

## **Atomic spectrometry update. Environmental analysis**

Owen T. Butler,<sup>a\*</sup> Warren Cairns,<sup>b</sup> Jennifer M. Cook,<sup>c</sup> and Christine M Davidson.<sup>d</sup>

<sup>a</sup>Health and Safety Laboratory, Harpur Hill, Buxton, UK SK17 9JN

\*owen.butler@hsl.gov.uk

<sup>b</sup>CNR-IDPA, Universita Ca' Foscari, 30123 Venezia Italy

<sup>c</sup>British Geological Survey, Keyworth, Nottingham, UK NG12 5GG

<sup>d</sup>University of Strathclyde, Cathedral Street, Glasgow, UK G1 1XL

This is the twenty-fifth 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 2008 and August 2009. In the analysis of air, work is focused on the need to collect and characterise ultrafines; determination of elements such as Be, Hg and PGEs in air samples; application of SRXRF techniques and advances in the development of field deployable aerosol mass spectrometry systems. In the analysis of water, significant areas of activity currently focus on elemental speciation of As, Cr, Hg and Sn. Work in increasing method sensitivities through the use of vapour generation and optimization of extraction and preconcentration procedures continues. The increased global awareness of the need to monitor levels of potentially toxic elements (PTE) in soils is desirable and this is reflected in a growing body of published literature from authors in the Middle East, Asia and Africa. However, a potential criticism of some studies is that they simply report the concentrations of analytes in particular soils or plants, without providing sufficient information on analytical quality control and with little assessment of their environmental significance, e.g. those levels that are a threat to human health. In the field of geological analysis, 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 in geochemical analysis. Feedback on this review is most welcome and the lead author can be contacted using the email address provided.

- 1 Air analysis
  - 1.1 Sampling techniques
  - 1.2 Laboratory based measurements
    - 1.2.1 Sample preparation
    - 1.2.2 AAS, AFS and ICP based measurement techniques
      - 1.2.2.1 Elemental analysis
      - 1.2.2.2 Isotopic analysis
    - 1.2.3 X-ray based measurement techniques
    - 1.2.4 Other measurement techniques
  - 1.3 Field and on-line measurements
    - 1.3.1 AFS and AES based measurement techniques
    - 1.3.2 X-ray based measurement techniques
    - 1.3.3 Mass spectrometry measurement techniques
    - 1.3.4 Other measurement techniques
- 2 Water analysis
  - 2.1 Sample preparation
    - 2.1.1 Sampling procedures
    - 2.1.2 Pre-concentration, extraction and separation procedures
  - 2.2 Speciation
  - 2.3 Instrumental analysis
    - 2.3.1 Atomic emission spectrometry
    - 2.3.2 Vapour generation methods
    - 2.3.3 X-ray fluorescence spectrometry
    - 2.3.4 Inductively coupled plasma mass spectrometry
    - 2.3.5 Laser induced breakdown spectroscopy
  - 2.4 Data quality and method standardisation
- 3 Analysis of soils, plants and related materials
  - 3.1 Sample preparation
    - 3.1.1 Sample dissolution and extraction
    - 3.1.2 Pre-concentration procedures
  - 3.2 Instrumental analysis
    - 3.2.1 Atomic absorption spectrometry
    - 3.2.2 Atomic emission spectrometry
    - 3.2.3 Atomic fluorescence spectrometry

3.2.4	Inductively coupled plasma mass spectrometry
3.2.4.1	Laser ablation ICP-MS
3.2.4.2	Solution based ICP-MS
3.2.5	Accelerator mass spectrometry
3.2.6	Laser-induced breakdown spectrometry
3.2.7	X-ray fluorescence spectrometry
3.3	Analytical quality control
4	Analysis of geological materials
4.1	Reference materials
4.2	Solid sample introduction
4.2.1	Laser ablation ICP-MS
4.2.2	Laser-induced breakdown spectroscopy
4.3	Sample treatment
4.3.1	Sample dissolution
4.3.2	Separation and preconcentration
4.3.3	Speciation studies
4.4	Instrumental analysis
4.4.1	Atomic absorption and atomic fluorescence spectrometry
4.4.2	Atomic emission spectrometry
4.4.3	Inductively coupled plasma mass spectrometry
4.4.4	Other mass spectrometric techniques
4.4.5	X-ray techniques
5	Glossary of terms
6	References

# 1 Air Analysis

This section highlights noteworthy areas of research and development in the analysis of aerosols, particulates and gases by atomic spectrometric techniques that have been published since the last Update<sup>1</sup>.

## 1.1 Sampling techniques

The need to collect sufficient sample for analysis over short time scales or to collect particulates over a wide particle size range has led to developments in *new air sampling systems*. Researchers in California<sup>2</sup> continue to develop their versatile aerosol concentration enrichment system coupled to an electrostatic collector that was reported last year<sup>1</sup>. In order to collect ambient particles for chemical and toxicological studies, modifications to the design involved separating the charging zone from the ionisation zone to minimise the potential for possible chemical reactions between sampled particles and ions generated in the corona region of the electrostatic precipitator (ESP). They were able to demonstrate high particle collection efficiency of greater than 90 % and, through developments of the ESP collection substrate, were able to demonstrate uniform particle deposition, a desirable feature for cellular exposure studies. In the United Kingdom, researchers have developed a sampler for the size-selective sampling of particles over a wide particle size range<sup>3</sup>. They used an elegant way of collecting particles over this wide range by employing a combination of a cascade impactor for larger particles,  $> 0.25 \mu\text{m}$ , and a diffusion collector to collect nanoparticles. A key development was the interface between these two units as their operating principles are different. A cascade impactor collects larger particles first and then particles of a smaller size in sequence, depending upon the number of

collection plates used. In contrast, a diffusion collector, here employing nylon nets with different fibre diameters and fibre densities, collects smaller particles first. Hence if there were not spacing between the particle cutoff sizes, it would present difficulties in the reconstruction of the particle size distribution of airborne material once sampled. An interface was successfully achieved resulting in a sampler that had 11 stages, 5 of which involved the diffusion particle collector, covering the range 20  $\mu\text{m}$  down to 1 nm. The sampler was tested by sampling in a lead crystal glass manufacturing plant where, depending upon the work activity involved, the fraction of lead nanoparticles was found to vary between 10 and 70 % of the total lead that was collected and quantified.

Monitoring workers' exposure to airborne particles in the workplace through the use of *personal samplers*, i.e. samplers mounted on people, is an ongoing activity in many countries. The increased awareness that exposure to engineered nanoparticles should be measured and the need to enhance the wearability of such samplers has led to a number of innovations in this field. Liden and Surakka<sup>4</sup> have developed a miniaturised personal sampler for measuring occupational exposure to airborne particles in the breathing zone. Existing samplers tend to be large, so it is impractical to mount them on the face close to the mouth and nasal area. Hence they tend to be mounted on the torso and it has been shown that, owing to spatial variations in airborne particle concentrations around a working individual, sampling away from the direct breathing zone may not be fully representative. This mini-sampler is to be worn mounted on a headset, modified from a professional microphone headset, which can, for example, be mounted behind a welder's face shield. The authors suggest that, whilst this design is most applicable for fume sampling, it may be used for personal sampling of the inhalable fraction of other workplace aerosols, provided that the

majority of the particles are below 20  $\mu\text{m}$ . In a similar vein, Hsiao *et al.*<sup>5</sup> have published work that they have carried out on the development of two mini-cyclones as size selective inlets for a mini condensation particle counter for personal use. These devices were designed to remove particles larger than 1.0 and 0.3  $\mu\text{m}$  at a nominal flow rate of 0.3  $\text{l min}^{-1}$ . Their physical size is smaller than a US quarter coin! Work carried out will also be applicable in designing inlets for other miniaturised filter based samplers. A caveat about miniaturisation is that the physical quantities of dust that can be sampled will be reduced, resulting in the need to apply sensitive analytical techniques such as ICP-MS for, say, elemental analysis. The importance of minimising laboratory and field blank contamination will also need to be addressed.

*Comparative performance testing of samplers* is welcome, not only given the plethora of designs available, but also because preferences exist in different countries for particular models. It is useful to compare the performance of personal samplers against their equivalent area or static sampler, as there is a growing interest in monitoring an individual's exposure to particulates, particularly in the urban environment, where historically airborne particulate concentration data have been derived from static samplers. Mjestic and coworkers<sup>6</sup> compared the size-resolved trace metal concentrations derived from using three commercially  $\text{PM}_{2.5}$  personal samplers with those obtained from a reference  $\text{PM}_{2.5}$  static sampler. Co-location studies were carried out at two urban sites. Data obtained, following analysis of filters samples for a range of metals by ICP-MS, demonstrated that there were reproducible biases for the three designs relative to the reference static sampler. Park *et al.*<sup>7</sup> evaluated the performance of six different aerosol samplers by challenging them with polydisperse fly ash spheres in a controlled test chamber. Likewise, Reynolds and coworkers<sup>8</sup> compared the performance of personal samplers for

inhalable and respirable particulates using agriculturally derived dusts in both field and wind tunnel settings.

The assessment of *sampling artefacts, inefficiencies and losses* is an ongoing field of interest. Kumar *et al.*<sup>9</sup> considered the losses of ultrafine aerosol (< 100 nm) in long sampling lines and found that losses for particles < 20 nm were important and needed to be considered if sampling lines longer than 1 m were required. Timko *et al.*<sup>10</sup> reported evidence that carbon-impregnated conductive silicone tubing used in many aerosol sampling systems can introduce two types of experimental artefacts, namely the absorption of CO<sub>2</sub> that requires a number of minutes to reach equilibrium and emission from the tubing of organic contaminants containing siloxanes that are adsorbed onto collected particles travelling through the sampler. Italian researchers looked at both organic and inorganic sampling artefacts associated with sampling the ambient PM<sub>2.5</sub> mass fraction of suspended airborne particles<sup>11</sup>. The focus was on the positive biases caused by co-sampled organic vapours obtained when attempting organic carbon measurements, and negative or positive biases in aerosol nitrate measurements due to evaporative losses of ammonium nitrate or adsorption of nitric acid on the filter. In an attempt to address sampling issues with semi-volatile aerosols, Kim and Raynor<sup>12</sup> have taken a new approach by using a modified virtual impactor design to collect and separate vapour and particulate phases. In a conventional virtual impactor, designed to preconcentrate particles, typically 90 % of the air sampled moves towards the so called ‘major flow’ direction which is perpendicular to the air nozzle, while the remaining 10 % of air goes towards the ‘minor flow’ direction, which is parallel to the air nozzle, i.e. particles are preconcentrated into this minor flow. In their modified design, this flow ratio is reversed, i.e. vapour is drawn off using 10 % of the airflow. Whilst sampling on

filters predominates, Miljevic *et al.*<sup>13</sup> have re-examined the efficiency of impingers with fritted nozzle tips for collection of ultrafines and near ultrafine particles (< 220 nm) and determined collection efficiencies higher than those reported with previous impinger designs. It was noted that this collection efficiency is a combination of the filter-like performance of the fritted nozzle tip, which has a porous glass frit, and the impingement of particles in the liquid collection solution.

*Deposition sampling* continues to be used as a means of assessing atmospheric particulate pollution. Austrian researchers<sup>14</sup> assessed the extent of pollution from pyrotechnics and fireworks by measuring the extent of contamination of pristine snow by barium nitrate. They found levels some 600-fold greater than those in uncontaminated snow. Researchers have compared the lead pollution records in a number of *Sphagnum* peat bogs in both the British Isles and the Czech Republic with known lead emission rates<sup>15</sup>. They suggest that regional differences in deposition rates of gasoline-derived Pb in the U.K. warrants further study. French researchers, based in Grenoble, studied the dust deposit on the bark surfaces of trees<sup>16</sup>. Using SEM-EDAX and ICP-MS techniques they determined that a typical deposit was ~ 80 % organic in nature, ~ 10 % was of geological origin, which they termed the atmospheric geogenic fraction, and ~ 10 % of an elemental anthropogenic origin, which they termed the anthropogenic atmospheric elements fraction (AAEF). Using the SEM-EDAX data of the deposit and that of the average local soil composition, they suggest that it is possible to estimate the elemental content of AAEF directly attributable to anthropogenic activities. In this way, they found that most of the Cd, Cu, Pb, Sb, Sn and Zn was in this AAEF fraction.



## 1.2 Laboratory based measurements

### 1.2.1 Sample preparation

*Risk of contamination* during air sampling, handling of filters and their subsequent analysis is a recurring theme. Upadhyay and coworkers<sup>17</sup> have evaluated the trace metal content of commonly used cellulose (CL), polypropylene (PP), polyurethane (PUF) and quartz fiber (QF) collection substrates (filters). Test samples were digested in a mixture of HNO<sub>3</sub>/HCl/H<sub>2</sub>O<sub>2</sub>/HF in a closed vessel with microwave assistance and analysed by ICP-MS. Results showed that the elemental concentrations of blanks were in the order QF > PUF > PP > CL with a high variability for PUF and PP blanks from different sample lots relative to QF. Quartz filter substrates showed consistent blanks from lot to lot with a reproducibility of better than 10 % for the majority of elements. The results suggest that QF filters used in a high volume air sampler can be a suitable filter for trace elements. Sampling for organic moieties is also possible, hence the potential for reducing sampling logistics. Italian researchers have optimised an ICP-MS based procedure for the determination of 20 elements in airborne particulate matter and paid close attention to understanding and minimising contributions from blanks<sup>18</sup>.

*Fraction studies of airborne particles involving sequential extraction procedures* continue to attract interest. Berlinger *et al.*<sup>19</sup> have undertaken a critical evaluation of sequential leaching procedures for the determination of Mn and Ni species in welding fume. The well-known Zatka sequential extraction, developed for Ni species in refinery dusts, and a four-step sequential extraction procedure for Mn were applied. Although these procedures worked well on simulated dust mixtures using stoichiometrically pure metal salts, the authors concluded that such operationally defined leaching procedures have major limitations in the analysis of

‘real-world’ complex dust mixtures found in an industrial setting. They recommend that complimentary analytical techniques such as XPS, XRD and TEM-EDX be used to decipher results from such extraction studies.

Maxwell and coworkers<sup>20</sup> have developed a *sample clean up procedure* involving ion exchange resins to remove co-existing metallic species that can potentially cause spectral interferences in the determination of Be by ICP-AES in workplace dusts. Further work on the measurement of beryllium is discussed below.

## **1.2.2 AAS, AFS and ICP based measurement techniques**

### **1.2.2.1 Elemental analysis**

Atomic spectrometric methods such as AAS and ICP are now well established for the measurement of elemental species in airborne particulate matter collected using filtration sampling. Whilst AAS and ICP-AES continue to be used for the analysis of samples derived from the atmosphere, particularly in developing nations, elsewhere, *ICP-MS* is now starting to dominate this measurement arena. Presented here is a cross section of published papers where the benefits of multi-elemental trace analysis by ICP-MS are apparent. Lamaison *et al.*<sup>21</sup> used a DRC equipped ICP-MS to determine key elements, such as As, Cr, Ni and V, that can be subject to isobaric interferences. Ammonia was used as the reaction gas and NIST SRM 1648 urban particulate matter was analysed to validate the procedure. Method detection limits were 450, 1210, 780 and 26 ng/L for As, Cr, Ni and V respectively. Grotti *et al.*<sup>22</sup> have developed a sensitive method for the determination of ultra trace elements deposited in snow samples using QICP-MS. Following a preconcentration step involving evaporation, samples were injected into the plasma *via* a PFA micronebuliser coupled to a total consumption sample introduction system. Polyatomic interferences were removed by ammonia gas in the DRC. Limits of detection were in the range 0.02 – 0.45 pg g<sup>-1</sup>,

allowing the determination of Cd, Co, Cr, Cu, Fe, Mn, Pb, V and Zn in Antarctic snow samples. Moreno and coworkers<sup>23</sup> identified atmospheric pollution events from oil refineries through the specific use of La/Ce and La/Sm elemental ratios in digested air filter samples. Zeolitic catalytic convertors used in this industry can be highly enriched in REE. For example, a spent convertor sample recently submitted for analysis in this author's laboratory was found to contain ~ 3 % (m/m) La in the powdered sample. Hu *et al.*<sup>24</sup> present a comprehensive set of trace element emissions measured from state-of-the-art retrofits for heavy duty diesel vehicles and compared these to a baseline of a vehicle without a retrofit. The control technologies tested consisted of combinations of diesel oxidation catalysts (DOC), diesel particulate filters (DPF) and selective catalytic reduction (SCR) designed to reduce particulate matter and NO<sub>x</sub> emissions from diesel engines. Test vehicles were exercised on a heavy-duty chassis dynamometer to replicate driving conditions. Tailpipe emissions were sampled onto Teflon filters and subjected to a closed vessel, microwave-assisted digestion procedure involving an *aqua regia*/HF mixture. The water-soluble fraction was also determined by leaching filters in distilled water for 6 hours. A suite of 49 major and trace elements were quantified using HR ICP-MS. It was found that a DPF significantly reduced the emissions of trace elements by some 85% as compared to baseline. Total trace elements as a percentage of particulate matter from the retrofitted vehicles were comparable to the baseline vehicle, implying that the reduction in trace metals was in concert with the reduction of particulate matter. It was noted that the zeolite-based SCR system showed a higher water soluble fraction of the emissions of most metals than did the vanadium-based SCR system. There was considerable release of V and Ti, presumably from the SCR wash coating, and further work is planned to elucidate the oxidation state of the emitted V species.

*ICP-MS as an elemental detector as part of a hyphenated analytical system*

also continues to attract attention. Gligorovski *et al.*<sup>25</sup> used a LA-ICP-MS approach in conjunction with an image analysis system to interrogate size-segregated atmospheric particles collected with cascade impactors. The authors suggest that the whole impaction spot requires mapping because artifacts generated by impactors can lead to distorted impaction spots, i.e. the presence of halos or satellite spots. Researchers at the University of Pau determined new volatile Se and Te species in fermentation gases produced by composting duck manure<sup>26</sup>. Fermentation gases were sampled using Tedlar™ gas bags, preconcentrated in a cryogenic trap and analysed using a GC-ICP-MS system. Instrument calibration was performed using a mixer system that allowed the simultaneous addition of nebulised liquid standards. The authors suggest that this approach, although semi-quantitative in nature with an estimated error of  $\pm 30\%$ , was sufficient for this exercise. The absolute detection limits ranged between 0.006 pg for Bi species and 4.0 pg for Se species. Corresponding relative detection limits range from 1.2 pg m<sup>-3</sup> to 799 pg m<sup>-3</sup> for a 5 l compost gas sample. Gilfedder and coworkers<sup>27</sup> determined iodine species in rain, snow and aqueous leaches of airborne particulate, using an IC-ICP-MS system. They showed that soluble organically bound iodine was the dominant fraction with minor components of iodide and iodate species.

Specific elements continue to attract the interest of researchers. Human exposure to *Be-containing aerosols* can result in Be sensitisation, a cell-mediated immune response. Hence the current 8-hour time-weighted occupational exposure limit value in many countries, currently at 2 µg m<sup>-3</sup>, will in time reduce to 20 - 200 ng m<sup>-3</sup>. Consequently, attention is now being focused on measurement surveys to ascertain whether workplaces, in particular non-nuclear industries that handle Be-containing materials, can meet these possible new limit values. A French study,

conducted between 2004 and 2006, collected both air filter samples and surface swab samples from 95 work premises for subsequent analysis by ETAAS and ICP-AES<sup>28</sup>. It was found that some 15 % of air measurements exceed the current  $2 \mu\text{g m}^{-3}$  exposure limit value. Work activities within foundries and in aluminium production were the major culprits. Exposure levels in other metalwork activities were lower but still some 30 % of air measurements exceeded the revised ACGIH recommended  $50 \text{ ng m}^{-3}$  limit value. Surface swab samples were also analysed and it was noted that the average Be value exceeded the  $3 \mu\text{g per } 100 \text{ cm}^{-2}$  threshold value recommended by the US Department of Energy. Other researchers have examined surface levels of Be in a military ammunition plant<sup>29</sup> and Be levels in CAISiFrit, a recycled product produced from spent pot lining used in the aluminium smelting industry<sup>30</sup>.

There is ongoing interest in measuring *mercury as a global pollutant*. Pirrone *et al.*<sup>31</sup> set out future challenges in our understanding of atmospheric cycling of this element. Analytically they suggest that knowing the precise chemical composition of reactive oxidised gas phase mercury species would be useful for understanding atmospheric chemical interactions. Canadian researchers have carried out kinetic and product studies of the reaction of gaseous mercury with molecular iodine, atomic iodine and iodine oxide radicals at tropospheric pressure within a reaction chamber<sup>32</sup>. Reaction products were analysed in the gas phase and from deposits found on the walls of the chamber. Analytical techniques used included CVAFS, chemical and electron impact mass spectrometry, GC-MS, MALDI-TOF and HRTEM equipped with an energy dispersive spectrometer. The major reaction products identified were  $\text{HgI}_2$ ,  $\text{HgO}$  and  $\text{HgIO}$  or  $\text{HgOI}$ . Glenz and coworkers<sup>33</sup> investigated the appropriateness of packing materials in preventing the release of mercury vapour from broken fluorescent lamps. They concluded that a double-boxed package incorporating

a laminated foil bag was required to prevent fugitive emissions. Most of the synthetic gypsum generated from wet flue gas desulphurisation (FSD) scrubbers is currently being used for plasterboard production. Oxidised mercury species can be trapped in such scrubbers when utilised on coal fired power stations. American researchers have undertaken a feasibility study of identifying mercury species within FSD gypsum and plasterboard products using a solid sampling thermal desorption method<sup>34</sup>. Another American group has investigated the release potential of gaseous mercury from aerated concrete that had been cured in controlled laboratory experiments<sup>35</sup>. The concrete contained waste by-products such as coal fly ash or coal fly ash and powdered activated carbon. Mercury emitted from such experiments was sampled onto iodated carbon traps and subsequently analysed using CVAFS. The mercury flux from exposed concrete surfaces to free air ranged from 0.77 to 11.1 ng m<sup>-2</sup> hr<sup>-1</sup> although it was calculated that less than 0.02 % of the total quantity of mercury within the solid material was released. Coal fired power stations dominate in China and consequently a number of studies of environmental mercury, involving laboratory based AAS/AFS techniques, have been published, including the determination of total and methyl mercury in wet deposition fluxes<sup>36</sup> and mercury in size-fractionated particles in urban air<sup>37</sup>. Studies involving real time *in situ* measurements from around the globe are reviewed below.

Interest in the *release of PGEs into the wider environment from automobiles* equipped with catalytic convertors continues. Researchers based in Rome have undertaken a study to determine the exposure of the city's tram drivers by mounting a static sampler system on their vehicles<sup>38</sup>. Mean values determined in TSP/PM<sub>10</sub>/PM<sub>2.5</sub> particles were 82/58/15 pg m<sup>-3</sup> for Pd, 20/14/9 pg m<sup>-3</sup> for Pt and 4/3/2 pg m<sup>-3</sup> for Rh. The authors suggest that, whilst the levels are 8 – 11 orders of magnitude below

values thought to cause effects on workers handling such elements in an occupational setting, they nevertheless suggest that periodic monitoring in the future would be sensible. In 2004 and 2005 Chinese researchers recorded levels of platinum in Shanghai air<sup>39</sup>. They found average levels in PM<sub>10</sub> particles of  $1.69 \pm 0.93 \text{ pg m}^{-3}$  in the centre of the city and an urban background value of  $0.54 \pm 0.03 \text{ pg m}^{-3}$ . These levels are lower than those recorded elsewhere in Western urban environments, suggesting a lag time in the availability of catalytically equipped cars. Spanish researchers have developed an isotope dilution procedure to internally correct the HfO isobaric interference on Pt<sup>40</sup>.

In this review period, a number of papers on *trends in elemental species in airborne particulate matter* have been published. These include: a seasonal variability study between 1999 and 2003 of crustal and marine trace elements in the aerosol at the Neaumayer research station in the Antarctica<sup>41</sup>; a 25-year record of atmospheric trace metal concentrations from the Norwegian Birkenes research station<sup>42</sup>; a 5-year study from 2001 of trace metals collected in aerosol samples in Beijing<sup>43</sup>; a study conducted between 1994 and 2007 to determine the Pd content in road tunnel dust samples<sup>44</sup>; and a long-term (1974 – 2000) trend of Hg in Arctic air<sup>45</sup>.

#### **1.2.2.2 Isotopic analysis**

Interest in using isotopic analysis for atmospheric tracer studies continues and involves the investigation of different elemental species. *Lead isotopic analysis* can be a very efficient tool for tracing the sources of local and global pollution. A review (159 references) of lead isotopes in environmental sciences focussing on the use of ICP-MS has been published<sup>46</sup>. Deposition repositories, as an historical archive of global lead fallout, continue to attract attention, including the analysis of samples from corals<sup>47</sup>, tree-bark pockets<sup>48</sup> and sediment profiles from a salt marsh<sup>49</sup>.

Ketterer and Szechenyi<sup>50</sup> present a review (182 references) on the determination of *plutonium and uranium* by ICP-MS, including the use of SF-ICP-MS to monitor  $^{240}\text{Pu} / ^{239}\text{Pu}$  ratios in fall-out particles from thermonuclear testing events. The isotopic composition of single particles containing U and Pu, arising from nuclear safeguard activities, has been measured by both ICP-MS and TIMS<sup>51</sup>. Particles were initially deposited on carbon planchets, for examination by SEM-EDX, and then transferred to a silicon wafer and subsequently dissolved in acid. The results obtained by both techniques for CRMs showed good agreement with the certified values within the expected uncertainty. Chinese researchers have undertaken a study on the analysis of the isotopic ratio of U-bearing particles in swipe samples by fission-track-TIMS (FT-TIMS)<sup>52</sup>. In summary, uranium-bearing particles in the samples were located using a FT procedure. Optical microscopy was used to aid the transfer of the particle to a Re filament for TIMS analysis. Hungarian researchers describe the application of a LA-SF-ICP-MS procedure for the isotopic analysis of individual UOX particles<sup>53</sup>. The methodology was deemed suitable for measuring  $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{236}\text{U}$  and  $^{238}\text{U}$  in single actinide particles with lateral dimensions down to 10  $\mu\text{m}$ . Measurement precision was improved using a slow ablation rate and by obtaining several replicate spectra from the same particle. High mass resolution ( $R = 4000$ ) was required in some cases to avoid spectral interferences. A multinational team has estimated the total global fallout of  $^{236}\text{U}$  on Earth as  $\sim 900\text{kg}$ <sup>54</sup>. The  $^{236}\text{U}$  fallout was deduced from measurements of  $^{236}\text{U}$ ,  $^{239+240}\text{Pu}$  and  $^{137}\text{Cs}$  in surface soils which are influenced solely by global fallout. Concentrations of  $^{239+240}\text{Pu}$  and  $^{238}\text{U}$  were determined by alpha spectrometry, while the  $^{236}\text{U} / ^{238}\text{U}$  ratio was measured using AMS. Consistent  $^{236}\text{U} / ^{239}\text{Pu}$  ratios of between 0.212 and 0.253 were determined, allowing this global fallout figure to be calculated.



*Isotopic ratios of Fe<sup>55</sup> and Zn<sup>56-58</sup> in airborne particulate* have been reported in aerosols collected downwind of metallurgical processes, leading to the suggestion that these isotope systems could be used as a new means of tracing air pollutant sources.

Szidat<sup>59</sup> has published a review(33 references) of recent developments in *radiocarbon analysis* of carbonaceous aerosols. Behrens and co-workers have developed a GC combustion IRMS system for the high precision measurement of delta <sup>13</sup>C in atmospheric methane extracted from ice core samples<sup>60</sup>. Swiss researchers optimised an automated gas sampling and IRMS system for air analysis<sup>61</sup>. Tuzson *et al.*<sup>62</sup> describe a compact and cryogen-free, quantum cascade, laser-based absorption spectrometer designed for *in situ*, continuous and high precision isotope ratio measurements of atmospheric CO<sub>2</sub>.

