cr fixed to Fe^{III} hydroxide precipitates, and that microwave digestion of the samples before the measurement of total Cr gave the best results.

Plutonium isotopes have been determined in seawater by semiconductor alpha spectrometry, ICP-MS and Accelerator Mass Spectrometry[185]. All the techniques were able to produce depth profiles and the results were comparable between all three analytical methods.

A review of Bi determination in environmental matrices has been published[186] (148 references), with the objective of establishing a range of typical concentrations for this element in natural water. The authors report that this objective was impossible to achieve due to the wide variability in the published data. The detection limits of most methods published after 2000 are well above those required and are therefore of limited usefulness. Analysis of existing information on total Bi concentrations and its chemical speciation in seawater reveals that the uncritical reproduction of old data is widespread. The gauntlet has been thrown down! It should be picked up by the readers of this update as there is obviously a need for sensitive, accurate and precise measurements of Bi and its species in natural waters.

A blind intercomparison exercise has been carried out to *validate the standard portable flow injection chemiluminescence method for the determination of Fe in seawater*[187] against ID-ICP-MS. To investigate the effect of the seawater matrix, samples were collected at various depths (0-200 m) from different water masses in the Atlantic Ocean. These were filtered through 0.02 μm and 0.2 μm pore size filters. The results showed good agreement over the concentration range of 0.15–2.1 nM of Fe. Where disagreement occurred the authors put this down to random error caused by contamination during handling and matrix effects, rather than systematic errors.

Sector field ICP-MS and TIMS have been compared for *B isotope ratio measurements* in Water Framework Directive monitoring programs[188]. As expected, the precision of $\delta^{11}B$ measurements by sector field ICP-MS (2 σ = ± 2.6‰) was poorer than that obtained using a TIMS instrument (2 σ = ± 0.3‰). However, ICP-MS was found to be a suitable screening method although the superior precision of TIMS allowed the tracing of nitrate pollution sources.

3 Analysis of soils, plants and related materials

This section highlights new developments and improved analytical methods that use atomic spectrometry for the determination of trace metal(loids) and their associated elemental species in environmental water samples since the last Update [1].

3.1 Sample preparation

3.1.1 Sample extraction and dissolution

Methods for ultrasound-assisted extraction of both organic compounds and metals from food and soil have been reviewed (160 references) by Tadeo *et al.*[189]. Elik[190] developed a procedure in which 0.5 g of soil, ground to < 63 μm particle size, was sonicated for 30 minutes in a mixture of HNO_3:HCl (4+1). Results for Mn, Ni and Pb in CRM and roadside soils were similar to those from hotplate digestion, with precisions < 2% . A group from the University of the Basque Country[191] developed an ultrasound extraction that they propose as an alternative to US EPA Method 3051A Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils. Best compromise conditions, determined according to a central composite design with three variables and five levels, were a 6-minute irradiation in a 6.8 mol L^{-1} mixture of 45% HNO_3 and 55% HCl. Results for some elements were close to those obtained by the US EPA method, but recoveries were < 50% for Al, Fe and V. Another Spanish group[192] used a range of CRMs to develop dedicated ultrasound-assisted extraction methods for animal tissue, plant tissue and inorganic matrices (soil, sediment, fly ash and sewage sludge).

Assessing the bioavailable metal fraction in soil is important but there is still little consensus on the best reagent(s) to use. Bortolon and Gianello[193] recommended the Mehlich-1 extractant (0.05 mol L^{-1} HCl + 0.0125 mol L^{-1} H$_2$SO$_4$, pH 1.2) over 1 mol L^{-1} KCl or 0.1 mol L^{-1} HCl in their study of 441 Brazilian soils. However, Schroder *et al.*[194], following a major inter-comparison involving 23 laboratories, concluded that the Mehlich-3 recipe (0.2 mol L^{-1} CH$_3$COOH + 0.25 mol L^{-1} NH$_4$NO$_3$ + 0.013 mol L^{-1} HNO$_3$ + 0.015 mol L^{-1} NH$_4$F + 0.001 mol L^{-1} EDTA) constituted a suitable extractant for assessing plant-available Cu, K, Mg, Mn and Zn, but not Ca or Fe. A simple water leaching procedure[195] was applied to assess element bioaccessibility in 161 soils from two transects across the United States as part of the North American Soil Geochemical Landscapes Project. Sixty-three elements were measured in the extracts by ICP-AES or ICP-MS.

An attempt has been made[196] to harmonise *dynamic fractionation methods for metals in soils* by comparing results obtained by sequential injection micro-column extraction and the rotating coiled column extraction methods on NIST SRM 2711 Montana soil and GBW 07511 Sediment. A 5-step procedure was used: water soluble/exchangeable; acid soluble; easily reducible; easily oxidisable and moderately reducible. The residual fraction was also analysed after microwave digestion in *aqua regia*. Similar trends in metal distribution were generally found with the two methods.

The stability of arsenic species during sample pre-treatment and extraction is of considerable current interest, as discussed in a review by Rubio *et al.*[197] with 70 references. A comparison[198] of four extraction procedures applied to two CRMs and five soils, using HPLC-ICP-MS detection, found that microwave-assisted extraction in 1 mol L^{-1} H$_3$PO$_4$ + 0.5 mol L^{-1} ascorbic acid gave good As recovery and minimised conversion of As^{III} to As^V. Similar findings were reported by other workers[199] using IC-ICP-MS. They recommended 1 mol L^{-1} H$_3$PO$_4$ for the extraction of inorganic As species from soils but noted that, even when extracts were stored at 4 °C in darkness, the As^{III} peak area decreased over time. The same research group[200] recommended the use of protein-extracting solution at pH 5.6 for isolation of As^{III}, As^V, DMA and MMA from spinach, claiming that no interspecies conversion occurred in extracts over 45 days. Meanwhile, a study on the uptake and transformation of As by *Sinapis alba* (White Mustard)[201] found highest extraction efficiency, reproducibility and stability of arsenic species in extracts when samples of dry, homogenised plant tissue were extracted in water, without use of liquid nitrogen.

Species stability during extraction is also discussed in a review[40] (94 references) focusing on recent developments in EU regulation and analytical methods relevant to Cr. A study[202] has been carried out to assess whether naturally-occurring substances co-extracted from plant tissue can affect Se speciation. Using HPLC-ICP-MS it was discovered that the presence of two phenolic antioxidants, rutin and tannin, at a ratio of 1:100 w/w, decreased the signal for Se^{IV}. In addition, the Se^{VI} was found to be unstable during 4 days at 4 °C.

A high-throughput *microwave-assisted digestion* method suitable for plant samples weighing as little as 1-20 mg has been developed[203]. The procedure, which typically involved treatment of ≤ 5 mg of sample with 125 μL of H_2O_2 and 250 μL of HNO_3, was carried out using a 64-position rotor with 5 mL disposable glass vials. Results for NIST SRM 1515 Apple leaves were similar to certified values for Al, Ca, Cu, K, Mg, Mn, P and Zn for a 1 mg sample, but 5 mg was required for accurate quantification of Mo and S. The method was applied to single rice grains and small batches of *Arabidopsis* seeds, yielding results similar to conventional digestion of larger samples. Microwave digestion was found superior to open vessel digestion for the measurement of rare earth elements in tomato plants[204]. Procedures without HF addition, e.g. treatment of 0.5 g of sample with 6 mL HNO_3 + 2 mL H_2O_2, gave lower blanks than when HF was added. Limits of detection from around 0.02 to 2 μg kg^{-1} were obtained by both quadrupole ICP-MS and SF-ICP-MS.

3.1.2   Preconcentration procedures

Numerous *procedures for preconcentrating analytes from plant or soil extracts and digests* have been reported since our previous Update[1]. But many appear to be relatively minor variations on methods already in the literature, differing only in the target analyte or precise details of the experimental conditions. Selected methods that provide results for CRMs or other validation checks are summarised in Tables 1-3. Most were developed specifically for soil or plant analysis, but also listed are methods for water or food analysis that involved soil or plant CRMs. Additionally, a flotation method for preconcentration of Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn[205] has been reported (preconcentration factor 125; LOD 1.3 – 2.4 mg mL^{-1}) together with dispersive liquid-liquid micro-extraction procedures for Co[206] (preconcentration factor 16, LOD 0.9 μg L^{-1}) and Pd[207] (preconcentration factor 350; LOD 0.007 μg L^{-1}).

3.2 Instrumental analysis

3.2.1 Atomic absorption spectrometry

Interest in *continuum source atomic absorption spectrometry* noted in our previous Update[1] has continued. Oliveira *et al.*[208] successfully used HR-CS-FAAS to determine both macro and micronutrients in acid digests of NIST SRMs 1573a Tomato leaves, 1570 Spinach leaves and 1547 Peach leaves, before applying the method developed to samples of orange and sugarcane. Boron, Cu, Fe, Mn, Mo and Zn were measured at their main atomic lines; Ca and Zn at their secondary lines; Mg by side pixel registration on the secondary line wing; P by use of the non-resonance line at 213.618 nm, and S on the basis of the molecular band of CS at 258.055 nm. The simultaneous determination of Cd and Fe in sewage sludge by HR-CS-ETAAS has been demonstrated[209]. Cadmium was measured at the main resonance line of 228.802 nm and Fe at a secondary line (228.725 nm). Samples were introduced to the atomiser as slurries. A short temperature program was used with no pyrolysis but with two atomisation steps: 1300 °C for Cd and 2300 °C for Fe. Calibration with respect to aqueous standards yielded good agreement with certified values for CRMs BCR 144R Domestic sewage sludge and 146R Industrial sewage sludge. Methods involving HR-CS-ETAAS with solid sample introduction have also been reported for the determination of Ag in soil[210] and Sb in sediment[211].

Slurry sampling with conventional (line source) FAAS has been used to determine Mn in leaves of cassava (*Manihot esculenta crantz)*[212]. Samples were dried, milled, sieved to < 100 μm particle size, and sonicated for 20 minutes in 2 mol L^{-1} HNO$_3$ before aspiration. A method for measuring Mn and Zn in tea leaves[213] reported optimal performance when 200 mg of ground sample was sonicated for 10 minutes in 2 mol L^{-1} HNO$_3$ + 2 mol L^{-1} HCl + 2.5% Triton X-100$^®$, in the proportions 50:12:38. Results were statistically similar to those obtained following acid digestion of the same samples (paired t-test at 95% confidence interval).

Slurry sampling ETAAS has also experienced renewed interest. Methods have been reported for the determination of As and Sb[214] and for Cd, Hg, Pb and Se[215] in soil (the latter in Japanese with English abstract), Sn in sediment[216], and V[217] and Cd, Cu, Pb and Ni[218] in plant material.

Applications of AAS in speciation analysis include a method coupling FAAS with HPLC[219], specifically an IonPac CS5A bifunctional ion-exchange column, which allowed a Polish group to separate three classes of Al species in water extracts of soil from the vicinity of an aluminium smelter. The first peak eluted corresponded to AlF_2^+ and/or AlF_4^-, the second to AlF^{2-} and/or AlF_3, and the third to Al^{3+}. Researchers in Brazil[220] used a Box-Behnken design to optimise a method for determination of As^{III} (directly) and total As (following reduction) in slurries of phosphate fertilisers by HG-AAS. Speciation of inorganic Se in soil digests by ETAAS[134] was achieved by workers in Iran. Their approach involved measurement of total Se, electrodeposition of Se^{IV} on a mercury-coated electrode, and then measurement of Se^{VI} in the spent electrolyte.

A recently available *commercial background correction method for AAS – high speed self-reversal* – has been evaluated[221] for its ability to remove spectral interference from As in the determination of Cd. This occurs in As-rich soils because the weak As line at 228.812 nm is only 0.01 nm from a sensitive Cd line. The method not only overcame the As problem but also appeared to eliminate the need to add chemical modifier (Pd) in the determination of Cd in 0.01 mol L^{-1} $CaCl_2$, a reagent often used to assess phytoavailability.

3.2.2   Atomic emission spectrometry

Spectral interference between As and Cd, and also the interference of Fe on As, Cd and Pb, have been overcome[222] by the use of *electrothermal vaporisation inductively coupled plasma atomic emission spectrometry*. Researchers successfully separated the analytes using a three-step temperature programme. Cadmium vaporised during the first step (760 °C, 40 s) and As and Pb during the second (1620 °C, 20 s), but the majority of the Fe remained until step 3 (2250 °C, 10 s). Reasonable results were obtained from the direct analysis of Chinese soil GBW7411, using NIST SRM 2710 Montana soil as the calibration standard. Detcheva *et al.*[223] claimed to have overcome the need for matrix-matched standards in their analysis of 17 elements in plant materials by ETV-ICP-AES. After optimisation of the sample carbonisation procedure and the introduction of appropriate gaseous modifiers (CCl_4, $CHCl_3$, CCl_2F_2 or C_3H_8), they proved that satisfactory calibration could be achieved not only with plant CRM but also with dried aqueous standards or graphite standards.

There has been interest in *non-ICP excitation methods for atomic emission spectrometry*. Work on tungsten coil atomic emission spectrometry has included the first demonstration of the measurement of In and V by this technique[146]. Results obtained for Cr, Ga, In and V in nitric acid digests of NIST SRM 2711 Montana soil were statistically similar to certified values, although RSDs were at least 15% for all analytes and 36% for V. Limits of detection, based on summation of results at multiple wavelengths for each element, were 4, 80, 20 and 300 μg L^{-1} for Cr, Ga, In and V, respectively. An article in Japanese with English abstract[224] described a simple, cheap approach for the measurement of Pb in soil based on liquid electrode plasma atomic emission spectrometry. The sample was extracted with water, then Pb was separated from other elements in the extract by SPE. A small amount of sample extract was placed in a narrow channel and a high voltage applied from both ends, generating a micro-plasma. A LOD of 1.3 mg L^{-1} was achieved and calibration was linear up to 800 mg L^{-1}. A two-jet argon arc plasmatron[225] has been used to study the effect of major elements K, Na, Ca, Mg and Fe on the determination of trace elements in natural samples including rock, soil and ashed plant material. Matrix interferences could be controlled by careful selection of operating conditions and use of reference samples.

3.2.3   Atomic fluorescence spectrometry

The role of *hydride generation atomic fluorescence spectrometry (HG-AFS)* in speciation analysis has been reviewed[50] (147 references). Approaches involving coupling of HG-AFS with both chromatographic and non-chromatographic separations were described for As, Hg, Sb and Se species. Meanwhile, a new non-chromatographic separation and determination of Sb^{III} and Sb^{V} in mushrooms by HG-AFS has been reported[226]. As in previous work on As by some of the same researchers (see the 2009 Update[1]), the method uses different experimental conditions and proportional equations to obtain the species concentrations. The determination of As by HG-AFS using a dielectric barrier discharge atomiser was also reported in the 2008 Update[227]. This technique has now advanced, with new methods reported for the determination in soil of both Bi[228] and Te[229], the latter in Chinese with English abstract.

The *single-ring electrode radio-frequency capacitively coupled plasma torch* previously used to measure Cd and reported in the previous Update [1] has now been applied successfully to the determination of Zn[230] in soil, water and biological reference materials. The LOD was 8.2 µg L^{-1} and RSD values were < 10% (n = 10).

Ezer[182] described the first application of *continuous flow hydride generation-laser induced fluorescence (HG-LIF)* for trace measurement of Pb. After optimisation of hydride generation conditions, the LOD was 0.3 µg L^{-1} using the 405.8 nm line and the dynamic range was 0.5-50 µg L^{-1}. Results similar to those from ICP-AES were obtained for a multi-element solution, but not when the techniques were applied to an acid digest of a contaminated river sediment (316 mg kg^{-1} by HG-LIF *vs.* 501 mg kg^{-1} by ICP-AES at 220.4 nm and 735 mg kg^{-1} at 217.0 nm). Ezer attributed these discrepancies to spectral interference in ICP-AES caused by the unusually high levels of iron present in the sample, up to 245,000 mg kg^{-1}.

The feasibility of using sample combustion and gold amalgamation in *the determination of Hg by cold vapour-AFS* was demonstrated for the first time by Cizdziel *et al.*[231]. They coupled together a cold vapour atomic fluorescence spectrometer and a combustion-based cold vapour-AAS mercury analyser in a configuration that allowed analyte from a single combustion event to be measured sequentially by both techniques. Results obtained by AAS and AFS for a range of environmental and biological samples were highly correlated (R^2 = 0.998). However, the sensitivity was higher with AFS and the LOD lower (0.002 ng for AFS *vs.* 0.016 ng for AAS).

3.2.4 Inductively coupled plasma mass spectrometry

Researchers at the University of Copenhagen[232] have described *a high-throughput semi-quantitative ICP-MS method* for trace element fingerprinting in plants. More than 70 elements covering the mass range from ^{7}Li to ^{238}U could be measured in plant digests in less than 60 s. As expected, accuracy was poorer than in full quantitative mode, but application of principal component analysis allowed three different genotypes of rice to be distinguished on the basis of their trace element profiles.

There is growing *use of ICP-MS for measuring ratios of stable and long-lived isotopes*. However, although the addition of oxygen gas to the collision/reaction interface[166] allowed ^{129}I to be measured in environmental samples from around a

nuclear reprocessing plant, the method was not sensitive enough to measure ^{129}I/^{127}I ratios in relatively uncontaminated environmental samples. Sahoo et al.[233] avoided this problem in their study of soils from Chernobyl by measuring ^{127}I by ICP-MS but ^{129}I by AMS. Current concentrations of ^{129}I, together with knowledge of the ^{129}I/^{131}I ratio discharged by the damaged reactor, were used to calculate the amounts of the short-lived radionuclide ^{131}I ($t_{1/2}$ = 8 days) deposited in the vicinity of the plant in the period April-May 1986. This allowed the probable radiation dose to the local population arising from ^{131}I to be estimated. Meanwhile, a Canadian research group[234] has developed a method of measuring ^{107}Ag/^{109}Ag using MC-ICP-MS and performed the first study of isotopic fractionation of silver in a range of environmental CRMs. Silver was isolated from samples by a two-stage column procedure involving anion and cation-exchange resins. Mass discrimination and instrument drift were corrected using a combination of Pd internal standard and standard-sample-standard bracketing. Precision better than 0.015‰ (2 σ) was obtained which is adequate for measuring δ^{107}Ag/^{109}Ag fractionation in natural samples. There is also continuing interest in isotope ratio measurements by MC-ICP-MS as a tool to improve understanding of the biogeochemical cycling of Hg[235].

Two detailed studies focus on *the optimisation of collision/dynamic reaction cell conditions in the measurement of Se*. Pick et al.[236] used 1.1 mL min^{-1} CH$_4$ as a reaction gas to reduce polyatomic interference from ^{40}As^{40}As on ^{80}Se in the analysis of HNO$_3$/H$_2$O$_2$ digests of plants and animal feedstuffs. Results were comparable to those obtained by both collision cell ICP-QMS and SF-ICP-MS; the latter measured ^{77}Se since it could not resolve ^{80}Se from the interferent. Floor et al.[237] applied a collision cell in the analysis of volcanic soils. Best results were obtained by the addition of ca. 2% methanol to the sample digests and quantifying ^{78}Se using a collision/reaction cell pressurised with hydrogen.

Brazilian workers[238] optimised a method for measuring Dy, Eu, Sm, Te and Yb in soil and sediment by *slurry sampling ETV-ICP-MS*. Powdered sample (50 mg) ground to < 50 μm particle size was sonicated in a mixture of 0.8 mL HNO$_3$, 0.4 mL HF and 0.4 mL H$_2$O$_2$, then introduced to the instrument along with NaCl carrier. Results for four CRMs were within the certified ranges.

The use of chromatographic methods with ICP-MS remains of major interest, with applications becoming more widespread and routine. Interesting examples from

the past year include the measurement of organophosphates in sediment[239] by gas chromatography ICP-MS, and a rapid automated method for the separation of Pu[240] from potential interferent Hg, Pb, Th and U by sequential injection extraction chromatography using TEVA$^®$ sorbent followed by ICP-MS. The procedure, which was validated by the analysis of CRMs IAEA 375 Soil and IAEA 135 Sediment, proved capable of handling the large samples – up to 200 g of soil, 20 g of seaweed, or 200 L of water – typically required in environmental radiochemical analysis. Size exclusion chromatography ICP-MS was used to investigate the speciation of Fe and Zn in barley[241] as part of a study focused on the growing worldwide problem of human trace element deficiency. Phosphorus and S were also measured, as $^{47}PO^+$ and $^{48}SO^+$ ions after addition of oxygen to the octapole reaction cell, because they are major constituents of phytic acid and protein, respectively. Most of the Fe co-eluted with P and most of the Zn with S suggesting that, in cereal grains, Fe is mainly associated with phytic acid and Zn with peptides. Lombi *et al.*[242] also found evidence of Fe phytate in their analysis of rice grains by HPLC-ICP-MS and X-ray techniques, and of an association between Zn and S consistent with metal binding to phytochelatins or metallothionein. A HPLC-ICP-MS method[243], employing a mixed mode (anion-exchange with reversed phase) column, provided baseline separation of selenocystine, Se-methyl-selenocysteine, selenomethionine, methylseleninic acid, selenite, γ-glutamyl-methyl-selenocysteine and selenate in standard solutions. Selenium-methyl-selenocystiene, selenomethionine and selenate were identified in extracts of watercress grown in Se-enriched soil. The identities of the two organic species were confirmed by on-line HPLC-ESI-MS-MS.

3.2.5 Accelerator Mass Spectrometry

Techniques used for measuring ^{14}C have been reviewed (273 references) by Povinec *et al.*[244] who conclude that AMS will dominate this measurement arena in the future.