### **1.2.3 X-ray based measurement techniques**

Lippmann<sup>63</sup> suggests that *semi-continuous atmospheric monitoring* data, with at least a 4-hour resolution, is required to understand more fully the impact on human health. Instrumentation that can provide this information has been available for a number of years for gaseous species. Likewise, (near) real-time instrumentation, as reported in this review over the last few years and further on is this particular review, for ionic and carbon species such as nitrates, sulphates and elemental/organic carbon is now becoming available. However, the determination of mass concentrations of trace elements in ambient air, with a time resolution of better than one day remains somewhat elusive. It is therefore encouraging to see further developments in the *rotating DRUM impactor sampler-SRXRF approach*<sup>64</sup>. Size-segregated airborne particles are collected onto a rotating polypropylene film, which is advanced on any hourly basis, to provide high temporal resolution. As the total aerosol mass collected

in one hour is around 10 µg, experimental detection limits in the low ng range are thus required to measure the resultant trace metal content. This could be achieved only with a SRXRF approach and it was found that more commonly available laboratory-based XRF techniques were not sensitivity enough.

*Synchrotron radiation TXRF and XANES techniques* are an exciting development for the characterisation and speciation of airborne particles. Fittschen *et al.*<sup>65</sup> characterised size-segregated aerosol samples collected in Hamburg with a Berner impactor and determined that 20 minutes of sampling time was sufficient to collect sample material for the elemental determination of most metals. Subsequent SR-XANES analysis showed that Fe(III) species predominated in all the particle size fractions. In a similar fashion, Groma and coworkers<sup>66</sup>, this time using a May cascade impactor, determined ultra trace levels of metals at pg m<sup>-3</sup> at the Ferihegy airport in Budapest. They conclude that such is the sensitivity of this approach that it is possible to match the time scale of sampling to the time scale of the emission event under investigation. Aeolian mineral dust archived in ice cores represents a time capsule for assessing historic environmental and climatic changes. Here the identification of the dust mineralogy can play a key role. A European research group has presented the first preliminary SR-XANES experiments on mineral dust extracted from Alpine and Antarctic ice cores[99/100]. Results show that it was possible to examine the iron inclusion mineral fraction on insoluble dust in the 1 – 10 µg mass range.

Japanese researchers have employed an in-air µ-PIXE system to assess the content and spatial distribution of asbestos and other metals in lung tissues *in vitro*<sup>68</sup>. Traditionally it has been an onerous task examining lung tissue sections for evidence of asbestos, as samples have to be plasma ashed and mounted for electron microscopic analysis. The novel system could identify the location of asbestos bodies

from the Fe, Mg and Si signatures. It was noted that the Fe and Si contents were higher in lungs with asbestosis than in lungs without asbestosis. Researchers at the ion beam facility at Surrey University in the UK concluded that PIXE analysis aided the conventional SEM-EDX analysis of gunshot residues (GSR). Complementary information was obtained on trace elements that were undetectable by the SEM technique, thus strengthening the discrimination between different types of GSR<sup>69</sup>.

Characterisation of *individual airborne particles* using x-ray techniques continues to be a fertile area for research. Asian research groups<sup>70-71</sup> have used x-ray microprobe techniques to characterise single particles collected during Asian dust storm events. In particular, Ma and Kim<sup>70</sup> compared filter packs, a low pressure Andersen impactor and a micro-orifice uniform deposit impactor (MOUDI) to ascertain their performance as potential samplers for discrete particles. They found that the MOUDI allowed more particle mass to be collected without overloading the collection substrate, since it could rotate and present a large surface area for deposition. However, this MOUDI sampler, like the other samplers investigated, produced particle clusters and it was found that the microprobe analysis is restricted to individual particles deposited at edges of spots.

X-ray techniques are providing useful in the interrogation of *nuclear derived particles* as part of safeguard programs. IAEA researchers are using SEM-EDX to interrogate particles obtained via swabs for verification purposes<sup>72</sup>. Particle manipulation and relocation procedures have been developed so that surface morphological, elemental, isotopic and depth profiling information can be obtained using a combination of analytical techniques including SIMS and focused ion beam etching techniques. European researchers have undertaken solid state speciation and ascertained the potential bioavailability of depleted uranium (DU) particles recovered

from Kosovo and Kuwait<sup>73</sup>. A combination of synchrotron-based radiation techniques such as  $\mu$ -XRF,  $\mu$ -XRD and  $\mu$ -XANES were used and it is interesting to note that most of the DU particles dissolved in dilute HCl after one week of immersion, thus indicating that a majority of such DU material could be considered bioaccessible.

*X-ray powder diffraction* is a suitable method for identifying and quantifying airborne particulate matter containing crystalline phases. Bye *et al.*<sup>74</sup> have developed a procedure for examining airborne respirable non-fibrous  $\alpha$ -silicon carbide (SiC). Instrument calibration standards were prepared from respirable grade SiC powder suspensions in an ethanol/water mixture, which were filtered through polycarbonate filters. Absorption corrections were obtained with the polycarbonate filter placed above a silver filter in the goniometer. A calibration range of 100 – 1000  $\mu\text{g}$  per filter was produced and the calculated instrument detection limit was 12  $\mu\text{g}$  per filter. In a subsequent survey of Norwegian factories making SiC, airborne levels of between 12 and 890  $\mu\text{g m}^{-3}$  were found, which can be benchmarked against a limit value suggested by ACGIH of 3000  $\mu\text{g m}^{-3}$ . Stacey and co-workers<sup>75</sup> have undertaken an international comparison to determine the crystallinity of calibrant dust materials used in the analysis of  $\alpha$  quartz. Each of the collaborators was asked to prepare and analyse filter standards in the range 1.5 – 6 mg per filter prepared from various in-house calibrant dust materials. Following absorption and drift correction, they were then asked to compare the value for the slope of the relationship between instrumental response and filter mass loading for each powder to that obtained using the standards prepared using the benchmark NIST SRM 1878a. In this way it was possible to cross certify these various in-house materials for crystallinity. Readers wishing to learn more about developments in X-ray techniques should consult our companion Update on X-ray fluorescence spectrometry<sup>76</sup>.

#### **1.2.4 Other measurement techniques**

*Combustion techniques* are often used to determine carbon species in airborne particulate matter, typically operationally defined as organic and elemental carbon species. However, carbonate-derived carbon can be an important fraction of atmospheric particles, particularly where specific sources such as construction dust are present. Jankowski and co-workers have developed an operationally defined thermal program to quantify this carbonate-carbon fraction (CC) in air filter samples<sup>77</sup>. In their proposed method, pre-treatment of the filter by heating to 460 °C for 60 minutes is used to remove both OC and EC and thus the resultant total carbon measurement equates to the carbonate-carbon fraction. Measurements conducted on urban air filter samples compared favourably with carbonate-carbon values derived via calculation from an ionic mass balance, i.e. cations and anions determined on these filters by IC. The authors suggest that it is now possible to measure CC, OC and EC with a total carbon analyzer using a three-step procedure. Watson and co-workers assessed sampling artifacts arising from adsorption of semi-volatile organic vapours onto filters. These can be major causes of uncertainty in OC and EC measurements<sup>78</sup>. A US-Swiss consortium evaluated the OC extractability from three model particulate matrices: wood smoke, diesel exhaust and urban particulate matter<sup>79</sup>. They compared fractionation by hot pressurized water and sequential organic solvent Soxhlet extraction and evaluated these extraction efficiencies using thermal optical transmittance (TOT), reflectance and total organic carbon analysis. They found that comparable OC yields were obtained with both extraction procedures accounting for some 45 – 60 % of OC as determined by TOT. These studies suggest that a significant portion of OC can remain unextractable.

### 1.3 Field and on-line measurements

#### 1.3.1 AES and AFS based measurement techniques

Park *et al.*<sup>80</sup> have developed a *LIBS* system with a sheath air focusing system for the qualitative analysis of fine and ultrafine metal aerosols. However it was found that performance was limited for particles below 100 nm in size due to the weak intensity of emitted light. Therefore the system was modified to preconcentrate particles by including an aerodynamic lens focusing system and a particle collection substrate. They found that it was then possible to detect Cu particles, ~ 60 nm in size, after preconcentration for 5 minutes onto this collection substrate. The system was then subjected to a multi-metal test aerosol generated from an atomised ICP-MS grade multi-element solution. They observed that the LIBS response increased with increasing the collection time, i.e. response was proportional to the mass of each metal collected. It was noted however that the sensitivity of LIBS response to different masses varied from element to element due to changes in local plasma conditions such as plasma temperature, electron density and extent of ionization. More extensive research on matrix effects are planned and such knowledge would be required to enable the development of quantitative analytical procedures.

As reported last year<sup>1</sup>, *real-time in situ measurements of mercury in the atmosphere* continue to be reported. Swedish researchers have reported data from a field study around Göteborg in 2005 using a Tekhran™ mercury speciation analyser<sup>81</sup>. Results show that the average concentrations for gaseous elemental mercury (GEM), reactive gaseous mercury (RGM), particulate bound mercury (Hg<sub>p</sub>) and total gaseous mercury (TGM) were  $1.96 \pm 0.38 \text{ ng m}^{-3}$ ,  $2.53 \pm 4.09 \text{ pg m}^{-3}$ ,  $12.50 \pm 5.88 \text{ pg m}^{-3}$  and  $1.63 \pm 0.19 \text{ ng m}^{-3}$  respectively. In a similar study conducted also in 2005 using the same instrumentation, Korean researchers measured average concentrations of  $3.22 \pm 2.10 \text{ ng m}^{-3}$ ,  $27.2 \pm 10.3 \text{ pg m}^{-3}$  and  $23.9 \pm 19.6 \text{ pg m}^{-3}$  for

TGM, RGM and Hg<sub>p</sub> respectively<sup>82</sup>. A joint US-Japanese research group has published data obtained during a sampling campaign in 2004 at the Cape Hedo Observatory on Okinawa Island downwind of Asian sources<sup>83</sup>. They recorded average concentrations of  $2.04 \pm 0.38 \text{ ng m}^{-3}$ ,  $4.5 \pm 5.4 \text{ pg m}^{-3}$  and  $3.0 \pm 2.5 \text{ pg m}^{-3}$  for GEM, RGM and Hg<sub>p</sub> respectively. American researchers at the Storm Peak Laboratory high in the Colorado Rocky Mountains recorded an average GEM value of  $1.51 \pm 0.12 \text{ ng m}^{-3}$  during a sampling campaign between October 2006 and May 2007<sup>84</sup>. Another American research group recorded an average TGM value of  $1.4 \pm 0.2 \text{ ng m}^{-3}$  from a sampling campaign in northern Wisconsin during 2002-2004<sup>85</sup>. These geographically dispersed studies demonstrate the uniformity of background levels of mercury in the atmosphere.

The *Tekhran*<sup>TM</sup> AFS instrument used in the above studies is typically calibrated at relatively high mass loadings, i.e. more than 100 times the instrumental detection limit, using an onboard permeation calibration system. Swartzendruber et al.<sup>86</sup> concluded that this instrument's default peak integration algorithm should be modified if sub-optimal sample loading is undertaken, i.e. < 10-15 pg per analytical cycle. Alternatively, the full fluorescence peak can be recorded and processed off-line using procedures that they claim can improve precision and thus reduce the detection limit achievable.

### **1.3.2 X-ray based measurement techniques**

*Field deployable XRF instruments* combined with air samplers to provide near real time *in situ* measurement capability are being commercially developed, but published work has focused on the use and validation of hand held portable XRF systems. Researchers at NIOSH in the United States<sup>87</sup>, building upon work reviewed in previous Updates, have assessed the potential of a radio-isotope source instrument to

measure elements commonly encountered in workplace air that may be collected on air filters, namely Cr, Cu, Fe, Mn, Ni, Pb and Zn. The evaluation included an assessment of LoD as a function of analysis time and as a function of filter type. The authors also assessed the uniformity of instrumental response to selected elements across the surface of the instrument's 10 x 20 mm probe window by measuring 2-mm square pieces of Cu, Fe, Ni and Pb at different locations under the x-ray beam. They conclude that, in light of previously published work and this beam uniformity study, consideration needs to be given to the type of air sampler employed, as the dust deposition pattern on the filter will vary from design to design. This author concurs with this assessment and advocates the use and preparation of XRF calibrant filter standards specific to the air sampler design in question. The potential to undertake field-based XRF analysis of filters using the mini-sampler design reviewed in section 1.1 is of particular interest.

### **1.3.3 Mass spectrometry measurement techniques**

The use of *ATOFMS* presents an opportunity to understand the sources of atmospheric metals from point source emitters impacting receptor sites through the integration of meteorological data and fast time-resolved single particle characterisation. British researchers studied the size distribution and the elemental composition of airborne particles in the vicinity of a large integrated steelworks<sup>88</sup>. Measurements with *ATOFMS* showed six particle classes associated with differing processes within this steel mill. Activities that contributed most particles included iron making, steel/coke making and the rolling mills. A *MOUDI* sampler was co-located with the *ATOFMS* to provide time-integrated particle size analysis. Extraction, digestion and analysis of the Teflon filter substrates by IC and ICP-MS techniques provided particle size analysis on a species by species basis. In a similar vein, US researchers used



A TOFMS to estimate the contribution of point sources to an industrially impacted location<sup>89</sup>. They suggest that information derived from wind direction and particle composition can potentially be used to validate point source emissions inventories or to locate previously unidentified sources impacting such receptor sites. The authors evaluated the relationship between ATOFMS data and atmospheric concentrations by comparing 24-hour integrated peak areas for metal ions of interest with 24-hour integrated elemental concentrations obtained from XRF analysis of filter samples from co-located air samplers. For certain elements, a good correlation was found, but this was less obvious for other elements where the authors noted isobaric interferences with ATOFMS or where there are sensitivity issues with XRF analysis. The comparisons support a semi-quantitative relationship between integrated ATOFMS signal and ambient air concentrations. The authors conclude that this measurement approach has some advantages over more conventional statistically based source apportionment analyses, including eliminating the need for *a priori* knowledge concerning point sources. However, it is acknowledged that the development of higher resolution single particle mass spectrometers is required to reduce the impact of troublesome isobaric interferences.

Development work to *improve time of flight mass spectrometer capabilities* is ongoing. Wu and co-workers have characterised the volatile fraction of laboratory generated aerosol particles by coupling a thermodenuder to a mass spectrometer<sup>90</sup>. However, they noted a need to be careful in the interpretation of volatility measurements because some molecular structures may change after being heated. Kamphus *et al.*<sup>91</sup> compared the performance of two different aerodynamic lenses capable of focusing particles with diameters ranging from 80 – 800 nm and 300 – 3000 nm respectively. Matthew *et al.*<sup>92</sup> studied sampling efficiency as a function of

particle phase type using laboratory generated aerosols. They noted higher sampling efficiencies for liquid particles and liquid coated particles compared to solid particles. This they attributed to the fact that wet or coated particles tended to stick upon impact with the vaporiser/ioniser element within the mass spectrometer, while a significant fraction of solid particles bounced upon impact and were lost prior to the vaporisation/ionisation and detection steps.

Swedish researchers have refined the design of their aerosol mass spectrometer design<sup>93</sup>. The instrument employs an aerodynamic inlet system for efficient sampling of particles into a vacuum. Particles impact on a hot platinum surface and are ionised. This Pt surface has a box-like design that limits problems associated with particle bounce effects and incomplete ionisation. The main difference between this new instrument and the original design is that the quadrupole mass spectrometer previously used has now been replaced by a TOFMS. This change makes it possible to obtain a complete spectrum for each detected particle instead of just one pre-selected ion mass when using the earlier quadrupole design. The instrument is capable of detecting and recording complete alkali mass spectra for individual nanometer-size aerosol particles in the range 50 – 500 nm. The authors see the potential for this instrument in aerosol research where some of the major types of atmospheric particles such as sea salt particles, mineral dusts and particles emitted from biomass burning have an appreciable alkali content.

American researchers have developed a new aircraft compatible single particle mass spectrometer - SPLAT II - that provides significantly improved performance over an earlier design<sup>94</sup>. An aerodynamic lens system is used to form a very narrow particle beam, with low divergence, thus enabling the efficient transport of particles into the instrument. Once the particles pass this inlet and two skimmers, they enter the

high vacuum area where their presence is detected by light scattering. Two optical detection stages using Nd:YAG lasers operating at 532 nm are employed. Spherical particles in the size range 125 – 600 nm can be detected with 100% efficiency. Detection efficiencies dropped for particles outside this range. For example, efficiencies dropped to ~ 20% at a nominal 1000 nm particle size and to ~ 40% at a nominal 100 nm particle size, and to ~ 1.5% at a nominal 70 nm particle size. The detection probability of asymmetrical particles was only ~3 times lower than spherical particles of the same size. The time for particles to transverse these two optical detection stages can be measured using timing gates and hence their velocity determined. Using this information, a particle vacuum aerodynamic diameter can be calculated. This detection system is also used to trigger the two-step, twin laser process to generate ions. An IR laser is used to evaporate the particle and a selectable time-delayed UV laser pulse is used to ionise the particles. The instrument is able to characterise the composition of particles containing both semivolatile and non-volatile compounds and could typically size ~ 500 particles and record up to 100 individual particle mass spectra per second.

#### **1.3.4 Other measurement techniques**

The *in situ semi-continuous measurement of the ionic composition of particles* using a particle into liquid sampler coupled to ion chromatography, described in detail in previous Updates, has now been employed by American researchers at several rural locations in the United States<sup>95</sup>. Comparison of such measurements conducted at 15 minute intervals with parallel traditional 24-hour integrated denuder/filter pack measurements by laboratory-based IC analysis revealed generally good agreement between the two techniques. The slopes (field v laboratory analysis) of zero intercept best fit lines for summed data from all the sampling locations were 0.97, 0.95 and 1.02 for ammonium, nitrate and sulphate ions with  $r^2$  values of 0.92, 0.96 and 0.98

respectively. Linear regression slopes for individual sampling sites ranged from 0.80 – 0.96 for ammonium ion measurements, 0.87 – 0.95 for nitrate ion measurements and 0.94 – 1.08 for sulphate ion measurements. Measurements of ammonium ion *in situ* were however typically 4 – 20 % lower than laboratory-derived results. This was attributed to difficulties in measuring ammonium ion concentrations approaching instrumental detection limits that were found at many of the rural sites, as well as suspected loss through ammonium volatilisation in the on-line system.

Laboratory-based *thermal combustion techniques* are commonly used to measure carbon species in airborne particulate matter. In recent years, semi-continuous field-based systems have been deployed in a number of countries. Bauer *et al.*<sup>96</sup> undertook a comparative analysis of two Sunset OC/EC analysers co-deployed in the field and suggested modifications that could improve reproducibility between instruments. Grover and co-workers modified a Sunset analyser to include a dual-oven mode so that semi-volatile OC, non-volatile OC and EC could be measured<sup>97</sup>.

Understanding the *role and mechanisms of halogen species in atmospheric chemical pathways*, in particular their role in the depletion of the ozone layer, requires highly time-resolved and sensitive field instruments. Mahajan *et al.*<sup>98</sup> describe the use of long path Differential Optical Absorption Spectrometry for the determination of BrO species at ppt levels at the marine boundary layer. Bale and co-workers have developed an ultra-sensitive UV resonance fluorescence system to determine iodine species in the marine boundary layer<sup>99</sup>. It is anticipated that future Updates will see a greater use of such sensitive, field-deployable instruments and the commercialisation and miniaturisation of such systems.

## 2 Water Analysis

This section highlights new developments and improved analytical methods that use atomic spectroscopy for the determination of trace metal(loid)s and their associated elemental species in environmental water samples reported since the last Update<sup>1</sup>. As with previous Updates in this series, significant areas of activity currently focus on elemental speciation, vapour generation and preconcentration and extraction procedures.

### 2.1 Sample preparation

#### 2.1.1 Sampling procedures

A passive *sampler* for obtaining time-weighted average concentration data for organotin species in water has been described<sup>100</sup>. The receiving phase was an Empore<sup>TM</sup> C<sub>18</sub> disk overlaid with a cellulose acetate diffusion membrane. The organotin compounds were eluted from the C<sub>18</sub> disk with a 1 + 3 mixture of methanol and acetic acid using ultrasound, prior to ethylation and measurement by GC-ICP-MS or GC-FPD. Detection limits in water after the collection of 14-day samples ranged from 0.2 ng L<sup>-1</sup> to 7.5 ng L<sup>-1</sup>. De Baar and co-workers<sup>101</sup> have developed a new ultra clean sampler for seawater that can contain up to 24 GO FLO sample containers, making it 3 to 4 times faster to use than the standard GO FLO sampler system. Field trials showed that results comparable with literature values for Fe in the Atlantic were obtained with this sampling system.

#### 2.1.2 Preconcentration, extraction and separation procedures

Development of “novel” preconcentration and separation techniques continues to be a fertile source of articles. The main trends seem to be the trial of every existing and potential chelating agent for use with cloud point extraction, or as a chemical modifier

for chemical and or biological adsorbents, as well as the miniaturisation of existing techniques, such as single drop micro-extraction.

*Cloud point extraction* (CPE) as a technique has recently been reviewed<sup>102</sup> (178 references) for a period covering 2004 to 2008. The authors noted that it is an interesting analytical tool, as it is as effective as traditional liquid-liquid extraction techniques, but avoids the use of large amounts of toxic or flammable solvents. It has a wide range of applicability including preconcentration prior to speciation and can be used with most inorganic analysis techniques. Many studies seem to be aimed at the preconcentration of a single analyte, but occasionally methods are published for multi-elemental preconcentration<sup>103</sup> from matrices such as high salinity waters<sup>104</sup> prior to analysis using multi-elemental instruments. An interesting trend is the use of online CPE. For instance, a PTFE knotted coil reactor has been successfully used to retain the surfactant-rich phase prior to elution with acidified methanol and analysis by ETAAS<sup>105</sup>. Normally CPE is used for the preconcentration of cations, however it has been reported that mixed micelle CPE can be used for the preconcentration of anionic species<sup>106</sup>. Cetyltrimethylammonium bromide and Triton-X114 were successfully used to form extractable complexes of the anionic species of Au and Tl with microwave-assisted phase separation. Under the conditions reported, preconcentration factors of 125 for Au and 110 for Tl and LODs of 0.12 pg mL<sup>-1</sup> for Au and 0.02 pg mL<sup>-1</sup> for Tl were found.

The use of *solid phase extraction* for inorganic analysis has been reviewed<sup>107</sup> (30 references, in Japanese with English abstract). Multi-walled carbon nanotubes continue to be investigated as a potential stationary phase for preconcentration. Gold present in water has been shown to adsorb quantitatively on them in a pH range between 1 and 6 and can be eluted with a solution of 3% thiourea in 1 mol L<sup>-1</sup> HCl<sup>108</sup>.

Under the experimental conditions reported, a preconcentration factor of 75 was found resulting in a method LOD of  $0.15 \text{ pg L}^{-1}$  with FAAS detection. The use of gold coated silica for mercury preconcentration<sup>109</sup> has been described. Gold nanoparticles immobilised on a silica surface can trap various mercury species which are then thermally desorbed directly into an AFS cell for quantification. For a 7 mL sample a detection limit of  $180 \text{ pg L}^{-1}$  was achieved with a precision of  $<3.2 \%$  at the  $5 \text{ ng L}^{-1}$  concentration level and a spike recovery of  $> 90\%$ .

*Miniaturized preconcentration methods* have been reviewed<sup>110</sup> (99 references). This review reported on the adaptation of liquid-liquid extraction for use with small volumes of extractant solution and covered three main miniaturized methodologies: single drop microextraction, hollow fiber liquid phase microextraction and dispersive liquid-liquid microextraction. Single drop microextraction seems to be particularly suited to ETAAS and ETV-ICP-MS instrumentation and its use has been reported for the preconcentration of Co, Hg and Pb from water samples<sup>111</sup>. Head space single drop microextraction has been successfully used to preconcentrate the hydrides of As, Bi, Hg, Pb, Sb and Sn from aqueous solutions<sup>112</sup>. Hydride generation was carried out in a closed vial and the hydrides trapped in an aqueous single drop containing  $\text{Pd}^{\text{II}}$ ; enrichment factors of between 9 (for As) and 138 (for Bi) were obtained for a 210 s trapping time with consequent LODs ranging from  $0.2 \text{ } \mu\text{g L}^{-1}$  for As to  $0.01 \text{ } \mu\text{g L}^{-1}$  for Bi.

## **2.2 Speciation**

*The determination of arsenic species* has been dominated by non-chromatographic methods. Elci *et al.*<sup>113</sup> determined the inorganic species of As in water after selective co-precipitation of  $\text{As}^{\text{III}}$  with  $\text{Ce}^{\text{IV}}$  hydroxide followed by ETAAS determination, while a Japanese group<sup>114</sup> used lead pyrrolidinedithiocarbamate as a co-precipitation

collector for  $\text{As}^{\text{III}}$  followed by NAA determination of arsenic in hot spring and river waters. In both cases,  $\text{As}^{\text{V}}$  was assumed to be the difference between the total arsenic and the  $\text{As}^{\text{III}}$  concentration. The capacity of ADPC as a complexing agent for  $\text{As}^{\text{III}}$  at pH 3 – 4 was used by three Chinese groups. One group<sup>115</sup> retained the  $\text{As}^{\text{III}}$ -ADPC complexes on a micro-column packed with carbon nanofibers prior to ICP-MS detection. The second group<sup>116</sup> used hollow fiber liquid phase micro-extraction followed by ETAAS detection to determine total and  $\text{As}^{\text{III}}$  concentrations. The third group<sup>117</sup> retained the  $\text{As}^{\text{III}}$ -ADPC complex on an octadecyl immobilised silica mini-column and  $\text{As}^{\text{V}}$  on an anion exchange resin mini-column with HG-AFS detection of As after species elution. Campillo *et al.*<sup>118</sup> have described the use of GC-AES for the determination of dimethylarsinic acid (DMA), monomethylarsonic acid (MMA) and inorganic arsenic in sea water. The arsenic species were derivatized using methyl thioglycolate. This is a reducing agent so all the inorganic As is reduced to  $\text{As}^{\text{III}}$ . The derivatized As species were extracted into cyclohexane and injected in splitless mode onto a low polarity HP-5 capillary column. The LODs varied from 0.05 ng mL<sup>-1</sup> for DMA to 0.8 ng mL<sup>-1</sup> for inorganic arsenic.

*The speciation of chromium in water* continues to be of interest. The methods published in this review period are dominated by the use of micro-columns packed with chemical adsorbents<sup>119-121</sup>, biological adsorbents<sup>122-123</sup> or natural fibres<sup>124</sup>. Chen *et al.*<sup>125</sup> investigated the use of carbon nano-fibres as a solid phase for a micro-column coupled to ICP-MS. They found that  $\text{Cr}^{\text{III}}$  was selectively adsorbed between pH 3.25 and 4.0 and could be eluted with 1.0 mol L<sup>-1</sup> nitric acid. A preconcentration factor of 100 was achieved resulting in LODs of 0.015 ng mL<sup>-1</sup> for  $\text{Cr}^{\text{III}}$  and 0.033 ng mL<sup>-1</sup> for  $\text{Cr}^{\text{VI}}$ . Ma and Tanner<sup>126</sup> determined  $\text{Cr}^{\text{III}}$  and  $\text{Cr}^{\text{VI}}$  in water by isotope dilution using an ICP-MS instrument fitted with a reaction cell. They co-precipitated  $\text{Cr}^{\text{III}}$  with  $\text{Fe}^{\text{III}}$



hydroxide and obtained the total Cr concentration by the subsequent addition to the sample of Fe<sup>II</sup> hydroxide, which reduces the Cr<sup>VI</sup> *in situ* to Cr<sup>III</sup> and the Fe<sup>III</sup> hydroxide formed in the redox reaction precipitates the Cr<sup>III</sup> thus formed. Spectroscopic interferences were best removed using ammonia as the reaction gas. The inter-conversion from Cr<sup>III</sup> to Cr<sup>VI</sup> species varied between 5.9 to 9.3% and the reverse conversion (Cr<sup>VI</sup> to Cr<sup>III</sup>) was between 0.9 and 1.9%. The method LODs were 0.4 µg L<sup>-1</sup> for Cr<sup>III</sup> and 0.04 µg L<sup>-1</sup> for Cr<sup>VI</sup>.

*The determination of vanadium species in water*<sup>127</sup> has been achieved by complexing with EDTA the cationic and anionic tetravalent and pentavalent species, which were subsequently separated on a short anion exchange column in less than 6 mins using 4 mM carbonate buffer doped with 5 mM sodium EDTA as a mobile phase. Pre-column complexation prevented species inter-conversion on contact with air; recoveries ranged from 98-103% and the repeatability was 5.5% for V<sup>IV</sup> and 1.4% for V<sup>V</sup>. The LODs were 0.16 mg L<sup>-1</sup> for V<sup>IV</sup> and 0.025 mg L<sup>-1</sup> for V<sup>V</sup>. Chloride interferences were resolved chromatographically and V<sup>V</sup> was found to be the dominant species in mineral water bottled in PET. A Chinese group<sup>128</sup> determined vanadium species in seawater by solid phase extraction at pH 4.5 on a Chelex 100 microcolumn followed by sequential elution of V<sup>V</sup> with 0.1 M ammonium hydroxide and elution of V<sup>IV</sup> with 0.2 N perchloric acid. Recovery was > 92% from synthetic seawater spiked with 40 nM of the V species, with detection limits of 0.5 nM for each species. Analysis of estuarine water from China showed that the dominant chemical form was V<sup>V</sup> with V<sup>IV</sup> levels changing seasonally.

*The analysis of tin and its species in natural waters* continues to be of great interest. Xiao *et al.*<sup>129</sup> preconcentrated Sn species after derivatisation with sodium tetraethylborate using headspace single drop microextraction prior to GC-ICP-MS

detection of MBT, DBT and TBT in seawater; the LODs for each species were 1.4, 1.8 and 0.8 ng L<sup>-1</sup> respectively. Concentrations in Chinese seawater were found to be 31 ng L<sup>-1</sup> for MBT, 79 ng L<sup>-1</sup> for DBT and 32 ng L<sup>-1</sup> for TBT. Another Chinese group<sup>130</sup> successfully determined MMT, DMT and TMT in seawater using coupled HPLC-HG-ICP-MS. Tin species were separated by reversed phase HPLC, and potassium borohydride and acetic acid were used to generate the hydrides. Detection limits of 0.27, 0.09 and 0.04 ng L<sup>-1</sup> were found for MMT, DMT and TMT respectively; the precision at a concentration of 10 ng L<sup>-1</sup> was < 1.4% for each species. Species recovery from seawater ranged between 95 and 107% and the MMT and DMT species were detected in unspiked seawater in the range 1.0-1.5 ng L<sup>-1</sup> for MMT and 0.3-0.6 ng L<sup>-1</sup> for DMT. Solid phase micro-extraction (SPME) has successfully been coupled to HPLC-ICP-MS for the determination of TBT, TPhT, TMT and TPrT in water samples<sup>131</sup>. The organometallic species were extracted onto a coated fibre and desorbed in static mode in the SPME-HPLC interface. The organotin compounds were separated isocratically using a water-acetonitrile-acetic acid mobile phase. Detection limits were between 6 and 185 ng L<sup>-1</sup> and the method was successfully applied to the determination of these species in freshwaters and seawater taken from leisure ports.

Because of *the high toxicity of mercury and its organometallic species*, preconcentration techniques continue to be developed for their determination at natural concentrations. A timely review (44 references) on the preconcentration techniques currently used contains recommendations for the most appropriate *in situ* sampling methods<sup>132</sup>. Ito *et al.*<sup>133</sup> have successfully combined *in situ* propylation of mercury species with stir bar sorptive extraction and thermal desorption GC-MS detection. Detection limits of < 0.2 ng mL<sup>-1</sup> were achieved for EtHg, MeHg, DEtHg

and iHg with spike recoveries of 93-131%. The detection limits are not yet sufficient for the analysis of natural waters, but the method appears to be promising. Methyl mercury, PhHg and iHg species have been determined at trace levels after preconcentration using CPE<sup>134</sup>. The target mercury species were transformed into hydrophobic chelates by reaction with sodium diethyldithiocarbamate and subsequently extracted into a surfactant-rich phase of Triton X-114 at 40 °C. It was found that EtHg partially decomposed during this process, but the other species appeared to be stable. After extraction, the species were separated on a reversed phase HPLC column with detection by ICP-MS. At a concentration of 0.5 ng mL<sup>-1</sup> the precision was found to vary between 2.3 and 5.3% depending on the species being detected, with LODs in the range 6 – 13 ng L<sup>-1</sup>. Methyl mercury concentrations have been successfully determined in lake water using species-specific isotope dilution with purge and trap GC-ICP-MS<sup>135</sup>. An instrumental LOD of 0.06 pg L<sup>-1</sup> was sufficient to determine MeHg in lake water where it is typically present at concentrations of < 0.04 ng L<sup>-1</sup>. The use of isotope dilution allowed artifactual inorganic mercury methylation to be monitored during the analytical procedure; it was found to be minor.

*Total, labile and inert fractions of silver* have been determined in seawater<sup>136</sup> using batch adsorption on Chelex 100 resin. Total Ag was determined directly by ICP-MS and the complexation mechanisms of Ag were investigated using the Gibbs-Donnan model.

The *free aluminium ion in ground water* has been separated from its fluoride complexes using HPLC prior to FAAS detection<sup>137</sup>. The separation was achieved in less than 8 mins on an IonPac CS5A column using ammonium chloride buffered at pH 3 as the mobile phase.

The *behaviour of Gd chelates* during sewage treatment has been investigated<sup>138</sup>. Because they are widely used in magnetic resonance imaging and known to have varying toxicities, they were determined in waste waters from hospitals. The Gd chelates were separated using a hydrophobic interaction chromatography column (HILIC) with subsequent ICP-MS detection. The macrocyclic, non-ionic compounds were found to be the most abundant in the environment.

A method for the *determination of the redox species of molybdenum in seawater* has been developed<sup>139</sup> in which Mo<sup>V</sup> is retained as its tartrate complex on XAD 7HP resin after pH adjustment of a 60 mL sample to pH 7. The water collected after retention is treated with 0.5 mL of 10 % (v/v) SnCl<sub>2</sub> to reduce the Mo<sup>VI</sup> present in solution to Mo<sup>V</sup>, which is then complexed and selectively retained on the column. The Mo<sup>V</sup> complexes are quantitatively eluted with eight 5 mL elutions with a 1 N acidic acetone solution (1 + 9 nitric acid in acetone) which are combined, dried and re-dissolved in 5 mL of 0.1 N nitric acid. Detection is by ETAAS; the LOD for each species was *ca.* 0.2 nM and the analytical precision 10%.

*Multi-elemental speciation methods* are important because they allow us to obtain more information from a limited quantity of sample. After separating by HPLC the redox species of Cr and Se with an anion exchange column, Bednar *et al.*<sup>140</sup> compared the performance of an ICP-MS instrument with a standard configuration to that of an instrument with a reaction cell. At least for these species, there was no gain in using the instrument equipped with a cell. Both instruments achieved LODs of 1 µg L<sup>-1</sup> per species and were capable of determining the redox species of Cr and Se in surface water, ground water and municipal tap waters. Further speciation developments can be found in our companion Update<sup>141</sup>.

## 2.3 Instrumental analysis

### 2.3.1 Atomic emission spectroscopy

Since the last Update<sup>1</sup>, the focus on atomic emission spectroscopy has been to improve the detection limits by using either preconcentration methods or vapour generation methods, the latter will be dealt with in Section 2.3.2. *Cloud point extraction* has been successfully used to simultaneously preconcentrate Hf<sup>V</sup>, Th<sup>IV</sup>, U<sup>IV</sup> and Zr<sup>IV</sup> ions in aqueous samples<sup>142</sup>. Complexes were formed with dibenzoylmethane and Triton X-114 was used as the surfactant. The subsequent surfactant-rich phase was diluted with a 1 + 4 (v/v) mixture of methanol and 1 M HNO<sub>3</sub> before ICP-AES determination of the analytes. Enrichment factors of between 37 to 43 were obtained resulting in LODs between 0.1 and 1.0 µg L<sup>-1</sup>.

A Chinese group<sup>143</sup> has separated the *inorganic species of arsenic and selenium* on an alkyl silica microcolumn modified with cetyltrimethylammonium bromide. The species were selectively retained by adjusting the pH of the samples to pH 2.0 or 6.5 and eluting them with 1.0 M HNO<sub>3</sub>. Detection limits were 0.15 µg L<sup>-1</sup> for As<sup>V</sup> and 0.1 µg L<sup>-1</sup> for Se<sup>VI</sup>.

### 2.3.2 Vapour generation methods

Vapour generation continues to be important for improving the sensitivity of atomic spectrometric methods for the hydride forming elements. A new type of hydride atomizer for use with AFS, *the flame in-gas shield miniature hydride atomizer*, has been developed<sup>144</sup>. It compared favourably with the standard miniature diffusion flame hydride atomizer, resulting in sensitivity improvements of up to 5.5 times.

*Hydride trapping prior to atomisation* continues to be investigated. An iridium-coated tungsten coil was used to trap antimony hydride<sup>145</sup>, a gold-coated tungsten coil was successfully applied to selenium hydride trapping<sup>146</sup> and an iridium-coated graphite tube was used to trap cadmium vapour prior to AAS determination<sup>147</sup>.

Trivalent antimony and total Sb have been determined by *head space single drop microextraction* with *in situ* hydride generation followed by ETAAS detection<sup>148</sup>. Antimony hydride is generated by the addition of NaBH<sub>4</sub> to the sample in a head space vial and the hydride is trapped onto a 3 µL drop of 30 mg L<sup>-1</sup> Pd(NO<sub>3</sub>)<sub>2</sub> formed at the tip of a microsyringe in the headspace above the sample. After a 180 s preconcentration trapping time, the drop is withdrawn into the syringe, removed from the sample vial and injected into the graphite furnace of an ETAAS instrument where the Pd also acts as a modifier. Total Sb is determined by reduction of all the Sb present to Sb<sup>III</sup> before addition of the NaBH<sub>4</sub>. In this way a preconcentration factor was 176 was achieved, resulting in a LOD for Sb<sup>III</sup> of 25 pg ml<sup>-1</sup>.

An *online method for the redox speciation of Sb* has also been developed with ICP-AES detection<sup>149</sup>. The Sb<sup>III</sup> is selectively retained on a micro-column containing L-proline immobilised on to controlled pore glass. The Sb<sup>V</sup> is detected after online reduction by HG-ICP-OES during the loading phase, Sb<sup>III</sup> is then eluted using 2 M HCl and detected without further reduction. For an 8 mL sample a preconcentration factor of 11 was achieved with a LOD of 90 ng L<sup>-1</sup> for Sb<sup>III</sup> and 900 ng L<sup>-1</sup> for Sb<sup>V</sup>; the sum of Sb<sup>III</sup> and Sb<sup>V</sup> was in good agreement with the certified value of Sb for the CRM used and results by ICP-MS analysis of effluent waters.

Sensitivity for the *detection of ammonium and organically bound nitrogen* by ICP-AES in natural and waste waters has been improved by the development of a vapour generation method<sup>150</sup>. Ammonia vapour is generated by the addition of concentrated NaOH followed by detection at 174.273 nm using an axial ICP-AES instrument. Detection limits of 10 – 25 mg L<sup>-1</sup> as N were achieved with an analytical precision of between 0.6 and 4.6 % RSD for a concentration range of 25 – 1000 mg L<sup>-1</sup>

<sup>1</sup>. The advantages of this method are that it is faster than the standard Kjeldahl method and more sensitive than solution nebulisation ICP-AES for the same analysis.

### **2.3.3 X-ray fluorescence spectroscopy**

*Solid phase extraction procedures in conjunction with TXRF* have been developed for the determination of metals in seawater. Staniszewski and Freimann<sup>151</sup> adjusted the pH of a 120 g sample of seawater to 2.2, added 10 ml of a 5 % *m/v* L-cysteine solution and heated it to 85 °C for 60 mins to reduce all the arsenic to As<sup>III</sup>. The sample was cooled, the pH adjusted to about 5 and the analytes complexed by the addition of a sodium dibenzylthiocarbamate (NaDBC) solution. The complexes were loaded onto silica gel columns, eluted using a chloroform-methanol mixture and a 50 µL aliquot was pipetted onto a quartz sample carrier and evaporated to dryness for analysis by TXRF. Detection limits were about 10 ng L<sup>-1</sup> for As and sufficient for the routine detection of Cu, Fe, Ni, Pb, U and Zn in North Sea water. The disadvantage of this method is that the addition of L-cysteine reduces Mn and Se to forms that do not complex with NaDBC, so they are undetectable with this methodology. Membrane extraction has been used to isolate Co, Cu, Ni and Zn from water and seawater prior to measurement by TXRF<sup>152</sup>. The elements were selectively extracted as anionic complexes of 4-(2-pyridylazo)resorcinol onto a PVC membrane deposited onto the centre of a quartz reflector modified with tricaprylyl methyl ammonium chloride (Aliquat-336). Detection limits of between 0.7 and 1.3 ng mL<sup>-1</sup> for the metals studied were achieved.

### **2.3.4 Inductively coupled plasma mass spectrometry**

*Sector field ICP-MS* continues to be the method of choice for the determination of trace elements in the cryosphere and pristine environments. Silver and Tl have been determined in Arctic snow, firn and ice<sup>153</sup> and heavy metals and metalloids have been determined in ice collected from Antarctica<sup>154</sup>. Both studies required the development

and use of specialised clean room protocols that could be applied to other fields involving ultratrace analysis.

However, *collision cell and reaction cell instruments* are challenging this predominance. Grotti and co-workers<sup>22</sup> have demonstrated that a quadrupole instrument equipped with a reaction cell and fitted with a total consumption microsample introduction system can achieve detection limits low enough to determine Cd, Co, Cr, Cu, Fe, Mn, Pb, V and Zn in Antarctic snow. Samples were preconcentrated by freeze drying a 10 mL aliquot and re-dissolving the residue in 200  $\mu\text{L}$  of 0.05 % v/v nitric acid. The high plasma solvent load ( $20 \text{ mg min}^{-1}$ ), caused by the use of an electrically heated evaporation chamber, is partially compensated for by tuning for low oxides levels; ammonia was used as a reaction gas to reduce isobaric interferences.

*Preconcentration techniques* previously used in conjunction with AAS continue to be investigated for use with ICP-MS. Lanthanum co-precipitation has been used to successfully separate the oxo-anions of As, Sb, V and W from seawater<sup>155</sup>. The two-step method consists of a precipitation stage and a separation stage. In the first stage, 20 mL of sample are adjusted to pH 9.5 with ammonium hydroxide, to which 0.2 mL of a  $5 \text{ g L}^{-1}$  solution of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  are added. The precipitate formed is collected on a  $0.2 \mu\text{m}$  membrane filter and re-dissolved in 2 mL of 2 M  $\text{HNO}_3$ . In the second stage, this solution is diluted two-fold and passed through an AG 50W-X8 cation exchange resin column to remove the lanthanum. Extraction recoveries range from 80 to 96% with a preconcentration factor of 5, resulting in analytical LODs ranging from 0.3 to  $1.0 \text{ ng L}^{-1}$ . The same group applied this method in tandem with preconcentration on a Chelex® 100 column to quantify 56 elements in the waters of Lake Baikal<sup>156</sup> using a sector field ICP-MS. Single-walled



carbon nanotubes have been evaluated as a potential solid phase extraction medium for rare earth elements<sup>157</sup>. It was found that REEs are retained quantitatively in a pH range from 3.0 to 8.0 and can be eluted completely with 1 M HNO<sub>3</sub>. Enrichment factors of up to 75-fold were achievable with recoveries of about 90% resulting in LODs of between 0.25 and 0.57 pg mL<sup>-1</sup>, with a precision of better than 5% RSD (n=9) at the 1.0 ng mL<sup>-1</sup> concentration level.

An *Fe-specific resin with multi-collector ICP-MS* has been used to determine the isotopic composition of dissolved Fe at its open ocean concentration range (0.1-1 nM)<sup>158</sup>. Dissolved Fe is preconcentrated using a Nitriloacetic Acid (NTA) superflow® resin (Qiagen) followed by purification using an AG1x4 anion exchange resin. A measurement precision of 0.13 ‰ RSD was achieved with a desolvating nebuliser (Aridus II). The concentrations of Fe in seawater have been measured by isotope dilution multi-collector ICP-MS<sup>159</sup>. A preconcentration step utilizing the NTA superflow® resin was necessary. It was reported that this resin quantitatively extracts Fe at a pH as low as 1.7, even in oxidised seawater (after addition of H<sub>2</sub>O<sub>2</sub>), eliminating the need for buffering of the sample. To reach a preconcentration of 100 times from a 50 mL sample, the eluate from the column is evaporated and re-dissolved in 0.05 M HNO<sub>3</sub>. Using this method the blanks were kept below 0.06 nmol L<sup>-1</sup> and the LOD per session varied between 0.020 and 0.069 nmol L<sup>-1</sup>.

### **2.3.5 Laser induced breakdown spectroscopy**

The use of LIBS as a sensor for *bulk water analysis* is being investigated by a number of workers. It has been shown to be capable of detecting toxic metal contaminants in waste waters from a dairy production plant<sup>160</sup> after ablation of the water surface in a flow cell. To expand the applicability of this technique, LIBS has been carried out in the laboratory at simulated oceanic pressures of up to 2.76 x 10<sup>7</sup> Pa<sup>161</sup> and the pulse energy and gate delay optimised. It was found that water pressure

had little effect on the peak intensity, that short gate delays of < 200 ns had to be used at all pressures and that low laser energy pulses of < 60 mJ could be used. It is hoped that this technique could be used to monitor *in situ* the bulk composition of hydrothermal vent fluids.

#### **2.4 Data quality and method standardisation**

An *interlaboratory comparison* of the ultratrace determination of REEs has been published<sup>162</sup>. Sector field, time of flight and quadrupole based ICP-MS systems were compared for the determination of REEs in ice core samples after digestion and sub-boiling preconcentration. It was found that sector field ICP-MS is still the instrument of choice for this specialized application. Measurements from quadrupole based instruments agreed well with those from sector field instruments but had higher RSDs, and the results from the time of flight instrument suffered from a small positive bias. The results of a proficiency testing exercise involving 47 Spanish laboratories for the use of ICP-MS for the determination of 16 elements in natural waters have been published<sup>163</sup>; assigned values for 12 of the elements were provided by isotope dilution analysis. The analytical results were evaluated by different scoring procedures according to European Directive 98/83/EC. The procedures used for outlier elimination (Cochran and Grubbs test, Hampel test and a combination of the Cochran and Hampel tests) were critically compared.

Lytle and co-workers<sup>164</sup> compared an in-house microwave digestion procedure followed by ICP-MS measurement using US EPA method 200.8 with the AFS-based US EPA methods 245.7 and 1631E for the analysis of total *mercury in waste water and industrial effluents*. They showed that heating the samples in closed vessels at 50 °C for 6 hours, as suggested in methods 245.7 and 1631, should be done to obtain reliable values for total mercury. Room temperature digestion with BrCl as described

in method 1631E or with  $\text{KBrO}_3/\text{KBr}$  as in method 245.7 for waters is ill suited to industrial effluent and waste water samples as it gives a negative bias. It is suspected that only the easily oxidisable fraction is measured when room temperature digestion followed by AFS detection of mercury is used.

A robust method for the *determination of the strontium isotopic signature of mineral water* has been validated<sup>165</sup>. Commercially available pre-packed columns filled with a Sr-specific resin were used to remove isobaric interferences. Mass bias correction was carried out internally using the  $^{88}\text{Sr}$  to  $^{86}\text{Sr}$  ratio and the method was found fit for purpose for comparing mineral waters from different geological backgrounds.

### 3 Analysis of soils, plants and related materials

Numerous articles have been published since the previous Update<sup>1</sup> featuring the application of atomic spectrometry to the analysis of soils and plants.

#### 3.1 Sample preparation

##### 3.1.1 Sample dissolution and extraction

Various *comparisons of sample digestion procedures* have been aimed at optimising procedures for isolating analytes from specific sample matrices. Vaisanen *et al.*<sup>166</sup> applied microwave digestion, ultrasound-assisted digestion and dry ashing in the analysis of a pine needle reference material NIST SRM 1474a by ICP-AES. The best accuracy was obtained with dry ashing followed by ultrasound-assisted dissolution of the ash in 50% *aqua regia*. The speed of the ultrasound step – 3 minutes – partially offset the relatively long ashing time of 5 h. Dry ashing at 550 °C was also recommended in the analysis of rice and wheat samples by Srivastava *et al.*<sup>167</sup>. Mixtures of nitric acid with hydrogen peroxide or perchloric acid were found suitable for the digestion of swine manure prior to the determination of 13 elements by ICP-AES<sup>168</sup> but sulfuric acid with hydrogen peroxide gave inconsistent results. Japanese workers<sup>169</sup> reported low recoveries for several analytes (Cd, Co, Cu, Ni, Pb and Zn), which they attributed to a combination of volatilisation losses and alloying reactions with platinum crucibles, when alkali fusion was used in the analysis of sewage sludge reference material BCR 144R. Even with their preferred method of microwave digestion, HF was required to obtain quantitative recoveries for Nb, Ta and Hf. In contrast, Mariet *et al.*<sup>170</sup> substituted successfully NH<sub>4</sub>F for HF/HClO<sub>4</sub> in the digestion of lichen, soil and rock CRMs prior to multi-element determination by ICP-MS. Four

combinations<sup>171</sup> of HCl, HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and HF have been evaluated for the microwave-assisted digestion of highly calcareous soils prior to analysis by ICP-AES, using BCR 141R as a test substrate. Extremely poor recoveries, < 5% of certified values, were obtained for Al when HF was used, and H<sub>2</sub>O<sub>2</sub> appeared to have negligible influence on extraction efficiencies. Hence, *aqua regia* was recommended.

*Element-specific sample digestion procedures* have been reported for several analyses. Sintering with Na<sub>2</sub>CO<sub>3</sub> and ZnO at 560 °C gave recoveries of ≥ 96% in the determination of Br and Cl by SF-ICP-MS in a variety of waste materials<sup>172</sup> including sewage sludge reference materials BCR 144R and 146R. Bolou-Bi<sup>173</sup> described an improved method for extraction of Mg for measurement of δ<sup>26</sup>Mg in alkali-rich CRMs such as soils and plants by MC-ICP-MS. Grinberg and Sturgeon<sup>174</sup> used several reference materials, including NIST SRM 1572 Citrus leaves and NIST SRM 2709 San Joaquin soil, to evaluate a new method for the extraction of I. The procedure involves thermal decomposition of samples, followed by capture of I<sub>2</sub> in 5% (v/v) acetic acid. This solution is then irradiated with UV light, generating free radicals that undergo photochemical reactions to produce volatile I species suitable for measurement by ICP-MS.

Spike recovery experiments with samples of maize and oak leaves suggested that treatment of 1 g of dried plant material with 10 mL of *aqua regia* for 16 h at room temperature, followed by reflux for 2.5 h, was suitable for *the determination of Pd, Pt and Rh* in plants by USN-ICP-MS<sup>175</sup>. Pre-treatment with HNO<sub>3</sub> followed by microwave-assisted digestion in HF and then treatment of the cooled digest with boric acid was preferred for the determination of the same analytes in road dust by ETAAS<sup>176</sup>, *aqua regia* being unsuitable because of interferences from chloride in furnace atomisers.

A six-stage extraction has been developed to explore *the speciation of Se* in freeze-dried garlic<sup>177</sup>. The stages are water extraction, enzymatic cell wall lysis, proteolysis, HCl extraction, sulfite extraction and CS<sub>2</sub> extraction, indicating concentrations of water soluble Se, cell-wall bound Se, protein bound Se, inorganic Se bound to organic matter, elemental Se, and selenide, respectively. Extraction methods for Se speciation in vegetables were summarised in a review by Pyrzyńska (75 references)<sup>178</sup>.

The environmental chemistry of Sb has been reviewed<sup>179</sup> and the need for *improved analytical methods for Sb* highlighted. Hjortenkrans *et al.*<sup>180</sup> have described the optimisation of methods for the recovery of Sb from urban samples, including soils.

Lomonte *et al.*<sup>181</sup> reported an optimised *procedure for the isolation of Hg* from biosolids using mineral acids, H<sub>2</sub>O<sub>2</sub> and hotplate digestion. Two detailed reviews on the extraction and determination of Hg species focus on the use of SPME<sup>182</sup> (55 references) and on methods for extraction of analytes from soils and sediment samples<sup>183</sup> (170 references).

Arsenic speciation remains an active topic of investigation and research has continued to develop *species-conserving methods for extracting As from plants*. Schmidt *et al.*<sup>184</sup> used a two-stage sequential extraction – deionised water followed by 1 g L<sup>-1</sup> cellulase in 0.1 M phosphate buffer at pH 7 – to isolate As<sup>III</sup>, As<sup>V</sup>, MMA and DMA from *Tropaeolum majus* (Indian Cress). A Polish research group<sup>185</sup> measured the same analytes in specimens of *Calamagrostis arundinacea* (Reed Grass) and *Athyrium filix-femina* (Lady Fern) growing in the vicinity of a disused gold and arsenic mine. The compounds were isolated from dried, milled, sieved plant material by sonication in distilled water followed by shaking with 4% sodium dodecylsulfate

surfactant. Other workers<sup>186</sup> suggested that two separate extractions should be performed, one in water and one in a 9+1 methanol-water mixture, to obtain a complete profile of As species in the submerged freshwater plant *Ceratophyllum demersum* (Coontail).

Development of *ultrasound-assisted digestion methods* continues to be of interest. Kazi *et al.*<sup>187</sup> studied sonication time, temperature of the ultrasonic bath and acid composition to optimise procedures that could be performed in *ca.* 30 minutes and gave extraction efficiencies equivalent to conventional acid digestion. Recoveries for Cd, Cr, Ni and Pb determined by ETAAS in a range of environmental and biological RMs were 96 to 102%. Other workers<sup>188</sup> reported that < 10 min treatment of dust samples with an ultrasonic probe, using either 0.05 mol L<sup>-1</sup> EDTA or 2 mol L<sup>-1</sup> HCl extractants, yielded recoveries of Cu, Pb and Zn similar to those achieved by conventional extraction.

Research to develop *more rapid versions of the BCR sequential extraction procedure* has continued, although there are reservations over whether this goal can be justified given the operationally-defined nature of the protocol and the fact that it was originally developed as a harmonised procedure to allow comparable results to be obtained by different laboratories, and so must be performed exactly as prescribed. Workers in Pakistan have proposed two modifications: that researchers working in warm climates may reduce the shaking time at each step from 16 h (overnight) to 8-10 h since higher ambient laboratory temperatures lead to more rapid extraction<sup>189</sup> and that the procedure may be performed with microwave assistance in less than 10 mins<sup>190</sup>. The microwave procedure was developed using CRM BCR 483 (Sewage sludge amended soil) but was not applied to CRMs certified for analytes extractable by the BCR procedure, e.g. BCR 701 Lake sediment, to check whether equivalent

performance would be obtained for substrates other than that used in method development.

A potentially significant advance in this area is the replacement of current, static methods with *dynamic sequential extraction procedures* that more accurately simulate environmental processes, e.g. the percolation of rainwater through soil. Both sequential injection micro-column extraction and sequential injection stirred-flow chamber extraction<sup>191</sup> have been explored using the same reagents as the conventional BCR protocol, ICP-AES and a coal fly ash CRM. These procedures are readily automated, can be performed in < 4 h, appear not to be operationally-defined and show considerable promise for further development.

### **3.1.2 Preconcentration procedures**

A large number of publications have described *methods for the isolation or preconcentration of metals from aqueous samples, including soil and plant digests*. Some procedures involving cloud point extraction are summarised in Table 1, procedures involving co-precipitation in Table 2, and procedures involving sorbent systems in Table 3. Most are intended specifically for analysis of soils, plants and related materials, but methods for water or food analysis are included if plant or soil CRMs were used in their validation.

## **3.2 Instrumental analysis**

### **3.2.1 Atomic absorption spectrometry**

An important development is the advent of commercial instrumentation for *high resolution continuum source flame atomic absorption spectrometry*. Brazilian workers<sup>192</sup> have used this equipment to develop a method for sequential measurement



of Cu, Fe, Mn and Zn in 0.005 mol L<sup>-1</sup> DTPA extracts of agricultural and reference soils. Options for increasing the linear range for determination of Fe, which is typically present at a higher concentration than the other analytes, were explored, including measurement on the wings of the main spectral line at 248.327 nm ('side pixel registration') and use of the secondary line at 252.744 nm. The results obtained were in agreement with target values for reference soils, spiked recoveries were > 92% and LODs were around 5.0 µg L<sup>-1</sup> for Cu, Mn and Zn, 55 µg L<sup>-1</sup> for Fe measured at 252.744 nm and 150 µg L<sup>-1</sup> for Fe measured at 248.325 nm. A HR-CS-FAAS method for the determination of S in plants, based on the 257.961 nm molecular absorption of carbon monosulfide, has been described (in Chinese with English abstract) by Wang and Li<sup>193</sup>.