Several developments focusing on *the measurement and application of isotopes of plutonium* were presented at the 11th International Conference on AMS (Rome, September 2008). Chamizo *et al.*[245] reported that $^{240}Pu/^{239}Pu$ ratios can now be measured on the compact AMS system at the Centro Nacional de Acceleradores in Seville and presented sediment core data that confirmed weapon-grade Pu, released during an accident on land, had been transported into the marine environment.

Bisinger et al.[246] applied a combination of AMS and alpha particle spectrometry to samples of soil, moss and sediment. The AMS technique was used to measure the β⁻ emitter ^{241}Pu, and the α-emitters ^{239}Pu and ^{240}Pu, which cannot be distinguished by alpha spectrometry because of their similar decay energies. The ^{238}Pu, which suffers interference from ^{238}U in AMS, was measured by alpha spectrometry. This approach allowed Pu released from Chernobyl to be distinguished from Pu released by other sources, Tims et al.[247-248] proposed that Pu isotopes derived from atmospheric weapons testing could prove a valuable alternative to the more commonly used ^{137}Cs as a tracer for soil erosion and sediment accumulation in major world rivers.

3.2.6 Laser-induced breakdown spectroscopy

The overall *suitability of LIBS for the determination of trace metals in soil* remains a subject of debate. Essington et al.[249] analysed a suite of 65 soils from Tennessee using a Nd:YAG laser at 532 nm, with beam energy 25 mJ per pulse, pulse width 5 ns and 10 Hz repetition rate. Spectra were collected from 200 to 600 nm and the Si emission at 288.16 nm was used as an internal standard. Results were deemed disappointing. In general, only elements present at concentrations above 500 mg kg^{-1} could be quantified, data did not correlate well with results obtained by ICP-AES, and analytical uncertainties of up to 48% were obtained. In contrast, Popov et al.[250] reported LODs between 1 mg kg^{-1} for V and 140 for Mn using 1064 nm laser irradiation (360 mJ per pulse, 8 ms pulse duration) and a spatially-confined plasma generated in a 4 mm diameter polished brass chamber. However, repeatability was found to be highly dependent on the position of the focal point of the laser relative to the sample surface. Another study[251] applied two-level factorial design to optimise laser pulse energy, delay time and integration time gate for the measurement of Al, Ca, Fe, K, Mg, Mn and Ti in soil. A key finding was that different analytes and matrices have different optimal conditions.

Numerous *element specific LIBS methods for soil analysis* have been reported. Double-pulse LIBS and normalisation of results to the Fe emission line at 248.814 nm successfully increased signal-to-noise ratio in the measurement of As[252] in mine tailing soils. A screening method for Cd[253] used soil and sediment CRMs for calibration and achieved a LOD of 1.3 mg kg^{-1}. Similar LOD values were reported for Cd and Zn[254] by Indian researchers using spiked soil calibrants and Si as internal

standard. The potential of LIBS to measure U in soils and on surfaces as an aid in the detection of nuclear material associated with weapons of mass destruction has been assessed[255]. The LOD in soil measured at a stand-off distance of around 75 cm was 0.5% w/w. Articles in Chinese with English abstracts describe further LIBS studies focusing on Cu[256], Cr and Sr[257] and Pb[258].

The *determination of total carbon content in soil by LIBS* has attracted interest. Two different ablation/excitation modes have been compared[259]: a double laser pulse *vs.* the superposition of a single laser pulse and a spark discharge. Measurements were made at 247.86 nm in the first case, but at 833.52 nm in the second to avoid spectral overlap with W lines from the electrodes. Both methods produced curved calibration graphs. However, results for topsoils with C contents ranging from approximately 1 to 8% were broadly similar to those from a commercial CHNOS analyser. Martin *et al.*[260] obtained linear correlations between emission at 247.85 nm and soil C content, but these were dependent on soil type. A multivariate approach – construction of a robust calibration model based on several C emission lines – helped overcome this problem, but study of a broader range of soils was recommended.

Several workers have sought to *optimise experimental or calibration procedures for application of LIBS to plants*. A novel chemometric approach[261] has been used to obtain the best compromise working conditions for the simultaneous measurement of macronutrents and micronutrients in plants, with NIST SRM 1570a Spinach leaves as the test sample. Some of the same researchers compared univariate and multivariate calibration[262] in the measurement of B, C, Fe, Mn and Zn in plant CRM and samples. They found that the development of a specific calibration model for each analyte, based on partial least squares regression and only the spectral regions containing analyte emission lines, was preferred. Meanwhile, workers interested in the development of LIBS methods that do not require external calibration studied the fundamental characteristics of the ablation plasma generated from the skin of potato[263]. The temporal evolution in electron density and temperature showed that local thermal equilibrium (LTE) – a pre-requisite for calibration-free LIBS – occured only if high ablation energy (20 mJ) was used and sufficient time (600 ns) allowed after impact of the laser pulse for LTE to be established.

An attempt to develop *a high-throughput LIBS method for the routine analysis of crop plants*[264] was partially successful. The method generally produced results

within 10% of values obtained by AAS or ICP-AES for Ca, K, Mg and P when applied to samples of rape and wheat, which are chemically similar to the barley and poppy leaves used for calibration. But poorer performance was obtained then the method was applied to a range of CRM representing widely different plant types and tissues, such as GBW 07603 Bush branches and NIST SRM 1575 Pine needles.

3.2.7   X-ray spectrometry

Several *reviews of X-ray techniques* have been published: Lombi and Susini[265] provided a useful introduction (201 references) to synchrotron-based analytical methods for plants and soils; Thieme *et al.*[266] discussed X-ray microscopy as an imaging tool in soil and environmental science (51 references); and Janssens *et al.*[267] described advances in instrumentation and methods for micro-X-ray fluorescence analysis, with examples from environmental, nuclear, biological, industrial and cultural heritage areas (97 references).

Portable X-ray fluorescence (PXRF) spectrometry and laboratory based systems have been compared. Radu and Diamond[268] studied the highly-contaminated Silvermines site in Ireland and obtained satisfactory correlations between data from the portable instrument and results from AAS analysis of *aqua regia* digests of the same 17 soils (R^2 values of 0.991, 0.959, 0.995 and 0.843 for As, Cu, Pb and Zn, respectively). Spectra of a variety of CRMs and cultural heritage objects[269] obtained by PXRF were compared with spectra from a laboratory instrument. Results suggested that, despite poorer limits of detection, PXRF could be useful for analysing artefacts that cannot be moved because of their size, weight or value. The ability to carry out multi-element analysis, on both solid and liquid samples, at remote locations, using a single portable instrument system, was demonstrated by an Australian research group[164]. They used Amberlite IRC748 cation-exchange resin to develop an in-field preconcentration technique that allowed PXRF to quantify Cu, Ni, Pb and Zn in water samples at concentrations as low as 20 μg L^{-1}. Analytes were collected from 1 L of water buffered to pH 5.5 with 2 mol L^{-1} ammonium acetate, then eluted in 15 mL of 3 mol L^{-1} HNO$_3$. Results obtained were generally within $\pm$ 20% of ICP-MS data except where concentrations approached the PXRF limits of detection.

High resolution micro-PIXE images of leaves from the Ni hyperaccumulator *Hybanthus floribundus* (Violaceae)[270] were obtained following optimisation of the ion beam of the microprobe at the Australian Nuclear Science Technology Organisation. Using an ion source current of almost 1 nA and a 3 μm spot, sub-cellular resolution was achieved. The study showed that both Ca and Ni are accumulated in the cell walls of the plant epidermis.

A rapid *X-ray absorption near edge spectrometry (XANES)* method has been developed and applied successfully to map Pu species[271] in a 'hot' particle from a nuclear test site in the Pacific Ocean. Only Pu^{IV} species were found. Haverkamp and Marshall[272] used XANES to measure Ag in *Brassica juncea* (Indian Mustard) grown hydroponically, and to follow the reduction of Ag^I to Ag^0. They discovered that there is a limit to the amount of Ag that the plant can store as metal nanoparticles (ca. 0.35% dry weight) with the remainder accumulated as salt. In other work, difficulties in distinguishing between As^{III}-S and As^{III}-O species in plants[273] based on XANES spectra alone, were overcome by parallel application of EXAFS to the samples. The combination of information from X-ray absorption spectrometry and chromatography coupled to mass spectrometry, for speciation analysis in environmental samples, has been reviewed[116] (91 references).

3.3   Reference materials

Several studies have reported new information on *isotopic fractionation or speciation of analytes in CRMs*. The Hg isotopic composition[274] of two new reference materials and nine established CRMs has been measured. The CRMs include soils, sediment, jasperoid, ore deposit, fly ashes and lichen and have $\delta^{202}Hg$ values from -1.75 to +0.11 ‰. Scientists from the European Commission's Institution for Reference Materials and Measurements[275] have reported not only $^{240}Pu/^{239}Pu$ but also, for the first time, $^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ isotope ratios in IAEA 135 Irish Sea sediment, IAEA 368 Pacific Ocean sediment, IAEA Soil 6 and SRM 4354 Freshwater lake sediment. Measurements were made by TIMS with multiple ion counting. The $^{87}Sr/^{86}Sr$ isotope ratios[276] in soil CRMs BCR 141 Calcareous loam soil and BCR 142 Light sandy soil have been determined by MC-ICP-MS as part of wider assessment of the suitability of a commercial resin for isolation of Sr from Ca-rich samples. Mandiwana and Panichev[277] determined V^V in 0.1 mol L^{-1} Na_2CO_3 extracts of five

soil CRMs certified for total V content by ETAAS, finding concentrations ranging from 3.6 to 86 µg g^{-1} equating to 4 to 88% of the certified values.

Table 1.   **Preconcentration methods involving cloud point extraction used in the analysis of soils, plants and related materials**

Analyte(s)	Matrix	Digestion	Surfactant	Chelator	Detector	Comments	CRMs	Reference
Cd, Pb	Tobacco	HNO_3	Triton X-114®	2-(bromo-2-pyridylazo)-5-diethyl-amino-phenol	TSFFAAS	LOD 4.0 µg kg^{-1} for Cd, 13 µg kg^{-1} for Pb	GBW 08505 Tea leaves, 08501 Peach leaves	[278]
Co, Cu, Pb	Canned fish, honey, tea, tomato sauce, water	Microwave HNO_3/H_2O_2	Triton X-114®	1-phenylthiosemicarbazide	FAAS	LOD 1.0, 0.7, 3.4 µg L^{-1} for Co, Cu and Pb, respectively; RSD 1.7-4.8% (n=7)	NIST SRM 1515 Apple leaves, GBW 07605 Tea	[279]
Cu, Fe	Plant materials	Microwave HNO_3/H_2O_2	Triton X-114®	1,2-thiazolylazo-2-naphthol	FAAS	Preconcentration factor 30; LOD 1.0 µg L^{-1} for Cu, 10 µg L^{-1} for Fe	NIST SRMs 1515 Apple leaves, 1547 Peach leaves, 1572 Citrus leaves, 1573a Tomato leaves	[280]
Mn	Flaxseed flower, oat, shrimp powder, soy flour, wheat flour	HNO_3	Triton X-114®	2-[2'-(6-methyl-benzothiazolylazo)]-4-bromophenol	FAAS	Preconcentration factor 17; LOD 0.7 µg L^{-1}	NIST SRMs 1515 Apple leaves, SRM 1570a Spinach leaves	[281]
Ni	Plant materials	Microwave	Triton X-114®	1,2-thiazolylazo-2-naphthol	FAAS	Preconcentration factor 30; LOD 5 µg L^{-1}	CRMs	[282]

Table 2   **Preconcentration methods involving precipitation used in the analysis of soils, plants and related materials**

Analyte(s)	Matrix	Carrier	Detector	Comments	CRMs	Reference
Cd, Co, Cr, Cu, Fe, Mn, Pb	Soil, water	N-cetyl N,N,N trimethylammonium bromide	FAAS	Preconcentration factor 10; LOD 0.2 -17 μg L^{-1}	BCR 141R Calcareous loam, CRM 025-050 Soil	[283]
Cr	Cheese, fish, meat, tea, water, wheat	Ni^{2+}/2-nitroso-1-naphthol-4-sulfonic acid	FAAS	Preconcentration factor 50; LOD 1.3 μg L^{-1}	GBW 07605 Tea, 0703 Bush branches and leaves	[284]
Cr	Water	3-ethyl-4-(*p*-chlorobenzylidenamino-4,5-dihydro-1H-1,2,4-triazol-5-one	FAAS	Preconcentration factor 50; LOD 1.0 μg L^{-1}	NIST SRM 1573a Tomato leaves, GBW 0703 Bush branches and leaves	[285]
Mn	Food, water	Zirconium (IV) hydroxide	FAAS	Preconcentration factor 50; LOD 0.75 μg L^{-1}	NIST SRMs 1515 Apple leaves, 1568a Rice flour	[286]

Table 3. **Preconcentration methods involving solid phase extraction used in the analysis of soils, plants and related materials**

Analyte(s)	Matrix	Substrate coating	Column substrate	Detector	Notes	CRMs (or other validation)	Reference
Au	Soil, water	Benzoylthiourea	Silica gel	FAAS	Preconcentration factor 267; LOD 1.4 μg L^{-1}	NIST SRMs 2709 San Joaquin soil, 2710 Montana soil	[287]
Au, Pd	Soil, wastewater	Aminopropyl-	MCM-41 and MCM-48	FAAS	Preconcentration factors 800 for Au, 400 for Pd; LOD 0.06 μg L^{-1} for Au and 0.1 μg L^{-1} for Pd	Spike recovery	[288]
Cd	Tea leaves, water	None	B_2O_3/TiO_2 composite	FAAS	Preconcentration factor 50; LOD 1.4 μg L^{-1}	GBW 07605 Tea leaves	[289]
Cd	Soil, tobacco, water	2-(2-quinolinylazo)-4-methyl-1,3-dihydroxydibenzene	Graphitised carbon black	FAAS	Preconcentration factor 500; LOD 0.05 μg L^{-1}	Comparison with ICP-MS	[290]
Cd, Co, Cu, Ni, Pb	Pea, potato	Carboxylic acid	Silica gel	ICP-AES	Analytes as 1,10-phenanthroline complexes; LOD 2.1 – 4.4 μg L^{-1} except Pb (18 μg L^{-1})	CTA-OTL-1 Oriental tobacco leaves	[291]
Cd, Co, Cu, Ni, Pb, Zn	Potato	1,10-phenanthroline	Silica gel	ICP-AES	LOD 6 - 30 μg L^{-1}	CTA-OTL-1 Oriental tobacco leaves	[292]
Cd, Pb	Plants, water	Sodium dodecyl sulfate-1-(2-pyridylazo)-2-naphthol	Nanometer sized γ alumina	FAAS	Preconcentration factor 250; LOD 0.15 μg L^{-1} for Cd, 0.17 μg L^{-1} for Pb	NIST SRM 1640 Natural water	[293]

Analyte	Matrix	Reagent	Sorbent	Detection	Figures of merit	CRMs	Ref.
Cr, Fe	Food, plants	None	Single-walled carbon nanotubes	FAAS	LOD 4.1 μg L^{-1} for Cr, 2.1 μg L^{-1} for Fe	IAEA 336 Lichen, CRM 025-050 Metals on soil, BCR 032 Moroccan phosphate rock	[294]
Cr, Fe, Pb, Th, Ti	Water	2-nitroso-1-naphthol	MCI GEL CHP20P	ICP-MS	Preconcentration factor 20; LOD 0.03 – 0.6 μg L^{-1}	BCR 114R Sewage sludge, BCR 141R Calcareous loam, SRMs 1568a Rice flour, 1577b Bovine liver	[295]
Cu	Tea leaves	None	Surface ion imprinted silica gel	AAS		GBW 07301a Sediment, 07401 Soil	[296]
Cu	Water	Dimethylglyoxime	Silica gel		LOD 6.0 μg L^{-1}	NIST SRMs 1515 Apple leaves, 1643e Simulated freshwater	[297]
Hg	Plants, waters	1,5-diphenylcarbazide	Magnetic nanoparticles	CVAAS	LOD 0.16 μg L^{-1}	GBW 08603 Water	[298]
Mn	Cassava, corn, rice	4-(5'-bromo-2'-thiazolylazo)orcinol	Polyurethane foam	FAAS	Preconcentration factor 17; LOD 0.7 μg L^{-1}	NIST SRMs 1570a Spinach leaves, 1573a Tomato leaves, 1575a Pine needles	[299]

4   ANALYSIS OF GEOLOGICAL MATERIALS

4.1 Reference Materials

Developments in analytical techniques have fuelled a demand for *reference materials that are characterised as comprehensively as possible*. Values for Br, Cl, F and I in six igneous rock RMs (including BHVO-2 from the USGS and JB-2, JR-1 JG-1 and JG-1b from the GSJ) were obtained by combining extraction by pyrohydrolysis with detection by IC and ICP-MS[300]. Scrutiny of the data and associated errors indicated that the nature of the geological material had a greater influence on the data distribution than the absolute halogen concentration. It was concluded that basalts are more suitable as RMs for halogens, even though their halogen contents are lower than those of granites and rhyolites, where halogens can be heterogeneously distributed in 0.5 g sub-samples. Selenium is difficult to determine in silicate rocks because the aggressive reagents employed to dissolve the rock can lead to loss of Se by volatilisation, even at relatively low temperatures. For this reason, Savard *et al.*[301] employed INAA after preconcentration on thiol-cotton fibre to estimate the Se content of 26 geological RMs. They proposed consensus values for seven of the RMs and gave suggested or information Se values for the rest, supported by a literature compilation of Se values for all these RMs. In an alternative approach, Forrest and colleagues[302] used HG-ICP-MS and ID to obtain Se and Te data for basalt RMs. Method LODs were 0.01 ng g^{-1} for Se and 0.003 ng g^{-1} for Te, well below the concentrations expected in basalts, but more work is required to confirm the accuracy of their data. As part of a study of the geochemical behaviour of W, Babechuk and co-workers[303] have published their long-term data for a number of USGS and GSJ RMs. They concluded that some of the materials are heterogeneous and contaminated with respect to W. Although strictly outside the remit of this Update, the reader's attention is drawn to the simultaneous determination of C, H, N and S in 27 geochemical RMs using an automated elemental analyser[304].

The preparation and characterisation of *five new sediment RMs* from the China Sea and continental shelf has been reported[305]. These are in the form of ultra-fine powders with an average particle size of <4 μm. Twelve laboratories participated in the co-operative study and recommended values for over 50 analytes were assigned in compliance with Chinese national norms.

With an increasing requirement for RMs with certifications that comply, as far as possible, with *metrological standard ISO Guide 35*, two CRMs initially prepared and certified by the Central Geological Laboratory of Mongolia have been recertified[306]. Serpentinite GAS and alkaline granite OShBO were recertified under the direction of the International Association of Geoanalysts. While it was possible to increase the number of elements certified for OShBO from 21 to 30, the greater analytical difficulties posed by the serpentinite matrix in meeting the more stringent metrological requirements resulted in 12 rather than 15 elements being certified for GAS. Uncertainties for these values were established in accordance with international protocols and traceability of the certified values was demonstrated by concurrent analyses of existing matrix-matched CRMs by all participating laboratories.

New analytical data on reference glasses and other RMs suitable for the calibration of LA-ICP-MS are available. Hu et al.[307] reported values for Ag, As, Au, B, Be, Bi, Cd, Ge, In, Ir, Mo, Pd, Pt, Re, Rh, Sb, Sn, Tl and W in MPI-DING, USGS silicate glasses and the NIST 610 series of glasses by 193 nm ArF excimer LA-ICP-MS. Small amounts of nitrogen were added to the central channel of the plasma to improve the LODs and reduce oxide interferences, resulting in LODs between 0.1 and 10 ng g^{-1}. In general, for most elements, any chemical heterogeneities were smaller than the analytical uncertainty. A combination of EPMA, LA-ICP-MS and SHRIMP was used to determine Se in NIST SRMs 610, 612, 614 and a range of glass geological RMs[308]. Initially, the Se content of NIST SRM 610 was verified by EPMA and SHRIMP, and used to constrain the Se concentration in NIST SRM 612. The latter was then employed as an external calibrant in the determination of Se in the other geological materials by LA-ICP-MS. After a detailed examination of potential interferences from geological matrices, low uncertainties for *in situ* analysis were obtained by measuring ^{77}Se and correcting for ^{154}Sm^{2+} and ^{154}Gd^{2+}. Unfortunately, there is virtually no overlap in the materials analysed in this study and those measured by INAA for Se[301]. Two new USGS carbonate RMs, MACS-1 and MACS-2, doped with trace elements at various concentrations, were analysed by ICP-MS after dissolution and by LA-ICP-MS[309]. Differences of <10% relative between the solution and laser data were obtained for all elements except Cu and Zn in MACS-1 and Co, Cr and Zn in MACS-2, which has a lower trace element content. Good agreement was observed between LA-ICP-MS calibrations based on the MACS RMs and NIST SRM 612 glass when analysing landfill calcites. Although these carbonate RMs were

promising, the NIST glass was considered to be easier to use and had the advantage of containing all the elements of interest. However, the production of other carbonate RMs was thought to be highly desirable. Two candidate RMs, spinel lherzolite LSHC-1 and amphibole Amf-1, are being developed at the Institute of Geochemistry in Irkutsk[310]. Indicative values for REE, Hf, Nb, Ta, Th, U, Y and Zr obtained by solution and LA SF-ICP-MS, together with INAA and XRF data, have been published. High resolution mode was required to overcome interferences for some elements in the solution work, whereas all elements could be measured at low mass resolution during LA-ICP-MS because of low oxide formation in this mode.