There is still interest in *slurry and solid sample introduction for AAS*. Flores *et al.*<sup>194</sup> prepared pressed pellets containing powdered plant material and high purity graphite which, when burned in O<sub>2</sub> in a quartz cell located above the burner in FAAS, allowed the quantitative determination of Cd and Pb. The main advantage over previous work was that a larger pellet mass, up to 100 mg (25 mg sample + 75 mg graphite for Cd, 50 mg sample + 50 mg graphite for Pb) could be accommodated, leading to improved LODs of 0.012 µg g<sup>-1</sup> for Cd and 0.10 µg g<sup>-1</sup> for Pb. Electrothermal AAS with Zeeman effect background correction has been used with solid sampling in the measurement of Cd, Hg, Mn and Pb in aquatic plants<sup>195</sup> and with slurry sampling in the measurement of Pb and Sn in sediments<sup>196</sup>. A method for direct Hg speciation in solid samples, involving controlled thermal release of analytes followed by quantification by AAS, has been proposed by Shuvaeva *et al.*<sup>197</sup>.

Relatively few publications have featured developments in *electrothermal atomic absorption spectrometry* relevant to soils and plants, although there was one

report<sup>198</sup> of an improved matrix modifier (4 µg palladium + 1600 µg citric acid + 1000 µg ammonium fluoride) for the measurement of Sn in *aqua regia* digest with platform atomisation. One potentially significant advance, however, is the novel atomiser described by Gilmutdinov and Nagulin<sup>199</sup>. This has two independent power supplies, allowing the upper and lower parts to be heated at different rates. Atomisation takes place in two stages. The sample is injected, pyrolysed and vaporised as normal, but vapour is then condensed on the cooler, upper part of the tube. Once condensation is complete, the upper section is heated rapidly and analyte re-released for measurement. Potential interferents that are permanent gases are lost at the primary vaporisation stage, and atoms released at the second stage enter a high temperature environment, as occurs with platform atomisation. Hence, interference effects are reduced.

New or improved methods have been proposed for the determination of several elements by *hydride generation atomic absorption spectrometry*. Flow injection HG-AAS was used by Zhang and Adeloju<sup>200</sup> for the determination of As, Bi and Se in sediments and by Liang *et al.*<sup>201</sup> for measuring Pb in food, water and soil. Kozak *et al.*<sup>202</sup> employed HPLC-HG-AAS to study temporal changes in inorganic As speciation in marine sediments deposited on land in SW Thailand by the 2004 tsunami. They concluded that the material was enriched in exchangeable forms of As, especially As<sup>III</sup>, relative to local soil and that, although the concentrations of exchangeable As did not show a consistent trend, the ratio of As<sup>III</sup> to As<sup>V</sup> decreased markedly following two rainy seasons. Sun and Suo optimised methods for the measurement of Cd<sup>147</sup> and Ni<sup>203</sup> in environmental samples and CRMs by HG-ETAAS with *in situ* trapping of the hydride species in graphite tubes coated with iridium or iridium-platinum.

### 3.2.2 Atomic emission spectrometry

Although no longer widely-used, *flame atomic emission spectrometry* has remained popular with soil scientists for the determination of major cations. A new multi-syringe flow injection system for determining K in soil extracts by FAES has been described<sup>204</sup>. Different interface configurations were compared and problems previously encountered because of variability and interruption in the flow of solution to the flame were overcome.

*Hydride generation inductively coupled plasma atomic emission spectrometry* has been proposed<sup>150</sup> as an alternative to the standard Kjeldahl method for the measurement of nitrogen in samples of soil, water and fertiliser. Nitrogen species were converted to ammonia and swept into the ICP for measurement at 174 nm. Advantages claimed included higher sample throughput relative to Kjeldahl nitrogen determination and improved signal-to-noise ratio, sensitivity and limit of detection relative to conventional (non HG) ICP-AES.

An improved *double chamber electrothermal vaporisation system* for AES was described (in Japanese with English abstract)<sup>205</sup>. Under optimised conditions the system produced a LOD for Cd of 0.2 ng mL<sup>-1</sup>.

### 3.2.3 Atomic fluorescence spectrometry

Chinese workers<sup>206</sup>, using *hydride generation atomic fluorescence spectrometry*, have demonstrated that bi-anode electrochemical HG is a successful alternative to chemical HG in the determination of As. The method, which had a LOD of 0.64 µg L<sup>-1</sup> and a precision of 2.0% at 60 µg L<sup>-1</sup> (n = 13), gave results consistent with certified values for reference soil GBW07406 and recoveries of 100 ± 3% when used to analyse

spiked samples of animal feed. HG-AFS was also used with on-line microwave irradiation in a method for speciation of As and Sb<sup>207</sup>.

A new type of atomisation cell for AFS, the single ring electrode radio-frequency capacitively coupled plasma torch, has been proposed by Frentiu *et al.*<sup>208</sup>. The torch was used with an electrodeless discharge lamp source and charged coupled detector for the measurement of Cd. A LOD of 4.3 ng mL<sup>-1</sup> was obtained. Results for analysis of a reference soil and water sample were close to target values and similar to data obtained by ICP-AES.

### **3.2.4 Inductively coupled plasma mass spectrometry**

#### **3.2.4.1 Laser ablation ICP-MS**

Studying the *distribution of trace elements in plant tissues by laser ablation ICP-MS* can provide useful information on the uptake and translocation of essential and non-essential elements. Researchers in Germany have been particularly active in this area, in collaboration with workers from Brazil and China. Detailed images of the distribution of Cd, Cu, Fe, Mg, Mn, Pb and Zn in thin sections of *Nicotiana tabaccum* (Tobacco) leaf, shoot and stem have been obtained<sup>209</sup>. Analytes were quantified using matrix-matched standards (spiked powdered tobacco leaves) and <sup>13</sup>C as an internal standard to correct for changes in signal caused by variable sample thickness and water content. Two closely related publications by the same group<sup>210-211</sup> describe the application of the approach to the copper-tolerant plant *Elsholtzia splendens* (Shiny elsholtzia) using spiked portions of NIST SRM 1515 Apple leaves for calibration. Some of the same data are presented for a third time in a more general article concerning element mapping in biological tissues<sup>212</sup>, along with other applications, e.g. imaging of trace elements in brain tumours and in polyacrylamide gels.

Monticelli *et al.*<sup>213</sup> developed a *LA-ICP-MS method for analysis of tree rings* and applied it to *Larix decidua* (European larch) growing near a large uranium ore body. Special attention was paid to optimising sample preparation procedures: samples were sanded and then the surface was pre-ablated to remove potential contaminants prior to analysis. Calibration was with respect to pressed pellets of homogenised cedar wood, in which concentrations of trace elements had been previously determined by acid digestion and solution ICP-MS, again using <sup>13</sup>C as an internal standard. Analyte concentrations were compared with elemental records from a lake sediment core to assess whether tree rings represented a suitable archive of environmental pollution in the area. Data for Cu, U and Zn matched the sedimentary record, but data for Cd and Pb did not.

Researchers in Florida<sup>214</sup> developed a *LA-ICP-MS method for the analysis of soil and sediments* that yielded similar results to those from solution ICP-MS and which they claimed could be used for routine analysis. Grinding the sample to particles of < 1 µm diameter improved the reproducibility and allowed analysis to be performed without the use of any binder. A British team<sup>215</sup> studied microscopic uranium oxide grains in soil from the vicinity of a uranium processing plant and discovered that, although all the particles contained DU, the isotopic composition varied between grains. This case study used MC-ICP-MS to obtain the accurate <sup>235</sup>U/<sup>236</sup>U and <sup>235</sup>U/<sup>238</sup>U ratios necessary for nuclear forensic applications.

French researchers developed a *novel, in-cell method for isotope dilution analysis*<sup>216</sup> that yielded results similar to certified values for Cu, Pb, Sn and Zn in soil and sediment RMs. Two pellets are mounted in the ablation cell: a sample pellet and a pellet containing an isotopically enriched solid spike. By using a specialised, low-power (<100 µJ pulse<sup>-1</sup>) femtosecond IR laser capable of operating at a pulse

repetition rate of 10 kHz, and a fast beam scanning system, it proved possible to perform quasi-simultaneous ablation of the two pellets and obtain efficient mixing of sample and spike aerosols *en route* to the plasma.

#### 3.2.4.2 Solution based ICP-MS

Examples of *analysis of solution samples by MC-ICP-MS* include a study of Si isotopic composition in plants from a forest in Sweden by Engstrom *et al.*<sup>217</sup> and a re-assessment of Pb isotope ratios in peat cores from Canada and Scotland by Kylander *et al.*<sup>218</sup>. An automated on-line method for the measurement of Sr isotopes was developed by Galler *et al.*<sup>219</sup> and applied successfully to samples of *Asparagus officinalis* (Asparagus).

*Coupling of chromatographic methods to ICP-MS* continues to be of interest because of the useful information that hyphenated techniques can provide on trace element speciation in soils and plants. Anion exchange chromatography ICP-MS was used to measure phosphate, glyphosphate and aminomethylphosphate in soil extracts<sup>220</sup>. The addition of helium to the octopole collision cell eliminated interference from  $^{14}\text{N}^{16}\text{O}^1\text{H}^+$  and  $^{15}\text{N}^{16}\text{O}^+$  on the measurement of  $^{31}\text{P}$ , but reduced the sensitivity of the method. Krasnodebska-Ostrega *et al.*<sup>221</sup> also applied IC-ICP-MS to study Tl speciation in *Sinapis alba* (Indian mustard), revealing that  $\text{Tl}^{\text{I}}$  was the dominant species in plant leaf extracts, whilst researchers in Germany used the same technique to determine Sb species in *Pteris vittata* (Chinese break fern). Afton and Caruso<sup>222</sup> used a combination of size exclusion chromatography ICP-MS and capillary reversed phase chromatography ICP-MS to study Hg and Se speciation in extracts of *Allium fistulosum* (Green onion). They found evidence of a Se-Hg association within a protein-containing macromolecule.

Other researchers have performed speciation analysis by *combining chromatography with elemental and molecular mass spectrometry*, usually by directing components separated in a chromatograph to both ICP-MS and electrospray ionisation mass spectrometry (ESI-MS). At the University of Cincinnati, researchers have developed a method<sup>223</sup> to measure four Se species ( $\text{Se}^{\text{IV}}$ ,  $\text{Se}^{\text{VI}}$ , selenomethionine and selenocystine) and four As species ( $\text{As}^{\text{III}}$ ,  $\text{As}^{\text{V}}$ , MMA and DMA) by ion-pairing reversed phase chromatography ICP-MS and ion-pairing reversed phase chromatography ESI-ion trap-MS. Analysis takes only 18 minutes and is applicable to a wide variety of sample matrices, including water, urine and plant extracts. In Aberdeen, UK, a comparison has been conducted<sup>224</sup> between on-line and off-line measurement of As species in plant extracts by reversed phase-HPLC-ICP-MS/ESI-MS. When root extracts of *Thunbergia alata* (Black-eyed Susan vine) were prepared off-line by SEC and freeze drying, < 2% of the As present was found to be bound to peptides, e.g. phytochelatins; when the measurement was conducted directly on the extract it was found that 83% of the arsenic was peptide-bound. This large discrepancy was attributed to instability of As-peptide species during the preliminary fractionation and freeze-drying steps. Since freeze-drying may compromise the results of As speciation analysis, it was recommended that samples of plant tissue should be stored 'fresh' at 193 K. The combination of IC-ICP-MS and ESI-MS was used by an Australian group<sup>225</sup> to study Zn-aminopolycarboxylic species in work on chelate-assisted phytoremediation of contaminated soil.

*Other developments in ICP-MS* include a new computational method<sup>40</sup> to overcome interferences from hafnium oxide in the determination of Pt in dust and lichen by isotope dilution analysis, and a procedure<sup>226</sup> to measure  $^{90}\text{Sr}$  in the presence of high concentrations of  $^{90}\text{Zr}$  that was applied to soil samples from the vicinity of the

Chernobyl Nuclear Power Plant. The isobaric interference was overcome by a combination of sample pre-treatment with a Sr-specific resin (from Eichrom Technologies) and use of oxygen as the reaction gas in the DRC of a quadrupole ICP-MS. Direct coupling of asymmetric flow field-flow fractionation to ICP-MS<sup>227</sup> has facilitated investigation of the critical role of colloids in the environmental transport of PTE. This new method was applied to soil leachates. It provided results for As, Cd, Sb, Se, Sn and Pb in reasonable agreement with those of a previously validated, off-line procedure involving leachate fraction collection, freeze drying and HNO<sub>3</sub> digestion.

Several *review articles* have featured ICP-MS: Hou *et al.*<sup>228</sup> described the use of the technique in the measurement of <sup>129</sup>I in the atmosphere, water, soil, sediments and biota (164 references); Komarek *et al.*<sup>46</sup> discussed environmental applications involving lead isotopes (159 references); Ketterer and Szechenyi<sup>50</sup> considered historical developments and future trends in the determination of Pu and other transuranic elements by, in particular, SF-ICP-MS (182 references).

### **3.2.5 Accelerator mass spectrometry**

Applications in radiocarbon dating are abundant but the only analytical publications of note are a review of methods for the measurement of <sup>129</sup>I, which includes AMS<sup>228</sup>, and the report that Pu isotopic speciation is, for the first time, possible using the compact AMS instrument housed at the Centro Nacional de Acceleradores in Seville, Spain<sup>229</sup>.



### 3.2.6 Laser-induced breakdown spectroscopy

Sensei *et al.*<sup>230</sup> published a useful summary of key issues in *the application of LIBS to soils* and also quantified Cr, Cu, Pb, V and Zn in Italian soils having a range of characteristics (texture, organic matter, pH, conductivity, CaCO<sub>3</sub> content). Chromium was the focus of a study by Gondal *et al.*<sup>231</sup>. They optimised and applied a LIBS method to monitor the remediation of artificially contaminated soils in a laboratory test rig, as a step towards development of a field LIBS system for on-site contamination assessment. However, researchers from the University of Malaga, Spain, have already achieved this goal for Pb<sup>232</sup>. Their LIBS instrument consists of a probe incorporating a Q-switched Nd:YAG laser and associated optics, connected by fibre-optics to a compact cross Czerny-Turner spectrometer (spectral range 370 – 460 nm) with linear CCD array. The spectrometer, laser power supply and electronic systems fit in a backpack. The instrument is controlled wirelessly by a PDA. Calibration was evaluated using pellets containing mixtures of soil and Pb(NO<sub>3</sub>)<sub>2</sub>, which were then digested in 50% HNO<sub>3</sub> and analysed by FAAS. Similar results were obtained by the two techniques. The LOD of the LIBS measurement at 405.8 nm was 190 µg g<sup>-1</sup>. This proved adequate for the measurement of Pb *in situ* in material deposited inside a road tunnel with high traffic density, although other workers<sup>233</sup> have achieved a lower LOD, 45 µg g<sup>-1</sup>, for the measurement of Pb by LIBS using the UV emission line at 220.3 nm.

Brazilian researchers<sup>234</sup> have used linear discriminant analysis to build a soil classification model based on *chemometric processing of LIBS spectra*. Three algorithms for the selection of variables were compared to obtain the best sub-set of spectral data to construct the model: the successive projection algorithm, the genetic algorithm and a stepwise formulation. In contrast, a group from the Canadian Space

Agency<sup>235</sup> used *a priori* selection of particular wavelengths corresponding to the spectral emissions of specific elements (Al, Ca, Fe, Mg, Mn, Si and Ti) in their development of an artificial neural network for interpretation of LIBS spectra. The results obtained for major mineral components of rock samples were within 15% of XRF data.

Particular challenges exist in the *LIBS analysis of plants*. When high-energy laser pulses are used, the moisture in fresh tissue samples affects the plume dynamics, leading to irreproducibility. However, when low-energy is used, the tissue must first be desiccated otherwise emission lines are broad and sensitivity is poor. Ohta *et al.*<sup>236</sup> coated fresh leaves of *Rhododendron obtusum* (Kurume azalea) or *Citrus unshiu* (Satsuma orange) with metallic colloid and used localised surface plasmon resonance to reduce peak widths and enhance signal intensity in the detection of nutrients such as Ca and Fe with low-energy (< 1 mJ per pulse) LIBS. The effects of 20 nm and 80 nm diameter colloidal silver particles, and 80 nm colloidal gold particles, were compared. Use of 80 nm silver particles was preferred. A LIBS system noted in the previous Update<sup>1</sup> for its application to Pb mapping has now been compared with LA-ICP-MS for imaging of Ag and Cu distribution in leaves of *Helianthus annuus* (Sunflower)<sup>237</sup>.

Various developments in environmental applications of LIBS were discussed at the 4<sup>th</sup> *Euro Mediterranean Symposium on Laser Induced Breakdown Spectroscopy*, Paris, 10–13 September 2007, papers from which have been published in a special edition of *Spectrochimica Acta Part B: Atomic Spectroscopy* (Vol 63, Issue 10, Oct 2008). Topics covered included the measurement of macronutrients (Ca, K, Mg and P)<sup>238</sup> and trace elements in plants<sup>239</sup>; the development and use of portable LIBS systems for analysis of soils<sup>240-243</sup> and studies aimed at optimising the

performance of the combined Raman/LIBS instrument<sup>244</sup> scheduled to carry out *in situ* analysis of rocks and soils during the European Space Agency's next mission to Mars.

### 3.2.7 X-ray fluorescence spectrometry

Mosselman *et al.*<sup>245</sup> described the first application of the UK's new national synchrotron facility, Diamond Light Source, to *the measurement of PTE in soil samples*. The speciation of Pb and Zn in contaminated soil undergoing remediation with bonemeal, and the associations of Ni with iron and manganese oxides in laterite, were investigated. Meanwhile, at the European synchrotron facility in Grenoble, Eeckhout *et al.*<sup>246</sup> used valence-to-core X-ray emission spectroscopy to study the speciation of Cr. This element is naturally enriched in soils from the city of Turin because of serpentine in the local area. However, when an urban soil from the city was studied, spectra suggested that Cr was most probably present as the metal, phosphides and/or carbides rather than the expected oxide species. This highly surprising result was attributed to contamination of the sample with anthropogenic Cr in the form of waste from a nearby steel-making plant. There has also been interest in small X-ray instruments. Optimised operating conditions for the measurement of As, Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, Ti, V and Zn in soil and sediment samples<sup>247</sup> using the compact MiniPal 4 EDXRF spectrometer have been reported.

Lagunas-Solar *et al.*<sup>248</sup> evaluated novel *methods for the preparation of plant tissue prior to X-ray analysis*. Described later in more detail<sup>249</sup>, the optimised procedure involves the addition of 50 – 100 mg of dried, powdered sample to 3 mL of 30% H<sub>2</sub>O<sub>2</sub> which is then exposed for 5 min at 90 °C to pulsed UV photons from a KrF excimer laser (248 nm, 1 x 3 cm<sup>2</sup> beam profile, ~ 80 MW cm<sup>-2</sup> beam energy). The

resulting digest is filtered and then analytes are preconcentrated by co-precipitation as carbamates and collected on membrane filters. PIXE analysis of the membranes yielded results close to certified values for NIST SRMs 1570a Spinach leaves and 1547a Peach leaves. Australian workers<sup>250</sup> continued their comparison described in our previous Update<sup>1</sup> of freeze-drying and freeze-substitution in tetrahydrofuran for PTE imaging in hyperaccumulator plants by micro-PIXE. Significant loss of As occurred with the freeze-substitution method.

Awane *et al.*<sup>251</sup> reported a procedure for *grazing exit micro-XRF* that involves placing an X-ray absorber, in this case a 2.2 mm thick silicon wafer chip, between the plant leaf sample and the detector and measuring at an exit angle of  $< 2^\circ$ . After careful optimisation of the measurement geometry, it was possible to measure specifically analytes located on the surface of the leaf, but to exclude analytes inside the leaf. This method could be especially useful for the measurement of PTE in airborne particles deposited on plant surfaces, without interference from PTE within the plant tissue.

Several applications of *X-ray speciation and mapping* have been reported, including a study of the transport of Cu and Mn across the soil/root interface in *Populus tremuloides* (Quaking aspen)<sup>252</sup>. Use of XANES showed that both elements were reduced, to Cu<sup>I</sup> and Mn<sup>II</sup>, in the rhizosphere. PIXE<sup>253</sup> has revealed information on the accumulation of P in the mycelia of the arbuscular mycorrhizal fungus *Glomus intraradices* and showed that levels of P influence the uptake of other essential elements in fungal spores. A combination of genetic, physiological and X-ray analyses revealed new information about the uptake and translocation of Cs in *Arabidopsis thaliana* (Thale cress)<sup>254</sup>. Both micro-SXRF and micro-XANES were employed, and a comparison was made between the wild type and a Cs-tolerant

mutant to investigate the biochemical mechanisms involved in Cs toxicity. The chemical forms of S in tree rings of the Norway spruce<sup>255</sup> have also been studied.

Several *reviews and comparisons* are noteworthy. Necemer *et al.*<sup>256</sup> compared EDXRF, TXRF and micro-PIXE with INAA and FAAS for the measurement of Br, Ca, Cd, Fe, K, Pb, Rb, Sr and Zn in powdered leaves of *Thlaspi praecox* (Penny cress) and *Juglans regia* (Common walnut). Useful comments were provided on the sample preparation requirements, cost of equipment, analytical characteristics (LODs, accuracy, precision) and scope and applicability of the techniques. A review (150 references)<sup>257</sup> of the application of TXRF to a broad range of biological samples includes information on methods for the analysis of plant extracts and exudates. Progress relating specifically to the measurement of PTE in vegetal samples by XRF is discussed by Margui *et al.*<sup>258</sup>.

### **3.3 Analytical quality control**

The preparation of a new *certified reference material*, NIST SRM 2701 Cr<sup>VI</sup> in contaminated soil, has been described<sup>259</sup>. This material was created in response to the growing need for evaluation of sites contaminated with chromite ore processing residue. It has a Cr<sup>VI</sup> content of approximately 500 mg kg<sup>-1</sup>. Japanese workers<sup>260</sup> have produced a series of standard soils for XRF analysis by spiking forest soil with aqueous standard solutions, whilst a French team<sup>173</sup> used a specially adapted sample preparation procedure to obtain new information on magnesium isotopic composition in plant CRMs.

*Inter-laboratory comparison exercises* have focused on the measurement of total Hg in soils, sediments and fish tissue<sup>261</sup>, total PTE in soils<sup>262</sup>, Cd and Pb in the medicinal plant *Herba Desmodii Styracifolii*<sup>263</sup> and Cr<sup>VI</sup> in soil<sup>259</sup>, the latter in

association with the creation of the CRM described in the previous paragraph. Yip *et al.*<sup>264</sup> have reviewed international inter-comparisons conducted under the auspices of the Comité Consultatif pour la Quantité de Matière in the period 1998 to 2007. This article, containing 144 references, includes a detailed discussion of the strengths and limitations of various methods for inorganic analysis, and provides strategic recommendations for future research.

**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	Notes	CRMs	Ref
Au, Tl	Seawater, tapwater	Microwave <i>Aqua regia</i>	Mixed cetyltrimethyl ammonium bromide and Triton X-114	None (analytes extracted as chloride complexes $\text{AuCl}_4^-$ and $\text{TlCl}_3^{2-}$ )	ICP-MS	Preconcentration factors 125 and 110; LOD 0.12 and $0.02 \text{ pg mL}^{-1}$ for Au and Tl, respectively. RSD < 2.2% at $10\text{-}40 \text{ pg mL}^{-1}$ (n = 6).	NIST SRMs 1653c and 1643d Trace elements in water, 2709 San Joaquin soil, 2711 Montana soil, NRCC NASS-5 Open ocean seawater	<sup>106</sup>
Cu, Ni	Maize starch, potato starch, rice flour	$\text{HNO}_3$	Triton X-114	2-(2'-benzothiazolylazo)-5-(N,N-diethyl)aminophenol	FAAS	Preconcentration factors 29 and 25; LOD 0.1 and $0.4 \text{ }\mu\text{g g}^{-1}$ ; RSD 6.4% and 1.0% at $75 \text{ }\mu\text{g L}^{-1}$ (n = 10) for Cu and Ni, respectively.	NIST SRMs 1515 Apple leaves, 1570a Spinach leaves, 1573a Tomato leaves	<sup>265</sup>
Mn	Corn flour, infant formula, rice flour	$\text{HNO}_3$	Triton X-114	4-(5'-bromo-2'-thiazolylazo)orcinol	FAAS	Preconcentration factor 14. LOD $0.5 \text{ }\mu\text{g L}^{-1}$ .	NIST SRMs 1568a Rice flour, 1573a Tomato leaves	<sup>266</sup>

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

Analyte(s)	Matrix	Carrier	Detector	Notes	CRMs	Ref
As	Water	Aluminium hydroxide	HG-AAS	Measurement of As <sup>V</sup> , oxidation of As <sup>III</sup> → As <sup>V</sup> for measurement of total As, calculation of As <sup>III</sup> by difference. Preconcentration factor 25. LOD 0.012 µg L <sup>-1</sup> .	NIST SRM 2711 Montana soil, LGC6010 Hard drinking water	<sup>267</sup>
Cd, Co, Cr, Cu, Fe, Mn, Pb	Dialysis solutions, seawater	Tetrakis(pyridine)-nickel(II)bis(thiocyanate)	FAAS	Preconcentration factor 75 (50 for Cd). LOD 0.01 – 2.4 µg L <sup>-1</sup> .	NIST SRM 2711 Montana soil, HPS certified waste water trace metals Lot #D532205	<sup>268</sup>
Cd, Cr, Mn, Ni, Pb	Sediment, soil, tea, tobacco, water	Cu(II)-dibenzylthiocarbamate	FAAS	LOD 0.34 – 0.87 µg L <sup>-1</sup> .	NIST SRMs 2711 Montana soil, 1515 Apple leaves	<sup>269</sup>
Cr	Water (including tannery waste water)	5-chloro-3-{4-(trifluoromethoxy)phenylamino}indolin-2-one	FAAS	Measurement of Cr <sup>III</sup> , reduction of Cr <sup>VI</sup> → Cr <sup>III</sup> for measurement of total Cr, calculation of Cr <sup>VI</sup> by difference. Preconcentration factor 40. LOD 0.70 µg L <sup>-1</sup> . RSD 5% at 250 µg L <sup>-1</sup> (n = 10).	HPS CRMs TMDW-500 Drinking water, SA-C Sandy soil C	<sup>270</sup>
Cr	Various solid and liquid samples	3-phenyl-4- <i>o</i> -hydroxybenzylidenamino-4,5-dihydro-1,2,4-triazole-5-one	FAAS	Measurement of Cr <sup>III</sup> , reduction of Cr <sup>VI</sup> → Cr <sup>III</sup> for measurement of total Cr, calculation of Cr <sup>VI</sup> by	HPS CRM TMDW-500 Drinking water, NIST SRM 1573a Tomato leaves	<sup>271</sup>



				difference. Preconcentration factor 100. LOD $0.50 \mu\text{g L}^{-1}$ .		
Cr, Pb	Coal, sediment, soil	Cu(II)-5-chloro-2-hydroylaniline	FAAS	Preconcentration factor 50. LOD $1.2 \mu\text{g L}^{-1}$ for Cu, $2.7 \mu\text{g L}^{-1}$ for Pb.	GBW 07309 Stream sediment, NIST SRM 1633b Coal fly ash	<sup>272</sup>
REE	Apple leaves	Yttrium phosphate	ICP-AES	LOD $3 \text{ ng L}^{-1}$ (Yb, Lu) – $99 \text{ (Er) ng L}^{-1}$ .	NIST SRM 1515 Apple leaves	<sup>273</sup>

**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	Detect or	Notes	CRMs (or other validation)	Ref
Ag, Cd, Co, Cr, Cu, Ni, Pb	Biological, soil and water samples	N/a	Diaion SP-850	ETAAS	Analytes as 2-(2-quinolinylazo)resorcin complexes. LOD 0.14 – 0.36 $\mu\text{g L}^{-1}$ .		274
Ag, Cd, Co, Cu, Ni, Pb	Biological, soil and water samples	N/a	MCI GEL CHP 20Y	ETAAS	Analytes as 2-(2-quinolinylazo)-4-methyl-1,3-dihydroxybenzene complexes. Preconcentration factor 300. LOD $\sim 1.0 \text{ ng L}^{-1}$ .	GBW 08458 Rice, GBW 08126 Human hair	275
Ag, Ni	Sediment, soil, tea, tobacco, water	Bacillus sphaericus	Chromosorb 106	FAAS	LOD 1.0 $\mu\text{g L}^{-1}$ for Ag, 1.4 $\mu\text{g L}^{-1}$ for Ni.	NIST SRM 2711 Montana soil, GBW 07310 Stream sediment	276
Al	Hair, tea, water	N/a	Glycerol-bonded silica gel	FAAS	Preconcentration factor 500. LOD 2 $\text{ng mL}^{-1}$ . RSD 2.2% at 2 $\mu\text{g mL}^{-1}$ (n = 7).	None (spike recovery experiments)	277
Al	Soil	Eriochrome Cyanine R	Anion exchange resin (styrene-divinylbenzene copolymer with quaternary ammonium groups)	ICP-AES	Preconcentration factor 200. LOD 0.6 $\text{ng mL}^{-1}$ .	None ( <i>cf.</i> spectrophotometric measurement)	278
Au	Sediment soil, water	N/a	Dowex M 4195	FAAS	Preconcentration factor 31. LOD 1.6 $\mu\text{g L}^{-1}$ .	None (spike recovery experiments)	279

Cd, Pb	Liver, pear leaves, water	Ofloxacin	Silica gel	ICP-AES	Preconcentration factor 100. LOD 0.29 ng mL <sup>-1</sup> for Cd, 0.13 ng mL <sup>-1</sup> for Pb. RSD < 3% at 1.0 µg mL <sup>-1</sup> (n = 5).	GBW 08301 River sediment	<sup>280</sup>
Cd, Co, Cu, Ni	Mushroom, water	N/a	Amberlite XAD-2000	FAAS	Analytes as ammonium pyrrolidinedithiocarbamate complexes. Preconcentration factor 200. LOD 0.07 – 0.23 µg L <sup>-1</sup> .	HPS CRMs TMDW-500 Drinking water, SA-C Sandy soil C	<sup>281</sup>
Cd, Co, Cu, Ni, Pb	Soil, sediments	a) 4-phenylthiosemicarbazide; b) 2,3-dihydroxybenzaldehyde; and c) 2-thiophenecarboxaldehyde	Amberlite XAD	FAAS	Preconcentration factor 13. LOD a) 0.15 – 6.3 µg L <sup>-1</sup> b) 0.75 – 8.6 µg L <sup>-1</sup> c) 1.8 – 4.4 µg L <sup>-1</sup> .	SO-2 Soil, LGC 6157 Sediment, NRCC MESS-3 Sediment	<sup>282</sup>
Cd, Co, Ni, Zn	Apple leaves, urine, water	2,4,6-trimorpholino-1,3,5-triazin	Silica gel	FAAS	Preconcentration factors 100 (Co, Ni), 50 (Cd, Zn). LOD 0.20 – 0.30 ng mL <sup>-1</sup> . RSD ~ 2% at 50 ng mL <sup>-1</sup> (n = 5).	None (spike recovery experiments)	<sup>283</sup>
Cd, Pb	Apple leaves, water	Acetylacetone	Polyurethane foam	FAAS	Preconcentration factor > 220. LOD 0.07 µg L <sup>-1</sup> for Cd, 0.09 µg L <sup>-1</sup> for Pb.	None (spike recovery experiments)	<sup>284</sup>
Cr	Soil, water	Polyatomic donors	Silica gel	ICP-AES	Separate measurement of Cr <sup>III</sup> and Cr <sup>VI</sup> .	Spike recovery and <i>cf.</i> spectrophotometry for Cr <sup>VI</sup>	<sup>285</sup> in Japanese

Cu	Alloy, sediment	N,N'-bis(4-phenylazo salicylaldimine) 3-chloro-1,2-phenylenediamine	C-18 membrane disc	FAAS	Preconcentration factor 550. LOD 0.015 $\mu\text{g L}^{-1}$ .	NIES No. 2 Pond sediment, NKK No. 920 Aluminium alloy	<sup>286</sup>
Cu, Fe, Zn	Chickpea, dialysis solutions, tea, vitamin tables, walnut, water	<i>Bacillus thuringiensis israelensis</i>	Dowex optipore V-493	FAAS	Preconcentration factor 37. LOD 1.1 $\mu\text{g L}^{-1}$ for Cu, 2.0 $\mu\text{g L}^{-1}$ for Fe, 0.14 $\mu\text{g L}^{-1}$ for Zn.	NRCC SLRS-4 Riverine water, NIST SRM 1515 Apple leaves	<sup>287</sup>
Cu, Ni	Canned fish, hair, meat, tea, water	N/a	Dowex optipore SD-2	FAAS	Analytes as 5-methyl-4-(2-thiazolylazo)resorcinol complexes. Preconcentration factor 50. LOD 1.0 $\mu\text{g L}^{-1}$ for Cu, 1.9 $\mu\text{g L}^{-1}$ for Ni.	NIST SRM 1515 Apple leaves, GBW 07603 Aquatic and terrestrial biological products	<sup>288</sup>
Hg	Water	N/a	Sheep wool	AFS	Measurement of $\text{Hg}^{\text{II}}$ and methylmercury. LOD 0.01 $\text{ng mL}^{-1}$ . RSD $\sim$ 3.0% at 4.0 $\text{ng mL}^{-1}$ (n = 6).	NIST SRM 1547 Peach leaves	<sup>289</sup>
Hg	Chinese traditional medicines, water	N/a	Ion-imprinted amino-functionalised silica gel	ICP-AES	Measurement of $\text{Hg}^{\text{II}}$ . LOD 0.25 $\mu\text{g L}^{-1}$ . RSD 2.5% at 50 $\mu\text{g L}^{-1}$ (n = 8).	GBW 08603 River sediment	<sup>290</sup>
Nd	Sediment, soil	N/a	Ion-imprinted polymer	ICP-AES	LOD 6.1 $\text{ng mL}^{-1}$ . RSD 2.9% at 0.25 $\text{mmol L}^{-1}$ (n = 8)	GBW 07301a Sediment, GBW 07401 Soil	<sup>291</sup>

Pb	Liver, pear leaves, water	N/a	Ion-imprinted amino-functionalised silica gel	ICP-AES	Preconcentration factor 100. LOD 0.20 $\mu\text{g L}^{-1}$	GBW 08301 River sediment, 08504 Cabbage, 08511 Pig liver	<sup>292</sup>
REE (La, Gd and Yb)	Water	N/a	Single-walled carbon nanotube	ICP-MS	Preconcentration factor 75. LOD 0.25 – 0.57 $\text{pg mL}^{-1}$ . RSD < 5% at 1.0 $\text{ng mL}^{-1}$ (n = 9).	GBW 07603 Bush branches and leaves	<sup>157</sup>

n/a = not applicable

## 4 ANALYSIS OF GEOLOGICAL MATERIALS

### 4.1 Reference materials

*A comprehensive review of the use and development of RMs (391 refs) recorded in the geochemical literature published in 2006 and 2007 confirms the vital role that RMs play in analytical geochemistry*<sup>293</sup>. For bulk rock analysis, RMs supplied by the USGS and GSJ continue to be popular because of their homogeneity, extensive characterisation and wide range of rock types. However, most of these materials are not certified by ISO-compatible procedures and there is rarely a proper assessment of uncertainty. Much effort continues to be directed at providing new high precision data for RMs, thus enabling reliable up-to-date reference values to be determined. Although many RMs exist, the review concludes that there is still a pressing need for more, particularly certified rock RMs, homogeneous RMs suitable for mineral microanalysis and well characterised RMs for isotope determinations, including so-called delta zero materials for normalisation in stable isotope analysis.

Many geoanalysts will appreciate the investment made by the Max-Planck Institute in Germany in establishing the *GeoReM database*. This resource (<http://georem.mpch-mainz.gwdg.de>) currently contains information on ca. 1800 RMs relevant to analytical geochemistry and environmental research, including “preferred values” and their uncertainties. It is important, however, that not only geoanalysts but those who interpret geochemical data appreciate the role of RMs in providing confidence in the quality of the data and the associated uncertainties. It was therefore pleasing to note an article in *Chemical Geology*<sup>293</sup> that emphasizes the importance of

RMs and the inclusion of RM data in papers to demonstrate the validity of geochemical results.

A geochemical database of thirty-five RMs from four countries was used to evaluate the *performance of nine single outlier tests* with thirteen variants<sup>294</sup>. They concluded that the kurtosis test was the most powerful one for detecting discordant outliers in such geochemical RM databases. This contribution was part of an ongoing exercise to review statistical methods for processing such databases and should be useful for identifying discordant outliers in many other fields.

*New concentration data* for Ag, Au and Ir by INAA in 70 geochemical RMs, covering a broad compositional range, have been published<sup>295</sup>. Values for Cd and Hg were also presented for some of these materials. Reliable results for Au and Ir down to concentrations of a few ng g<sup>-1</sup> were obtained, whereas the relatively high LOD for Ag precluded its detection below 0.1 µg g<sup>-1</sup>. A particularly high RSD for Au (45%) was reported for WMG-1 (mineralised gabbro PGE material from CCRMP), which was attributed to the heterogeneous distribution of Au particles at the scale of a 2 g test portion. The Ir concentration in the serpentinite UB-N (CRPG, France) compared favourably to published results obtained by ID ICP-MS methods but heterogeneity was inferred for Au, Hg and Sb. During an evaluation of a Milestone DMA-80 mercury analyser<sup>296</sup>, values for Hg in 33 stream sediment and soil RMs were determined. The DMA-80 produced results that were in close agreement with published data for all samples except one, with a LOD of 1 ng g<sup>-1</sup>. Concentrations of Nb and Ta in a variety of glass RMs were determined by LA-ICP-QMS using a 193 nm ArF excimer laser<sup>297</sup>. Analytical precision was less than 10% at contents greater than 0.1 µg g<sup>-1</sup>. The results suggested that the reference values for Nb and Ta in NIST SRM 610 published by Pearce and co-workers in 1997 need to be revised upwards by

16% for Nb and 28% for Ta. It was concluded that most of the measurement uncertainty in the original data was analytical rather than due to chemical heterogeneities on a scale of 24  $\mu\text{m}$ .

Two new candidate *mineral RMs* have been characterised by the Smithsonian Institution specifically for the analysis of micas and feldspars in granitic pegmatites<sup>298</sup>. Stewart lepidolite (STL-1) and Zapot amazonite (ZA-1) were sourced from pegmatite deposits with unusually high Cs and Rb concentrations. They improved the accuracy of XRF measurements of micas and feldspars by eliminating the need to extrapolate calibrations based on existing RMs. Progress has been made in finding a RM suitable for the microanalysis of rutile in applications such as Zr thermometry, provenance studies and U-Pb dating<sup>299</sup>. Four rutile crystals, about a centimetre across, were shown to be homogeneous to within  $\pm 10\%$  for many of 15 trace elements determined by a variety of techniques<sup>299</sup>. The trace element concentrations of the crystals span a broad compositional range and provisional values for Hf, Nb, Sb, Sn, Ta, U, W and Zr were reported. One of the grains had a relatively high U content and provided U-Pb ages that were in excellent agreement with its regional geological context. Data indicated that some of the grains may also be useful as calibration material for *in situ* Hf isotope studies.

The rapid growth in studies of many new isotope systems has resulted in an increasing demand for *well characterised RMs for isotope determinations*, including materials with well defined delta zero values for normalisation<sup>300</sup>. New data supplied by Blichert-Toft<sup>301</sup> supports the use of the 91500 zircon for interlaboratory comparisons of radiogenic Hf isotope determinations. She argued that the larger spread in  $^{176}\text{Hf}/^{177}\text{Hf}$  from *in situ* measurements, compared with data from solution chemistry, probably reflected uncertainties arising from the corrections required for



prominent isobaric overlaps inherent in the analytical protocol for *in situ* analysis, rather than any significant heterogeneity. She provided a recommended value for the Hf isotopic composition of 91500 zircon, calculated by pooling her mean value with those from published studies using solution chemistry. The GJ-1 zircon series, derived from African pegmatites, distributed by GEMOC<sup>302</sup> is an alternative source of RMs for *in situ* measurements of  $^{176}\text{Hf}/^{177}\text{Hf}$ . Twenty four splits from two different GJ-1 zircons were analysed by solution ID MC-ICP-MS to determine their Lu/Hf and Hf isotopic compositions (as well as Hf and Lu contents). Isotope measurements by LA-MC-ICP-MS, using a 193 nm excimer laser, yielded homogeneous  $^{176}\text{Hf}/^{177}\text{Hf}$  data identical to the value, within analytical uncertainties, to that obtained from the solution work. Nasdala *et al.*<sup>303</sup> proposed zircon M257 as a RM for the determination of U-Pb ages by SIMS. This flawless, cut gemstone specimen from Sri Lanka satisfies the requirements for such a candidate material, in that it is homogeneous, has a concordant U-Pb isotopic system, a very low level of non-radiogenic Pb, as well as relatively high Pb and U concentrations, resulting in high count rates and good counting statistics. Its characteristics make zircon M257 a desirable RM for other microprobe techniques, such as LA-ICP-MS. However, the decision has been taken to restrict its use to ion microprobe laboratories to ensure its continued availability for at least one decade. New gravimetrically prepared U isotope RMs, the IRMM-074 series, have been prepared and certified<sup>304</sup>. Although primarily designed for the nuclear industry, these materials may be of interest to geoanalysts for the calibration of secondary electron multipliers widely used in isotope mass spectrometry. Two procedures, one static and the other dynamic, were proposed to assess the linearity of electron multipliers in MC-ICP-MS and TIMS instruments respectively.

The *measurement of boron isotopes* presents many challenges, including obtaining comparable results from SIMS, TIMS and ICP-MS. Because previous attempts to assess systematic differences in B isotope determinations produced a spread of data much greater than that predicted from the reported precisions, Aggarwal *et al.*<sup>305</sup> organised an inter-laboratory comparison based on materials that did not require any sample preparation. Two liquid standards (designated JABA and JABB), spanning the known natural range of B isotope ratios, were synthesized from salts enriched in  $^{11}\text{B}$  and  $^{10}\text{B}$ . Each laboratory was asked to measure the two boric acid liquid standards relative to an aliquot of NBS 951 also provided and to include an uncertainty estimate. There was no bias between the different analytical techniques, although it was noted that the ICP-MS techniques may produce higher  $\delta^{11}\text{B}$  values if the  $\text{Ar}^{4+}$  ion is not resolved out adequately. It was observed that the uncertainties in the measurement of  $\delta^{11}\text{B}$  were often underestimated – a common complaint in such exercises! Guidelines to assist the comparison of measurements between different laboratories were proposed.

Three methods were employed to measure the abundance of  $^9\text{Be}$  in *geological RMs* JA-2 (andesite) and JB-2 (basalt) from the GSJ<sup>306</sup>. These materials were chosen for this study because their  $^9\text{Be}$  content had been determined previously by another research group. Consistent  $^9\text{Be}$  data were obtained by ICP-QMS using standard addition and column separation methods, whereas reliance on a method employing an indium internal standard gave results that were about 10% lower. The  $^{10}\text{Be}$  abundance measurements were made on five occasions over a ten month period; the uncertainty of the  $^{10}\text{Be}/^9\text{Be}$  ratio was estimated to be 10% ( $1\sigma$ ).

*Revised reference values for IAEA sulfur isotope RMs* S-2 and S-3 have been recommended by workers from NIST<sup>307</sup>. These RMs are chemically pure and

homogenous silver sulfide materials, synthesized from a gypsum and sphalerite respectively. The revised values were determined using gas source IRMS and double spike multi-collector TIMS. The latter technique provided an independent method from the more traditional gas analyses, and gave confidence that the revised values were unbiased as well as being more precise than previous ones.

*Variations in Ca isotopes* can be used to study biomineralisation processes. The matrix of NIST SRMs 915a and 915b (artificial calcium carbonate) make them suitable for the analysis of marine organisms that have calcite structures, such as foraminifera, coral or coccolithophores. In contrast, NIST SRM 1486 (bone meal) is more appropriate for studies of vertebrate organisms with an apatitic skeleton. With this application in mind, Heuser and Eisenhauer<sup>308</sup> have published  $\delta^{44}\text{Ca}/^{40}\text{Ca}$  values for SRM 915b (a replacement for SRM 915a which is out of stock) and SRM 1486; the isotope ratios are quoted relative to SRM 915a.

## **4.2 Solid sample introduction**

### **4.2.1 Laser ablation ICP-MS**

For an overview of *recent trends in LA-ICP-MS with special reference to the Earth sciences*, an authoritative article by Sylvester<sup>309</sup> should be consulted (105 refs). As noted in last year's Update<sup>1</sup>, which covers a similar time period to Sylvester's review, the main themes include: the potential of fs lasers; ablation cell design; fractionation studies and *in situ* isotope measurements. In addition, he provides a critique of measurement uncertainties in LA-ICP-MS, taking examples from trace element determinations in mineral, pressed powder or fused beads, and radiometric ages derived from U-(Th)-Pb measurements. Total uncertainties for trace element concentrations were estimated to be ca. 10% (95% confidence limits) when errors on

the calibration values of RMs are taken into account. Similarly, the ages claimed for zircon and other U-rich accessory phases may only be accurate to about 2% (2sd) when uncertainties associated with Pb/U fractionation are included.

Although LA-ICP-MS is a relatively mature technique, improvements in its analytical performance, particularly to reduce matrix-dependent fractionation, are still desirable. A group at ISAS Dortmund<sup>310</sup> have provided *practical suggestions for improved performance* with both fs and ns laser technology, along with ideas for future experiments for a better understanding of the relevant processes. In a study of aerosol transport in LA-ICP-MS, Wälle and co-workers<sup>311</sup> measured detection efficiencies (defined as the ratio of ions reaching the detector to atoms released by LA) of silicate glasses, zircon and pure silicon using UV-ns- and NIR-fs-LA-ICP-QMS protocols. The detection efficiency for ns-LA of silicate glass using helium as the in-cell carrier gas was almost independent of laser wavelength and pulse duration. In contrast, the use of argon as the carrier gas suppressed the detection efficiency by up to a factor of 5 through less efficient conversion of the aerosol to ions and poorer ion transmission inside the ICP-MS instrument. Because aerosol expansion within the ablation cell can be a significant source of non-stoichiometric sampling, Hu *et al.*<sup>312</sup> devised a means of sampling the aerosol plume close to the ablation site of a 193 nm excimer laser. They monitored the composition of the expanding plume at different positions by changing the sampling distance between the nozzle tip of the gas outlet and the ablation site. Placing the nozzle tip inside the ablation cell led to an increase in peak height and reduction in signal width. This in turn shortened the washout time to approximately 2 s and almost eliminated the effects of aerosol recirculation in the cell. However, the positioning of the nozzle tip inside the cell was critical and further effort is required to develop the strategy for routine use.

The *analytical performance of fs lasers* continues to attract attention. The capability of a fs laser operating at 785 nm was assessed by replicate spot analysis of NIST and USGS glasses for 63 major, minor and trace elements<sup>313</sup>. A NIST SRM 612 glass was used as an external standard for calibration and <sup>43</sup>Ca as an internal standard to correct for matrix effects, drift and ablated mass. The measured concentrations were within 10% of the published values for most elements with RSDs of <10% in most cases, with little evidence of matrix effects. The authors felt that more work was required to establish the relative benefits of using fs lasers with different wavelengths, i.e. IR *versus* UV, as there did not appear to be any obvious advantages to compensate for the extra complexities of working in the UV. Ikehata *et al.*<sup>314</sup> demonstrated the use of a fs laser system operating at 780 nm, coupled with MC-ICP-MS, for the measurement of the Cu isotopic composition of pure copper metal and Cu-rich minerals at spot sizes down to 15 µm. The precision and accuracy obtained were comparable to those obtained by conventional solution MC-ICP-MS, e.g. 0.05‰ (2sd) for long term reproducibility, and significantly better than previous data for *in situ* Cu isotope determinations by ns LA-MC-ICP-MS.

The use of *liquid standards for calibration with fs LA-ICP-MS* has been explored<sup>315</sup>. Silicate glasses and brass were ablated at 265 nm in either single spot or scanning mode. Ablated aerosols were mixed with nebulised standards, either as a liquid or desolvated aerosol, using a Y-piece just before entry into an ICP-QMS instrument. Similar precisions were achieved under wet and dry plasma conditions, although selective loss of Cu occurred inside the desolvation unit. Liquid standards have the advantage of providing more flexibility in calibration strategies for a wide range of solids; in addition, better precisions can be attained because of the smaller uncertainty in their nominal values compared to solid standards. However, the

fractionation effects observed for Zn and Cd in liquid calibration standards limits their application in LA-ICP-MS generally.

Most analysis by LA-ICP-MS relies on one or more internal standards to correct for the varying mass of material ablated, either calculated from stoichiometry or obtained by an alternative analytical technique. Consequently, *an analytical strategy that does not involve the use of internal standards* is of interest. One method proposed for silicate minerals was to determine a comprehensive set of elements by LA-ICP-MS, convert them to equivalent oxide concentrations, scale the oxides to 100% and then convert them back to elemental concentrations<sup>316</sup>. It was concluded that oxide scaling produced data of similar accuracy and precision to those obtained using either NIST SRM 610 as an external calibration standard or a Ca, Fe or Si internal standard when analysing a range of glass CRMs. In a similar approach by Liu and co-workers<sup>317</sup>, an ablation yield correction factor (AYCF), calculated by normalising the sum of the metal oxides to 100 wt%, was used to correct for the absolute amount of material ablated. By applying an AYCF and employing several USGS reference glasses for calibration, it was shown that MPI-DING glasses could be analysed with an accuracy of better than 5% for major elements and between 5-10% for most trace elements, without any internal standardisation. Major element data for anhydrous minerals were generally consistent, within 5% uncertainty, with those obtained by EPMA, but minerals containing higher concentrations of anions (Cl, F, S and OH) were not amenable to this strategy as all the matrix elements need to be determined for good accuracy.

*Routine geological applications of LA-ICP-MS* abound as commercial instrumentation finds its way into more laboratories worldwide. Ablating NiS buttons to determine PGEs has been tried many times as a way of circumventing the need for

chemical dissolution. Resano *et al.*<sup>318</sup> devised a protocol to obtain accurate PGE concentrations with RSDs below 10% and LODs around 10 ng g<sup>-1</sup> when analysing platiniferous ores. This involved sampling 40-75 g of ore, grinding the NiS buttons, preparing a pellet of the powder using a polyethylene wax binder, ablating a line profile for 2-3 minutes per sample, using ammonia in a DRC to cope with all the spectral interferences and preparing matrix-matched calibration standards, combined with monitoring <sup>61</sup>Ni as an internal standard. The key factor in an improved protocol<sup>214</sup> for the analysis of soils and sediments by LA-ICP-MS was the reduction of the particle size to less than 1 µm. This provided representative sampling at the micro-scale, as well as better cohesion of the samples so that powder pellets could be made without the addition of a binder. Muller and co-workers<sup>319</sup> found that the accuracy of P determinations in crystalline quartz by LA-ICP-MS was comprised by an ICP-MS related background interference. Because published concentrations of P for a suite of RMs were poorly constrained, the RMs were analysed by phosphorus accelerator implantation and SIMS to provide independent and precise values on which to base the LA-ICP-MS calibration. However, the source of the <sup>31</sup>P background remained unclear and had to be corrected for empirically. It has been demonstrated that an excimer 193 nm LA system in conjunction with ICP-QMS is capable of producing accurate REE data in a variety of reference glasses at a spatial resolution of 24 µm<sup>320</sup>.

Laser ablation ICP-MS is currently one of the most sensitive and versatile microanalytical technique for determining the *composition of fluid inclusions*. The determination of S in fluid inclusions, however, is problematical because of its high first ionisation potential, polyatomic interferences from oxygen dimers on <sup>32</sup>S and <sup>34</sup>S and high blank levels. Guillong *et al.*<sup>321</sup> found that ICP-QMS and SF-ICP-MS were

equally well suited to the measurement of S in quartz, within certain limitations. The precision and accuracy, which were comparable for the two techniques, were not limited by interferences, but by an unknown source of S contamination in the quartz host mineral. Nevertheless, a method employing a careful baseline correction was developed to determine S as part of a multielemental suite, providing a LOD for S of ca.  $100 \mu\text{g g}^{-1}$  in brine inclusions of  $60 \mu\text{m}$  diameter. Recent experiments have shown that stray light from a 193 nm excimer laser can permanently modify the gas species in adjacent fluid inclusions<sup>322</sup>. Ablation for 40 s with a laser fluence of  $\sim 24 \text{ J cm}^{-2}$  produced new gas species in inclusions up to  $210 \mu\text{m}$  from the pit. These changes were attributed to molecular photodissociation induced by stray UV laser light. Although there was no evidence of any changes in the bulk chemistry of the inclusions, modification in the gas species would impact on temperatures calculated from microthermometry or Raman analysis, thus making it important to undertake these measurements on fluid inclusions prior to LA-ICP-MS.

There is no doubt that LA-MC-ICP-MS has had a dramatic impact on the field of isotope geochemistry over the last decade. A *review of recent isotope ratio applications* (146 refs)<sup>3</sup> noted a significant increase in publications in areas such as palaeoclimate and oceanography as a result of more funding opportunities in research associated with climate change.

*Developments in geochronology* continue to be of widespread interest, particularly dating of zircons in studies of the timing and nature of crustal and mantle events<sup>323</sup>. Key developments in LA-ICP-MS instrumentation and recent advances in U-Pb zircon geochronology have been reviewed by Cocherie and Robert<sup>324</sup>. To demonstrate the capabilities of the technique compared to TIMS and SIMS, they analysed four zircons covering a ages from 290 to 2440 Ma using a 213 nm laser



coupled to an MC-ICP-MS instrument equipped with a multi-ion counting system; this allowed static acquisition of all peaks of interest with high sensitivity. Precisions of better than 1% and 3% (2 sigma) were obtained for  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{206}\text{Pb}/^{238}\text{U}$  respectively. They concluded that the expected improvements in laser systems and the technology of ion counters should result in the performance of LA-ICP-MS rivalling that of SIMS for *in situ* age determinations. In order to overcome the complications associated with analysing intricately zoned zircon crystals, Johnston and colleagues<sup>325</sup> developed a novel method of sampling and analysing zircon volumes as small as 12-14  $\mu\text{m}$  in diameter and 4-5  $\mu\text{m}$  in depth (<3 ng of zircon). Channeltron detectors were required to monitor the intensities of the Pb peaks because of the low yields from the small diameter craters and slow laser pulse rate. The U-Pb isotopes were measured by MC-ICP-MS, using a 30-second acquisition routine followed by data reduction offline based on a total ion counting method; the measurement errors were calculated as a function of the number of counts. This rapid small-volume protocol was able to reproduce the ages of eight zircon standards to within 2% of published ages obtained by ID-TIMS. An automated method for U-Pb dating of zircon by LA-SF-ICP-MS with a single collector was described by Frei and Gerdes<sup>326</sup>. Accurate and precise U-Pb ages were obtained from single spots with relatively high spatial resolution (20-30  $\mu\text{m}$  wide and 15-20  $\mu\text{m}$  deep) in ablation times of 30 s. The analytical points were preset so that data could be acquired in automated mode for up to 16 hours per day. Proven calibration and data reduction strategies were employed to correct for elemental fractionation, sample transport, ionisation and instrumental mass bias. Protocols devised for U-Pb dating of zircons by LA-MC-ICP-MS have been successfully applied to the isotopic analysis of microscopic uranium oxide grains<sup>215</sup>. Precision and accuracy were assessed by replicate analyses of natural uraninite grains

and the relative uncertainty for  $^{235}\text{U}/^{238}\text{U}$  was 0.2% ( $2\sigma$ ). Previous research demonstrated that  $^{207}\text{Pb}/^{206}\text{Pb}$  could be monitored accurately during Hf isotope determinations in homogenous zircon chips without degrading the Hf isotope data. This strategy was applied to the analysis of zircons with complicated growth histories<sup>327</sup>. The concurrent measurement of Pb and Hf isotopes was conducted in an alternating two cycle routine. Although the  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio by itself is not an unambiguous indicator of the time of zircon growth, particularly in complex systems, the estimated ages were used to detect changes between domains of different ages during ablation, which might otherwise led to inaccurate Hf isotope ratios and spurious geological interpretations. The technique was applied to a case study of detrital zircons from modern river sands in the Himalayas. Of relevance is a study by Kent<sup>328</sup> who compared measurements of Pb isotope ratios by LA-MC-ICP-MS using parallel Faraday cup and ion counter detector array with those made using solely Faraday cups<sup>328</sup>. He demonstrated that both approaches produced accurate and precise data, although where the Pb ion beam was expected to be relatively small, the combined Faraday cup and ion counter array provided a significant improvement in precision.