There is a continuing requirement for *well characterised isotopic standards*. Amini and co-workers[311] reported $\delta^{44}Ca/^{40}Ca$ values (relative to NIST SRM 915a) for various igneous and metamorphic rocks, including several international RMs. The MPI-DING glasses were shown to be isotopically homogeneous at the millimetre scale and it was concluded that they were suitable RMs for Ca isotope measurements by LA-ICP-MS or ion microprobe. Molybdenum isotope ratios are typically reported relative to an in-house laboratory RM as there is no internationally accepted standard RM for Mo isotopes. Consequently, Wen *et al.*[312] used MC-ICP-MS to investigate the Mo isotopic composition of six synthetic reference solutions. These were found to have identical Mo isotopic values, despite their different chemical compositions. The authors proposed that NIST SRM 3134 Mo solution should be adopted as the delta zero RM when reporting the Mo isotopic composition of natural samples. A stream sediment, RM JSd-1 issued by the GSJ, has been characterised for 50 major, minor and trace elements, plus Hf, Nd, Pb and Sr isotope ratios[313]. The original JSd-1 powder displayed heterogeneity for Group II elements (Hf, Mo, Nb, Sb, Sn, Ta and Zr); this problem was eliminated on regrinding the material. The emergence of new analytical methods for measuring Hg isotopic compositions has accentuated the need for a wide range of RMs to validate and assure the accuracy of such data. Estrade and co-workers[274] have reported the Hg isotopic compositions of nine RMs, including soils, ores and sediments using cold vapour MC-ICP-MS. In addition, two solutions with $\delta^{202}Hg$ values at the extremities of the range of natural Hg variations were proposed as secondary RMs and are available from the CRPG.

4.2 Solid sample introduction

4.2.1 Laser ablation ICP-MS

Laser ablation ICP-MS is routinely employed in many geochemical laboratories for *in situ* elemental and isotopic analysis. However, for a complete *quantitative analysis of silicate rocks*, it often necessary to combine major element data from EPMA with trace element data obtained by LA-ICP-MS, using a major element measured by EPMA as an internal standard. Humayun *et al.*[314] describe the coupling of a 193 nm laser system to SF-ICP-MS to produce 20–50 μm diameter craters for major element determinations in natural silicate glasses. Relative intensity factors were obtained by averaging duplicate analyses of six MPI-DING glass RMs, which cover virtually the full range of major element compositions occurring in natural silicate glasses. The USGS glass RMs BHVO-2G and BCR-2G were run as independent QC materials and demonstrated precisions of 1–4% and accuracy better than ±5% for all major constituents. Because the methodology employed did not depend on any of the unique features of SF-ICP-MS, it should be applicable to quadrupole ICP-MS. Regnery and colleagues[315] established conditions for the accurate determination of Co, Cr, K, Mn, Ni, Sc, Ti, V and Zn by LA-ICP-MS when these elements are present at low abundances (<2–400 μg g^{-1}) in geological samples. Possible interferences from molecular ions in the mass range 39 to 67 were investigated systematically using SF-ICP-MS and critical concentration limits for each isotope established. A mass resolution of 4000 was preferred for reliable results. As an example of the application of LA-ICP-MS to complex geological samples, Cook and co-workers[316] used the technique to distinguish between trace elements in solid solution and those in micro-inclusions in samples of sphalerite (ZnS) from 26 ore deposits.

The *influence of sample matrix on laser ablation characteristics* is still the subject of much research. Gaboardi and Humayun[317] examined elemental fractionation during laser ablation of a range of silicate glass standards at 213 nm. They observed that the transparency of the material was a significant factor within the NIST SRM 61X series. In contrast, all the non-transparent glasses analysed (MPI-DING and USGS glasses BHVO-2G and BCR-2G) showed no matrix-dependent fractionation and could be employed interchangeably for calibration. For many elements in non-transparent materials, the greatest obstacle in the accuracy of measurement by LA-ICP-MS was the uncertainty in the reported RM concentrations. They concluded that calibration with transparent standards should be avoided unless

an element with a similar temperature of condensation to the analytes was available for normalisation.

In a study of the *fractionation of alkali elements during laser ablation at 213 nm*, LA-ICP-MS and SIMS were used to determine differences in sample composition before and after laser interaction with various silicate reference glasses[318]. Trends in fractionation of alkali elements were found to be different from those of other lithophile elements such as Ca and REEs. The rate of fractionation varied between different sample matrices and between different alkali elements in the same matrix. A combination of thermally-driven diffusion and size-dependent particle fractionation was thought to be responsible for these observations. The significance of this research is that elements such as Si and Ca, which are often used to correct for ablation yield in quantitative analysis of silicate rocks by LA-ICP-MS, are strongly influenced by thermal effects adjacent to the LA craters. Because these effects are very different for Ca and Si, for example, the choice of internal standard will affect the precision and accuracy of analysis.

Fundamental studies of femtosecond lasers have demonstrated reduced elemental fractionation compared to ns laser ablation, mainly because of the much smaller amount of heat transfer into material around the ablation crater. Research into the structural changes resulting from infrared (800 nm) fs LA in monazite by Seydoux-Guillaume and co-workers[319] highlighted the intense damage induced by the high-pressure shock wave associated with a fs laser pulse. They showed that these mechanical effects largely dominated the thermally-induced ones and were limited to a thin layer (200 nm) of resolidified nanocrystalline monazite. Although in the fs LA regime most of the energy goes into producing mechanical defects, it is still necessary to understand the cause of the remaining chemical fractionation observed. Hence investigations by Claverie *et al.*[320] on the influence of high repetition rates on elemental fractionation in silicate glass NIST SRM 610 in IR fs LA-ICP-MS are relevant. Working with wet plasma conditions to minimise fractionation within the ICP, a special arrangement of pulses was used to produce craters 100 μm in diameter. Two scanning speeds, five laser repetition rates and three fluence values were evaluated. Fractionation related to particle size was observed by monitoring $^{238}U/^{232}Th$ ratios. This was minimised by using high repetition rates and low scanning speeds, both of which had the effect of diluting the large particles ejected from the sample surface with a larger number of smaller particles originating from deeper

levels in the sample. High repetition rates had little influence on elemental fractionation whereas the fluence value was a major factor, with high fluence values resulting in lower fractionation. However, SEM measurements revealed no significant differences in the particle size and structure of the laser-generated particles whatever the ablation conditions. Short particle washout times from ablation cells are particularly desirable for applications such as 2-D imaging or depth profiling. With this in mind, Lindner et al.[321] describe their optimised cell geometry, based on computational fluid dynamics, for use with a fs laser operating at 795 nm at high repetition rates. Washout times of 140 ms were achieved, allowing single-pulse analysis with a 7 Hz laser repetition rate.

Recent reports of the use of fs LA in geochemical applications have been dominated by the *measurement of Fe isotopes*. Steinhoefel and co-workers[322] verified the accuracy and reproducibility of Fe isotope data in a range of iron siliceous matrices obtained by UV fs LA-MC-ICP-MS at high spatial resolution using non-matrix-matched calibration. Careful consideration of corrections for Cr isobaric interferences was necessary for samples with high Cr contents. Related studies included the measurement of Fe and Si isotope signatures in banded iron formations[323] and the use of the Fe isotopic composition of individual pyrite grains in Precambrian shallow marine carbonates as a proxy for redox conditions in ancient seawater[324].

Several developments in the *measurement of Pb isotopes by LA-ICP-MS* have been reported. Analytical problems unique to the determination of Pb isotopes in pyrite have been addressed by Woodhead et al.[325]. Technical issues included the low melting point of sulfide, highly variable and often high Pb contents, and the potential presence of relatively radiogenic inclusions. They concluded that controlled ablation of pyrite can be achieved only at low laser fluence and that, under these conditions, calibration with natural pyrite standards is preferred. Where pyrites contain hundreds to thousands of ppm of Pb, MC-ICP-MS can provide Pb isotope data of a comparable quality to that of TIMS. However, quadrupole ICP-MS was utilised where Pb concentrations were inappropriate for Faraday cup detection or where age corrections for radiogenic ingrowth required simultaneous measurement of Pb, Th and U. In such cases, pooling of data from multiple spot analyses could improve the analytical precision markedly but needed to be undertaken with care. At the other end of the scale, Souders and Sylvester[325] evaluated the extent to which matrix matching is

necessary for Pb isotope measurements of feldspar and sulfide minerals with low Pb contents (<70 μg g^{-1} Pb). The analytical methodology involved a 193 nm excimer laser coupled to MC-ICP-MS and standard-sample-standard bracketing to correct for mass discrimination. Somewhat to their surprise, acceptable results were obtained when feldspars containing <40 μg g^{-1} Pb were analysed against silicate glass standards, in spite of the large differences in the physical and chemical responses of the feldspar minerals and silicate glasses to the LA conditions used in the study. Similarly, for sulfides that contained little or no mercury, the mean Pb isotope ratios obtained were within 0.40% of the average TIMS measurements made on the same grains, with only subtle differences in the results between matrix-matched (sulfide) and non-matrix-matched (glass) standards. However, for samples containing significant amounts of mercury, external calibration standards that are matrix-matched in terms of their Hg/Pb ratios are required to correct properly for the isobaric interference of ^{204}Hg on ^{204}Pb.

A novel approach to *laser ablation U-Pb geochronology* is described by Cottle and co-workers[326]. Their method aims to acquire accurate isotopic data from single laser pulses while minimising sample destruction and maximising the spatial resolution of the analyses. Data were obtained using an in-house low volume ablation cell that facilitates the production of a high density particle stream with short sample washout of ca. 0.5 s. Isotope ratios from an individual laser pulse were calculated by integrating the total number of counts for the entire pulse after subtracting the baseline and assigning an uncertainty based on counting statistics. This method eliminates the effects of differing detector response times in MC-ICP-MS and provides an alternative way of quantifying transient signals. Results indicated that sample consumption could be reduced by as much as 90% without significant loss of precision, with a depth resolution of about 0.1 μm per pulse. Hence this technique has the potential to generate accurate age information from zoned and complex accessory minerals.

Patterns of fractionation with crater depth can vary markedly between laboratories and with changes in operating conditions. Thus an improved method of correcting for downhole fractionation effects observed when acquiring data for U-Pb geochronology by LA-ICP-MS has been proposed by Paton *et al.*[327]. They suggest a general approach in which users develop an appropriate model of downhole fractionation based upon their own data acquired during each analytical session, rather

than attempting to fit the data to a preconceived fractionation model. This methology is capable of producing high quality ages that are accurate to within 1% of accepted values and allows analytical uncertainties to be estimated using a single reference standard in a manner that best reflects the actual uncertainties of individual spot analyses. A data reduction module that implements this protocol is available as part of a software package designed for the rapid reduction of large quantities of data with maximum feedback to the user at each stage.

The feasibility of determining *Li isotope ratios* in natural and synthetic glasses by LA-MC-ICP-MS has been demonstrated[328]. Because of the large relative difference in abundance between the two Li isotopes, asymmetric tuning of the quadrupole lenses was required for simultaneous measurement of ^{7}Li and ^{6}Li on a Faraday – ion counter configuration. The NIST series of standard glasses proved to be unsuitable for external calibration. After evaluation of USGS and MPI-DING standard glasses, USGS BCR-2G was selected as the bracketing standard by reason of its moderate Li content and isotopic composition. This protocol yielded accurate Li isotope data with an external δ^7Li precision (2σ) of <1‰ at Li concentrations of 3-35 ppm.

Although *in situ measurements of Sr isotopes* are routinely made by LA-ICP-MS, most materials studied have high Sr contents and low Rb/Sr ratios. Samples with low Rb/Sr ratios and young ages are still analysed by TIMS after separation because of the requirement for high precision data. Jochum and co-workers[329] have demonstrated the potential of analysing silicates with low Sr concentrations of 30 to 400 µg g^{-1} using single collector SF-ICP-MS combined with a 193 nm Nd:YAG LA system. Corrections made in the determination of ^{87}Sr/^{86}Sr included dead time of the ion counting system, blanks, isobaric interferences of Kr and Rb, and mass discrimination for Sr and Rb. An external precision (1 SD) of about 0.0002–0.0004 was achieved for Sr contents of 100–400 µg g^{-1} and spot sizes of 50 µm. A comparison of LA-ICP-MS data obtained for glass RMs agreed with high precision TIMS data within the limits of uncertainty. Mainly because of isobaric interferences from ^{87}Rb, the technique is restricted to samples with Rb/Sr ratios of ca <0.1.

4.2.2   Laser-induced breakdown spectroscopy

Laser-induced breakdown spectroscopy is often employed as a *rapid on-line analytical technique for quality control* in a range of industries. Systems designed to

characterise pulverised coal feed to power stations for organic and inorganic components have been described[330],[331]. Chemometric methods combined with LIBS were applied by Death *et al*[332] in the routine quantitative analysis of iron, nickel and lead/zinc ores. In addition, they investigated the potential of applying both PCA and principal components regression to LIBS data for broad mineralogical as well as elemental analysis of mineral ores during exploration and ore processing.

The ongoing development of *portable LIBS instruments for geochemical fingerprinting* by the US military has been described[333],[334],[335]. The focus of these studies is the utilisation of full broadband LIBS spectra between 200 and 965 nm for rapid material discrimination and identification in the field. Harmon *et al.*[333] discuss the particular problems associated with using LIBS to identify minerals and to differentiate between minerals with similar structures with a high degree of accuracy. By comparing a single LIBS spectrum against a library of LIBS spectra a high degree of correct classification was achieved for carbonates, feldspars and pyroxenes. However, it proved more difficult to correctly identify different varieties of beryl, which is representative of a group of minerals with a fixed major element composition and a high degree of trace element variability. These experiments were performed with a bench-top instrument, as were the ones reported by Alvey and co-workers[335] who were able to discriminate between garnets of different composition using similar methodology. In another study, the performances of a commercial single-pulse LIBS system, a laboratory bench-top double pulse LIBS system and a prototype standoff LIBS system designed for analysis at a distance of 25m were compared[334]. The chemometric techniques of partial least squares discriminant analysis (PLS-DA) and PCA were applied to the spectra to classify the materials and to identify the distinguishing characteristics of a large suite of carbonate, fluorite and silicate geological samples. The laboratory double-pulse system did not provide any advantage for sample classification over the single-pulse system, except for soil samples. The stand-off LIBS system provided comparable results to the laboratory systems, demonstrating its potential for its intended application of geochemical fingerprinting. The work also showed how PCA can be used to identify spectral differences between similar sample types based on minor impurities.

4.2.3   Slurry sample introduction

A useful review of *slurry nebulisation for sample introduction to spectroanalytical techniques* has been published by Ferreira and co-workers [336]. Critical variables that need to be thoroughly investigated for proper performance of slurry-based procedures are discussed in detail, along with the most appropriate calibration methods for accurate quantification. They recognise that a major hindrance in the development of slurry methods is the preparation of stable suspensions within the timeframe of the assay. A compilation of analytical applications of slurry sampling, particularly ones published between 2004 and 2009, is included. Slurry sampling has been employed in the determination of Sn in marine sediments by ETAAS[216]. Suspensions were prepared in 7% nitric acid, and niobium selected as the permanent modifier with the addition of $BaCl_2$ to reduce interference from sulfur compounds. The introduction of slurried geological samples into ETV-ICP-MS for the determination of some REEs has been investigated[238]. Under optimum operating conditions, LODs of 200, 20, 30, 10 and 10 pg g^{-1} were reported for Dy, Eu, Sm, Tb and Tm respectively, with precisions of better than 10%.

4.3   Sample Treatment

4.3.1   Sample dissolution

Geoanalysts always need to exercise care in the choice of the *materials used in the physical preparation of rock powders*. Although natural agate has long been regarded as the best grinding material available for trace element analysis, Takamasa and Nakai[337] demonstrated that agate mills can be sources of Ag, Cr, W and U contamination, and that agate, even from a single locality, can exhibit large variations in elements such as Ba, Sr and U. Of the mills tested, one made of artificial crystalline quartz gave the least contamination but was not mechanically robust enough for grinding hard rocks such as basalt. An alumina ceramic hand mill was capable of pulverising most geological samples with little contamination but could contribute Cs and W. As always, the choice of mill needs to be assessed according to the target elements to be analysed, especially those present at trace levels in the samples.

New digestion protocols suitable for geological materials continue to be published, although it is often difficult to detect much of any novelty. Makishima and colleagues[338] lament the lack of appreciation by geochemistry students of the behaviour of different elements during sample decomposition using HF. They provide

an overview of the problems involved and precautions required. A microwave-assisted digestion procedure with HNO_3–H_2O_2–HF (2+1+1) in high-pressure vessels for the determination of As in mining residues from gold beneficiation plants by FAAS was reported to be fast and accurate[339]. However, its accuracy could only be evaluated by standard addition, there being no suitable CRM.

The use of *ultrasound energy to assist the extraction of analytes from solid samples* has been advocated as a safe and relatively cheap alternative to microwave-assisted procedures[191, 340]. De Vallejuelo *et al.*[191] describe the use of an ultrasonic probe in a procedure involving various HNO_3–HCl mixtures for leaching trace elements from sediments. The method was capable of extracting 13 elements in 6 mins with similar recoveries to those obtained using the microwave-assisted EPA 3051 method, which is based on extraction with HNO_3 only. One drawback of the use of the probe was that, although the procedure is rapid, the samples had to be treated individually. In contrast, Ilander and Vaisanen[340] employed an ultrasonic water bath, which allowed them to process 30 fly ash samples simultaneously in 18 mins prior to the determination of Cr, Cu, Ni Pb, V and Zn by ICP-AES[340]. Variations included a one-step protocol employing *aqua regia* and HF (1+1) and a two-step procedure, in which samples are first leached with 0.1 M HNO_3 and then a HNO_3–HF mixture (1+1). Data from the analysis of NIST SRM 1633b (coal fly ash) enabled the authors to claim that this was the first time a digestion method using ultrasound had achieved a greater extraction efficiency for Cr and Ni than an equivalent EPA microwave-based method.

All *sample pre-treatment must be appropriate for the specific geochemical application* to which it relates. Revillon and Hureau-Maxaudier[341] revisited methods for the complete digestion of sediments, including refractory phases such as zircons. Alkali fusion with NaOH–Na_2O_2 followed by preconcentration with $Fe(OH)_3$–$Ti(OH)_4$ was ruled out because not all the elements of interest were fully recovered and the blanks were too high for measurements of Sr and Pb isotope ratios. Of the four acid digestion procedures they tested, their preferred option was a combination of HF, HNO_3 and $HClO_4$ acids in high pressure digestion vessels for 7 days at 160°C. Complete dissolution and very low blanks were achieved, making it suitable for a broad range of analysis, including isotopic characterisation. In contrast, Townsend and co-workers[342] recommended partial extraction with 1 M HCl in a study of Pb

isotopic signatures in Antarctic marine sediment cores, in preference to total dissolution with HF. This partial extraction offered the greatest discrimination between contaminated and natural samples as over 90% of the easily extractable Pb was anthropogenic.

4.3.2   Separation and preconcentration

Several *adaptations of classical methods for the determination of the platinum group elements* (PGEs) have been published. Sun *et al.*[343] developed a fire assay method capable of providing Re recoveries of up to 75%, by using Fe–Ni sulfide as a collector and $Na_2B_4O_7$ as a flux. After fusion and cooling, the sulfide bead disintegrated into a powder on contact with water, before HCl was added, the solution heated and the insoluble residue collected. Osmium was distilled from the residue as OsO_4 for the measurement of Os concentrations by ID-ICP-MS or Os isotopes by N-TIMS. The remaining solution was then treated further prior to the measurement of the other PGEs by ICP-MS, with Re determined by ID. The accuracy of this procedure was validated by the analysis of several PGE CRMs and LODs (3σ) between 0.7 pg g^{-1} for Os and 25 pg g^{-1} for Pd were reported. Khanna and Siddaiah[344] sought to optimise various parameters in the NiS fire assay method for the successful fusion of chromitite and sulfide-rich samples. The NiS beads were dissolved in *aqua regia* and analysed for Pd and Pt by ICP-MS without any further treatment. Although the method was thought to be promising, recoveries for Pd and Pt in the CRMs measured were on the low side. An improved Carius tube technique designed specifically for Re-Os dating in hydrothermal pyrites has been reported[345]. The pyrite sample is first digested with HNO_3 in an open Carius tube and any Os released collected in 10 mol l^{-1} HCl cooled in an ice bath. After the sulfides had totally reacted, the HCl solution was injected back into the Carius tube, before adding Re and Os spikes and digesting the sample in *aqua regia* in a sealed tube for about 10 h at 200°C. By pre-treating the sample in an open Carius tube and thus preventing a build up of NO_x later on, the sample mass could be increased to about 3 g, which was important for dating hydrothermal pyrites that contain low concentrations of Os and Re.

Simple methods for the determination of gold and other precious metals continue to attract interest. One of the more novel approaches involved the use of a microcolumn packed with powdered leaves from the *Azadirachta Indica* tree for the

separation and preconcentration of Au and Pd in geological materials prior to their determination by ICP-AES[346]. Disappointingly, data for only one RM were reported. El-Naggar and co-workers[347] employed brilliant green as the complexing agent in cloud point extraction for selective preconcentration of trace amounts of Au in silicate rocks. Brilliant green is a basic water soluble dye, which has the advantage of being stable in acidic solution. Problems with the introduction of the highly viscous surfactant-rich phase into a FAAS instrument were circumvented by dilution with methanol. Acceptable results were obtained for three CRMs with Au contents between 500 and 5000 ng g^{-1}.