Caddock and co-workers<sup>329</sup> investigated strategies for making accurate  $^{34}\text{S}/^{32}\text{S}$  measurements by *HR-MC-ICP-MS* in sulfide and sulphate minerals using solution and laser ablation sample introduction. Major isobaric interferences from molecular  $\text{O}_2^+$  ions were removed by applying sufficient mass resolution and determining S intensities on interference-free plateaus. Memory effects and residual oxygen-tailing were small, typically  $<0.2\text{‰}$ , and mathematically removed by on-peak zero subtraction and by bracketing samples with standards giving similar signal intensities (within 20%). However, matrix effects were shown to be significant, up to 0.7‰,

making it essential to use appropriate matrix-matched standards to correct for instrumental mass bias.

#### **4.2.2 Laser-induced breakdown spectroscopy**

The LIBS technique is an option when *fast, inexpensive in situ analysis* is required. For this reason LIBS has found application in the mining and mineral processing industries. Because LIBS is a surface technique, a link between the sample surface and the bulk composition has to be assumed or demonstrated. Researchers from CSIRO Minerals in Australia<sup>330</sup> have explored the combination of LIBS and principle components regression for fast and accurate multi-elemental analysis of iron ore pellets. Robust calibration models were determined for Al, Fe, K and Si, while the results for Mn were “encouraging”. Phosphorus, present at low levels in the ores, proved to be the most difficult element to determine accurately. The next step would be to transfer this protocol to the analysis of loose chipped material at the mine site and on conveyor belts. Another geological application of LIBS is the analysis of crusts in karstic formations<sup>331</sup>. A portable LIBS system has been developed and assessed for the *in situ* characterisation of speleothems in a large cave system in Spain. A laser beam from a Q-switched Nd:YAG laser was focussed onto the target surface and the plasma emission collected by a fibre optic cable and guided to the slit of a compact spectrometer. The irregular morphology of the cave system did not affect the instrument, although other factors such as the high humidity had to be overcome. Qualitative measurements of Al, C, Ca, Fe, Mg, Mn, Sr, Si and Ti were obtained, together with depth profiles of Sr/Ca ratios that could be used as indicators for paleoclimatology and paleohydrology.

## 4.3 Sample treatment

### 4.3.1 Sample dissolution

The quality of analytical data is often limited by the manner in which the samples are prepared prior to measurement. Thus a reminder of some of the key aspects of preparing environmental samples for analysis is always welcome<sup>332</sup>, although much of this review is primarily concerned with waters.

A two-stage *microwave-assisted digestion* procedure using HNO<sub>3</sub>, HCl, HF and H<sub>3</sub>BO<sub>3</sub> has been developed for the analysis of sulfide ores by ICP-AES<sup>333</sup>. In the first stage, 0.2 g of sample was digested with a combination of HNO<sub>3</sub>, HCl and HF in a closed Teflon vessel in a microwave oven at 200 °C for 30 min. After cooling, H<sub>3</sub>BO<sub>3</sub> was added and the vessel reheated to 170 °C for 15 min. Analysis of six CRMs indicated recoveries between 95 and 105%, with precisions of 5% or better, for a range of major and trace elements. In the absence of a published method for the microwave digestion of komatiites (primitive lava), Nna-Mvondo *et al.*<sup>334</sup> devised their own based on a two-step procedure, which they found to be more effective than a single one. A combination of HF, HNO<sub>3</sub> and water was employed in the first digestion step, which was followed by drying down on a hot plate at 105 °C and adding HCl to the residue, before the second microwave digestion. Two USGS basalt CRMs were analysed for 17 elements by ICP-MS. Acceptable recoveries of 90-120% were obtained, except for Cu (51%) and Pb (165%) in BCR-2; a mitigating factor may be that the concentrations supplied by USGS for these elements are information values only.

In the Carius tube method, which is often used to *digest refractory PGE minerals*, the samples are dissolved in *aqua regia* in a sealed glass tube at high

temperatures. However, Qi and Zhou<sup>335</sup> demonstrated that this procedure underestimated the total PGE content of an ultramafic rock, because some of the PGE remained in the silicate residue. Complete recoveries were obtained by treating the residue from the Carius tube digestion with HF and combining the resulting solution with that from the Carius tube prior to Os distillation.

A combination of HNO<sub>3</sub> and HF is conventionally employed in the acid digestion of silicate rocks, often in conjunction with HClO<sub>4</sub>. However, a *safer substitute for HF* is desirable as many laboratories prohibit its use because of its highly corrosive and toxic nature. Mariert and co-workers<sup>170</sup> assessed the use of ammonium fluoride in place of HF and HClO<sub>4</sub> in an acid digestion of three CRMs, including a basalt and a soil. More H<sub>2</sub>O<sub>2</sub> was employed, compared to the method with HF and HClO<sub>4</sub>, to compensate for the oxidising effect of HClO<sub>4</sub>. The results obtained for up to 16 elements by ICP-MS were within 10% of the reference values, with precisions of 8% or better. It was concluded that the procedure with NH<sub>4</sub>F was as effective as that using HF and HClO<sub>4</sub>, although the presence of NH<sub>4</sub>F provided new possibilities for polyatomic interferences through the formation of complexes with NH<sub>3</sub>, as well as the potential for elements like As, Sb and Ta to form colloidal hydroxides in ammoniacal solutions.

### **4.3.2 Separation and preconcentration**

In recent years, many alternative substances have explored to improve the *separation and preconcentration of trace elements in solid-phase extractions*. Some that have found utility in this respect are carbon nanotubes, ion-imprinted polymers, biosorbents and nanometer material. An overview of the application of these and other solid sorbants in analytical procedures has been published<sup>336</sup>. The potential of multiwalled carbon nanotubes (MWTs) for the separation and preconcentration of Au in

geological and water samples has been investigated<sup>108</sup>. Gold was adsorbed quantitatively on a microcolumn packed with MWTs and then eluted with 3% thiourea in 1 mol L<sup>-1</sup> HCl prior to measurement by FAAS; an enrichment factor of 75 was achieved.

The *extraction chromatography resins UTEVA and TRU*, produced by Eichrom Technologies, have found widespread application in the separation of one or more of the actinide elements. A systematic study of the properties of these two resins has been undertaken using model solutions and geological RMs spiked with <sup>232</sup>Th, <sup>238</sup>U, <sup>237</sup>Np, <sup>239</sup>Pu and <sup>241</sup>Am<sup>337</sup>. The first four nuclides were determined simultaneously by ICP-MS; <sup>241</sup>Am was measured by  $\gamma$ -spectrometry. A procedure for separating Pu, Th and U on UTEVA resin was successfully applied to different sample types, whereas another one for the separation of Am, Pu, Th and U using TRU resin still required validation.

A fusion or sinter with Na<sub>2</sub>O<sub>2</sub> prior to measurement by ICP-MS is a powerful method for the *determination of REE concentrations in geological materials*. In a modified procedure for the determination of low levels of REE in ultramafic and sulfide samples, Sun and Sun<sup>338</sup> used graphite crucibles for the Na<sub>2</sub>O<sub>2</sub> fusion at 750 °C. The REE were then separated and preconcentrated by inorganic coprecipitation assisted by triethanolamine, before determination by ICP-MS following a 20-fold dilution. Limits of detection ranged from 4.46 ng g<sup>-1</sup> for Ce to 0.02 ng g<sup>-1</sup> for Tm and the blanks were shown to be comparable to those obtained from a HF-HClO<sub>4</sub> acid digestion; it should be noted that the comparison values were published in 1992!

Balaram<sup>339</sup> has reviewed methods for the *determination of PGEs* in exploration studies. He concluded that, in spite of advances in instrumental methods, traditional fire assay methods will not be replaced in the near future because of the

advantages they offer in terms of the relatively large mass of sample analysed and specialised sample attack for difficult materials such as chromite.

A two-step process for the determination of Se in small quantities (c. 50 mg) of sulfide minerals was developed<sup>340</sup>. After dissolution in 2M HNO<sub>3</sub>, transition metals were removed by precipitation as metal hydroxides under alkaline conditions to prevent sorption of Se, followed by further metal removal by chelating resin. Analysis of the RM CCu-1c, a copper concentrate supplied by CCRMP, by HG high resolution ICP-MS demonstrated quantitative Se recoveries of  $100 \pm 5\%$  with a LOD of  $4 \mu\text{g g}^{-1}$ .

*Separation chemistries for isotope ratio measurements* continue to evolve. A new method developed for the sequential separation of Pb, Nd and Sr was designed to minimise the number of evaporation steps<sup>341</sup>. This resulted in a higher throughput, especially when MC-ICP-MS was employed, although the solutions prepared were also suitable for TIMS. After a HF-HClO<sub>4</sub> digestion, the isotopes of interest were purified in a three-step separation procedure. The first column, containing Sr resin, separated Sr and Pb from the REE. In the second stage, the light REE were collected on a column packed with the cation exchange resin AG50W-X10. Finally Nd was separated from Sm on a column containing Ln resin. Measurements of Nd and Sr isotope ratios in RM JB-3 (basalt, GSJ) verified the chemistry and mass spectrometry strategies in this study. Makishima and Nakamura<sup>342</sup> devised a method of preconcentrating Hf, Mo, Nb, Ta, W and Zr by coprecipitation with titanium and applied it to studies of the Lu-Hf isotope system. Silicate RMs (basalt and peridotite) were digested with HF-HClO<sub>4</sub> after the addition of titanium and Lu/Hf spike solutions. Subsequent drying to eliminate fluorine encouraged the formation of titanium compounds. The sample was then dissolved in nitric acid and centrifuged to collect the titanium oxide/hydroxide precipitate. The supernatant containing Lu, Nd,

Pb, Sm and Sr was retained and used to determine isotope ratios by MC-ICP-MS after sequential purification. The Ti precipitate was redissolved and Hf was separated from the other elements using UTEVA column chemistry. The yields for Hf, Mo, Nb, Ta, W and Zr were between 84 and 98% and total blanks of 16, 2.4, 3, 11, 0.4 and 60 pg were reported for Hf, Lu, Nd, Pb, Sm and Sr respectively. Magnesium isotope ratios have been determined in a wide variety of environmental materials, including silicate and carbonate rocks, using an adaptation of two existing methods for the separation of Mg from complex matrices<sup>173</sup>. After dissolution, transition metals were removed using an AG-MP1 anion-exchange resin, and then the Mg was separated from alkali (Na, K) and bivalent cations ( $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Sr}^{2+}$ ) by two passes through a column containing AG50W-X12 cation-exchange resin. Magnesium recoveries of  $100\pm 8\%$  were achieved. The Mg isotope ratios of 11 RMs were determined using two different MC-ICP-MS instruments and the  $\delta^{26}\text{Mg}$  values plotted against the corresponding published values. All points lay on a 1:1 line, showing that the Mg separation protocol did not induce any systematic shift in the Mg isotope ratios. The long term reproducibility, assessed by repeated measurements of Mg standard solutions and natural RMs, was 0.14%.

### 4.3.3 Speciation studies

For a full discussion of *developments in elemental speciation*, the recent Update on this subject should be consulted<sup>141</sup>.

Procedures developed for the determination of *organotin compounds in marine sediments* are often a compromise between cost, availability of equipment and the efficacy of separation, sensitivity and selectivity. Consequently, numerous methods for their determination have been published. In their review of the analytical



techniques available, Staniszewska and co-workers<sup>343</sup> supply practical solutions to some of the problems most frequently encountered in such analysis. Expensive equipment and time-consuming analytical procedures are normally required to separate the organotin species from a complex organic matrix and preconcentrate them to a level that permits their measurement by highly selective and sensitive chromatographic techniques. One such example is the method involving headspace single drop microextraction combined with GC-ICP-MS detection reported by Xiao *et al.*<sup>344</sup>. However, a low cost procedure, based on HPLC with UV detection, has been developed for butyltins in sediment and water samples<sup>345</sup>. The extraction involved the use of hexane containing 0.05-0.5% tropolone and 0.2% NaCl in water at pH 1.7. Separation of the butyltins was performed in isocratic mode on an ultra cyanopropyl column with a mobile phase of hexane containing 5% THF and 0.03% acetic acid. The efficacy of this method was confirmed using standard GC-MS techniques, with LODs of 0.70 µg ml<sup>-1</sup> for TBT and 0.50 µg ml<sup>-1</sup> for DBT, similar to those obtained by GC-MS. A new self-tuning single mode focussed microwave technology has been evaluated for the extraction of organotin (and organomercury) compounds from marine sediments and organisms<sup>346</sup>. The results obtained using species-specific ID GC-MS demonstrated that MBT, DBT and TBT could be extracted quantitatively in a fast, reliable and routine manner.

A review<sup>183</sup> (176 refs) of chemical reagents employed to *extract different Hg species from soils and sediments* concluded that there was little consensus, and that a standard protocol and appropriate RMs were required. Researchers were advised to select the most appropriate reagent depending on the nature of the sample and Hg species under investigation, and validate their procedure as far as possible. A method based on the thermal evaporation of Hg species from solid samples in combination

with AAS has been described<sup>197</sup>. The procedure relies on the differences in the thermal characteristics of HgCl<sub>2</sub>, CH<sub>3</sub>HgCl and HgS. A Hg analyser with a pyrolytic attachment was modified by equipping it with a thermocouple for temperature control in the dosing unit and a homemade device for moving the unit inside the atomiser. Samples were mixed with aluminium oxide (1+4) and 10 mg placed in the dosing unit, which was heated at a rate of 1°Cs<sup>-1</sup> under an air flow of 1 L min<sup>-1</sup>. The total area under the peak of the thermal release profile was considered as the analytical signal for Hg quantification. Detection limits were calculated to be 0.70, 0.35 and 0.20 ng for HgCl<sub>2</sub>, CH<sub>3</sub>HgCl and HgS respectively. A range of different extraction methods and reagents were compared for the measurement of Hg species in coal<sup>347</sup>. Microwave-assisted extraction at 90 W for 5 min using TMAH provided the highest recoveries of MeHg and EtHg in their original form.

#### **4.4 Instrumental analysis**

##### **4.4.1 Atomic absorption and atomic fluorescence spectrometry**

A short *review of developments in AAS* applied to the analysis of geological materials confirmed that most of these are concerned with analyte preconcentration rather than technical improvements<sup>348</sup>. An on-line system containing a mini-column packed with Amberlite XAD-4 modified with a Schiff base was developed to preconcentrate Cd, Co, Cu, Ni and Pb from *aqua regia* digests of soils and sediments<sup>282</sup>. Treatment of the acid digests with sodium fluoride and buffering to pH 6 prior to column separation prevented the large concentrations of iron present from overloading the capacity of the column. The analytes were eluted from the column with 0.1 M nitric acid directly into a FAAS instrument; the accuracy of the proposed method was evaluated by the analysis of CRMs. A simple FI system, consisting of one peristaltic pump and a

solenoid valve, was successfully employed for the rapid determination of As, Bi and Se in sediments by HG-AAS<sup>200</sup>. To ensure the analytes were in the correct oxidation state, they were pre-reduced off-line using hydroxylamine hydrochloride for Se and a mixture of KI and ascorbic acid for As and Bi. Interference from transition metals was eliminated by the addition of thiourea and EDTA to the sodium borohydride reductant. The use of water as carrier streams for the sample and reagent provided a stable baseline and better sensitivity. Under optimised conditions, a throughput of 360 samples per hour was achieved.

In *thermospray flame furnace AAS* the sample is introduced into a nickel tube positioned on a standard burner head. Although the power of detection obtained with this technique is promising, the low temperature of the flame restricts the technique to volatile elements. To overcome this disadvantage, an on-line derivatisation strategy for improving the sensitivity of Co has been developed<sup>349</sup>. Lake and marine sediment CRMs were digested by a microwave-assisted acid decomposition involving HF. After adjusting the final solution to pH 3, on-line derivatisation using DDTC as the complexing agent provided a LOD of 7  $\mu\text{g L}^{-1}$  and Co values within the stated limits of uncertainty.

*Chemical vapour generation AFS* is widely used for the determination of the classic hydride-forming elements. In a novel development, room temperature ionic liquids (RTILs) have been exploited to enhance the chemical vapour generation (CVG) of Ag, Au and Cu<sup>350</sup>. The addition of N-butylpyridinium tetrafluoroborate (a typical RTIL) was shown to improve the CVG of these elements and reduce the interference from various transition elements. It was proposed that the RTIL prevented metal nanoparticles, which form the volatile metal species reaching the

atomiser, from coalescing. The RTIL-enhanced FI-CVG-AFS method was validated by the measurement of Ag and Au in ore grade CRMs.

#### **4.4.2 Atomic emission spectrometry**

Many of the *developments in geological applications of ICP-AES* are concerned with sample preparation and introduction rather than the technique itself, and therefore may be applicable to ICP-MS as well. This is well illustrated in reviews by Linge<sup>351</sup> and Evans *et al.*<sup>352</sup>. Thus Padmasubashini and Murty<sup>353</sup> investigated the use of chitin for solid phase extraction and preconcentration of Hf, Mo, W and Zr from geological materials. After an alkali fusion, ascorbic acid was added to the sample solutions to complex the iron present, which would otherwise interfere with the preconcentration step. Powdered chitin was added and the solution left to stand for 2 hours, with intermittent stirring, before filtration. The filter paper containing the chitin was ignited and the residue digested with a HF-HCl-H<sub>2</sub>SO<sub>4</sub> mixture, evaporated twice and finally taken up in 5% HCl. The method has the advantage of considerably reducing the TDS arising from the sample matrix and fusion; reported LODs by ICP-AES were 0.13 µg g<sup>-1</sup> for Hf, Mo and Zr, and 0.13 µg g<sup>-1</sup> for W. As indicated in Section 4.3.2, nanometer material is now finding favour as an absorbent for solid phase extraction. Nanometric TiO<sub>2</sub> immobilised on silica gel has been used to preconcentrate Pd and Pt from geological samples prior to measurement by ICP-AES<sup>354</sup>. The samples (peridotite and low platinpalladium ore CRMs from the IGGE) were roasted at 600 °C for one hour prior to a HF-based mixed acid digestion, resulting in a final solution in HCl adjusted to pH 7. They were then loaded onto a PTFE micro-column containing immobilised nanometer TiO<sub>2</sub> and eluted with 3% m/v thiourea in 1 mol l<sup>-1</sup> HNO<sub>3</sub>, providing an enrichment factor of 100. Recoveries of between 92 and 102% were obtained for

CRMs containing between 58-570  $\mu\text{g g}^{-1}$  Pd and Pt. Major cations and anions had no obvious influence on the adsorption of Pd and Pt under the conditions selected.

*Microwave plasma optical emission spectrometry* is a minority interest, usually performed on home-made instruments. A method for the determination of As in environmental samples, based on electrochemical hydride generation for sample introduction into a microwave plasma, has been proposed<sup>355</sup>. A continuous flow thin layer electrolysis cell with a Pt cathode was used to generate hydrides electrochemically at the surface of the cathode, which was separated from the anode compartment by a cation exchange membrane. A masking agent of L-cysteine or KI-ascorbic acid (1+1) was required to negate interferences from other transition metals such as  $\text{Cu}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$  and  $\text{Ni}^{\text{II}}$ ; a coal fly ash CRM was used to validate the procedure.

#### **4.4.3 Inductively coupled plasma mass spectrometry**

Now that ICP-QMS instrumentation equipped with reliable cell technology is well-established, it is used on a routine basis to provide comprehensive *multielement analysis of geological and environmental materials*. This has not discouraged a flurry of papers emphasizing the flexibility and power of quadrupole ICP-MS for geochemical analysis; these may provide some pointers for relatively inexperienced analysts<sup>356, 357, 358</sup>. The method proposed by de Madinabeitia *et al.*<sup>357</sup> involved fusion with  $\text{LiBO}_2$  and dissolution in  $\text{HNO}_3$  with a few drops of HF to stabilise the HFSE. The use of high dilution factors, e.g. 1:6500, together with actions like cone conditioning, specific washout solutions and the analysis of drift correction standards provided control on and correction for signal drift during the measurement of major and ultratrace elements by ICP-QMS. A similar approach was employed by Niolaeva and co-workers<sup>358</sup> to determine REEs and HFSEs using a high resolution ICP-MS

with ultrasonic nebulisation to improve the LODs. A method previously applied to the analysis of soil and sediments for REEs plus Ba, Hf, Sc, Th, Y and Zr has been revised so that it is now more widely applicable, particularly to rocks containing highly resistant minerals<sup>359</sup>. The procedure, which involves an alkaline fusion (NaOH-Na<sub>2</sub>O<sub>2</sub>) and co-precipitation on iron hydroxides, now includes the addition of a Tm spike prior to fusion to provide accurate data even when there is loss of sample during analysis. It is unusual for the boron content of rocks to be routinely measured alongside other trace elements, such as the HFSEs, because of the ease with which it is volatilised under acid conditions. By adding mannitol to the HF-HNO<sub>3</sub> acid mixture, Nagaishi and Ishikawa<sup>360</sup> stabilised B as a boron-mannitol complex, together with fluoro-HSFE ions such as NbF<sub>6</sub><sup>2-</sup> and ZrF<sub>6</sub><sup>2-</sup>. Instead of aspirating this solution directly into an ICP-MS instrument with the aid of an HF-resistant sample introduction system and ID spikes, as in previous publications, they manipulated the sample through stages of evaporation, addition of internal standards and dissolution, while keeping the temperature well below 100 °C to minimise any loss of B. A five-minute rinse with 0.015 M HF/0.15 M HNO<sub>3</sub> between samples provided effective washout with negligible damage to the glass components. Fourteen GSJ and 3 USGS rock RMs were analysed in this study to demonstrate that B, Hf, Nb, Ta and Zr could be determined with satisfactory precision and accuracy without the use of ID.

Multi-collector ICP-MS methodology now dominates the literature on isotope ratio measurements and has spawned a rapid growth in Earth science applications. The breadth and diversity of these applications is reflected in *several recent reviews*, such as that by Woodhead<sup>361</sup>. A special issue of *Chemical Geology* from the 17th Goldschmidt conference in August 2007, highlighted the results presented on stable isotopes in high-temperature geochemistry. The preface to this issue gives some

background to recent developments in this field<sup>362</sup>. An overview<sup>46</sup> (159 refs) of the use of Pb isotopes as tracers of environmental pollution contains a useful summary of published data of the Pb isotope composition, mainly  $^{206}\text{Pb}/^{207}\text{Pb}$ , of different anthropogenic sources. Aggarwal and co-workers<sup>363</sup> provided a couple of case studies using Pb and Sr systems in their review of the application of isotope geochemistry in forensic science. Science administrators might well take heed of an article on the development of geochronology in the state of Victoria, Australia<sup>364</sup> and the lessons learnt on the most effective way to set up, manage and support complex research facilities.

The influence of *non-spectral matrix effects on the accuracy of Pb isotope ratio* measurements by MC-ICP-MS has been investigated<sup>365</sup>. These effects can, in theory, be corrected using external normalisation, but this is only reliable if the element chosen to monitor instrumental mass fractionation responds to the sample matrix in a similar manner to the analyte. Doping experiments demonstrated that non-spectral matrix effects resulted in inaccuracies ranging from -150 to +120 ppm per amu in Pb isotope ratios corrected for mass bias using thallium. Although small, these values are significant for mantle geochemistry studies. The inaccuracy resulted from per mil level variations in the Tl to Pb mass bias ratio induced by the residual matrix components, such as aluminium, calcium, iron and magnesium, present after purification by anion exchange chromatography. The matrix also caused increased Pb and Tl sensitivity. The addition of a common matrix of magnesium to samples and standards was proposed as a viable alternative to thorough purification to reduce or eliminate non-spectral matrix effects.

The advantages of ICP-MS, and particularly SF-ICP-MS, for the *determination of Pu isotopes and other transuranic elements* has been documented

(182 refs)<sup>50</sup>. This review emphasizes the new and emerging studies of transuranic elements in earth and environmental sciences made possible by low cost and widely available ICP-MS data. Liao *et al.*<sup>366</sup> adapted and optimised a published method for the determination of Pu isotopes in marine sediments to the analysis of freshwater lake sediments. A strong base anion exchange resin, AG MP-1M, was used to separate the Pu isotopes, with concentrated HBr as the final eluant prior to measurement by SF-ICP-MS. Because of the relatively simple sample preparation procedure, this method is stated to be cost-effective and well suited to the analysis of large numbers of sediment samples. However, their mean <sup>240</sup>Pu/<sup>239</sup>Pu atom ratio of 0.144 for NIST SRM 4354 (freshwater lake sediment) was lower than those reported by other laboratories. The authors suggested that this discrepancy may be because the material is isotopically heterogeneous – it will be interesting to see whether any other laboratory substantiates this claim. A new protocol for the separation and measurement of Pa, Th and U isotopes in marine sediments by MC-ICP-MS has been published<sup>367</sup>. Although Th and U were completely dissolved after the first microwave-assisted digestion with HNO<sub>3</sub>, HF and HCl, a second digestion with reverse *aqua regia* (2+1 HNO<sub>3</sub>/HCl) on a hot plate was employed to ensure that all Pa had dissolved and spike equilibration achieved. The elements of interest were separated and then the Pa fraction was purified further using Dowex AG1-X8 anion exchange resin, providing good separation of U from Pa; typical <sup>231</sup>Pa/<sup>238</sup>U ratios measured in the Pa fraction were around  $6 \times 10^{-3}$ . A rapid method for determining <sup>241</sup>Am in marine sediments by isotope dilution SF-ICP-MS combined with extraction chromatography has been developed<sup>368</sup>. A selective CaF<sub>2</sub> co-precipitation procedure followed by extraction chromatography separation and purification using Eichrom TRU resin was employed to remove the major elements and preconcentrate <sup>241</sup>Am. A high efficiency



sample introduction system combined with SF-ICP-MS enabled the authors to achieve a detection limit of  $0.32 \text{ fg g}^{-1}$ , which was better than that by alpha spectrometry, and allowed depth profiles of  $^{241}\text{Am}$  in sediment cores to be studied.

Investigations into the systematics of so-called “*non traditional*” *stable isotopes* continue to flourish. Whilst a high degree of precision permits a range of geological questions to be addressed, confirming the accuracy of the data remains a challenge, as bias can easily be introduced during chemical preparation and analysis. For this reason, the standard addition method was used to verify the accuracy and precision of Mg and Ca isotope data by MC-ICP-MS<sup>369</sup>. Although good agreement with published values was obtained for the analysis of seawater, there were discrepancies between the estimates of  $\delta^{26}\text{Mg}$  in silicate material and those reported previously for the same samples, possibly through an artefact induced by the chemical purification of Mg prior to analysis.

A new procedure developed for the determination of *Cr isotope ratios in geological samples* by MC-ICP-MS<sup>370</sup> employed a two column separation system of anion and cation exchange resins to avoid any potential matrix effect and isobaric interferences, while maintaining high recovery of Cr. Measurement precisions (2s) of 110, 60 and 100 ppm for  $^{50}\text{Cr}/^{52}\text{Cr}$ ,  $^{53}\text{Cr}/^{52}\text{Cr}$  and  $^{54}\text{Cr}/^{52}\text{Cr}$  respectively were reported. Inexplicably, for some geological matrices, this methodology was not effective in reducing the concentrations of iron and titanium below 2% relative to the Cr concentrations in the eluate. As a result, only  $^{53}\text{Cr}/^{52}\text{Cr}$  could be measured in such samples. Significant differences in Cr isotope ratios were found between basic igneous rocks and organic-rich shale, as well as between that shale and its natural combustion products.