4.3.3 Speciation studies

For a *comprehensive review of recent developments in elemental speciation*, the reader is referred to the ASU on this subject (245 refs)[3]. While it is recognised that the most sophisticated and complete information on speciation is derived from hyphenated techniques, particularly those that involve separation by chromatographic techniques such as GC and HPLC coupled to ICP-MS, they represent a minor proportion of the separation procedures available. In their review (177 refs) of non-chromatographic methods for speciation analysis, Vieira and co-workers[118] discuss extraction methods, including conventional solvent extraction, SPE, SPME and SDME, and derivatization techniques. They emphasize that these procedures, while not providing a complete spectrum of species, can provide sufficient information on elemental speciation for situations such as risk evaluation. Moreover, they can be less time-consuming, more cost-effective, more readily available and give competitive LODs.

4.4   Instrumental analysis

4.4.1   Atomic absorption and atomic fluorescence spectrometry

As noted in the Update on atomic spectrometry and related techniques[348], sample introduction continues to provide some novel developments. *In the case of AAS the emphasis has been on vapour generation*. A sensitive ETAAS method for the determination of Ni, based on the photochemical generation of Ni(CO)$_4$ – a highly toxic gas – and its trapping on the surface of a graphite furnace, is described by Zheng *et al.*[153]. The sample solution was mixed with formic acid in a FI system and

irradiated with UV light before being flushed into a gas-liquid separator. This was connected to a quartz tip that was manually inserted into the graphite furnace during the analyte trapping process and retracted prior to atomisation of the sample. A LOD of 8 pg mL^{-1}, based on a 2 ml sample volume, was reported and the method applied to various CRMs including a marine sediment. Xi and colleagues[349] employed *in situ* trapping of Te hydride with a platinum-coated tungsten coil in the development of a sensitive and simple method for the determination of Te by AAS. After trapping, the Te hydride was electrothermally vaporised into an electrically heated quartz tube atomiser for measurement. Sensitivity was enhanced 28 times compared to conventional HG-AAS. The LOD of 0.08 ng mL^{-1}, for 1 min trapping of 1.5 mL sample volume, was comparable or better than published levels involving on-line trapping and more sophisticated analytical techniques. Acceptable recoveries were obtained from soils and sediment CRMs with Te concentrations of 0.1–0.4 µg g^{-1}. The effect of room temperature ionic liquids (RTILs) on the chemical vapour generation (CVG) of Au have been studied using a FI-CVG-AFS system[350]. The RTILs were found to change the Au species so that they were more effective precursors for the CVG and facilitated the generation of small bubbles, which provide a protective micro-environment for the unstable Au volatile species and assist fast isolation of these species from the reaction mixture. Of the RTILs tested, 1-butyl-3-methylimidazolium tetrafluoroborate bromide provided a 24-fold improvement in sensitivity over no RTIL. Acceptable data were obtained for two Au ore CRMs. A useful review (87 refs) of the chemical interferences observed in the determination of As, Bi, Ge, Sb, Se, Sn and Te by hydride generation (HG) atomic spectrometric techniques has been provided by Kumar and Riyazuddin[351]. They also discuss various approaches to eliminate or minimise these interferences.

Dittert *et al.*[210] determined Ag in geological samples using direct solid sampling and *high resolution continuum source ETAAS*. For soils and sediments, good accuracy was achieved with calibration against aqueous standards. However, the analysis of rocks and ores required calibration against a CRM of similar composition, as the sulfur-rich matrices reduced the atomisation efficiency. An optimised atomisation temperature of 2300°C and the application of a least squares background correction algorithm resulted in a background-free spectrum. A LOD of 2 ng g^{-1} was obtained with RSDs of typically <15%.

In a *novel application of AAS for speciation analysis*, Campos and co-workers[352] interfaced a commercially available Hg analyser based on CV-AAS with HPLC separation for the determination of total inorganic Hg and MeHg in sediments. The detector contained a high intensity source, a multipath absorption cell and a system for Zeeman-effect background correction. Post-column CVG was performed with a UV lamp to decompose MeHg and reduction with sodium borohydride to generate Hg^0. For a 200 μL injection volume, the LOD was 50 ng L^{-1} for both species.

4.4.2   Atomic emission spectrometry

Petrova and co-workers[353] demonstrated that *Pd, Pt and Rh could be determined in complex matrices by ICP-AES* through systematic investigation of potential interferences from major element components. After digestion with a mixture of HNO_3, HCl and HF, the samples were quenched with boric acid before direct nebulisation using a conventional glass ICP sample introduction system. Optimum line selection and correction for interferences provided LODs of 1.4, 1.7 and 0.9 ng g^{-1} for Pd, Pt and Rh respectively, which was not sufficiently low to provide a reliable value for Rh in CRM SARM 7 (a Pt ore from the South African National Institute of Metallurgy). For geological and environmental materials with lower concentrations of these elements, effective preconcentration techniques are required prior to analysis. Torgov and co-workers[354] extracted PGEs from a sample digest using a mixture of p-alkyl aniline with petroleum sulfides in o-xylene, which provided 10-20 fold preconcentration. All the PGEs and Au were then back-extracted with ammonia and thiourea in a two-step procedure prior to analysis by ICP-AES. The method was applied to a range of raw materials and products from a factory processing copper-nickel ores.

A relatively inexpensive method for the *determination of REE in uraninite samples* by ICP-AES, based on solid phase extraction on activated carbon, has been developed[355]. After digestion with a mixture of HNO_3, HF and $HClO_4$, the solution was neutralised with NH_4OH and then excess NH_4OH added to precipitate U, Th and REEs as hydroxides. After washing and filtration, the precipitate was dissolved in HF and activated carbon added. The slurry was then filtered and the filter paper ignited to remove the activated carbon before dissolution in 10% HNO_3 and dilution prior to analysis. Uranium was almost entirely eliminated in this procedure (<10 μg mL^{-1} in

the final solution) but judicious selection of the REE emission lines was essential to minimise interference from the relatively large concentrations of Th.

A novel method of determining *bioavailable concentrations of As and Se in sediments* by HG-ICP-AES employed a commercial 'concomitant metals analyser' as a hydride generator[356]. This device is a modified cyclonic chamber developed to measure elements that form hydrides alongside those that do not. Multivariate techniques were employed in the optimisation of the procedure. It was found that interferences from transition metals such as cobalt, copper, iron and nickel could be minimised by using highly concentrated HCl solutions (6 mol L^{-1}). The bioavailable content of estuarine sediments was assessed using a microwave-assisted extraction with concentrated HNO$_3$ at 175°C and LODs of 0.025 µg g^{-1} for As and 0.030 µg g^{-1} for Se were obtained.

4.4.3 Inductively coupled plasma mass spectrometry

4.4.3.1 Quadrupole ICP-MS

Many people involved with the operation and application of modern ICP-MS instruments are not necessarily specialists in this field, as was usually the case in the early days of the technique. *A recent review* (124 refs) of quadrupole ICP-MS[357], written with the novice user in mind, is valuable in reminding all practitioners of the strengths and limitations of the technique, particularly now it is being applied to a vast range of sample types. Because ICP-MS has the sensitivity to determine trace elements at concentrations of ng L^{-1} and below, one of the constraints in realising the best possible detection limits is contamination in the laboratory. Rodushkin *et al.*[35] reviewed (43 refs) potential sources of contamination during sample preparation and instrumental analysis and proposed remedial strategies for ameliorating their impact on the results of multi-elemental analysis by ICP-MS. Papers on ETV-ICP-MS published in the last 10 years (186 refs) have been reviewed by Aramendía and co-workers[358]. From this evidence, it would appear that one of the main reasons why ETV has not been widely adopted as a sample introduction technique for ICP-MS is the lack of interest shown by the main manufacturers of analytical instrumentation in providing suitable instrumental systems and the associated methodological support. Wider acceptance is also hindered by the perception that it is a difficult technique to work with, together with the lack of well-defined standard conditions for analysis. This review seeks to provide the reader with a better understanding of ETV-ICP-MS

and proposes a guide for method development for challenging analytical applications based on existing literature. Advantages of coupling an ETV unit to newer types of ICP-MS instrumentation equipped with collision/reaction cells, TOF or SF spectrometers are also discussed. The contribution of quadrupole ICP-MS to the advancement of geochemical fingerprinting and its application in the earth and environmental sciences over several decades has also been reviewed (81 refs)[359].

The *widespread availability of reaction cells in ICP-MS instrumentation* has facilitated the determination of Se and other elements that suffer from spectral interferences from argon-based polyatomic ions. In a study of the Se content of volcanic soils, Floor *et al.*[237] recommended the addition of 2% methanol to the nitric acid extractions and the use of hydrogen as the cell gas while making measurements at ^{78}Se. Makishima and Nakamura[360] developed an ID-ICP-MS method for the determination of As, Ge, Se and Te in silicate samples, based on their finding that the use of helium as a reaction gas suppressed the formation of iron oxides, and Rb and Sr argide ions. A Ge-Se-Te spike was added during digestion with a HF-HNO$_3$-HBr mixture, before the sample was dried and re-dissolved with HF. The supernatant was directly aspirated into the ICP-MS instrument, using helium as the reaction gas for As, Ge and Te, and hydrogen for Se. Interferences were assessed and corrections applied where necessary. Limits of detection were 4, 2, 1 and 0.1 ng g^{-1} for As, Ge, Se and Te respectively. Advantages of this method included the capability to analyse very small amounts of material, as only 0.13 mg was required for a test portion, and the same solution could be used to determine Hf, Mo, Nb, S, Sb, Sn, Ta, Ti and Zr.

Quadrupole ICP-MS is capable of *providing sufficiently precise isotopic data* for a wide range of applications, at comparatively low cost. The challenge of measuring Li isotope ratios in natural carbonates was tackled by separating Li from the matrix elements on AG 50W-X8 cation-exchange resin and eluting with 6 ml of 0.5 N HCl[177]. Measurements of ^{6}Li/^{7}Li were made by ICP-QMS under cool plasma conditions (600W) to minimise interferences from ^{12}C^{2+} and ^{14}N^{2+}, using soft extraction, peak jumping and pulse detection mode combined with sample-standard bracketing. The method was optimised for natural carbonates containing 1-2 ppm of Li and a precision (2σ) of better than ±1.5‰ was achieved for this type of sample. Marelli *et al.*[361] proposed an alternative protocol for measuring ^{63}Cu/^{65}Cu ratios by ICP-QMS. Their modified bracketing approach incorporated regular monitoring of a blank solution, which was used to compensate for long-term drift in signal sensitivity.

Accurate ratios with RSDs as low as 0.025% (1s) were reported, with a faster throughput than normally achieved with a typical standard bracketing protocol. This precision was sufficient to discriminate between copper ores. It is worth noting here a parallel paper on the application of Cu isotope fractionation in mineral exploration of porphyry copper deposits based on MC-ICP-MS[362]. Although magnetic sector mass spectrometers dominate the field of ^{40}Ar/^{39}Ar geochronology, Schneider and colleagues[363] have demonstrated that a triple filter quadrupole mass spectrometer can be an economic alternative for ^{40}Ar/^{39}Ar dating when small sample sizes and very high precision measurements are not the first priority. The instrument was connected to a furnace extraction system designed for the incremental heating of large (500 mg) samples of young volcanic rocks. The system produced stable flat-topped peaks with good resolution and was capable of measuring Ar ratios with precisions in the 1‰ range. Rapid and accurate U-Th dating of ancient carbonates by ICP-QMS has been explored by Douville *et al.*[364]. The analytical procedure included a simplified chemical separation using Eichrom UTEVA® resin, which resulted in a very rapid extraction of Th and U from 100-1000 mg of carbonate on a micro-column. During the simultaneous measurement of Th and U isotopes, the count rate was maintained below 2 Mcps for each isotope in order to maintain data acquisition in pulse counting mode. Up to 50 U-Th dates could be measured per day by ICP-QMS with reproducibilities (2σ) of 3-4‰ for δ^{234}U and 1‰ for δ^{230}Th. Sensitivities of greater than 3 x 10^5 cps/ppb combined with low backgrounds (<0.5 cps) allowed U-Th dating of ancient deep-water corals (15-260 kyr) and stalagmites (30-85 kyr) at precisions of <2%. Kamber and Gladu[365] compared standard methods of Pb purification by anion-exchange for the measurement of Pb isotope ratios by ICP-QMS. They found that matrix removal was much more effective using a procedure based on HBr-HCl rather than HBr-HNO$_3$. A careful single-pass separation using HCl removed more than 99.9% of the silicate rock matrix except for very zinc-rich matrices. Elemental concentrations were determined on the sample digest first to allow accurate prediction of the expected ion signal and permit optimal spiking with Tl, if desired, for mass bias correction. Long-term reproducibility of data obtained for geological CRMs was better than 1% for Th/U and 1.5% for U/Pb, which was more than adequate for most geological applications of Pb isotopes. Godoy and co-workers[366] demonstrated that ICP-QMS is capable of determining the concentrations and isotopic compositions of Pu and U in environmental samples with sufficient precision and accuracy to satisfy

IAEA requirements. The separation procedure applied to soils and sediments involved acid leaching, followed by ion-exchange on Dowex 1X8 and extraction chromatography using 2 mL TEVA® and UTEVA® columns to produce separate Pu and U fractions. The samples were introduced into the ICP-QMS instrument via an ultrasonic nebuliser coupled to a membrane desolvation system. Several CRMs and working RMs were incorporated into the analytical scheme for mass bias corrections and ID measurements; the uncertainty calculations are given in detail in several appendices. The reader's attention is drawn to a similar separation procedure for the determination of Pu and U in coral soils by MC-ICP-MS[367].

4.4.3.2 Sector field ICP-MS

Considerable improvements in instrumentation, combined with improved access to the technique worldwide, have resulted in a dramatic increase in the number of isotopic measurements made by MC-ICP-MS over the past few years. A recent review[368] on the determination of isotope ratios by single collector and multicollector ICP-MS (182 refs) is an excellent tutorial for those new to the field. The capabilities of various types of ICP-MS instrumentation are addressed and issues surrounding mass discrimination and detectors are discussed. In covering a wide range of applications, including geochronological dating and provenance studies, this review provides an insight into some of the more important aspects of the published literature. In another review (170 refs) Yang[369] highlights the inconsistencies and errors evident in many MC-ICP-MS publications, including errors in mass bias correction models. She suggests some general rules to achieve precise and accurate measurements by MC-ICP-MS. The advantages and disadvantages of three mass bias correction procedures, depending on the elements and sample types measured, the chemical separation employed, plus the instrument used and its degree of stability, are discussed. She emphasizes the importance of reporting isotope ratio data with their associated combined uncertainties to facilitate comparison of results from different laboratories.

A comparatively simple and *rapid method for the determination of $^7Li/^6Li$ by MC-ICP-MS* has been applied to the analysis of silicate rocks and marine biogenic carbonates, as well as waters of varying salinities[178]. Sample digests were loaded onto columns containing AG 50W-X8 cation-exchange resin and eluted with 1 M HNO_3 in 80% methanol (cf ref[177] in section 4.4.3.1). To reduce the Li background signal, a new

desolvating sample introduction system with high sensitivity and low memory effects was employed, which reduced the amount of Li required for isotope measurements. A residual stable background of ~10 mV was achieved with a 120 s wash time; measurement of various CRMs demonstrated that this did not affect the accuracy of the Li ratios significantly.

Huang and colleagues[370] addressed several issues to improve the accuracy and precision of *Mg isotope measurements by MC-ICP-MS* and applied them to the analysis of 11 rock standards. Factors examined included the storage of the Mg standard solution, the effect of matrix elements (e.g. Al, Na, Mn and Ni) on the instrumental mass bias of Mg isotopes, the total Mg concentration of the nebulised solutions, interference from the $^{12}C^{14}N^+$ isobar, and the effect of Mg blank and organics leached from the resin during chemical purification. After dissolution, the samples were purified using a column filled with 0.5 mL BioRad AG50-X12 cation-exchange resin and Mg isotopes measured by sample-standard bracketing using HR-MC-ICP-MS. Prior to sample introduction, samples and standards were diluted to produce ~0.2 Mg ppm solutions in 0.3 N HNO_3, keeping the variation in ^{24}Mg intensity to within 5%. Even with the use of a desolvating nebuliser, the size of the $^{12}C^{14}N^+$ interference could be significant relative to the ^{26}Mg signal. Hence, it was important to ensure that the total Mg concentrations were high enough so that the contribution from $^{12}C^{14}N^+$ was minimal and that the concentrations of samples and stadards were closely matched. The long-term reproducibility of $\delta^{26}Mg$ for samples with relatively high MgO content was 0.11‰ (2 SD) and ~0.2‰ for granites with lower MgO content. Wombacher and co-workers[371] reported a method for the chemical separation of Ca, Fe and Mg on a 1 mL column of BioRad AG50W-X8 cation-exchange resin. This resin was preferred because of the somewhat faster fluid flow and less extensive cleaning required compared to X12 resin. For many geological matrices, Mg was separated by a single pass through the column. To separate Mg from Ca-dominated samples, such as carbonate, or effect a separation of Ca, Fe and Mg from the same sample aliquot, Ca and Fe were first separated in an additional step, using the same ion-exchange columns but higher acid molarities (10 M HCl). Following purification, Mg and Fe isotopes were determined by MC-ICP-MS, while Ca isotopes were measured by double-spike TIMS. Average external repeatabilities (2 σ) were ±0.16‰ for $^{26}Mg/^{24}Mg$, ±0.26‰ for $^{44}Ca/^{40}Ca$ and ±0.05‰ for $^{56}Fe/^{54}Fe$.

Dauphas *et al.*[372] developed a protocol for the *determination of Fe isotope ratios* in natural materials and evaluated the variables that can affect the accuracy of δ^{56}Fe measurements using HR-MC-ICP-MS. Chemical separation and purification involved two-step chromatography using columns containing 1 mL of AG1-X8 anion-exchange resin. The analyte concentrations of the sample and RM were matched within 5%; most critical was ensuring the acid molarity of the samples and standards were matched exactly (0.3 M HNO_3). The measurements were not sensitive to the presence of other transition elements in solution as long as their concentrations remained below ~10 ppm. Accurate δ^{56}Fe measurements in a range of natural materials with precisions of better than about 0.03‰ (2 SD) were routinely achieved. A similar procedure was adopted in a study of the Fe isotope composition of ordinary chondrites and their constituent components[373].

A method for the measurement of *Co, Cr, Fe, Mn and Ni concentrations in silicate samples by HR-MC-ICP-MS* without chemical separation or matrix matching has been described[374]. Chromium was determined by ID after the addition of a Cr spike at a judicious point after sample digestion to avoid its loss as $Cr_2O_2Cl_2$. The concentrations of the other elements were calculated by an ID-IS method developed previously by researchers at the same Japanese institute. Matrix effects were shown to be negligible down to a dilution factor of ~3000 for basalt and ~10^4 for peridotite, within an uncertainty of ±1%. A repeatability of about 1% was achieved, which is >10 times better than HR-ICP-MS and comparable to ID-TIMS.

Precautions need to be taken in the *measurement of Si isotope ratios by MC-ICP-MS* to avoid the introduction of mass dependent fractionation[375] and sulfur-induced offsets[376]. Samples are normally fused with NaOH and purified using cation-exchange. In a study of meteorite and terrestrial samples, Fitoussi and colleagues[375] found that the pH of the solutions loaded onto the cation-exchange column containing BioRad 50W-X12 resin was a critical parameter. They concluded that the solution should be adjusted to pH≥2.1 to avoid analytical artefacts. Because concentrations of anionic species in rocks are generally low, it is often assumed that they do not compromise Si isotope determinations. However, van den Borrn *et al.*[376] have demonstrated significant errors in the accuracy of such measurements by MC-ICP-MS in sulfur-rich materials. They recommend heating the sample powder at 1350°C in a stream of oxygen to remove sulfur prior to sample dissolution; this was shown to have no effect on the Si isotope ratios. Mechanisms to account for the observed offset in

δ^{26}Si values were explored. Isobaric interferences could be excluded because sulfur isotopes have higher masses than Si ones; their hypothesis was that sulfur in the matrix brought about changes in the instrumental mass bias.

The presence of high concentrations of sulfur can be particularly problematical in the *measurement of Cu isotopes* in some geological samples such as sulfides because of the formation of polyatomic species such as $^{32}S^{14}N^{16}O^1H$ that overlap with the ^{63}Cu isotope[377]. Although routine separation normally incorporates anion-exchange chromatography, variable column breakthrough can occur if the initial sulfur content is high. In these circumstances, a second separation of the Cu fraction was recommended, although it may be worth considering the simpler approach taken in the study of Si isotopes above[376].

A new procedure for the *quantitative separation of Mo and Re from geological samples* has been developed by Pearce and co-workers[378]. The chromatography employs 2 ml of BioRad AG 1-X8 anion-exchange resin in 10 mL columns, and involves the sequential use of three solutions: 1 mol L^{-1} HF/0.5 mol L^{-1} HCl, 4 mol L^{-1} HCl and 3 mol L^{-1} HNO$_3$ for loading, washing and collecting the Mo and Re fractions. In conjunction with a ^{100}Mo-^{97}Mo double spike and ^{185}Re single spike, the Mo isotope composition and Mo and Re abundances were determined by MC-ICP-MS. Quantitative recovery of Mo and Re from the column was confirmed and a long-term precision of <0.12‰ (2 σ) for ^{98}Mo/^{95}Mo established. This procedure offers some analytical advantages over others in current use and is suited to palaeo-redox studies requiring knowledge of Mo isotopic composition and the Re/Mo ratio from the same sample.

Poirier and Doucelance[379] demonstrated that the measurement of *$^{187}Re/^{185}Re$ ratios in geological materials by MC-ICP-MS* suffered from matrix effects that could not be corrected by the standard–solution bracketing technique. By spiking samples and calibrators with W, and measuring Re and W isotopes simultaneously, they were able to compensate for changes in mass bias induced by the matrix.