The determination of the platinum group elements (PGEs) in geological samples presents a variety of problems during both their preparation and measurement by ICP-MS. These are compounded by their low natural abundances and heterogeneous distribution. A procedure developed by Paleskii *et al.*<sup>371</sup> employed *isotope dilution to improve the accuracy of PGE measurements*. Samples were spiked with <sup>191</sup>Ir, <sup>190</sup>Os, <sup>106</sup>Pd, <sup>194</sup>Pt, <sup>185</sup>Re and <sup>99</sup>Ru before microwave digestion with a 1+3 mixture of HCl and HNO<sub>3</sub>. The analytes were separated from the matrix by cation exchange on BioRad AG 50Wx8 resin; the eluant obtained was suitable for direct analysis by an SF-ICP-MS instrument fitted with an ultrasonic nebuliser. To reduce memory effects to a minimum, wash solution was introduced for up to 10 minutes between samples. Detection limits ranged from 0.005 ng g<sup>-1</sup> to 0.2 ng g<sup>-1</sup> for Pd. Isotope dilution was also employed by Rodríguez-Castrillón and colleagues<sup>40</sup> to determine Pt in environmental samples containing comparatively high levels of hafnium without any chemical separation. Their method was based on calculating the contribution of hafnium oxide as an independent factor in the observed isotope pattern of Pt in a sample spiked with enriched <sup>194</sup>Pt. The procedure required the measurement of three Pt isotope ratios, which was performed on a quadrupole ICP-MS instrument. It was possible to correct for mass bias by an internal procedure, in which the regression variance was minimised, because the mass bias factor of hafnium oxide was virtually the same as that for Pt.

#### **4.4.4 Other mass spectrometric techniques**

*Thermal ionisation mass spectrometry (TIMS)* is still considered to be the technique of choice for isotopic measurements where the amount of sample is limited and small amounts of the element of interest are available. An example is the determination of

Sr isotope ratios in individual melt inclusions<sup>372</sup>. Micro-milling was preferred over laser ablation sampling, and the micro Sr separation chemistry using Eichrom Sr spec resin was modified for application to samples containing sub-ng amounts of Sr. All potential contributions to the blank were assessed; total procedural blanks were  $5.4 \pm 0.3$  pg Sr and  $1.9 \pm 0.7$  pg Rb. By applying blank corrections, the Sr isotope composition could be determined to an accuracy of better than 400 ppm on samples as small as 25 pg Sr. Harvey and Baxter<sup>373</sup> developed an improved TIMS method for high precision Nd isotope analysis of samples containing small amounts (1-10 ng) of Nd. Analysing Nd isotopes as  $\text{NdO}^+$  is a well known technique, often involving an oxygen bleed and/or silica gel. In this study, samples were loaded with a tantalum oxide phosphoric acid slurry, which provided the oxygen source. With external reproducibilities of 13-21 ppm ( $2\sigma$  RSD) and an internal precision of less than 10 ppm ( $2\sigma$  RSD), when combined with successful column chemistry, this method has the potential to expand the range of materials suitable for high precision Nd isotope measurements. Single crystal chemical abrasion ID TIMS has been used for U-Pb dating of zircon and rutile from the PGE-rich Merensky reef to provide a precise age of crystallisation for the Bushveld Complex<sup>374</sup>. During an investigation of Ni isotopic anomalies in iron meteorites and chondrites, Chen and co-workers<sup>375</sup> concluded that TIMS was the preferred analytical technique because of the numerous atomic and molecular mass interferences present in the determination of Ni by MC-ICP-MS. Improved analytical procedures resulted in a  $\text{Ni}^+$  ionisation efficiency of 1‰ and chemical separations reduced mass interferences to 1 ppm. Consequently, no interference corrections were necessary for the isotopes measured. Mass bias was corrected using  $^{62}\text{Ni}/^{58}\text{Ni}$ . When they applied this method to some meteorites analysed by other workers, they could not find any evidence to support previous descriptions of

Ni isotopic anomalies by workers using MC-ICP-MS. They concluded that complex astrophysical scenarios were not required to account for the very peculiar Ni isotope anomalies reported elsewhere.

An authoritative review (21 refs)<sup>376</sup> of *advances in secondary ion mass spectrometry (SIMS or ion probe)* during 2006-2007, highlighted significant developments in instrumentation, analytical methodology and the characterisation of new RMs. By the end of this period, total sampling masses down to the 10 fg range, spatial resolutions of better than 100 nm and uncertainties on major element isotope ratios of better than  $\pm 0.2\%$  were being reported. This paper also discusses some research results that were only possible because of the unique capabilities of SIMS.

Historical perspectives are often valuable to those new to a field. The story of the development of the *Sensitive High Resolution Ion Microprobe (SHRIMP)*, the first ion microprobe dedicated to geological isotopic analysis, is one such example<sup>377</sup>. The SHRIMP has often been regarded as an instrument solely used for U-Pb geochronology, whereas its capabilities are far more extensive. Advances in SHRIMP instrumentation include multiple collection and negative ion measurement for stable isotope analysis, as well as the construction of different versions for specific applications.

Technical improvements to the SHRIMP II enabled Ickert and co-workers<sup>378</sup> to determine the *in situ oxygen isotopic composition* of insulating materials such as silicates, carbonate, phosphates and oxides, on a scale of 25  $\mu\text{m}$  with better than 0.4‰ precision and accuracy at 95% confidence limits. Key aspects of this achievement included the introduction of a  $\text{Cs}^+$  source, a multiple collector, charge neutralisation using an oblique-incidence electron gun, Helmholtz coils and new sample mounts that reduce geometry effects. In another study<sup>379</sup>, oxygen isotopes in a

large lunar zircon were measured using a Cameca IMS1270 ion microprobe equipped with multicollectors. The authors demonstrated that the accuracy of such high precision (typically <0.2%,  $1\sigma$ ) analyses may be compromised by a combination of excessive surface relief and orientation factors. Bias could be avoided by locating the sample and standard close to each other. Where this was not possible, orientation along the x-axis of the mount was found to provide better accuracy.

Li *et al.*<sup>380</sup> developed a method of measuring  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios in young zircons using a large radius magnetic sector MC Cameca IMS-1280 SIMS instrument. Through a combination of multicollector mode, a NMR magnet controller and oxygen flooding techniques, an analytical precision of 0.2% or better was achieved without external standardisation. The precision of the zircon Pb–Pb determinations depended chiefly on the radiogenic Pb content; uncertainties in the  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios were very close to those expected from counting statistics.

The performance of the *Cameca NanoSIMS 50 ion probe* has been assessed for U–Pb dating of zircon with a 15  $\mu\text{m}$  spatial resolution<sup>381</sup>. A multicrystal zircon standard, QGNG from South Australia with a U–Pb age of 1842 Ma, was used as a reference for  $\text{Pb}^+/\text{UO}^+ - \text{UO}_2^+/\text{UO}^+$  calibration in multicollector mode. On the basis of a positive correlation between these ratios, the  $^{206}\text{Pb}/^{238}\text{U}$  ratios of the samples were determined. The  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios were measured by magnetic scanning in single collector mode. The  $^{206}\text{Pb}$ – $^{238}\text{U}$  ages obtained for standard zircons 91500 and SL13 agreed well with published ages within experimental error;  $^{207}\text{Pb}$ – $^{206}\text{Pb}$  ages were also comparable, although the experimental error was large. It has also been demonstrated that the *Cameca NanoSIMS 50 ion probe* is able to measure  $^{13}\text{C}/^{12}\text{C}$  ratios in early Precambrian organic matter with permil precision<sup>382</sup>. A  $\text{Cs}^+$  primary beam was rastered over a 5 x 5  $\mu\text{m}$  area in less than 30 minutes; grains smaller than 5  $\mu\text{m}$  could

be analysed if their surrounding matrix did not contain carbon. The procedures adopted are not universally applicable because of the matrix dependence of the C<sup>-</sup> secondary yields but many of the experimental observations would apply to any organic sample.

A short technical note<sup>383</sup> describes a simple technique for making a germanium-bismuth glass designed specifically for performing *coarse calibrations of SIMS instruments*. The Ge-Bi glass was doped with five trace elements selected to anchor specific points on the mass spectrum. While not suitable for the quantification of geological materials, its use greatly simplified the switch from low to high mass measurements.

Two large pegmatitic crystals of sodic pyroxene and sodic amphibole have been found to be suitable RMs for *in situ Li isotope determinations by SIMS*<sup>384</sup>. Although the crystals were isotopically homogeneous within the precision of the methods applied, there was a significant difference between the SIMS data and those obtained on micro-drilled material analysed by MC-ICP-MS. This indicated the presence of significant matrix effects in the SIMS determinations of Li isotopes in amphibole and pyroxene relative to the basalt glasses used for calibration. It was proposed that these two crystals serve as RMs to ensure the accuracy of Li isotope ratios measured by SIMS.

The capabilities and limitations of *ToF-SIMS as a tool in organic geochemical research* have been evaluated<sup>385</sup>. Although at an early stage, examples of its potential application in this field are: (i) the identification of biomarkers in oil-bearing fluid inclusions; and (ii) the identification of specific lipid biomarkers that might be assigned to particular organisms involved in biomineralisation. Important aspects of this research were the development of appropriate sample preparation

protocols, measurement of reference spectra from pure substances as an aid to spectrum interpretation, and validation of the ToF-SIMS results against established knowledge and methods.

With the increasing use of *accelerator mass spectrometry (AMS)* in geoscientific research, more precise data for  $^{10}\text{Be}$  and  $^{36}\text{Cl}$  will be required measurements at the  $10^{-14}$  level. Merchel *et al.*<sup>386</sup> outlined the special precautions that should be taken during sample preparation to ensure that low blank values are obtained consistently when working at this level. Dating surface rocks using cosmogenic  $^{10}\text{Be}$  can be problematical in the presence of contaminant  $^{10}\text{Be}$  produced in the Earth's atmosphere<sup>387</sup>. While quartz is relatively easily cleaned by acid leaching, carbonates are more difficult. Leaching experiments performed on different grain size fractions showed that atmospheric  $^{10}\text{Be}$  resided in the clay fraction and that partial leaching procedures failed to release  $^{10}\text{Be}$  because of instant reabsorption on the grain surfaces<sup>387</sup>. As a result,  $^{10}\text{Be}$  measurements in carbonates should be carried out on samples that do not contain clay minerals. Balco and Rovey<sup>388</sup> have described an improved procedure for dating buried paleosols using measurements of cosmic  $^{26}\text{Al}$  and  $^{10}\text{Be}$  in quartz grains. The procedure involves measuring  $^{26}\text{Al}$  and  $^{10}\text{Be}$  at multiple depths in the paleosol and calculating its age of burial from the resulting isochron. The only critical assumption required by this method is that the inherited  $^{26}\text{Al}$  and  $^{10}\text{Be}$  in the paleosol parent material are well-mixed vertically. Laser decomposition has been successfully employed to generate radiocarbon measurements from marine aragonite<sup>389</sup>. A Nd-YAG laser operating at 213 nm was used to produce  $\text{CO}_2$  by thermal decomposition of the aragonite. Agreement between  $^{14}\text{C}$  data obtained by laser decomposition AMS and conventional acid digestion prior to AMS, indicated that fractionation was not a concern. This is in contrast to the significant

fractionation that has been observed during stable isotope determinations of C and O of different carbonate minerals following laser decomposition. These results illustrated the potential promise for coupling laser decomposition to an AMS system that measures CO<sub>2</sub> directly.

#### 4.4.5 X-ray techniques

The annual Update on XRFS<sup>76</sup> is a *comprehensive review of recent developments in all aspects of XRF* (434 refs). The section on geological applications confirms that XRFS often supplies the routine major and trace element data as part of a multi-technique approach in geochemical studies.

*Methods of sample preparation* continue to evolve. Two methods of correcting for mineralogical effects in the measurement of pressed powders pellets by WD-XRF were evaluated<sup>390</sup>. The first involved checking the 2θ angle for each sample before the actual measurement and correcting for any shift in the peak; an improvement in the calibration obtained with 27 Chinese geological CRMs was demonstrated. In the second method, the peak intensity was replaced by the peak area to correct for any distortion of the peak shape; this required too much scanning time to be practicable. Zhang *et al.*<sup>391</sup> proposed another approach in which the samples were digested with *aqua regia* before mixing the sample solution with agarose gel. After boiling, a quasi-solid gel was formed on cooling to room temperature. This technique was successfully applied to the determination of Fe, Pb and Zn in concentrates of lead and zinc ores. Information from XRD can be crucial to the successful analysis of some difficult samples, such as slags and refractory materials, by confirming the mineralogical phases present and thus influencing the method of sample preparation<sup>392</sup>. Fused beads, while minimising any mineralogical effects, may result in loss of volatile elements like sulphur. To overcome this difficulty, Gazulla and co-



workers<sup>393</sup> added a known quantity of barium, which combined with the S in the sample to form BaSO<sub>4</sub> and thus suppressed the loss of S during the fusion process. An unusual procedure for determining Re by XRF in ores containing gold relied on the adsorption of perrhenate ions on activated charcoal after sample dissolution<sup>394</sup>. Not only did the preconcentration enhance the sensitivity but it allowed samples of differing compositions to be presented for analysis in a uniform matrix.

Although *bench top ED-XRF instruments* have been accepted for routine quality control in industrial settings, they still need to establish their credentials in geochemical studies for a wide range of elements. A recent study of the determination of major and trace elements in soils and sediments provides some figures of merit for a modern bench top model<sup>247</sup>. The samples were prepared as pressed powders, without a binder, and a spinner system in the spectrometer was employed to reduce any errors due to sample heterogeneity. After careful selection of measurement parameters, the precision of analysis was better than 0.5% for Fe, K, Mn and Ti and better than 5% for all other elements, with a minimum LOD of between 1 and 2 ppm for most elements.

On-line analysis of sediment cores by *XRF core scanners* has become increasingly popular because near-continuous records of element distributions can be obtained non-destructively with a minimum of analytical effort. However, one major disadvantage compared to conventional geochemical analysis is the problem of converting the output into elemental concentrations. Weltje and Tjallingii<sup>395</sup> have proposed a log ratio calibration model, derived from a combination of XRF theory, principles of compositional data analysis and empirical experience. The successful calibration of XRF core scanners by this technique would appear to represent a major advance in their use. The authors urge practitioners to abandon the general practice of

reporting the results from core scanners as raw intensities or peak integrals and adopt log ratios as the default format.

## **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
AToFMS	Atomic Time of Flight Mass Spectrometry
BCR	Community Bureau of Reference ( <i>of the European Community</i> )
CCRMP	Canadian Certified Reference Material Project
CPE	Cloud 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
DEtHg	Diethylmercury
DMA	Dimethyl arsenic acid
DMT	Dimethyltin
DPhT	Diphenyltin
DRC	Dynamic reaction cell
DTPA	Diethylenetriaminepentaacetic acid
DU	Depleted uranium
EC	Elemental Carbon
EDAX	Energy Dispersive Spectrometry
EDXRF	Energy Dispersive X-ray Fluorescence
EDTA	Ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
EN	European Committee for Standardisation
EMPA	Electron Microprobe Analyser
ESI-MS	Electrospray Ionisation-Mass Spectrometry
ETAAS	Electrothermal Atomic Absorption Spectrometry
EtHg	Ethylmercury
ETV-AAS	Electrothermal Vaporisation- Atomic Absorption Spectrometry

ETV-ICP-MS	Electrothermal Vaporisation-Inductively Coupled Plasma-Mass Spectrometry
EXAFS	Extended X-ray Absorption Fine Structure)
FAAS	Flame Atomic Absorption Spectrometry
FES	Flame Emission Spectrometry
FI	Flow Injection
FI-CV-ICP-MS	Flow injection-Cold Vapour-Inductively Coupled Plasma-Mass Spectrometry
FI-HG-QF-AAS	Flow injection-Hydride Generation-Quartz Furnace- Atomic Absorption Spectrometry
FI-ICP-MS	Flow injection-Inductively Coupled Plasma-Mass Spectrometry
FP	Fundamental Parameter
<i>fs</i>	Femto second
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
GC-FPD	Gas Chromatographic-Flame Photometric Detector
GC-ICP-MS	Gas Chromatography-Inductively Coupled Plasma-Mass Spectrometry
GC-IR-MS	Gas Chromatography-Isotope Ratio-Mass Spectrometry
GC-MS	Gas Chromatography-Mass Spectrometry
GC-TOF-MS	Gas Chromatography-Time of Flight-Mass Spectrometry
GEMOC	Geochemical Evolution and Metallogeny of Continents, MacQuarie University, Sydney, Australia
GF-AAS	Graphite Furnace-Atomic Absorption Spectrometry
GSI	Geological Survey of Japan
HFSE	High field strength elements
HG	Hydride Generation
HG-AAS	Hydride Generation-Atomic absorption Spectrometry
HG-AFS	Hydride Generation-Atomic Fluorescence Spectrometry
HG-QT-AAS	Hydride Generation-Quartz Tube- Atomic Absorption Spectrometry
HPLC	High Performance Liquid ChromatographyHPLC-HG-AAS High Performance Liquid Chromatography-Hydride Generation-Atomic Absorption Spectrometry

HPLC-HG-AFS	High Performance Liquid Chromatography-Hydride Generation-Atomic Fluorescence Spectrometry
HPLC-ICP-MS	High Performance Liquid Chromatography- Inductively Coupled Plasma-Mass Spectrometry
HR-CS-AAS	High Resolution-Continuum Source- Atomic Absorption Spectrometry
HR-ICP-MS	High Resolution-Inductively Coupled Plasma-Mass Spectrometry
HR-TEM	High Resolution-Transmission Electron Microscopy
IAEA	International Atomic Energy Agency
IAG	International Association of Geoanalysts
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-(Q)MS	Inductively Coupled Plasma (Quadrupole) Mass Spectrometry
ICP-TOF-MS	Inductively Coupled Plasma-Time of Flight-Mass Spectrometry
ID	Isotope Dilution
IGGE	Institute of Geophysical and Geochemical Exploration
iHg	Inorganic mercury
ID-ICP-MS	Isotope Dilution- Inductively Coupled Plasma-Mass Spectrometry
ID-MS	Isotope Dilution-Mass Spectrometry
IGGE	Institute of Geophysical and Geochemical Exploration
INAA	Instrumental Neutron Activation Analysis
IR	Infra Red
IRMM	Institute for Reference Materials and Measurements
IRMS	Isotope Ratio Mass Spectrometry
ISO	International Standards Organisation
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
LA-SF-ICP-MS	Laser Ablation-Sector Field-Inductively Coupled Plasma-Mass Spectrometry
LC-ICP-MS	Liquid Chromatography-Inductively Coupled Plasma-Mass Spectrometry
LC-MS	Liquid Chromatography-Mass Spectrometry
LC-MS-MS	Liquid Chromatography-Mass Spectrometry-Mass Spectrometry
LIBS	Laser Induced Breakdown Spectrometry
LOD	Limit of Detection
LOQ	Limit of Quantification
MA	Methylarsonic acid
MALDI-ToF	Matrix Assisted Laser Desorption Ionisation-Time of Flight
MBT	Monobutyltin
MC	Multi Collector
MC-ICP-MS	Multi Collector- Inductively Coupled Plasma-Mass Spectrometry
MDL	Method Detection Limit
MIP-AES	Microwave Induced Plasma- Atomic Emission Spectrometry
MMA	Monomethyl arsenic
MMT	MonomethyltinMeHg                      Methyl Mercury
MPhT	Monophenyltin
MSFIA	Multi-syringe flow injection analysis
MS/MS	Tandem Mass Spectrometry
NAA	Neutron Activation Analysis
Nd:YAG	Neodymium Doped:Yttrium Aluminum Garnet
NEXAFS	Near Edge X-ray Absorption Fine Structure
NIOSH	National Institute of Occupational Safety and Health
NIST	National Institute of Standards and Technology
<i>ns</i>	Nano second
OC	Organic Carbon
ORS	Octopole reaction cell

PDA	Personal digital assistant
PGE	Precious Group Element
PhHg	Phenylmercury
PIXE	Particle-Induced X-ray Emission
PFA	Perfluoroalkoxy
PLE	Pressurised Liquid Extraction
PTFE	Poly(tetrafluoroethylene)
P-EDXRF	Polarised-Energy Dispersive X-ray Fluorescence
<i>ps</i>	pico second
PTE	Potentially toxic elements ( <i>so called 'heavy metals'</i> )
PXRF	Portable X-ray Fluorescence
QICP-MS	Quadrupole Inductively Coupled Plasma-Mass Spectrometry
REE	Rare Earth Element
RM	Reference Material
RSD	Relative Standard Deviation
RSE	Relative Standard Error
RTIL	Room temperature ionic liquids
SARM	South African Reference Material
<i>sd</i>	Standard deviation
SEC	Size Exclusion Chromatography
SEM	Scanning Electron Microscopy
SEM-EDAX	Scanning Electron Microscopy-Energy Dispersive Spectrometry
SF-ICP-MS	Sector Field Inductively Coupled Plasma-Mass spectrometry
SHRIMP	Sensitive High mass Resolution Ion MicroProbe
SIMS	Secondary Ion Mass Spectrometry
SIRMS	Stable Isotope Ratio Mass Spectrometry
S/N	Signal to Noise ratio
SPE	Solid Phase Extraction
SPME	Solid Phase Microextraction
SRM	Standard Reference Material
SR	Synchrotron Radiation
SRXRF	Synchrotron Radiation X-ray Fluorescence
SRXANES	Synchrotron Radiation X-Ray Absorption Near Edge Structure

TBT	Tributyltin
TEM	Transmission Electron Microscopy
TEM-EDAX	Transmission Electron Microscopy- Energy Dispersive Spectrometry
THF	Tetrahydrofuran
TIMS	Thermal Ionisation Mass Spectrometry
TMAH	Tetramethylammonium hydroxide
TMT	Trimethyltin
TOC	Total organic carbon
TOF-MS	Time of Flight-Mass Spectrometry
TOF-SIMS	Time of Flight- Secondary Ion Mass Spectrometry
TOK	Thermal Optical Kinetic
TOT	Thermal Optical Transmission
TPhT	Triphenyltin
TPrT	Tripropyltin
TXRF	Total reflection X-ray Fluorescence
US EPA	United States Environmental Protection Agency
USGS	United States Geological Survey
USN-ICP-MS	Ultrasonic nebulisation inductively coupled plasma mass spectrometry
UV	Ultra Violet
WDXRF	Wavelength Dispersive X-ray Fluorescence
XAFS	X-ray Absorption Fine Structure Spectrometry
XANES	X-Ray Absorption Near Edge Structure
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
XRFS	X-ray Fluorescence Spectrometry
ZAAS	Zeeman Atomic Absorption Spectrometry

## 6 References

- 1 O. T. Butler, J. M. Cook, C. M. Davidson, C. F. Harrington and D. L. Miles, *Journal of Analytical Atomic Spectrometry*, 2009, **24**(2), 131-177.



- 2 B. Han, N. Hudda, Z. Ning, Y. J. Kim and C. Sioutas, *Aerosol Science and Technology*, 2009, **43**(8), 757-766.
- 3 B. Gorbunov, N. D. Priest, R. B. Muir, P. R. Jackson and H. Gnewuch, *Ann. Occup. Hyg.*, 2009, **53**(3), 225-237.
- 4 G. Liden and J. Surakka, *Ann. Occup. Hyg.*, 2009, **53**(2), 99-116.
- 5 T. C. Hsiao, D. R. Chen and S. Y. Son, *J. Aerosol. Sci.*, 2009, **40**(6), 481-491.
- 6 B. J. Majestic, J. J. Schauer, M. M. Shafer, P. M. Fine, M. Singh and C. Sioutas, *Journal of Environmental Engineering and Science*, 2008, **7**(4), 289-298.
- 7 J. M. Park, J. C. Rock, L. J. Wang, Y. C. Seo, A. Bhatnagar and S. Kim, *Atmos. Environ.*, 2009, **43**(2), 280-289.
- 8 S. J. Reynolds, J. Nakatsu, M. Tillery, T. Keefe, J. Mehaffy, P. S. Thorne, K. Donham, M. Nonnenmann, V. Golla and P. O'Shaughnessy, *Ann. Occup. Hyg.*, 2009, **53**(6), 585-594.
- 9 P. Kumar, P. Fennell, J. Symonds and R. Britter, *Atmos. Environ.*, 2008, **42**(38), 8819-8826.
- 10 M. T. Timko, Z. H. Yu, J. Kroll, J. T. Jayne, D. R. Worsnop, R. C. Mlake-Lye, T. B. Onasch, D. Liscinsky, T. W. Kirchstetter, H. Destailats, A. L. Holder, J. D. Smith and K. R. Wilson, *Aerosol Sci. Technol.*, 2009, **43**(9), 855-865.
- 11 R. Vecchi, G. Valli, P. Fermo, A. D'Alessandro, A. Piazzalunga and V. Bernardoni, *Atmos. Environ.*, 2009, **43**(10), 1713-1720.
- 12 S. W. Kim and P. C. Raynor, *Ann. Occup. Hyg.*, 2009, **53**(3), 239-248.
- 13 B. Miljevic, R. L. Modini, S. E. Bottle and Z. D. Ristovski, *Atmos. Environ.*, 2009, **43**(6), 1372-1376.
- 14 G. Steinhauser, J. H. Sterba, M. Foster, F. Grass and M. Bichler, *Atmos. Environ.*, 2008, **42**(37), 8616-8622.
- 15 M. Novak, Y. Erel, L. Zemanova, S. H. Bottrell and M. Adamova, *Atmos. Environ.*, 2008, **42**(40), 8997-9006.
- 16 M. Catinon, S. Ayrault, R. Clocchiatti, O. Boudouma, J. Asta, M. Tissut and P. Ravanel, *Atmos. Environ.*, 2009, **43**(5), 1124-1130.
- 17 N. Upadhyay, B. J. Majestic, P. Prapaipong and P. Herckes, *Analytical and Bioanalytical Chemistry*, 2009, **394**(1), 255-266.
- 18 G. Toscano, A. Gambaro, G. Capodaglio, W. R. L. Cairns and P. Cescon, *Journal of Environmental Monitoring*, 2009, **11**(1), 193-199.
- 19 B. Berlinger, M. Naray, I. Sajo and G. Zaray, *Annals of Occupational Hygiene*, 2009, **53**(4), 333-340.
- 20 S. L. Maxwell, M. A. Bernard, M. R. Nelson and L. D. Youmans, *Talanta*, 2008, **76**(2), 432-440.
- 21 L. Lamaison, L. Y. Allemant, A. Robache and J. C. Galloo, *Applied Spectroscopy*, 2009, **63**(1), 87-91.
- 22 M. Grotti, F. Soggia and J. L. Todoli, *Analyst*, 2008, **133**(10), 1388-1394.
- 23 T. Moreno, X. Querol, A. Alastuey and W. Gibbons, *Atmos. Environ.*, 2008, **42**(34), 7851-7861.
- 24 S. H. Hu, J. D. Herner, M. Shafer, W. Robertson, J. J. Schauer, H. Dwyer, J. Collins, T. Huai and A. Ayala, *Atmos. Environ.*, 2009, **43**(18), 2950-2959.
- 25 S. Gligorovski, J. T. Elteren and I. Grgic, *Science of the Total Environment*, 2008, **407**(1), 594-602.
- 26 R. Pinel-Raffaitin, C. Peckheyran and D. Amouroux, *Atmos. Environ.*, 2008, **42**(33), 7786-7794.