Yang and co-workers[380] present a three-column procedure for separating Hf, Lu, Nd, Rb, Sm and Sr from a single rock digest prior to *measurements of the Lu-Hf, Rb-Sr and Sm-Nd isotope systems* using MC-ICP-MS and TIMS. The simplified chemical separation employs mainly HCl as the eluting reagent, resulting in rapid purification in three working days. The same Chinese research group[381] demonstrated precise and accurate measurements of ^{143}Nd/^{144}Nd without separating Nd from Sm.

Instrumental mass discrimination was corrected using $^{146}Nd/^{144}Nd$ as an internal standard, after correction of the isobaric interference of ^{144}Sm on ^{144}Nd using interference-free $^{147}Sm/^{149}Sm$ for mass fractionation. Their data indicated that the mass discrimination of Sm and Nd was not the same and varied during an analytical session, hence the need to calculate mass biases for each element on individual samples. Martin *et al.*[382] showed that Nd extracted from the >63μm decarbonated fraction of deep sea sediments using a solution of 0.02 M hydroxylamine hydrochloride can provide high resolution records of Nd isotopes for interpretation in terms of deep water circulation. An excellent correlation with Nd isotope ratios obtained from cleaned fossil fish teeth from the same samples was noted. Yuan and co-authors[383] proposed a method based on a sectional power-law correction to provide precise and accurate measurements of $^{176}Lu/^{175}Lu$ by MC-ICP-MS, after spiking with ^{176}Lu and ^{178}Hf, and correcting for the interference of ^{176}Yb on ^{176}Lu. The success of this correction method meant that complete chemical separation of Yb from Lu was not a critical requirement and that simple one-step chemical chromatography could be employed. A systematic evaluation of the performance of Sr spec® resin in Sr isotope ratio measurements of samples with a complex or calcium-rich matrix has been carried out by a research group in Belgium[276]. Resin volumes between 250 and 2000 μL, depending on the absolute Sr mass loaded on the resin, were preferred over the smaller quantities often deployed (<300μL), to ensure complete recovery and matrix separation. Soil and bone CRMs were analysed but the method is likely to be applicable to a broad range of Sr isotope applications. They also demonstrated that it was possible to regenerate the resin without detectable loss of performance. The same laboratory developed a simplified procedure for the isolation of Sr and Pb from volcanic rock powders using this resin[384]. Savings in cost and time were made by reducing the steps for pre-cleaning the Sr spec® resin and cutting out the use of HBr without compromising the quality of the isotope ratio data obtained by MC-ICP-MS.

4.4.4 Other mass spectrometric techniques

A method for the *chemical separation of Cr, Cu, Fe, Ni and Zn prior to ID-TIMS* has been applied to the analysis of very small quantities of silicate samples[385]. The procedure involves a combination of cation and anion-exchange chromatography and Eichrom Ni specific resin. Concentrations of each element were determined by TIMS using W filaments and a Si-B-Al type activator for Cr, Fe, Ni and Zn, and a rhenium

filament and silicic acid – phosphoric acid activator for Cu. The analytical procedure was extended to obtain high precision isotope data for Cr.

Two new procedures for the *measurement of Ca and Cd isotopes in geological and biological materials* by TIMS have been published recently by the same lead author[386],[387]. The method for Cd[386] involves spiking with a mixed ^{106}Cd/^{108}Cd tracer prior to anion-exchange on AG1-X8 resin. It was found necessary to remove iron by solvent extraction into 4-methylpentan-2-one as traces of iron inhibit the thermal ionisation of Cd. The long-term reproducibility on the ^{112}Cd/^{110}Cd ratio was ±14 ppm (2 σ), based on 100 ng loads of standards treated as unknowns. The natural isotope fractionation of Ca is very limited, so excellent external precision and sensitivity are required in the measurement of Ca isotope ratios. Automated high pressure ion chromatography was shown to effect complete separation of Ca from K, Mg and Sr, thereby avoiding isobaric interferences, which is critical in TIMS[387]. Recoveries of close to 100% were achieved, leading to the absence of any fractionation of Ca isotopes during purification. This procedure will be a particular interest for applications that are not amenable to the use of the double spike technique.

Chen and co-workers[388] developed an improved protocol for the *determination of Ru isotopes in chondrites and meteorites by NTIMS*. Samples were dissolved with reverse *aqua regia* in Carius tubes and Ru separated by ion-exchange and further purified by distillation. This improved chemistry, plus the use of zone-refined, outgased Pt filaments, reduced the isobaric interferences from Mo to a level where no correction was necessary. Data were normalised to ^{99}Ru/^{101}Ru to correct for mass fractionation.

Algorithms commonly used to correct for mass dependent isotope fractionation in TIMS have been assessed using a large set of *Nd isotope data*[389]. The authors concluded that the exponential law is fully adequate to correct for mass fractionation at the current level of precision obtainable. However, this law assumes that sample evaporation takes place from a single, homogenous domain on the filament, which is probably not justified as mass fractionation is temperature dependent. They estimated that up to 50% of the external reproducibility could be explained by ion emission from multiple domains of somewhat different isotopic composition on the filament. Chu *et al.*[390] have developed a sensitive method for measurements of Nd isotopes as NdO$^+$ by TIMS using a single tungsten filament with TaF$_5$ as an ion emitter. Advantages of this procedure included higher sensitivity, a

more stable ion beam and no need for oxygen gas to be bled into the ion source chamber compared to previous methods based on NdO^+ determinations. Combined with a highly efficient and low-blank column chemistry to separate Nd from Sm, Ce and Pr, this method has the potential to determine Nd and Sm concentrations plus Nd isotopic compositions of geological materials with very low Nd and Sm contents.

Lasers are often employed for the extraction of noble gases from geological samples prior to the measurement of their isotopic composition by mass spectrometry. In K-Ar geochronology, the use of lasers to release argon from the sample can result in lower blanks and complete extraction of the argon in tens of seconds. Sole[391] reported the practicalities of using an infrared CO_2 laser for this purpose. In an alternative approach, Ignatiev *et al.*[392] extracted argon from geological samples with a continuous Nd-YAG laser. After preconcentration, the argon was separated from possible contaminants by passage through a chromatographic capillary column in a flow of helium. They demonstrated that argon isotope measurement by continuous flow IRMS could be used for the analysis of radiogenic argon in picogram quantities. The sensitivity and accuracy of the measurements were shown to be comparable to those provided by the classical static method, as well as being simpler and more reliable. A combination of three techniques to extract argon for Ar-Ar dating has been reported[393]. This involved stepwise heating of single grains and small separates with a laser, spot fusions with a UV laser on polished sections, and an *in vacuo* crushing technique for liberating radiogenic argon from fluid inclusions. An internally consistent thermal history was derived from the Ar-Ar ages obtained from these three sampling strategies. Zimmerman and co-workers[394] selected a 193 nm excimer laser to extract nitrogen captured in targets exposed to ions emitted by the Sun during a space mission. A low volume nitrogen purification line was employed, with a cryogenic trap to avoid loss of nitrogen by dilution in the line. After purification, the nitrogen was analysed by static mode mass spectrometry using electron multipliers and Faraday cup detectors. The blanks obtained by this procedure were an order of magnitude lower than those achieved by other workers.

Applications of *ion microprobe measurements in the study of zircons* have been widely reported in this review period. Some of the first determinations of oxygen isotope ratios in zircon from oceanic crust have been made by ion microprobe on zircon in polished rock chips of gabbro and veins in serpentinised peridotite drilled from the Mid-Atlantic Ridge[395]. Gordon *et al.*[396,397] used SIMS to acquire high

resolution depth profiles of the rims of natural zircons from high-grade metamorphic rocks. They demonstrated that the evolution of highly metamorphosed terrains, including the fluid history, could be revealed in unprecedented detail through data acquired at the sub-micrometre scale for U-Pb geochronology, Ti thermometry and oxygen isotope ratios using this technique. A rapid and accurate protocol[398] has been developed for the determination of U-Pb ages in ancient zircons using a fully automated multi-collector ion microprobe. Sample locations were determined off-line before the samples were loaded into the instrument, reference points calibrated and target positions visited sequentially. The zircons were screened initially, with a 5 s acquisition, and suitable candidates then analysed in a longer routine to obtain better measurement statistics, U/Pb and concentration data. In multi-collector mode the analytical time taken for a single mount containing 400 zircons is approximately 6 h; in single collector mode, the analysis takes about 17 h. These routines have been used to analyse over 100,000 zircons.

In many cases, ion microprobe is the preferred method for U-Pb and Th-Pb dating of minerals because it combines good analytical precision with μm-scale spatial resolution. Like all techniques, it is important to *quantify any matrix effects in SIMS*. Fletcher and co-workers[399] have made a comprehensive assessment of the effect of different matrix compositions on the ionisation efficiencies of different secondary ionic species during the dating of monazites. They concluded that matrix corrections could be applied without measuring all the LREEs, using ion probe data alone. In addition, other complications such as Pb-Pb fractionation and an isobar at ^{204}Pb, could be addressed without iterative data reduction. Observed variations in instrumental mass fractionation (IMF) during the measurement of radiogenic Pb isotopes in zircon by SIMS has been investigated[400]. The specific causes of variability in IMF were unclear, but generally reflected subtle differences in analytical conditions between instruments and between analytical sessions. It was recommended that an igneous zircon RM such as OD1, characterised for U-Pb isotopes by ID-TIMS, should be incorporated into the analytical routine to improve the accuracy and reproducibility, particularly when dating Precambrian events. Problems encountered in the determination of Pb and U isotopes in highly altered zircons from sediments overlying the Bangombé natural fission reactor in the Gabon using a SHRIMP have been described[401]. These zircons have very variable U contents from <100 to 59 000 ppm. The conventional U-Pb calibration technique for *in situ* analysis was found to be

unreliable for U contents greater than 2500 ppm. Accurate ages for these samples required U/Pb elemental ratios determined by EPMA prior analysis by ion probe.

A new method to measure the natural *$^{10}Be/^9Be$ ratio of a sample* directly with low energy AMS has been developed[402]. This AMS technique is faster and more precise compared to conventional analysis, which relies on the determination of the total Be concentration by another method, such as ICP-MS. Possible applications of this new method are $^{10}Be/^9Be$ dating or the reconstruction of the geomagnetic field strength from marine sediments. Chmeleff and co-workers[403] used a combination of MC-ICP-MS and scintillation counting to measure the half-life of ^{10}Be; a value of 1.387±0.012 My is recommended as a result of their investigations. They also prepared a ^{10}Be-rich master solution that is available as an absolute Be ratio standard for AMS measurements. The current debate over the half-life of ^{10}Be is relevant to the determination of cosmogenic $^{10}Be/^{21}Ne$ and $^{26}Al/^{21}Ne$ production rates in quartz by AMS[404].

In contrast to siliceous environments, there are few cosmogenic nuclides that can be used for *in situ dating of calcareous materials*. Thus, Merchel *et al.*[405] investigated nuclides such as ^{10}Be, ^{26}Al and ^{41}Ca as possible dating tools through cross-calibration with ^{36}Cl. They found that cosmogenic ^{10}Be in calcite is highly contaminated with atmospheric ^{10}Be, which is extremely difficult to remove quantitatively. Very low $^{41}Ca/Ca$ ratios (<5 x 10^{-15}) hinders the measurement of ^{41}Ca, whereas ^{26}Al can be easily determined in calcite, even though its production rate is only ~4.6%, and would merit further research.

The *accurate determination of Cl concentrations in terrestrial rock*s is important for the interpretation of *in situ* cosmogenic ^{36}Cl. The results of an inter-laboratory comparison[406] of Cl measurements by prompt gamma activation analysis and ID-AMS concluded there was no significant difference between the Cl concentrations obtained by either methods when analysing Icelandic basalts with Cl contents between 40 and 99 μg g^{-1}, with comparable uncertainties.

4.4.5 X-ray techniques

For a comprehensive *review* of developments in XRF, including all types of applications, the sister Update covering this subject should be consulted[5] (498 refs). On an historical note, an article celebrating pioneering research surrounding the first

practical applications of energy dispersive X-ray spectroscopy in EPMA, over 40 years ago, has been published[407].

Developments in *geological applications of XRF* have included an EDXRF method for the rapid determination of Ce, La, Nd, Pr and total REE content of rare earth ores from Mongolia[408]. Synthetic calibration standards were prepared from pure oxides of Ce, La, Nd and Pr in a matrix of SiO_2 and Al_2O_3. Artificial samples made by successive dilution of the calibration standards with oxides of known interfering elements, such as Ba, Nd and Sr, were used to calculate corrections for spectral overlaps. The measurement of the FeO content of rocks by WDXRF has been revisited by Finkelshtein and Chubarov[409]. From their experiments, they selected the $K\beta_{2,5} / K\beta_{1,3}$ ratio as the analytical signal. For igneous samples with a FeO/Fe_2O_{3total} of >0.25, they claimed that the accuracy of the XRF determination of FeO content was comparable to that of wet chemical analysis.

A variety of *micro X-ray techniques* can be employed to provide chemical information at high spatial resolution. Recent examples include the use of XANES to investigate whether REEs are incorporated in the carbonate phase or in other minor mineral phases, such as Fe-Mn oxides and phosphate, within a limestone[410]. Impact materials from the Barringer Meteor Crater have been examined by a combination of μ-XANES and μ-PIXE techniques[411], with a focus on understanding the complex character of their Fe-rich inclusions. Spatially resolved X-ray absorption and fluorescence techniques were employed to study the movement and speciation of a Np radiotracer in fractured granite core from the Swedish Aspo Hard Rock Laboratroy[412]. Elemental distributions were obtained from μ-XRF measurements and the Np oxidation state was determined by μ-XAFS. It was observed that the Np, originally introduced as Np^V, was reduced to Np^{IV} in the fractured granite and that the distribution of the Np^{IV} was correlated with that of zinc. From this, it was concluded that ZnS may have played a role in the reduction and subsequent immobilisation of the Np tracer.

5 Glossary of terms

Terms include the plural form.

AAS	atomic absorption spectrometry
ACGIH	American Conference of Governmental Industrial Hygienists
ADPC	ammonium pyrrolidinedithiocarbamate
AES	atomic emission spectrometry
AFS	atomic fluorescence spectrometry
AMS	accelerator mass spectrometry
AsB	arsenobetaine
ASTM	American Society for Testing And Materials,
ATOFMS	atomic time of flight mass spectrometry
BCR	Community Bureau of Reference (*of the European Community*)
CCRMP	Canadian Certified Reference Material Project
CEN	European Committee for Standardisation
CPE	clould point extraction
CRM	certified reference material
CRPG	Centre de Recherches Petrographiques et Geochimiques
CV	cold vapour
CV-AAS	cold vapour atomic absorption spectrometry
CV-AFS	cold vapour atomic fluorescence spectrometry
CVG	chemical vapour generation
DBT	dibutyltin
DDTC	diethyldithiocarbamate

DILLME	dispersive liquid liquid microextraction
DMA	dimethyl arsenic acid
DRC	dynamic reaction cell
EDAX	energy dispersive spectrometry
EDXRF	energy dispersive x-ray fluorescence
EN	European Standard
EPMA	electron probe microanalyser
ESI-MS	electrospray ionisation mass spectrometry
ETAAS	electrothermal atomic absorption spectrometry
ETV	electrothermal vaporisation
ETV-ICP-AES	electrothermal vaporisation inductively coupled plasma emission spectrometry
ETV-ICP-MS	electrothermal vaporisation inductively coupled plasma mass spectrometry
EU	European Union
EXAFS	extended x-ray absorption fine structure
FAAS	flame atomic absorption spectrometry
FAPES	furnace atomization plasma excitation spectrometry
FI-CVG-AFS	flow injection cold vapour atomic fluorescence spectrometry
FI-HG-ICP-AES	flow injection hydride generation inductively coupled plasma atomic emission spectrometry
fs	femto second
FTIR	fourier transform infrared
GBW	reference materials produced by the National Research Center for Certified Reference Materials in China
GC	gas chromatography
GC-FID	gas chromatographic flame ionization detector
GC-MS	gas chromatography mass spectrometry
GSJ	Geological Survey of Japan
HF-LPME	hollow fiber liquid phase microextraction
HG	hydride generation
HG-AAS	hydride generation atomic absorption spectrometry
HG-AFS	hydride generation atomic fluorescence spectrometry

HG-ICP-MS	hydride generation inductively coupled plasma mass spectrometry
HPLC	high performance liquid chromatography
HPLC-ICP-MS	high performance liquid chromatography inductively coupled plasma mass spectrometry
HR-CS-FAAS	high resolution continuum source flame atomic absorption spectrometry
HR-CS-ETAAS	high resolution continuum source electrothermal atomic absorption spectrometry
HR-ICP-MS	high resolution inductively coupled plasma mass spectrometry
HR-MC-ICP-MS	high resolution multi collector inductively coupled mass spectrometry
IAEA	International Atomic Energy Agency
IC	ion chromatography
IC-ICP-MS	ion chromatography inductively coupled plasma mass spectrometry
ICP-AES	inductively coupled plasma atomic emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
ICP-QMS	inductively coupled plasma quadrupole mass spectrometry
ID	isotope dilution
ID-ICP-MS	isotope dilution inductively coupled plasma mass spectrometry
INAA	instrumental neutron activation analysis
INRS	Institut National de Recherche et de Sécurité
IOM	Institute of Occupational Medicine
IR	infrared
IRMS	isotope ratio mass spectrometry
IS	internal standard
ISO	International Standards Organisation
JSAC	Japanese Society for Analytical Chemistry
LA	laser ablation
LA-ICP-MS	laser ablation inductively coupled plasma mass spectrometry
LA-MC-ICP-MS	laser ablation multi collector inductively coupled plasma mass spectrometry
LIBS	laser induced breakdown spectroscopy

LOD	limit of detection
LOQ	limit of quantification
LPME	liquid drop microextraction
MA	methylarsonic acid
MBT	monobutyltin
MC-ICP-MS	multi collector inductively coupled plasma mass spectrometry
MIBK	methyl isobutyl ketone
MMA	monomethyl arsenic
Nd:YAG	neodymium doped:yttrium aluminum garnet
NIOSH	National Institute of Occupational Safety and Health
NIST	National Institute of Standards and Technology
NRCC	National Research Council of Canada
ns	nano second
NTIMS	negative thermal ionisation mass spectrometry
PCA	principal component analysis
PGE	precious group element
PIXE	particle induced x-ray emission
PXRF	portable x-ray fluorescence
REE	rare earth element
RM	reference material
RSD	relative standard deviation
sd	standard deviation
SDME	single drop microextraction
SEM	scanning electron microscopy
SF	sector field
SF-ICP-MS	sector field inductively coupled plasma mass spectrometry
SFODME	solidified floating organic drop microextraction
SHRIMP	sensitive high mass resolution ion microprobe
SIDMS	speciated isotope dilution mass spectrometry
SIMS	secondary ion mass spectrometry
SPE	solid phase extraction
SPME	solid phase microextraction
SRM	standard reference material
SRXRF	synchrotron radiation x-ray fluorescence

TBT	tributyltin
TEM	transmission electron microscopy
TIMS	thermal ionisation mass spectrometry
TMAO	trimethylarsine oxide
TOF	time of flight
TPhT	triphenyltin
TXRF	total reflection x-ray fluorescence
US EPA	United States Environmental Protection Agency
USGS	United States Geological Survey
USN	ultrasonic nebulisation
UV	ultra violet
VOC	volatile organic compound
WDXRF	wavelength dispersive x-ray fluorescence
XAFS	x-ray absorption fine structure spectrometry
XANES	x-ray absorption near edge structure
XRD	x-ray diffraction
XRF	x-ray fluorescence

6   References

1   O. T. Butler, W. R. L. Cairns, J. M. Cook and C. M. Davidson, *J. Anal. At. Spectrom.,* 2010, **25**(2), 103-141.

2   A. Taylor, S. Branch, M. P. Day, M. Patriarca and M. White, *J. Anal. At. Spectrom.*, 2010, **25**(4), 453-492.

3   C. F. Harrington, R. Clough, H. R. Hansen, S. J. Hill and J. F. Tyson, *J. Anal. At. Spectrom.*, 2010, **25**(8), 1185-1216.

4   E. H. Evans, J. A. Day, C. Palmer and C. M. M. Smith, *J. Anal. At. Spectrom.*, 2010, **25**(6), 760-784.

5   M. West, A. T. Ellis, P. J. Potts, C. Streli, C. Vanhoof, D. Wegrzynek and P. Wobrauschek, *J. Anal. At. Spectrom.*, 2010, **25**(10), 1503-1545.

6   S. Carter, A. S. Fisher, P. S. Goodall, M. W. Hinds, S. Lancaster and S. Shore, *J. Anal. At. Spectrom.,* 2009, **24**(12), 1599-1656.

7   P. Gorner, X. Simon, R. Wrobel, E. Kauffer and O. Witschger, *Annals of Occupational Hygiene,* 2010, **54**(2), 165-187.

8   T. Lee, W. P. Chisholm, J. E. Slaven and M. Harper, *Aerosol Science and Technology,* 2009, **43**(10), 1042-1050.

9   C. H. Chen, P. J. Tsaia, C. Y. Lai, Y. L. Peng, J. C. Soo, C. Y. Chen and T. S. Shih, *Journal of Hazardous Materials,* 2010, **176**(1-3), 389-394.

10   T. R. Anthony, A. C. Landazuri, M. Van Dyke and J. Volckens, *Annals of Occupational Hygiene,* 2010, **54**(4), 427-442.

11   Y. Zhou and Y. S. Cheng, *Journal of Occupational and Environmental Hygiene,* 2010, **7**(2), 88-93.

12   T. Lee, S. W. Kim, W. P. Chisholm, J. Slaven and M. Harper, *Annals of Occupational Hygiene,* 2010, **54**(6), 697-709.

13   L. Morawska, H. Wang, Z. Ristovski, E. R. Jayaratne, G. Johnson, H. C. Cheung, X. Ling and C. He, *Journal of Environmental Monitoring,* 2009, **11**(10), 1758-1773.

14   Z. C. Wei, R. C. Rosario and L. D. Montoya, *Atmospheric Environment,* 2010, **44**(6), 872-876.

15   A. Miller, G. Frey, G. King and C. Sunderman, *Aerosol Science and Technology,* 2010, **44**(6), 417-427.

16   L. Li, D. R. Chen, C. Qi and P. S. Kulkarni, *Journal of Aerosol Science,* 2009, **40**(11), 982-992.

17   N. Bukowiecki, A. Richard, M. Furger, E. Weingartner, M. Aguirre, T. Huthwelker, P. Lienemann, R. Gehrig and U. Baltensperger, *Aerosol Science and Technology,* 2009, **43**(9), 891-901.

18   D. J. Phares and S. Collier, *Aerosol Science and Technology,* 2010, **44**(3), 173-181.

19   C. E. McDade, A. M. Dillner and H. Indresand, *Journal of the Air & Waste Management Association,* 2009, **59**(9), 1045-1048.

20   K. S. Lee, J. H. Jung, S. I. Keel, J. H. Yun, Y. J. Kim, H. K. Lee and S. S. Kim, *Aerosol Science and Technology,* 2010, **44**(7), 563-569.

21   L. Freville, J. C. Moulut, M. Grzebyk and E. Kauffer, *Annals of Occupational Hygiene,* 2010, **54**(6), 659-670.

22   D. G. Nash and D. Leith, *Journal of the Air & Waste Management Association,* 2010, **60**(2), 204-209.

23   A. Hagenbjork-Gustafsson, A. Tornevi, B. Forsberg and K. Eriksson, *Journal of Environmental Monitoring,* 2010, **12**(6), 1315-1324.

24   C. Lin, P. McKenna, R. Timmis and K. C. Jones, *Journal of Environmental Monitoring,* 2010, **12**(7), 1430-1436.

25   M. H. Garnett and I. P. Hartley, *Atmospheric Environment,* 2010, **44**(7), 877-883.

26   S. N. Lyman, M. S. Gustin and E. M. Prestbo, *Atmospheric Environment,* 2010, **44**(2), 246-252.

27   N. P. Hyslop and W. H. White, *Journal of the Air & Waste Management Association,* 2009, **59**(9), 1032-1039.

28   N. Kumar, V. Nixon, K. Sinha, X. S. Jiang, S. Ziegenhorn and T. Peters, *Journal of the Air & Waste Management Association,* 2009, **59**(11), 1308-1316.

29   E. G. Ferradas, M. D. Minarro, I. M. M. Terres and F. J. M. Martinez, *Atmospheric Environment,* 2010, **44**(21-22), 2640-2645.

30   M. S. Epstein, *Talanta,* 2010, **80**(3), 1467-1469.

31   V. Stone, B. Nowack, A. Baun, N. van den Brink, F. von der Kammer, M. Dusinska, R. Handy, S. Hankin, M. Hassellov, E. Joner and T. F. Fernandes, *Science of the Total Environment*, 2010, **408**(7), 1745-1754.

32   J. Kucera, V. Havranek and I. Krausova, *Journal of Radioanalytical and Nuclear Chemistry*, 2009, **281**(1), 123-129.

33   Y. S. Zhang, J. Zheng, M. Yamada, F. C. Wu, Y. Igarashi and K. Hirose, *Science of the Total Environment*, 2010, **408**(5), 1139-1144.

34   T. Tanaka, S. Inoba, S. Kawada, A. Kida, K. Kurusu, M. Furusaki, T. Tanosaki, N. Nishida, T. Maruta, Y. Watanabe, A. Ono, M. Sakata, K. Kakita and K. I. Takimoto, *Bunseki Kagaku*, 2010, **59**(2), 137-150.

35   I. Rodushkin, E. Engstrom and D. C. Baxter, *Analytical and Bioanalytical Chemistry*, 2010, **396**(1), 365-377.

36   K. X. Yang, M. E. Kitto, J. P. Orsini, K. Swami and S. E. Beach, *J. Anal. At. Spectrom.*, 2010, **25**(8), 1290-1297.

37   E. Szeles, Z. Varga and Z. Stefanka, *J. Anal. At. Spectrom.*, 2010, **25**(7), 1014-1018.

38   M. L. Sammut, Y. Noack, J. Rose, J. L. Hazemann, O. Proux, M. Depoux, A. Ziebel and E. Fiani, 2010, *Chemosphere*, **78**(4), 445-450.

39   M. Keane, S. Stone and B. Chen, *Journal of Environmental Monitoring*, 2010, **12**(5), 1133-1140.

40   N. Unceta, F. Seby, J. Malherbe and O. F. X. Donard, *Analytical and Bioanalytical Chemistry*, 2010, **397**(3), 1097-1111.

41   S. Jin, M. Kinoshita, Y. Suzuki and N. Furuta, *Bunseki Kagaku*, 2009, **58**(7), 617-622.

42   K. D. da Cunha, M. Santos, F. Zouain, L. Carneiro, G. Pitassi, C. Lima, C. V. B. Leite and K. C. P. Dalia, *Water Air and Soil Pollution*, 2010, **205**(1-4), 251-257.

43   H. Alsenz, F. Zereini, C. L. S. Wiseman and W. Puttmann, *Analytical and Bioanalytical Chemistry*, 2009, **395**(6), 1919-1927.

44   D. Lariviere, K. Benkhedda, S. Kiser, S. Johnson and R. J. Cornett, *Analytical Methods*, 2010, **2**(3), 259-267.

45   A. Mukhtar and A. Limbeck, *Analytica Chimica Acta*, 2009, **646**(1-2), 17-22.

46   M. Savio, P. H. Pacheco, L. D. Martinez, P. Smichowski and R. A. Gil, *J. Anal. At. Spectrom.*, 2010, **25**(8), 1343-1347.

47   K. X. Yang, K. Swami and L. Husain, *Spectroscopy Letters*, 2009, **42**(8), 458-466.

48   R. Dumarey, R. J. C. Brown, W. T. Corns, A. S. Brown and P. B. Stockwell, *Accreditation and Quality Assurance*, 2010, **15**(7), 409-414.

49   A. S. Brown, R. J. C. Brown, M. A. Dexter, W. T. Corns and P. B. Stockwell, *Analytical Methods*, 2010, **2**(7), 954-966.

50   D. Sanchez-Rodas, W. T. Corns, B. Chen and P. B. Stockwell, *J. Anal. At. Spectrom.*, 2010, **25**(7), 933-946.

51   D. W. Hahn, *Spectroscopy*, 2010, February, 23-28.

52   M. N. Fiddler, I. Begashaw, M. A. Mickens, M. S. Collingwood, Z. Assefa and S. Bililign, *Sensors*, 2009, **9**(12), 10447-10512.

53   Y. Suzuki, H. Sato, S. Hikida, K. Nishiguchi and N. Furuta, *J. Anal. At. Spectrom.*, 2010, **25**(7), 947-949.

54   R. J. C. Brown, K. E. Jarvis, B. A. Disch, S. L. Goddard and A. S. Brown, *Journal of Environmental Monitoring*, 2009, **11**(11), 2022-2029.

55   R. Jakob, A. Roth, K. Haas, E. M. Krupp, A. Raab, P. Smichowski, D. Gomez and J. Feldmann, *Journal of Environmental Monitoring*, 2010, **12**(2), 409-416.

56   S. Yonezawa, A. Hokura, K. Matsuda, T. Kimoto and I. Nakai, *Bunseki Kagaku*, 2010, **59**(1), 23-33.

57   P. Formenti, S. Nava, P. Prati, S. Chevaillier, A. Klaver, S. Lafon, F. Mazzei, G. Calzolai and M. Chiari, *Journal of Geophysical Research-Atmospheres*, 2010, **115**, 8.

58   E. Bontempi, A. Zacco, D. Benedetti, L. Borgese, P. Colombi, H. Stosnach, G. Finzi, P. Apostoli, P. Buttini and L. E. Depero, *Environmental Technology*, 2010, **31**(5), 467-477.

59   C. Liu, J. Hu and K. G. McAdam, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2009, **64**(11-12), 1294-1301.

60   S. Pattanaik, F. E. Huggins and G. P. Huffman, *Journal of Hazardous Materials*, 2010, **178**(1-3), 804-813.

61   R. B. Kellogg and R. D. Willis, *X-Ray Spectrometry*, 2009, **38**(4), 283-286.

62   D. Ceccato, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 2009, **267**(12-13), 2077-2079.

63   W. Gutknecht, J. Flanagan, A. McWilliams, R. K. M. Jayanty, R. Kellogg, J. Rice, P. Duda and R. H. Sarver, *Journal of the Air & Waste Management Association*, 2010, **60**(2), 184-194.

64   S. Ayrault, M. Catinon, R. Clochiatti, M. Tissut and J. Asta, *Journal of Radioanalytical and Nuclear Chemistry*, 2009, **281**(1), 131-136.

65   K. Ashley, M. J. Brisson, A. M. Howe and D. L. Bartley, *Journal of Occupational and Environmental Hygiene*, 2009, **6**(12), 745-750.

66   J. J. Niu, P. E. Rasmussen, A. Wheeler, R. Williams and M. Chenier, *Atmospheric Environment*, 2010, **44**(2), 235-245.

67   K. von Bobrutzki, C. F. Braban, D. Famulari, S. K. Jones, T. Blackall, T. E. L. Smith, M. Blom, H. Coe, M. Gallagher, M. Ghalaieny, M. R. McGillen, C. J. Percival, J. D. Whitehead, R. Ellis, J. Murphy, A. Mohacsi, A. Pogany, H. Junninen, S. Rantanen, M. A. Sutton and E. Nemitz, *Atmospheric Measurement Techniques*, 2010, **3**(1), 91-112.

68   N. Pirrone, S. Cinnirella, X. Feng, R. B. Finkelman, H. R. Friedli, J. Leaner, R. Mason, A. B. Mukherjee, G. B. Stracher, D. G. Streets and K. Telmer, *Atmospheric Chemistry and Physics*, 2010, **10**(13), 5951-5964.

69   Y. Wu, D. G. Streets, S. X. Wang and J. M. Hao, *Atmospheric Chemistry and Physics*, 2010, **10**(6), 2937-2946.

70   M. Takaoka, K. Oshita, N. Takeda and S. Morisawa, *Atmospheric Chemistry and Physics*, 2010, **10**(8), 3665-3671.

71   Z. G. Li, X. Feng, P. Li, L. Liang, S. L. Tang, S. F. Wang, X. W. Fu, G. L. Qiu and L. H. Shang, *Atmospheric Chemistry and Physics*, 2010, **10**(7), 3353-3364.

72   A. Dommergue, F. Sprovieri, N. Pirrone, R. Ebinghaus, S. Brooks, J. Courteaud and C. P. Ferrari, *Atmospheric Chemistry and Physics*, 2010, **10**(7), 3309-3319.

73   F. Sprovieri, N. Pirrone, R. Ebinghaus, H. Kock and A. Dommergue, *Atmospheric Chemistry and Physics*, 2010, **10**(17), 8531-8531.

74   J. R. Richards, T. T. Brozell, C. Rea, G. Boraston and J. Hayden, *Journal of the Air & Waste Management Association*, 2009, **59**(11), 1287-1295.

75   J. S. Le Blond, C. J. Horwell, B. J. Williamson and C. Oppenheimer, *Journal of Environmental Monitoring*, 2010, **12**(7), 1459-1470.

76   M. Cerqueira, C. Pio, M. Legrand, H. Puxbaum, A. Kasper-Giebl, J. Afonso, S. Preunkert, A. Gelencser and P. Fialho, *Journal of Aerosol Science,* 2010, **41**(1), 51-61.

77   L. Tumolva, J. Y. Park, J. S. Kim, A. L. Miller, J. C. Chow, J. G. Watson and K. Park, *Aerosol Science and Technology,* 2010, **44**(3), 202-215.

78   M. Methner, L. Hodson and C. Geraci, *Journal of Occupational and Environmental Hygiene,* 2010, **7**(3), 127-132.

79   J. S. Kinsey, Y. J. Dong, D. C. Williams and R. Logan, *Atmospheric Environment,* 2010, **44**(17), 2147-2156.

80   H. Winnes and E. Fridell, *Journal of the Air & Waste Management Association,* 2009, **59**(12), 1391-1398.

81   R. M. Healy, I. P. O'Connor, S. Hellebust, A. Allanic, J. R. Sodeau and J. C. Wenger, *Atmospheric Environment,* 2009, **43**(40), 6408-6414.

82   Z. G. Liu, V. N. Vasys, M. E. Dettmann, J. J. Schauer, D. B. Kittelson and J. Swanson, *Aerosol Science and Technology,* 2009, **43**(11), 1142-1152.

83   M. Fowler, H. Datson and J. Newberry, *Journal of Environmental Monitoring,* 2010, **12**(4), 879-889.

84   E. Cadena, J. Colon, A. Sanchez, X. Font and A. Artola, *Waste Manage.,* 2009, **29**(11), 2799-2807.

85   M. K. Lee, Y. Il Lee and H. I. Yi, *Atmospheric Environment,* 2010, **44**(20), 2401-2414.

86   S. Weinbruch, M. Ebert, H. Gorzawski, T. Dirsch, T. Berg and E. Steinnes, *Journal of Environmental Monitoring,* 2010, **12**(5), 1064-1071.

87   J. P. Putaud, R. Van Dingenen, A. Alastuey, H. Bauer, W. Birmili, J. Cyrys, H. Flentje, S. Fuzzi, R. Gehrig, H. C. Hansson, R. M. Harrison, H. Herrmann, R. Hitzenberger, C. Huglin, A. M. Jones, A. Kasper-Giebl, G. Kiss, A. Kousa, T. A. J. Kuhlbusch, G. Loschau, W. Maenhaut, A. Molnar, T. Moreno, J. Pekkanen, C. Perrino, M. Pitz, H. Puxbaum, X. Querol, S. Rodriguez, I. Salma, J. Schwarz, J. Smolik, J. Schneider, G. Spindler, H. ten Brink, J. Tursic, M. Viana, A. Wiedensohler and F. Raes, *Atmospheric Environment,* 2010, **44**(10), 1308-1320.

88   R. J. C. Brown, *Journal of Environmental Monitoring,* 2010, **12**(3), 665-671.

89   J. X. Qiao, X. L. Hou, M. Miro and P. Roos, *Analytica Chimica Acta,* 2009, **652**(1-2), 66-84.

90   M. Gallego-Gallegos, R. M. Olivas and C. Camara, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(5), 595-601.

91   N. Garcia-Otero, C. Teijeiro-Valino, J. Otero-Romani, E. Pena-Vazquez, A. Moreda-Pineiro and P. Bermejo-Barrera, *Analytical and Bioanalytical Chemistry,* 2009, **395**(4), 1107-1115.

92   A. N. Anthemidis and K. I. G. Ioannou, *Talanta,* 2009, **80**(2), 413-421.

93   M. Rezaee, Y. Yamini and M. Faraji, *Journal of Chromatography A*, 2010, **1217**(16), 2342-2357.

94   S. Z. Mohammadi, D. Afzali and Y. M. Baghelani, *Analytica Chimica Acta,* 2009, **653**(2), 173-177.

95   S. Z. Mohammadi, D. Afzali, M. A. Taher and Y. M. Baghelani, *Talanta,* 2009, **80**(2), 875-879.

96   S. Q. Li, S. Cai, W. Hu, H. Chen and H. L. Liu, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(7), 666-671.

97   J. L. Manzoori, M. Amjadi and J. Abulhassani, *Analytica Chimica Acta,* 2009, **644**(1-2), 48-52.

98   S. Dadfarnia and A. M. H. Shabani, *Analytica Chimica Acta*, 2010, **658**(2), 107-119.

99   M. S. Bidabadi, S. Dadfarnia and A. M. H. Shabani, *Journal of Hazardous Materials,* 2009, **166**(1), 291-296.

100   I. Lopez-Garcia, R. E. Rivas and M. Hernandez-Cordoba, *Analytical and Bioanalytical Chemistry*, 2010, **396**(8), 3097-3102.

101   M. Mohamadi and A. Mostafavi, *Talanta*, 2010, **81**(1-2), 309-313.

102   R. E. Rivas, I. Lopez-Garcia and M. Hernandez-Cordobo, *Analytical Methods*, 2010, **2**(3), 225-230.

103   I. Hagarova, *Chemicke Listy,* 2009, **103**(9), 712-720.

104   S. E. Pepper, D. R. Peterman, T. J. Tranter and B. M. White, *Journal of Radioanalytical and Nuclear Chemistry,* 2009, **282**(3), 909-912.

105   N. N. Meeravali and S. J. Jiang, *Talanta,* 2009, **80**(1), 173-178.

106   Y. J. Li and B. Hu, *Atomic Spectroscopy,* 2009, **30**(3), 104-111.

107   A. Kaur and U. Gupta, *Journal of Materials Chemistry,* 2009, **19**(44), 8279-8289.

108   C. R. Quetel, E. Vassileva, I. Petrov, K. Chakarova and K. I. Hadjiivanov, *Analytical and Bioanalytical Chemistry*, 2010, **396**(6), 2349-2361.

109   D. H. Chen, B. Hu, M. He and C. Z. Huang, *Microchemical Journal*, 2010, **95**(1), 90-95.

110   L. M. Ravelo-Perez, A. V. Herrera-Herrera, J. Hernandez-Borges and M. A. Rodriguez-Delgado, *Journal of Chromatography A*, 2010, **1217**(16), 2618-2641.

111   S. Z. Chen, C. Liu, M. Yang, D. B. Lu, L. Zhu and Z. Wang, *Journal of Hazardous Materials,* 2009, **170**(1), 247-251.

112   X. W. Zhao, N. Z. Song, Q. O. Jia and W. H. Zhou, *Microchimica Acta,* 2009, **166**(3-4), 329-335.

113   S. Ghaseminezhad, D. Aftali and M. A. Taher, *Talanta,* 2009, **80**(1), 168-172.

114   S. Z. Chen, L. Zhu, D. B. Lu, X. L. Cheng and X. R. Zhou, *Microchimica Acta*, 2010, **169**(1-2), 123-128.

115   X. L. Cheng, S. Z. Chen, X. Wang and C. Liu, *Atomic Spectroscopy*, 2010, **31**(3), 75-80.

116   J. Feldmann, P. Salaun and E. Lombi, *Environmental Chemistry,* 2009, **6**(4), 275-289.

117   M. Popp, S. Hann and G. Koellensperger, *Analytica Chimica Acta*, 2010, **668**(2), 114-129.

118   M. A. Vieira, P. Grinberg, C. R. R. Bobeda, M. N. M. Reyes and R. C. Campos, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(6), 459-476.

119   A. Gonzalvez, S. Armenta, M. L. Cervera and M. de la Guardia, *Trac-Trends in Analytical Chemistry*, 2010, **29**(3), 260-268.

120   C. Puls and A. Limbeck, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(10), 1434-1440.

121   I. Aydin, F. Aydin, A. Saydut and C. Hamamci, *Journal of Hazardous Materials,* 2009, **168**(2-3), 664-669.

122   M. Ghambarian, M. R. Khalili-Zanjani, Y. Yamini, A. Esrafili and N. Yazdanfar, *Talanta*, 2010, **81**(1-2), 197-201.

123   R. E. Rivas, I. Lopez-Garcia and M. Hernandez-Cordoba, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(4), 329-333.

124   A. A. Ammann, *Journal of Chromatography A*, 2010, **1217**(14), 2111-2116.

125   Y. K. Tsoi and K. S. Y. Leung, *J. Anal. At. Spectrom.*, **25**(6), 880-885.

126   G. B. Tonietto, J. M. Godoy, A. C. Oliveira and M. V. de Souza, *Analytical and Bioanalytical Chemistry*, **397**(5), 1755-1761.

127   G. D. Matos, E. B. dos Reis, A. C. S. Costa and S. L. C. Ferreira, *Microchemical Journal,* 2009, **92**(2), 135-139.

128   P. Hemmatkhah, A. Bidari, S. Jafarvand, M. R. M. Hosseini and Y. Assadi, *Microchimica Acta,* 2009, **166**(1-2), 69-75.

129   L. Y. Xing and D. Beauchemin, *J. Anal. At. Spectrom.*, 2010, **25**(7), 1046-1055.

130   K. Leopold, M. Foulkes and P. Worsfold, *Analytica Chimica Acta*, 2010, **663**(2), 127-138.

131   J. S. dos Santos, M. de la Guardia, A. Pastor and M. L. P. dos Santos, *Talanta,* 2009, **80**(1), 207-211.

132   H. T. Chen, J. G. Chen, X. Z. Jin and D. Y. Wei, *Journal of Hazardous Materials,* 2009, **172**(2-3), 1282-1287.

133   Y. G. Yin, M. Chen, J. F. Peng, J. F. Liu and G. B. Jiang, *Talanta*, 2010, **81**(4-5), 1788-1792.

134   N. M. Najafi, S. Seidi, R. Alizadeh and H. Tavakoli, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2010, **65**(4), 334-339.

135   E. Ghasemi, N. M. Najafi, S. Seidi, F. Raofie and A. Ghassempour, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(10), 1446-1451.

136   N. M. Najafi, H. Tavakoli, R. Alizadeh and S. Seidi, *Analytica Chimica Acta*, 2010, **670**(1-2), 18-23.

137   H. Altundag and M. S. Dundar, *Fresenius Environmental Bulletin,* 2009, **18**(11), 2102-2107.

138   Z. H. Yu, M. Jing, X. R. Wang, D. Y. Chen and Y. L. Huang, *Spectroscopy and Spectral Analysis,* 2009, **29**(10), 2855-2859.

139   M. C. C. Pericas, S. M. Lloret, S. T. Cartas and M. R. Alama, *Lc Gc Europe,* 2009, **22**(10), 506-+.

140   L. Segovia-Martinez, A. Bouzas-Blanco, P. Campins-Falco and A. Seco-Torrecillas, *Talanta*, 2010, **80**(5), 1888-1893.

141   T. Sano, H. Takagi, K. Nagano and M. Nishikawa, *Journal of Chromatography A*, 2010, **1217**(26), 4344-4346.

142   C. M. Xiong, Y. C. Qin and B. Hu, *Journal of Hazardous Materials*, 2010, **178**(1-3), 164-170.

143   V. N. Oreshkin and G. I. Tsizin, *Journal of Analytical Chemistry,* 2009, **64**(12), 1221-1225.

144   S. Gunduz, S. Akman, A. Baysal and M. Kahraman, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2010, **65**(4), 297-300.

145   G. L. Donati, C. P. Calloway and B. T. Jones, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(8), 1105-1110.

146   G. L. Donati, B. E. Kron and B. T. Jones, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(6), 559-564.

147   G. L. Donati, J. A. Nobrega, C. C. Nascentes and B. T. Jones, *Microchemical Journal,* 2009, **93**(2), 242-246.

148   X. D. Wen, P. Wu, L. Chen and X. D. Hou, *Analytica Chimica Acta,* 2009, **650**(1), 33-38.

149   M. Kovacs, M. H. Nagy, J. Borszeki and P. Halmos, *Journal of Fluorine Chemistry,* 2009, **130**(6), 562-566.

150   S. B. Adeloju and Y. L. Zhang, *Analytical Chemistry,* 2009, **81**(11), 4249-4255.

151   A. S. Ribeiro, M. A. Vieira, P. Grinberg and R. E. Sturgeon, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(5), 689-694.

152   I. Kula, Y. Arslan, S. Bakirdere, S. Titretir, E. Kenduzler and O. Y. Ataman, *Talanta,* 2009, **80**(1), 127-132.

153   C. B. Zheng, R. E. Sturgeon and X. D. Hou, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(10), 1452-1458.

154   C. B. Zheng, R. E. Sturgeon, C. S. Brophy, S. P. He and X. D. Hou, *Analytical Chemistry*, 2010, **82**(7), 2996-3001.

155   C. B. Zheng, R. E. Sturgeon and X. D. Hou, *J. Anal. At. Spectrom.*, 2010, **25**(7), 1159-1165.

156   J. Cmelik, J. Machat, V. Otruba and V. Kanicky, *Talanta*, 2010, **80**(5), 1777-1781.

157   I. N. I. Aretaki and N. G. Kallithrakas-Kontos, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(7), 979-982.

158   R. Juvonen, A. Parviainen and K. Loukola-Ruskeeniemi, *Geochemistry-Exploration Environment Analysis,* 2009, **9**, 173-178.

159   M. Ovari, C. Streli, P. Wobrauschek and G. Zaray, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(8), 802-804.

160   E. Margui, J. C. Tapias, A. Casas, M. Hidalgo and I. Queralt, *Chemosphere*, **80**(3), 263-270.

161   I. A. Tolokonnikov, A. T. Savichev and A. S. Moskalets, *Journal of Analytical Chemistry,* 2009, **64**(9), 921-925.

162   E. Margui, R. Van Grieken, C. Fontas, M. Hidalgo and I. Queralt, *Applied Spectroscopy Reviews*, 2010, **45**(3), 179-205.

163   Y. Yamini, N. Amiri and M. Karimi, *X-Ray Spectrometry,* 2009, **38**(6), 474-478.

164   E. S. Heiden, D. B. Gore and S. C. Stark, *X-Ray Spectrometry*, 2010, **39**(3), 176-183.

165   A. J. B. Cotta and J. Enzweiler, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(10), 1406-1413.

166   K. Li, E. Vogel and U. Krahenbuhl, *Radiochimica Acta,* 2009, **97**(8), 453-458.

167   M. Liezers, O. T. Farmer and M. L. Thomas, *Journal of Radioanalytical and Nuclear Chemistry,* 2009, **282**(1), 309-313.

168   S. M. Hong, K. Lee, S. G. Hou, S. D. Hur, J. W. Ren, L. J. Burn, K. J. R. Rosman, C. Barbante and C. F. Boutron, *Environmental Science & Technology,* 2009, **43**(21), 8060-8065.

169   P. Serapinas, G. Labarraque, P. Charlet, Z. Ezerinskis and V. Juzikiene, *J. Anal. At. Spectrom.*, 2010, **25**(5), 624-630.

170   C. H. Chung, I. Brenner and C. F. You, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(9), 849-856.

171   L. Yang, S. Willie and R. E. Sturgeon, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(7), 958-963.

172   L. Yang and R. E. Sturgeon, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(10), 1327-1335.

173   A. Milne, W. Landing, M. Bizimis and P. Morton, *Analytica Chimica Acta,* 2010, **665**(2), 200-207.

174   K. Tagami and S. Uchida, *Journal of Nuclear Science and Technology,* 2008, 128-132.

175   Y. B. Zhu, D. Rahmi, T. Umemura, H. Haraguchi and K. Chiba, *Journal of Nuclear Science and Technology,* 2008, 65-68.

176   M. Hattori, T. Shimamura, M. Iwashita, H. Ohashi and Y. Takaku, *Journal of Nuclear Science and Technology,* 2008, 161-165.

177   S. Misra and P. N. Froelich, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(11), 1524-1533.

178   K. F. Huang, C. F. You, Y. H. Liu, R. M. Wang, P. Y. Lin and C. H. Chung, *J. Anal. At. Spectrom.*, 2010, **25**(7), 1019-1024.

179   C. Chen and M. Sharma, *Analytical Chemistry,* 2009, **81**(13), 5400-5406.

180   H. Loudyi, K. Rifai, S. Laville, F. Vidal, M. Chaker and M. Sabsabi, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(10), 1421-1428.

181   Z. J. Chen, Y. Godwal, Y. Y. Tsui and R. Fedosejevs, *Applied Optics*, 2010, **49**(13), C87-C94.

182   M. Ezer, *International Journal of Environmental Analytical Chemistry*, 2010, **90**(9), 697-707.

183   N. Shokoufi, F. Shemirani and M. Shokoufi, *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy,* 2009, **74**(3), 761-766.

184   A. R. Kumar and P. Riyazuddin, *Microchemical Journal,* 2009, **93**(2), 236-241.

185   S. H. Lee, P. P. Povinec, J. Gastaud, J. J. La Rosa, E. Wyse and L. K. Fifield, *Journal of Radioanalytical and Nuclear Chemistry,* 2009, **282**(3), 831-835.

186   M. Filella, *Journal of Environmental Monitoring*, 2010, **12**(1), 90-109.

187   S. J. Ussher, I. Petrov, C. R. Quetel and P. J. Worsfold, *Environmental Chemistry*, 2010, **7**(2), 139-145.

188   K. Tirez, W. Brusten, D. Widory, E. Petelet, A. Bregnot, D. M. Xue, P. Boeckx and J. Bronders, *J. Anal. At. Spectrom.*, 2010, **25**(7), 964-974.

189   J. L. Tadeo, C. Sanchez-Brunete, B. Albero and A. I. Garcia-Valcarcel, *Journal of Chromatography A*, 2010, **1217**(16), 2415-2440.

190   A. Elik, *Asian Journal of Chemistry,* 2009, **21**(7), 5095-5103.

191   S. F. O. de Vallejuelo, A. Barrena, G. Arana, A. de Diego and J. M. Madariaga, *Talanta,* 2009, **80**(2), 434-439.

192   I. De La Calle, N. Cabaleiro, I. Lavilla and C. Bendicho, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(9), 874-883.

193   L. Bortolon and C. Gianello, *Revista Brasileira De Ciencia Do Solo*, 2010, **34**(1), 125-132.

194   J. L. Schroder, H. L. Zhang, J. R. Richards and M. E. Payton, *Journal of Aoac International,* 2009, **92**(4), 995-1008.

195   R. G. Garrett, G. E. M. Hall, J. E. Vaive and P. Pelchat, *Applied Geochemistry,* 2009, **24**(8), 1438-1453.

196   M. Rosende, E. Y. Savonina, P. S. Fedotov, M. Miro, V. Cerda and R. Wennrich, *Talanta,* 2009, **79**(4), 1081-1088.

197   R. Rubio, M. J. Ruiz-Chancho and J. F. Lopez-Sanchez, *Trac-Trends in Analytical Chemistry*, 2010, **29**(1), 53-69.

198   M. Giral, G. J. Zagury, L. Deschenes and J. P. Blouin, *Environmental Pollution*, 2010, **158**(5), 1890-1898.

199   M. M. Rahman, Z. L. Chen and R. Naidu, *Environmental Geochemistry and Health,* 2009, **31**, 93-102.

200   F. Rahman, Z. L. Chen and R. Naidu, *Environmental Geochemistry and Health,* 2009, **31**, 103-113.

201   L. Jedynak, J. Kowalska, M. Kossykowska and J. Golimowski, *Microchemical Journal*, 2010, **94**(2), 125-129.

202   P. Cuderman and V. Stibilj, *Analytical and Bioanalytical Chemistry*, 2010, **396**(4), 1433-1439.

203   T. H. Hansen, K. H. Laursen, D. P. Persson, P. Pedas, S. Husted and J. K. Schjoerring, *Plant Methods,* 2009, **5**, 11.

204   S. Spalla, C. Baffi, C. Barbante, C. Turretta, G. Cozzi, G. M. Beone and M. Bettinelli, *Rapid Communications in Mass Spectrometry,* 2009, **23**(20), 3285-3292.

205   M. Ghaedi, A. Shokrollahi, M. Montazerozohori, F. Marahel and M. Soylak, *Quimica Nova*, 2010, **33**(2), 404-410.

206   P. X. Baliza, L. S. G. Teixeira and V. A. Lemos, *Microchemical Journal,* 2009, **93**(2), 220-224.

207   M. Shamsipur, M. Ramezani and M. Sadeghi, *Microchimica Acta,* 2009, **166**(3-4), 235-242.

208   S. R. Oliveira, J. A. G. Neto, J. A. Nobrega and B. T. Jones, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2010, **65**(4), 316-320.

209   F. Vignola, D. L. G. Borges, A. J. Curtius, B. Welz and H. Becker-Ross, *Microchemical Journal*, 2010, **95**(2), 333-336.

210   I. M. Ditter, D. L. G. Borges, B. Welz, A. J. Curtius and H. Becker-Ross, *Microchimica Acta,* 2009, **167**(1-2), 21-26.

211   R. G. O. Araujo, B. Welz, F. Vignola and H. Becker-Ross, *Talanta,* 2009, **80**(2), 846-852.

212   F. D. Dias, L. S. Alves, W. N. L. dos Santos, J. M. David and S. L. C. Ferreira, *Analytical Letters,* 2009, **42**(14), 2206-2213.

213   M. A. Bezerra, J. T. Castro, R. C. Macedo and D. G. da Silva, *Analytica Chimica Acta*, 2010, **670**(1-2), 33-38.

214   P. Torok and M. Zemberyova, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2010, **65**(4), 291-296.

215   K. Fujita and T. Nakamura, *Bunseki Kagaku,* 2009, **58**(7), 609-615.

216   R. Dobrowolski, M. Otto and A. Adamczyk, *Microchimica Acta*, 2010, **168**(3-4), 355-362.

217   B. Ambrozini, V. R. A. Filho, S. R. Oliveira, L. V. S. Sacramento and J. A. G. Neto, *Food Chemistry,* 2009, **116**(4), 1024-1028.

218   R. A. Sanchez-Moreno, M. J. Gismera, M. T. Sevilla and J. R. Procopio, *Phytochemical Analysis*, 2010, **21**(4), 340-347.

219   M. Frankowski, A. Ziola-Frankowska and J. Siepak, *Microchemical Journal*, 2010, **95**(2), 366-372.

220   S. M. Macedo, R. M. de Jesus, K. S. Garcia, V. Hatje, A. F. D. Queiroz and S. L. C. Ferreira, *Talanta,* 2009, **80**(2), 974-979.

221   C. Waterlot and F. Douay, *Talanta,* 2009, **80**(2), 716-722.

222   A. Asfaw and G. Wibetoe, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(5), 363-368.

223   A. Detcheva, P. Barth and J. Hassler, *Analytical and Bioanalytical Chemistry,* 2009, **394**(5), 1485-1495.

224   M. Kumai, K. Nakayama, Y. Furusho, T. Yamamoto and Y. Takamura, *Bunseki Kagaku,* 2009, **58**(6), 561-567.

225   A. S. Cherevko and A. I. Syso, *Journal of Analytical Chemistry,* 2009, **64**(8), 806-814.

226 H. S. Ferreira, S. L. C. Ferreira, M. L. Cervera and M. de la Guardia, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(6), 597-600.

227 O. T. Butler, J. M. Cook, C. F. Harrington, S. J. Hill, J. Rieuwerts and D. L. Miles, *J. Anal. At. Spectrom.,* 2008, **23**(2), 249-286.

228 Z. Xing, J. Wang, S. C. Zhang and X. R. Zhang, *Talanta,* 2009, **80**(1), 139-142.

229 B. Kuermaiti, J. Wang, G. J. Han and Z. Xing, *Chinese Journal of Analytical Chemistry,* 2010, **38**(3), 357-361.

230 T. Frentiu, M. Ponta, M. Senila, A. I. Mihaltan, E. Darvasi, M. Frentiu and E. Cordos, *J. Anal. At. Spectrom.,* 2010, **25**(5), 739-742.

231 J. V. Cizdziel, C. Tolbert and G. Brown, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2010, **65**(2), 176-180.

232 K. H. Laursen, T. H. Hansen, D. P. Persson, J. K. Schjoerring and S. Husted, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(9), 1198-1207.

233 S. K. Sahoo, Y. Muramatsu, S. Yoshida, H. Matsuzaki and W. Ruhm, *Journal of Radiation Research,* 2009, **50**(4), 325-332.

234 Y. Luo, E. Dabek-Zlotorzynska, V. Celo, D. C. G. Muir and L. Yang, *Analytical Chemistry,* 2010, **82**(9), 3922-3928.

235 J. G. Wiederhold, C. J. Cramer, K. Daniel, I. Infante, B. Bourdon and R. Kretzschmar, *Environmental Science & Technology,* 2010, **44**(11), 4191-4197.

236 D. Pick, M. Leiterer and J. W. Einax, *Microchemical Journal,* 2010, **95**(2), 315-319.

237 G. H. Floor, M. Iglesias and G. Roman-Ross, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(7), 944-948.

238 F. G. Pinto, F. G. Lepri, T. D. Saint'Pierre, J. B. B. da Silva, L. M. Costa and A. J. Curtius, 2010, *Analytical Letters,* **43**(6), 949-959.

239 M. Garcia-Lopez, I. Rodriguez, R. Cela, K. K. Kroening and J. A. Caruso, *Talanta,* 2009, **79**(3), 824-829.

240 J. X. Qiao, X. L. Hou, P. Roos and M. Miro, *Analytical Chemistry,* 2009, **81**(19), 8185-8192.

241 D. P. Persson, T. H. Hansen, K. H. Laursen, J. K. Schjoerring and S. Husted, *Metallomics,* 2009, **1**(5), 418-426.

242 E. Lombi, K. G. Scheckel, J. Pallon, A. M. Carey, Y. G. Zhu and A. A. Meharg, *New Phytologist,* 2009, **184**(1), 193-201.

243 E. Peachey, K. Cook, A. Castles, C. Hopley and H. Goenaga-Infante, *Journal of Chromatography A,* 2009, **1216**(42), 7001-7006.

244 P. P. Povinec, A. E. Litherland and K. F. von Reden, *Radiocarbon,* 2009, **51**(1), 45-78.

245 E. Chamizo, M. C. Jimenez-Ramos, S. M. Enamorado, M. Garcia-Leon, R. Garcia-Tenorio, J. L. Mas, P. Masque, J. Merino and J. A. Sanchez-Cabeza, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms,* 2010, **268**(7-8), 1273-1276.

246 T. Bisinger, S. Hippler, R. Michel, L. Wacker and H. A. Synal, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms,* 2010, **268**(7-8), 1269-1272.

247 S. G. Tims, S. E. Everett, L. K. Fifield, G. J. Hancock and R. Bartley, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms,* 2010, **268**(7-8), 1150-1154.

248   S. G. Tims, S. M. Pan, R. Zhang, L. K. Fifield, Y. P. Wang and J. H. Gao, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 2010, **268**(7-8), 1155-1158.

249   M. E. Essington, G. V. Melnichenko, M. A. Stewart and R. A. Hull, *Soil Science Society of America Journal,* 2009, **73**(5), 1469-1478.

250   A. M. Popov, F. Colao and R. Fantoni, *J. Anal. At. Spectrom.*, 2010, **25**(6), 837-848.

251   E. C. Ferreira, J. M. Anzano, D. Milori, E. J. Ferreira, R. J. Lasheras, B. Bonilla, B. Montull-Ibor, J. Casas and L. M. Neto, *Applied Spectroscopy,* 2009, **63**(9), 1081-1088.

252   J. H. Kwak, C. Lenth, C. Salb, E. J. Ko, K. W. Kim and K. Park, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(10), 1105-1110.

253   D. Santos, L. C. Nunes, L. C. Trevizan, Q. Godoi, F. O. Leme, J. W. B. Braga and F. J. Krug, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(10), 1073-1078.

254   S. Pandhija, N. K. Rai, A. K. Rai and S. N. Thakur, *Applied Physics B-Lasers and Optics*, 2010, **98**(1), 231-241.

255   R. C. Chinni, D. A. Cremers, L. J. Radziemski, M. Bostian and C. Navarro-Northrup, *Applied Spectroscopy,* 2009, **63**(11), 1238-1250.

256   Z. K. Zheng, X. H. Ma, H. F. Zhao, L. Yu, M. Zhang and Y. B. Liao, *Spectroscopy and Spectral Analysis,* 2009, **29**(12), 3383-3387.

257   J. S. Huang, Q. L. Chen and W. D. Zhao, *Spectroscopy and Spectral Analysis,* 2009, **29**(11), 3126-3129.

258   Y. Lu, J. L. Wu, Y. Li, J. J. Guo, K. Cheng, H. M. Hou and R. E. Zheng, *Spectroscopy and Spectral Analysis,* 2009, **29**(11), 3121-3125.

259   M. V. Belkov, V. S. Burakov, A. De Giacomo, V. V. Kiris, S. N. Raikov and N. V. Tarasenko, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(9), 899-904.

260   M. Z. Martin, N. Labbe, N. Andre, S. D. Wullschleger, R. D. Harris and M. H. Ebinger, *Soil Science Society of America Journal*, 2010, **74**(1), 87-93.

261   L. C. Nunes, G. A. da Silva, L. C. Trevizan, D. Santos, R. J. Poppi and F. J. Krug, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(6), 565-572.

262   J. W. B. Braga, L. C. Trevizan, L. C. Nunes, I. A. Rufini, D. Santos and F. J. Krug, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2010, **65**(1), 66-74.

263   W. Q. Lei, V. Motto-Ros, M. Boueri, Q. L. Ma, D. C. Zhang, L. J. Zheng, H. P. Zeng and J. Yu, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(9), 891-898.

264   M. Pouzar, T. Cernohorsky, M. Prusova, P. Prokopcakova and A. Krejcova, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(7), 953-957.

265   E. Lombi and J. Susini, *Plant and Soil,* 2009, **320**(1-2), 1-35.

266   J. Thieme, J. Sedlmair, S. C. Gleber, J. Prietzel, J. Coates, K. Eusterhues, G. Abbt-Braun and M. Salome, 2010, *Journal of Synchrotron Radiation*, **17**, 149-157.

267   K. Janssens, W. De Nolf, G. Van Der Snickt, L. Vincze, B. Vekemans, R. Terzano and F. E. Brenker, *Trac-Trends in Analytical Chemistry*, 2010, **29**(6), 464-478.

268   T. Radu and D. Diamond, *Journal of Hazardous Materials,* 2009, **171**(1-3), 1168-1171.

269   S. Pessanha, A. Guilherme and M. L. Carvalho, *Applied Physics a-Materials Science & Processing,* 2009, **97**(2), 497-505.

270   R. Siegele, A. G. Kachenko, M. Ionescu and D. D. Cohen, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms,* 2009, **267**(12-13), 2054-2059.

271   M. Bielewski, M. Eriksson, J. Himbert, M. Betti, F. Belloni and G. Falkenberg, *Journal of Radioanalytical and Nuclear Chemistry,* 2009, **282**(2), 355-359.

272   R. G. Haverkamp and A. T. Marshall, *Journal of Nanoparticle Research,* 2009, **11**(6), 1453-1463.

273   J. G. Parsons, M. L. Lopez, H. Castillo-Michel, J. R. Peralta-Videa and J. L. Gardea-Torresdey, *Applied Spectroscopy,* 2009, **63**(8), 961-970.

274   N. Estrade, J. Carignan, J. E. Sonke and O. F. X. Donard, *Geostandards and Geoanalytical Research,* 2010, **34**(1), 79-93.

275   R. Jakopic, S. Richter, H. Kuhn and Y. Aregbe, *J. Anal. At. Spectrom.,* 2010, **25**(6), 815-821.

276   D. De Muynck, G. Huelga-Suarez, L. Van Heghe, P. Degryse and F. Vanhaecke, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(11), 1498-1510.

277   K. L. Mandiwana and N. Panichev, *Journal of Hazardous Materials,* 2010, **178**(1-3), 1106-1108.

278   F. P. Andrade, C. C. Nascentes and L. M. Costa, *Journal of the Brazilian Chemical Society,* 2009, **20**(8), 1460-1466.

279   D. Citak and M. Tuzen, *Food and Chemical Toxicology,* **45**(5), 1399-1404.

280   S. G. Silva, P. V. Oliveira and F. R. P. Rocha, *Journal of the Brazilian Chemical Society,* **21**(2), 234-239.

281   V. A. Lemos and G. T. David, *Microchemical Journal,* 2010, **94**(1), 42-47.

282   S. G. Silva, P. V. Oliveira, J. A. Nobrega and F. R. P. Rocha, *Analytical Methods,* 2009, **1**(1), 68-70.

283   S. Saracoglu and M. Soylak, *Food and Chemical Toxicology,* 2010, **45**(5), 1328-1333.

284   O. D. Uluozlu, M. Tuzen and M. Soylak, *Food and Chemical Toxicology,* 2009, **47**(10), 2601-2605.

285   O. D. Uluozlu, M. Tuzen, D. Mendil, B. Kahveci and M. Soylak, *Journal of Hazardous Materials,* 2009, **172**(1), 395-399.

286   D. Citak, M. Tuzen and M. Soylak, *Journal of Hazardous Materials,* 2010, **173**(1-3), 773-777.

287   S. S. Bozkurt and M. Merdivan, *Environmental Monitoring and Assessment,* 2009, **158**(1-4), 15-21.

288   H. Ebrahimzadeh, N. Tavassoli, M. M. Amini, Y. Fazaeli and H. Abedi, *Talanta,* 2010, **81**(4-5), 1183-1188.

289   O. M. Kalfa, O. Yalcinkaya and A. R. Turker, *Journal of Hazardous Materials,* 2009, **166**(1), 455-461.

290   Y. K. Li, Y. Huang, Y. R. Xu, P. Fan, Q. F. Hu and G. Y. Yang, *Asian Journal of Chemistry,* 2009, **21**(7), 5319-5327.

291   B. Puzio, B. Mikula and B. Feist, *Journal of Analytical Chemistry,* 2009, **64**(8), 786-790.

292   B. Mikula, B. Puzio and B. Feist, *Microchimica Acta,* 2009, **166**(3-4), 337-341.

293   M. Ezoddin, F. Shemirani, K. Abdi, M. K. Saghezchi and M. R. Jamali, *Journal of Hazardous Materials*, **178**(1-3), 900-905.

294   M. Soylak and Y. E. Unsal, *Food and Chemical Toxicology*, 2010, **48**(6), 1511-1515.

295   F. A. Aydin and M. Soylak, 2010, *Journal of Hazardous Materials*, **173**(1-3), 669-674.

296   J. J. Guo, Q. D. Su and W. E. Gan, *Journal of the Chinese Chemical Society,* 2009, **56**(4), 763-770.

297   B. Anilan, T. Gedikbey and S. T. Akar, *Clean-Soil Air Water*, 2010, **38**(4), 344-352.

298   Y. H. Zhai, S. E. Duan, Q. He, X. H. Yang and Q. Han, *Microchimica Acta*, 2010, **169**(3-4), 353-360.

299   V. A. Lemos, C. G. Novaes and M. A. Bezerra, *Journal of Food Composition and Analysis,* 2009, **22**(4), 337-342.

300   H. Balcone-Boissard, A. Michel and B. Villemant, *Geostandards and Geoanalytical Research,* 2009, **33**(4), 477-485.

301   D. Savard, L. P. Bedard and S. J. Bames, *Geostandards and Geoanalytical Research,* 2009, **33**(2), 249-259.

302   A. Forrest, R. Kingsley and J. G. Schilling, *Geostandards and Geoanalytical Research,* 2009, **33**(2), 261-269.

303   M. G. Babechuk, B. S. Kamber, A. Greig, D. Canil and J. Kodolanyi, *Geochimica Et Cosmochimica Acta*, 2010, **74**(4), 1448-1470.

304   R. Kubota, *Geostandards and Geoanalytical Research,* 2009, **33**(2), 271-283.

305   X. H. Wang, Y. M. Wang, Y. S. Gao, Y. Y. Huang, Z. Y. Wang and X. F. Shi, *Geostandards and Geoanalytical Research,* 2009, **33**(3), 357-368.

306   J. S. Kane, B. Batjargal and D. Erdenetsetseg, *Geostandards and Geoanalytical Research,* 2009, **33**(3), 295-308.

307   Z. C. Hu, Y. S. Liu, M. Li, S. Gao and L. S. Zhao, *Geostandards and Geoanalytical Research,* 2009, **33**(3), 319-335.

308   F. E. Jenner, P. Holden, J. A. Mavrogenes, H. S. O'Neill and C. Allen, *Geostandards and Geoanalytical Research,* 2009, **33**(3), 309-317.

309   L. Strnad, V. Ettler, M. Mihaljevic, J. Hladil and V. Chrastny, *Geostandards and Geoanalytical Research,* 2009, **33**(3), 347-355.

310   E. V. Smirnova, B. Flem, E. A. Anchutina, I. N. Mysovskaya, V. I. Lozhkin and L. L. Petrov, *Geostandards and Geoanalytical Research*, 2010, **34**(1), 49-65.

311   M. Amini, A. Eisenhauer, F. Bohm, C. Holmden, K. Kreissig, F. Hauff and K. P. Jochum, *Geostandards and Geoanalytical Research,* 2009, **33**(2), 231-247.

312   H. J. Wen, J. Carignan, C. Cloquet, X. K. Zhu and Y. X. Zhang, *J. Anal. At. Spectrom.*, 2010, **25**(5), 716-721.

313   B. N. Nath, A. Makishima, J. Noordmann, R. Tanaka and E. Nakamura, *Geochemical Journal,* 2009, **43**(3), 207-216.

314   M. Humayun, F. A. Davis and M. M. Hirschmann, *J. Anal. At. Spectrom.*, 2010, **25**(7), 998-1005.

315   J. Regnery, B. Stoll and K. P. Jochum, *Geostandards and Geoanalytical Research*, 2010, **34**(1), 19-38.

316   N. J. Cook, C. L. Ciobanu, A. Pring, W. Skinner, M. Shimizu, L. Danyushevsky, B. Saini-Eidukat and F. Melcher, *Geochimica Et Cosmochimica Acta,* 2009, **73**(16), 4761-4791.

317 M. Gaboardi and M. Humayun, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(9), 1188-1197.

318 J. Mikova, J. Kosler, H. P. Longerich, M. Wiedenbeck and J. M. Hanchar, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(9), 1244-1252.

319 A. M. Seydoux-Guillaume, R. Freydier, F. Poitrasson, F. X. d'Abzac, R. Wirth and L. Datas, *European Journal of Mineralogy*, 2010, **22**(2), 235-244.

320 F. Claverie, B. Fernandez, C. Pecheyran, J. Alexis and O. F. X. Donard, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(7), 891-902.

321 H. Lindner, D. Autrique, C. C. Garcia, K. Niemax and A. Bogaerts, *Analytical Chemistry,* 2009, **81**(11), 4241-4248.

322 G. Steinhoefel, I. Horn and F. von Blanckenburg, *Chemical Geology,* 2009, **268**(1-2), 67-73.

323 G. Steinhoefel, I. Horn and F. von Blanckenburg, *Geochimica Et Cosmochimica Acta,* 2009, **17**(18), 5343-5360.

324 M. Nishizawa, H. Yamamoto, Y. Ueno, S. Tsuruoka, T. Shibuya, Y. Sawaki, S. Yamamoto, Y. Kon, K. Kitajima, T. Komiya, S. Maruyama and T. Hirata, *Geochimica Et Cosmochimica Acta*, 2010, **74**(9), 2760-2778.

325 A. K. Souders and P. J. Sylvester, *J. Anal. At. Spectrom.*, 2010, **25**(7), 975-988.

326 J. M. Cottle, M. S. A. Horstwood and R. R. Parrish, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(10), 1355-1363.

327 C. Paton, J. D. Woodhead, J. C. Hellstrom, J. M. Hergt, A. Greig and R. Maas, *Geochemistry Geophysics Geosystems*, 2010, **11**, 36.

328 P. J. le Roux, *J. Anal. At. Spectrom.*, 2010, **25**(7), 1033-1038.

329 K. P. Jochum, B. Stoll, U. Weis, D. V. Kuzmin and A. V. Sobolev, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(9), 1237-1243.

330 J. Li, J. D. Lu, Z. X. Lin, S. S. Gong, C. L. Xie, L. Chang, L. F. Yang and P. Y. Li, *Optics and Laser Technology,* 2009, **41**(8), 907-913.

331 W. B. Yin, L. Zhang, L. Dong, W. G. Ma and S. T. Jia, *Applied Spectroscopy,* 2009, **63**(8), 865-872.

332 D. L. Death, A. P. Cunningham and L. J. Pollard, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(10), 1048-1058.

333 R. S. Harmon, J. Remus, N. J. McMillan, C. McManus, L. Collins, J. L. Gottfried, F. C. DeLucia and A. W. Miziolek, *Applied Geochemistry,* 2009, **24**(6), 1125-1141.

334 J. L. Gottfried, R. S. Harmon, F. C. De Lucia and A. W. Miziolek, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(10), 1009-1019.

335 D. C. Alvey, K. Morton, R. S. Harmon, J. L. Gottfried, J. J. Remus, L. M. Collins and M. A. Wise, *Applied Optics*, 2010, **49**(13), C168-C180.

336 S. L. C. Ferreira, M. Miro, E. G. P. da Silva, G. D. Matos, P. S. dos Reis, G. C. Brandao, W. N. L. dos Santos, A. T. Duarte, M. G. R. Vale and R. G. O. Araujo, *Applied Spectroscopy Reviews*, 2010, **45**(1), 44-62.

337 A. Takamasa and S. Nakai, *Geochemical Journal,* 2009, **43**(5), 389-394.

338 A. Makishima, R. Tanaka and E. Nakamura, *Analytical Sciences,* 2009, **25**(10), 1181-1187.

339 F. L. Pantuzzo, J. C. J. Silva and V. S. T. Ciminelli, *Journal of Hazardous Materials,* 2009, **168**(2-3), 1636-1638.

340 A. Ilander and A. Vaisanen, *Ultrasonics Sonochemistry,* 2009, **16**(6), 763-768.

341 S. Revillon and D. Hureau-Mazaudier, *Geostandards and Geoanalytical Research,* 2009, **33**(3), 397-413.

342   A. T. Townsend, I. Snape, A. S. Palmer and A. J. Seen, *Science of the Total Environment,* 2009, **408**(2), 382-389.

343   Y. L. Sun, Z. Y. Chu, M. Sun and X. P. Xia, *Applied Spectroscopy,* 2009, **63**(11), 1232-1237.

344   P. P. Khanna and N. S. Siddaiah, *Himalayan Geology*, **31**(1), 23-27.

345   L. Qi, M. F. Zhou, J. F. Gao and Z. Zhao, *J. Anal. At. Spectrom.*, 2010, **25**(4), 585-589.

346   S. S. Jibrin, C. Z. Huang, J. Li, N. Zhang and B. Hu, *Geostandards and Geoanalytical Research,* 2009, **33**(4), 469-476.

347   W. S. El-Naggar, T. A. Lasheen, E. A. Nouh and A. K. Ghonaim, *Central European Journal of Chemistry*, 2010, **8**(1), 34-40.

348   M. C. Saha and T. Bhattacharyya, *Atomic Spectroscopy,* 2009, **30**(5), 170-177.

349   M. Y. Xi, R. Liu, P. Wu, K. L. Xu, X. D. Hou and Y. Lv, *Microchemical Journal*, 2010, **95**(2), 320-325.

350   C. A. Zhang, Y. Li, P. Wu, Y. Jiang, Q. Liu and X. P. Yan, *Analytica Chimica Acta,* 2009, **650**(1), 59-64.

351   A. R. Kumar and P. Riyazuddin, *Trac-Trends in Analytical Chemistry*, 2010, **29**(2), 166-176.

352   R. C. Campos, R. A. Goncalves, G. R. Brandao, M. S. Azevedo, F. Oliveira and J. Wasserman, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(6), 506-512.

353   P. Petrova, S. Velichkov, N. Velitchkova, I. Havezov and N. Daskalova, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2010, **65**(2), 130-136.

354   V. G. Torgov, T. M. Korda, M. G. Demidova, E. A. Gus'kova and G. L. Bukhbinder, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(11), 1551-1557.

355   P. L. Mahanta, G. Chakrapani and R. Radhamani, *Atomic Spectroscopy*, 2010, **31**(1), 21-26.

356   W. D. Lopes, R. E. Santelli, E. P. Oliveira, M. D. B. de Carvalho and M. A. Bezerra, *Talanta,* 2009, **79**(5), 1276-1282.

357   K. L. Linge and K. E. Jarvis, *Geostandards and Geoanalytical Research,* 2009, **33**(4), 445-467.

358   M. Aramendia, M. Resano and F. Vanhaecke, *Analytica Chimica Acta,* 2009, **648**(1), 23-44.

359   B. S. Kamber, *Applied Geochemistry,* 2009, **24**(6), 1074-1086.

360   A. Makishima and E. Nakamura, *Geostandards and Geoanalytical Research,* 2009, **33**(3), 369-384.

361   M. Marelli, B. Giussani, I. Angelini, G. Artioli and S. Recchia, *J. Anal. At. Spectrom.*, 2010, **25**(6), 893-898.

362   R. Mathur, S. Titley, F. Barra, S. Brantley, M. Wilson, A. Phillips, F. Munizaga, V. Maksaev, J. Vervoort and G. Hart, *Journal of Geochemical Exploration,* 2009, **102**(1), 1-6.

363   B. Schneider, K. Kuiper, O. Postma and J. Wijbrans, *Quaternary Geochronology,* 2009, **4**(6), 508-516.

364   E. Douville, E. Salle, N. Frank, M. Eisele, E. Pons-Branchu and S. Ayrault, *Chemical Geology*, 2010, **272**(1-4), 1-11.

365   B. S. Kamber and A. H. Gladu, *Geostandards and Geoanalytical Research,* 2009, **33**(2), 169-181.

366   M. Godoy, J. M. Godoy, L. A. Roldao and L. Tauhata, *Journal of Environmental Radioactivity,* 2009, **100**(8), 613-625.

367 R. E. Martinelli, T. F. Hamilton, R. W. Williams and S. R. Kehl, *Journal of Radioanalytical and Nuclear Chemistry,* 2009, **282**(2), 343-347.

368 F. Vanhaecke, L. Balcaen and D. Malinovsky, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(7), 863-886.

369 L. Yang, *Mass Spectrometry Reviews,* 2009, **28**(6), 990-1011.

370 F. Huang, J. Glessner, A. Ianno, C. Lundstrom and Z. F. Zhang, *Chemical Geology,* 2009, **268**(1-2), 15-23.

371 F. Wombacher, A. Eisenhauer, A. Heuser and S. Weyer, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(5), 627-636.

372 N. Dauphas, A. Pourmand and F. Z. Teng, *Chemical Geology,* 2009, **267**(3-4), 175-184.

373 A. W. Needham, D. Porcelli and S. S. Russell, *Geochimica Et Cosmochimica Acta,* 2009, **73**(24), 7399-7413.

374 A. Makishima, A. Yamakawa, K. Yamashita and E. Nakamura, *Chemical Geology*, 2010, **274**(1-2), 82-86.

375 C. Fitoussi, B. Bourdon, T. Kleine, F. Oberli and B. C. Reynolds, *Earth and Planetary Science Letters,* 2009, **287**(1-2), 77-85.

376 S. van den Boorn, P. Z. Vroon and M. J. van Bergen, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(8), 1111-1114.

377 M. J. Pribil, R. B. Wanty, W. I. Ridley and D. M. Borrok, *Chemical Geology*, 2010, **272**(1-4), 49-54.

378 C. R. Pearce, A. S. Cohen and I. J. Parkinson, *Geostandards and Geoanalytical Research,* 2009, **33**(2), 219-229.

379 A. Poirier and R. Doucelance, *Geostandards and Geoanalytical Research,* 2009, **33**(2), 195-204.

380 Y. H. Yang, H. F. Zhang, Z. Y. Chu, L. W. Xie and F. Y. Wu, *International Journal of Mass Spectrometry*, 2010, **290**(2-3), 120-126.

381 Y. H. Yang, F. Y. Wu, L. W. Xie and Y. B. Zhang, *Analytical Letters*, 2010, **43**(1), 142-150.

382 H. D. Scher and M. L. Delaney, *Chemical Geology*, 2010, **266**(3-4), 329-338.

383 H. L. Yuan, S. Gao, C. L. Zong and M. N. Dai, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(11-12), 1228-1234.

384 I. Smet, D. De Muynck, F. Vanhaecke and M. Elburg, *J. Anal. At. Spectrom.*, 2010, **25**(7), 1025-1032.

385 A. Yamakawa, K. Yamashita, A. Makishima and E. Nakamura, *Analytical Chemistry,* 2009, **81**(23), 9787-9794.

386 A. D. Schmitt, S. J. G. Galer and W. Abouchami, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(8), 1079-1088.

387 A. D. Schmitt, S. Gangloff, F. Cobert, D. Lemarchand, P. Stille and F. Chabaux, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(8), 1089-1097.

388 J. H. Chen, D. A. Papanastassiou and G. J. Wasserburg, 2010, *Geochimica Et Cosmochimica Acta*, **74**(13), 3851-3862.

389 R. Andreasen and M. Sharma, *International Journal of Mass Spectrometry,* 2009, **285**(1-2), 49-57.

390 Z. Y. Chu, F. K. Chen, Y. H. Yang and J. H. Guo, *Journal of Analytical Atomic Spectrometry,* 2009, **24**(11), 1534-1544.

391 J. Sole, *Rapid Communications in Mass Spectrometry,* 2009, **23**(22), 3579-3590.

392 A. V. Ignatiev, T. A. Velivetskaya and S. Y. Budnitskiy, *Rapid Communications in Mass Spectrometry,* 2009, **23**(16), 2403-2410.

393   H. N. Qiu, J. R. Wijbrans, F. M. Brouwer, J. B. Yun, L. H. Zhao and Y. G. Xu, *Journal of Metamorphic Geology*, 2010, **28**(5), 477-487.

394   L. Zimmermann, P. Burnard, B. Marty and F. Gaboriaud, *Geostandards and Geoanalytical Research,* 2009, **33**(2), 183-194.

395   A. J. Cavosie, N. T. Kita and J. W. Valley, *American Mineralogist,* 2009, **94**(7), 926-934.

396   S. M. Gordon, M. Grove, D. L. Whitney, A. K. Schmitt and C. Teyssier, *Chemical Geology,* 2009, **262**(3-4), 186-201.

397   S. M. Gordon, M. Grove, D. L. Whitney, A. K. Schmitt and C. Teyssier, *Geology,* 2009, **37**(8), 735-738.

398   P. Holden, P. Lanc, T. R. Ireland, T. M. Harrison, J. J. Foster and Z. Bruce, *International Journal of Mass Spectrometry,* 2009, **286**(2-3), 53-63.

399   I. R. Fletcher, N. J. McNaughton, W. J. Davis and B. Rasmussen, *Chemical Geology*, 2010, **270**(1-4), 31-44.

400   R. A. Stern, S. Bodorkos, S. L. Kamo, A. H. Hickman and F. Corfu, *Geostandards and Geoanalytical Research,* 2009, **33**(2), 145-168.

401   M. Kikuchi and H. Hidaka, *Geosciences Journal,* 2009, **13**(3), 257-264.

402   M. Christl, C. Maden, P. W. Kubik, A. Muller, S. Ivy-Ochs, M. Suter and H. A. Synal, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 2010, **268**(7-8), 726-729.

403   J. Chmeleff, F. von Blanckenburg, K. Kossert and D. Jakob, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 2010, **268**(2), 192-199.

404   M. M. Goethals, R. Hetzel, S. Niedermann, H. Wittmann, C. R. Fenton, P. W. Kubik, M. Christl and F. von Blanckenburg, *Earth and Planetary Science Letters,* 2009, **284**(1-2), 187-198.

405   S. Merchel, L. Benedetti, D. L. Bourles, R. Braucher, A. Dewald, T. Faestermann, R. C. Finkel, G. Korschinek, J. Masarik, M. Poutivtsev, P. Rochette, G. Rugel and K. O. Zell, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 2010, **268**(7-8), 1179-1184.

406   L. Di Nicola, C. Schnabel, K. M. Wilcken and K. Gmeling, *Quaternary Geochronology,* 2009, **4**(6), 501-507.

407   K. Keil, R. Fitzgerald and K. F. J. Heinrich, *Microscopy and Microanalysis,* 2009, **15**(6), 476-483.

408   P. Zuzaan, N. Gansukh and D. Bolortuya, *X-Ray Spectrometry*, 2010, **39**(1), 52-56.

409   A. L. Finkelshtein and V. M. Chubarov, *X-Ray Spectrometry*, 2010, **39**(1), 17-21.

410   K. Tanaka, Y. Takahashi and H. Shimizu, *Geochemical Journal,* 2009, **43**(3), 143-149.

411   Z. Szikszai, I. Uzonyi, A. Z. Kiss, G. A. Sziki, D. Vantelon and P. Rozsa, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms,* 2009, **267**(12-13), 2229-2232.

412   M. A. Denecke, B. Brendebach, W. De Nolf, G. Falkenberg, K. Janssens and R. Simon, *Spectrochimica Acta Part B-Atomic Spectroscopy,* 2009, **64**(8), 791-795.