- 27 B. S. Gilfedder, S. C. Lai, M. Petri, H. Biester and T. Hoffmann, *Atmospheric Chemistry and Physics*, 2008, **8**(20), 6069-6084.
- 28 R. Vincent, J. Catani, Y. Creau, A. M. Frocaut, A. Good, P. Goutet, A. Hou, F. Leray, M. A. Andre-Lesage and A. Soyeux, *Ann. Occup. Hyg.*, 2009, **53**(4), 363-372.
- 29 W. T. Sanderson, S. Leonard, D. Ott, L. Fuortes and W. Field, *Journal of Occupational and Environmental Hygiene*, 2008, **5**(7), 475-481.
- 30 C. Muller, G. L'Esperance, P. Plamondon, G. Kennedy and J. Zayed, *Journal of Toxicology and Environmental Health-Part a-Current Issues*, 2008, **71**(16), 1091-1099.
- 31 N. Pirrone, I. M. Hedgecock and F. Sprovieri, *Atmos. Environ.*, 2008, **42**(36), 8549-8551.
- 32 F. Raofie, G. Snider and P. A. Ariya, *Canadian Journal of Chemistry-Revue Canadienne De Chimie*, 2008, **86**(8), 811-820.
- 33 T. T. Glenz, L. M. Brosseau and R. W. Hoffbeck, *J. Air Waste Manage. Assoc.*, 2009, **59**(3), 266-272.
- 34 J. Y. Lee, K. M. Cho, L. Cheng, T. C. Keener, G. Jegadeesan and S. R. Al-Abed, *J. Air Waste Manage. Assoc.*, 2009, **59**(8), 972-979.
- 35 D. W. Golightly, C. M. Cheng, P. Sun, L. K. Weavers, H. W. Walker, P. Taerakul and W. E. Wolfe, *Energy Fuels*, 2008, **22**(5), 3089-3095.
- 36 Y. N. Guo, X. B. Feng, Z. G. Li, T. R. He, H. Y. Yan, B. Meng, J. F. Zhang and G. L. Qiu, *Atmos. Environ.*, 2008, **42**(30), 7096-7103.
- 37 G. L. Xiu, J. Cai, W. Y. Zhang, D. N. Zhang, A. Bueler, S. C. Lee, Y. Shen, L. H. Xu, X. J. Huang and P. Zhang, *Atmos. Environ.*, 2009, **43**(19), 3145-3154.
- 38 I. Iavicoli, B. Bocca, S. Caroli, S. Caimi, A. Alimonti, G. Carelli and L. Fontana, *Journal of Occupational and Environmental Medicine*, 2008, **50**(10), 1158-1166.
- 39 Y. Yang, X. Li, Y. L. Li, M. Tan, W. Lu, G. Zhang and Y. Li, *Global Nest Journal*, 2008, **10**(2), 169-173.
- 40 J. A. Rodriguez-Castrillon, M. Moldovan and J. I. G. Alonso, *Analytical and Bioanalytical Chemistry*, 2009, **394**(1), 351-362.
- 41 R. Weller, J. Woltjen, C. Piel, R. Resenberg, D. Wagenbach, G. Konig-Langlo and M. Kriews, *Tellus Series B-Chemical and Physical Meteorology*, 2008, **60**(5), 742-752.
- 42 T. Berg, W. Aas, J. Pacyna, H. T. Uggerud and M. Vadset, *Atmos. Environ.*, 2008, **42**(32), 7494-7501.
- 43 T. Okuda, M. Katsuno, D. Naoi, S. Nakao, S. Tanaka, K. B. He, Y. L. Ma, Y. Lei and Y. T. Jia, *Chemosphere*, 2008, **72**(6), 917-924.
- 44 K. Leopold, M. Maier, S. Weber and M. Schuster, *Environmental Pollution*, 2008, **156**(2), 341-347.
- 45 C. S. Li, J. Cornett, S. Willie and J. Lam, *Sci. Total Environ.*, 2009, **407**(8), 2756-2759.
- 46 M. Komarek, V. Ettler, V. Chrastny and M. Mihaljevic, *Environment International*, 2008, **34**(4), 562-577.
- 47 H. Nazemiyeh, F. Bahadori, A. Delazar, M. Ay, G. Topcu, L. Nahar, R. R. T. Majinda and S. D. Sarker, *Natural Product Research*, 2008, **22**(16), 1385-1392.
- 48 M. Conkova and J. Kubiznakova, *Science of the Total Environment*, 2008, **404**(2-3), 440-445.

- 49 W. A. Marshall, R. Clough and W. R. Gehrels, *Science of the Total Environment*, 2009, **407**(8), 2734-2748.
- 50 M. E. Ketterer and S. C. Szechenyi, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2008, **63**(7), 719-737.
- 51 T. Shinonaga, F. Esaka, M. Magara, D. Klose and D. Donohue, *Spectroc. Acta Pt. B-Atom. Spectr.*, 2008, **63**(11), 1324-1328.
- 52 Y. Shen, Y. G. Zhao, S. L. Guo, J. Y. Cui, Y. Liu, J. H. Li, J. Xu and H. Z. Zhang, *Radiation Measurements*, 2008, **43**, S299-S302.
- 53 Z. Varga, *Anal. Chim. Acta*, 2008, **625**(1), 1-7.
- 54 A. Sakaguchi, K. Kawai, P. Steier, F. Quinto, K. Mino, J. Tomita, M. Hoshi, N. Whitehead and M. Yamamoto, *Sci. Total Environ.*, 2009, **407**(14), 4238-4242.
- 55 K. Kim, S. Cho, J. Suh, J. Won, J. Hong and S. Kim, *Current Applied Physics*, 2009, **9**(2), 306-310.
- 56 Y. Sivry, J. Riotte, J. E. Sonke, S. Audry, J. Schafer, J. Viers, G. Blanc, R. Freydier and B. Dupre, *Chemical Geology*, 2008, **255**(3-4), 295-304.
- 57 S. Gioia, D. Weiss, B. Coles, T. Arnold and M. Babinski, *Analytical Chemistry*, 2008, **80**(24), 9776-9780.
- 58 N. Mattielli, J. C. J. Petit, K. Deboudt, P. Flament, E. Perdrix, A. Taillez, J. Rimetz-Planchon and D. Weis, *Atmos. Environ.*, 2009, **43**(6), 1265-1272.
- 59 S. Szidat, *Chimia*, 2009, **63**(3), 157-161.
- 60 M. Behrens, J. Schmitt, K. U. Richter, M. Bock, U. C. Richter, I. Levin and H. Fischer, *Rapid Communications in Mass Spectrometry*, 2008, **22**(20), 3261-3269.
- 61 L. Malicsko, L. Pogany, A. L. Toth, V. Horvath and E. Beregi, *Crystal Research and Technology*, 2009, **44**(4), 425-432.
- 62 B. Tuzson, J. Mohn, M. J. Zeeman, R. A. Werner, W. Eugster, M. S. Zahniser, D. D. Nelson, J. B. McManus and L. Emmenegger, *Applied Physics B-Lasers and Optics*, 2008, **92**(3), 451-458.
- 63 M. Lippmann, *Journal of Exposure Science and Environmental Epidemiology*, 2009, **19**(3), 235-247.
- 64 N. Bukowiecki, P. Lienemann, C. N. Zwicky, M. Furger, A. Richard, G. Falkenberg, K. Rickers, D. Grolimund, C. Borca, M. Hill, R. Gehrig and U. Baltensperger, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2008, **63**(9), 929-938.
- 65 U. E. A. Fittschen, F. Meirer, C. Strelt, R. Wobrauschek, J. Thiele, G. Falkenberg and G. Pepponi, *Spectroc. Acta Pt. B-Atom. Spectr.*, 2008, **63**(12), 1489-1495.
- 66 V. Groma, J. Osan, S. Torok, F. Meirer, C. Strelt, P. Wobrauschek and G. Falkenberg, *Idojaras*, 2008, **112**(2), 83-97.
- 67 G. Cibin, A. Marcelli, V. Maggi, M. Sala, F. Marino, B. Delmonte, S. Albani and S. Pignotti, *Spectroc. Acta Pt. B-Atom. Spectr.*, 2008, **63**(12), 1503-1510.
- 68 Y. Shimizu, K. Dobashi, T. Kusakbe, T. Nagamine, M. Oikawa, T. Satoh, J. Haga, Y. Ishii, T. Ohkubo, T. Kamiya, K. Arakawa, T. Sano, S. Tanaka, K. Shimizu, S. Matsuzaki, M. Utsugi and M. Mori, *International Journal of Immunopathology and Pharmacology*, 2008, **21**(3), 567-576.
- 69 M. J. Bailey, K. J. Kirkby and C. Jeynes, *X-Ray Spectrom.*, 2009, **38**(3), 190-194.
- 70 C. J. Ma and K. H. Kim, *Atmos. Environ.*, 2008, **42**(29), 7022-7026.
- 71 H. Hwang, H. Kim and C. U. Ro, *Atmos. Environ.*, 2008, **42**(38), 8738-8746.

- 72 H. Ibrahim, A. N. Aziz, D. R. Syamsir, N. A. M. Ali, M. Mohtar, R. M. Ali and K. Awang, *Food Chemistry*, 2008, **113**(2), 575-577.
- 73 O. C. Lind, B. Salbu, L. Skipperud, K. Janssens, J. Jaroszewicz and W. De Nolf, *Journal of Environmental Radioactivity*, 2009, **100**(4), 301-307.
- 74 E. Bye, S. Foreland, L. Lundgren, K. Kruse and R. Ronning, *Ann. Occup. Hyg.*, 2009, **53**(4), 403-408.
- 75 P. Stacey, E. Kauffer, J. C. Moulut, C. Dion, M. Beuparlant, P. Fernandez, R. Key-Schwartz, B. Friede and D. Wake, *Ann. Occup. Hyg.*, 2009, **53**(6), 639-649.
- 76 M. West, A. T. Ellis, P. J. Potts, C. Strelis, C. Vanhoof, D. Wegrzynek and P. Wobruschek, *Journal of Analytical Atomic Spectrometry*, 2009, **24**(10), 1289-1326.
- 77 N. Jankowski, C. Schmidl, I. L. Marr, H. Bauer and H. Puxbaum, *Atmos. Environ.*, 2008, **42**(34), 8055-8064.
- 78 J. G. Watson, J. C. Chow, L. W. A. Chen and N. H. Frank, *J. Air Waste Manage. Assoc.*, 2009, **59**(8), 898-911.
- 79 A. Kubatova, T. J. Lahren, J. Beranek, I. P. Smoliakova, A. Braun and F. E. Huggins, *Aerosol Sci. Technol.*, 2009, **43**(7), 714-729.
- 80 K. Park, G. Cho and J. H. Kwak, *Aerosol Sci. Technol.*, 2009, **43**(5), 375-386.
- 81 J. Li, J. Sommar, I. Wangberg, O. Lindqvist and S. Q. Wei, *Atmos. Environ.*, 2008, **42**(36), 8382-8388.
- 82 S. H. Kim, Y. J. Han, T. M. Holsen and S. M. Yi, *Atmos. Environ.*, 2009, **43**(20), 3267-3274.
- 83 D. Chand, D. Jaffe, E. Prestbo, P. C. Swartzendruber, W. Hafner, P. Weiss-Penzias, S. Kato, A. Takami, S. Hatakeyama and Y. Z. Kajii, *Atmos. Environ.*, 2008, **42**(34), 7988-7996.
- 84 D. Obrist, A. G. Hallar, I. McCubbin, B. B. Stephens and T. Rahn, *Atmos. Environ.*, 2008, **42**(33), 7579-7589.
- 85 C. J. Watras, K. A. Morrison, J. L. Rubsam and B. Rodger, *Atmos. Environ.*, 2009, **43**(26), 4070-4077.
- 86 P. C. Swartzendruber, D. A. Jaffe and B. Finley, *Atmos. Environ.*, 2009, **43**(22-23), 3648-3651.
- 87 N. J. Lawryk, H. A. Feng and B. T. Chen, *J. Occup. Environ. Hyg.*, 2009, **6**(7), 433-445.
- 88 M. Dall'Osto, M. J. Booth, W. Smith, R. Fisher and R. M. Harrison, *Aerosol Sci. Technol.*, 2008, **42**(12), 981-991.
- 89 D. C. Snyder, J. J. Schauer, D. S. Gross and J. R. Turner, *Atmos. Environ.*, 2009, **43**(26), 4033-4042.
- 90 Z. J. Wu, L. Poulain, B. Wehner, A. Wiedensohler and H. Herrmann, *J. Aerosol. Sci.*, 2009, **40**(7), 603-612.
- 91 M. Kamphus, M. Ettner-Mahl, M. Brands, J. Curtius, F. Drewnick and S. Borrmann, *Aerosol Science and Technology*, 2008, **42**(11), 970-980.
- 92 B. M. Matthew, A. M. Middlebrook and T. B. Onasch, *Aerosol Science and Technology*, 2008, **42**(11), 884-898.
- 93 M. Svane, T. L. Gustafsson, B. Kovacevik, J. Noda, P. U. Andersson, E. D. Nilsson and J. B. C. Pettersson, *Aerosol Sci. Technol.*, 2009, **43**(7), 653-661.
- 94 A. Zelenyuk, J. Yang, E. Choi and D. Imre, *Aerosol Sci. Technol.*, 2009, **43**(5), 411-424.
- 95 T. Lee, X. Y. Yu, S. M. Kreidenweis, W. C. Malm and J. L. Collett, *Atmos. Environ.*, 2008, **42**(27), 6655-6669.

- 96 J. J. Bauer, X. Y. Yu, R. Cary, N. Laulainen and C. Berkowitz, *J. Air Waste Manage. Assoc.*, 2009, **59**(7), 826-833.
- 97 B. D. Grover, N. L. Eatough, W. R. Woolwine, D. J. Eatough and R. A. Cary, *J. Air Waste Manage. Assoc.*, 2009, **59**(8), 1007-1017.
- 98 A. S. Mahajan, H. Oetjen, J. D. Lee, A. Saiz-Lopez, G. B. McFiggans and J. M. C. Plane, *Atmos. Environ.*, 2009, **43**(25), 3811-3818.
- 99 C. S. E. Bale, T. Ingham, R. Commane, D. E. Heard and W. J. Bloss, *Journal of Atmospheric Chemistry*, 2008, **60**(1), 51-70.
- 100 R. Aguilar-Martinez, M. A. Palacios-Corvillo, R. Greenwood, G. A. Mills, B. Vrana and M. M. Gomez-Gomez, *Anal. Chim. Acta*, 2008, **618**(2), 157-167.
- 101 H. J. W. De Baar, K. R. Timmermans, P. Laan, H. H. De Porto, S. Ober, J. J. Blom, M. C. Bakker, J. Schilling, G. Sarthou, M. G. Smit and M. Klunder, *Mar. Chem.*, 2008, **111**(1-2), 4-21.
- 102 C. B. Ojeda and F. S. Rojas, *Analytical and Bioanalytical Chemistry*, 2009, **394**(3), 759-782.
- 103 J. Borkowska-Burnecka, M. Jakubiel and W. Zyrnicki, *Chemia Analityczna*, 2008, **53**(3), 335-346.
- 104 L. A. Escaleira, R. E. Santelli, E. P. Oliveira, M. D. B. de Carvalho and M. A. Bezerra, *International Journal of Environmental Analytical Chemistry*, 2009, **89**(7), 515-527.
- 105 R. A. Gil, J. A. Gasquez, R. Olsina, L. D. Martinez and S. Cerutti, *Talanta*, 2008, **76**(3), 669-673.
- 106 N. N. Meeravali and S. J. Jiang, *J. Anal. At. Spectrom.*, 2008, **23**(10), 1365-1371.
- 107 Y. Furusho, M. Ono, M. Yamada, K. Ohashi, T. Kitade, K. Kuriyama, S. Ohta, Y. Inoue and S. Motomizu, *Bunseki Kagaku*, 2008, **57**(12), 969-989.
- 108 P. Liang, E. H. Zhao, Q. O. Ding and D. Du, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2008, **63**(6), 714-717.
- 109 K. Leopold, M. Foulkes and P. J. Worsfold, *Analytical Chemistry*, 2009, **81**(9), 3421-3428.
- 110 F. Pena-Pereira, I. Lavilla and C. Bendicho, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2009, **64**(1), 1-15.
- 111 L. B. Xia, X. Li, Y. L. Wu, B. Hu and R. Chen, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2008, **63**(11), 1290-1296.
- 112 S. Gil, M. T. C. de Loos-Vollebregt and C. Bendicho, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2009, **64**(3), 208-214.
- 113 L. Elci, U. Divrikli and M. Soylak, *Int. J. Environ. Anal. Chem.*, 2008, **88**(10), 711-723.
- 114 J. Sano, Y. Kikawada and T. Oi, *Journal of Radioanalytical and Nuclear Chemistry*, 2008, **278**(1), 111-116.
- 115 S. Z. Chen, X. L. Zhan, D. B. Lu, C. Liu and L. Zhu, *Analytica Chimica Acta*, 2009, **634**(2), 192-196.
- 116 H. M. Jiang, B. Hu, B. B. Chen and L. B. Xia, *Analytica Chimica Acta*, 2009, **634**(1), 15-21.
- 117 M. L. Chen, Y. M. Huo and J. H. Wang, *Talanta*, 2009, **78**(1), 88-93.
- 118 S. Y. Dewhirst, M. A. Birkett, J. D. Fitzgerald, A. Stewart-Jones, L. J. Wadhams, C. M. Woodcock, J. Hardie and J. A. Pickett, *Journal of Chemical Ecology*, 2008, **34**(12), 1575-1583.
- 119 M. M. Hassanien, I. M. Kenawy, A. M. El-Menshawy and A. A. Ei-Asmy, *Journal of Hazardous Materials*, 2008, **158**(1), 170-176.

- 120 M. E. Mahmoud, A. A. Yakout, S. B. Ahmed and M. M. Osman, *J. Liq. Chromatogr. Relat. Technol.*, 2008, **31**(16), 2475-2492.
- 121 M. Ghaedi, K. Niknam, A. Shokrollahi and E. Niknam, *Journal of the Chinese Chemical Society*, 2009, **56**(1), 150-157.
- 122 A. M. Zou, X. Y. Tang, M. L. Chen and J. H. Wang, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2008, **63**(5), 607-611.
- 123 Y. Furusho, A. Sabarudin, L. Hakim, K. Oshita, M. Oshima and S. Motomizu, *Analytical Sciences*, 2009, **25**(1), 51-56.
- 124 R. P. Monasterio, J. C. Altamirano, L. D. Martinez and R. G. Wuilloud, *Talanta*, 2009, **77**(4), 1290-1294.
- 125 S. Z. Chen, X. L. Zhan, D. B. Lu, M. Yang and C. Liu, *Atomic Spectroscopy*, 2008, **29**(4), 124-128.
- 126 H. L. Ma and P. A. Tanner, *Talanta*, 2008, **77**(1), 189-194.
- 127 F. Aureli, S. Ciardullo, M. Pagano, A. Raggi and F. Cubadda, *J. Anal. At. Spectrom.*, 2008, **23**(7), 1009-1016.
- 128 D. Wang and S. A. Sanudo-Wilhelmy, *Marine Chemistry*, 2008, **112**(1-2), 72-80.
- 129 Q. Xiao, B. Hu and M. He, *Journal of Chromatography A*, 2008, **1211**(1-2), 135-141.
- 130 N. Y. Zahid, N. A. Abbasi, I. A. Hafiz and Z. Ahmad, *Journal of the Chemical Society of Pakistan*, 2008, **30**(6), 889-895.
- 131 A. Ugarte, N. Unceta, M. C. Sampedro, M. A. Goicolea, A. Gomez-Caballero and R. J. Barrio, *Journal of Analytical Atomic Spectrometry*, 2009, **24**(3), 347-351.
- 132 K. Leopold, M. Foulkes and P. J. Worsfold, *Trac-Trends in Analytical Chemistry*, 2009, **28**(4), 426-435.
- 133 R. Ito, M. Kawaguchi, N. Sakui, H. Honda, N. Okanouchi, K. Saito and H. Nakazawa, *Journal of Chromatography A*, 2008, **1209**(1-2), 267-270.
- 134 J. G. Chen, H. W. Chen, X. Z. Jin and H. T. Chen, *Talanta*, 2009, **77**(4), 1381-1387.
- 135 B. Jackson, V. Taylor, R. A. Baker and E. Miller, *Environmental Science & Technology*, 2009, **43**(7), 2463-2469.
- 136 P. Kangsepp and L. Mathiasson, *Waste Management & Research*, 2009, **27**(2), 147-158.
- 137 A. Ziola-Frankowska, M. Frankowski and J. Siepak, *Talanta*, 2009, **78**(2), 623-630.
- 138 J. Kunemeyer, L. Terborg, B. Meermann, C. Brauckmann, I. M. A. Scheffer and U. Karst, *Environmental Science & Technology*, 2009, **43**(8), 2884-2890.
- 139 D. L. Wang, R. C. Aller and S. A. Sanudo-Wilhelmy, *Marine Chemistry*, 2009, **113**(3-4), 250-256.
- 140 A. J. Bednar, R. A. Kirgan and W. T. Jones, *Analytica Chimica Acta*, 2009, **632**(1), 27-34.
- 141 C. F. Harrington, R. Clough, H. R. Hansen, S. J. Hill, S. A. Pergantis and J. F. Tyson, *J. Anal. At. Spectrom.*, 2009, **24**(8), 999-1025.
- 142 S. Shariati, Y. Yamini and M. K. Zanjani, *Journal of Hazardous Materials*, 2008, **156**(1-3), 583-590.
- 143 C. Xiong, M. He and B. Hu, *Talanta*, 2008, **76**(4), 772-779.
- 144 A. D'Ulivo, I. Paolicchi, M. Onor, R. Zamboni and L. Lampugnani, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2009, **64**(1), 48-55.
- 145 O. Alp and N. Ertas, *J. Anal. At. Spectrom.*, 2008, **23**(7), 976-980.

- 146 I. Kula, Y. Arslan, S. Bakirdere and O. Y. Ataman, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2008, **63**(8), 856-860.
- 147 H. W. Sun and R. Suo, *International Journal of Environmental Analytical Chemistry*, 2009, **89**(5), 347-356.
- 148 F. Pena-Pereira, I. Lavilla and C. Bendicho, *Microchimica Acta*, 2009, **164**(1-2), 77-83.
- 149 A. A. Menegario, P. Smichowski, P. S. Tonello, G. Polla, E. P. Oliveira and R. E. Santelli, *Anal. Chim. Acta*, 2008, **625**(2), 131-136.
- 150 A. M. Y. Jaber, N. A. Mehanna and S. M. Sultan, *Talanta*, 2009, **78**(4-5), 1298-1302.
- 151 B. Staniszewski and P. Freimann, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2008, **63**(11), 1333-1337.
- 152 N. Kallithrakas-Kontos and V. Hatzistavros, *X-Ray Spectrometry*, 2009, **38**(3), 229-233.
- 153 M. Krachler, J. C. Zheng, D. Fisher and W. Shotyk, *Sci. Total Environ.*, 2008, **399**(1-3), 78-89.
- 154 A. Marteel, C. F. Boutron, C. Barbante, P. Gabrielli, G. Cozzi, V. Gaspari, P. Cescon, C. R. Ferrari, A. Dommergue, K. Rosman, S. M. Hong and S. Do Hur, *Earth and Planetary Science Letters*, 2008, **272**(3-4), 579-590.
- 155 D. Rahmi, Y. Zhu, E. Fujimori, T. Hasegawa, T. Umemura, S. Konagaya and H. Haraguchi, *Anal. Sci.*, 2008, **24**(9), 1189-1192.
- 156 D. Rahmi, Y. B. Zhu, T. Umemura, H. Haraguchi, A. Itoh and K. Chiba, *Analytical Sciences*, 2008, **24**(11), 1513-1517.
- 157 S. Z. Chen, C. Liu, D. B. Lu and L. Zhu, *Atomic Spectroscopy*, 2009, **30**(1), 20-25.
- 158 F. Lacan, A. Radic, C. Jeandel, F. Poitrasson, G. Sarthou, C. Pradoux and R. Freydier, *Geophysical Research Letters*, 2008, **35**(24), 5.
- 159 J. de Jon, V. Schoemann, D. Lannuzel, J. L. Tison and N. Mattielli, *Anal. Chim. Acta*, 2008, **623**(2), 126-139.
- 160 T. Hussain and M. A. Gondal, *Bulletin of Environmental Contamination and Toxicology*, 2008, **80**(6), 561-565.
- 161 A. P. M. Michel and A. D. Chave, *Applied Optics*, 2008, **47**(31), G122-G130.
- 162 D. Dick, A. Wegner, P. Gabrielli, U. Ruth, C. Barbante and M. Kriews, *Anal. Chim. Acta*, 2008, **621**(2), 140-147.
- 163 J. A. Rodriguez-Castrillon, M. Moldovan and J. I. G. Alonso, *Journal of Analytical Atomic Spectrometry*, 2009, **24**(6), 815-824.
- 164 C. Lytle, J. Dahl, E. Farkas, J. Wilson and R. Myers, *Water Environment Research*, 2008, **80**(9), 823-831.
- 165 C. Brach-Papa, M. Van Bocxstaele, E. Ponzevera and C. R. Quétel, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2009, **64**(3), 229-234.
- 166 A. Vaisanen, P. Laatikainen, A. Ilander and S. Renvall, *International Journal of Environmental Analytical Chemistry*, 2008, **88**(14), 1005-1016.
- 167 P. Srivastava, P. C. Srivastava, U. Srivastava and U. S. Singh, *Communications in Soil Science and Plant Analysis*, 2008, **39**(13-14), 2046-2052.
- 168 R. L. R. Steinmetz, A. Kunz, V. L. Drenslar, E. M. D. Flores and A. F. Martins, *Clean-Soil Air Water*, 2009, **37**(3), 239-244.
- 169 S. Akatsuki, R. Yamanouchi, Y. Nakamoto, K. Yoshizumi, M. Ogaki, T. Yabutani, Y. Hayashi and J. Motonaka, *Bunseki Kagaku*, 2008, **57**(8), 659-666.

- 170 C. Mariet, O. Belhadj, S. Leroy, F. Carrot and N. Metrich, *Talanta*, 2008, **77**(1), 445-450.
- 171 B. Marin, E. I. B. Chopin, B. Jupinet and D. Gauthier, *Talanta*, 2008, **77**(1), 282-288.
- 172 H. Osterlund, I. Rodushkin, K. Ylinenjarvi and D. C. Baxter, *Waste Management*, 2009, **29**(4), 1258-1264.
- 173 E. B. Bolou-Bi, N. Vigier, A. Brenot and A. Poszwa, *Geostandards and Geoanalytical Research*, 2009, **33**(1), 95-109.
- 174 P. Grinberg and R. E. Sturgeon, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2009, **64**(3), 235-241.
- 175 M. Cyprien, M. Barbaste and P. Masson, *Int. J. Environ. Anal. Chem.*, 2008, **88**(8), 525-537.
- 176 G. Z. Tsogas, D. L. Giokas, A. G. Vlessidis and N. P. Evmiridis, *Talanta*, 2008, **76**(3), 635-641.
- 177 S. Mounicou, M. Dernovics, K. Bierla and J. Szpunar, *Talanta*, 2009, **77**(5), 1877-1882.
- 178 K. Pyrzyńska, *Food Chemistry*, 2009, **114**(4), 1183-1191.
- 179 M. Filella, P. A. Williams and N. Belzile, *Environmental Chemistry*, 2009, **6**(2), 95-105.
- 180 D. S. T. Hjortenkrans, N. S. Mansson, B. G. Bergback and A. V. Haggerud, *Environmental Chemistry*, 2009, **6**(2), 153-159.
- 181 C. Lomonte, D. Gregory, A. J. M. Baker and S. D. Kolev, *Chemosphere*, 2008, **72**(10), 1420-1424.
- 182 S. Diez and J. M. Bayona, *Talanta*, 2008, **77**(1), 21-27.
- 183 N. Issaro, C. Abi-Ghanem and A. Bermond, *Analytica Chimica Acta*, 2009, **631**(1), 1-12.
- 184 A. C. Schmidt, N. Haufe and M. Otto, *Talanta*, 2008, **76**(5), 1233-1240.
- 185 L. Jedynek, J. Kowalska, J. Harasimowicz and J. Golimowski, *Science of the Total Environment*, 2009, **407**(2), 945-952.
- 186 J. Zheng and H. Hintelmann, *Journal of Radioanalytical and Nuclear Chemistry*, 2009, **280**(1), 171-179.
- 187 T. G. Kazi, M. K. Jamali, M. B. Arain, H. I. Afridi, N. Jalbani, R. A. Sarfraz and R. Ansari, *Journal of Hazardous Materials*, 2009, **161**(2-3), 1391-1398.
- 188 D. Remeteiova, S. Ruzickova and R. Rusnak, *Microchimica Acta*, 2008, **163**(3-4), 257-261.
- 189 M. B. Arain, T. G. Kazi, M. K. Jamali, H. I. Afridi, N. Jalbani, R. A. Sarfraz, J. A. Baig, G. A. Kandhro and M. A. Memon, *Journal of Hazardous Materials*, 2008, **160**(1), 235-239.
- 190 M. K. Jamali, T. G. Kazi, M. B. Arain, H. I. Afridi, N. Jalbani, G. A. Kandhro, A. Q. Shah and J. A. Baig, *Journal of Hazardous Materials*, 2009, **163**(2-3), 1157-1164.
- 191 W. Boonjob, M. Rosende, M. Miro and V. Cerda, *Analytical and Bioanalytical Chemistry*, 2009, **394**(1), 337-349.
- 192 J. L. Raposo, S. R. de Oliveira, N. M. Caldas and J. A. G. Neto, *Analytica Chimica Acta*, 2008, **627**(2), 198-202.
- 193 Y. Wang and J. X. Li, *Spectroscopy and Spectral Analysis*, 2009, **29**(5), 1418-1421.
- 194 E. M. M. Flores, A. P. F. Saidelles, J. C. P. Mattos, E. I. Muller, J. S. F. Pereira, J. N. G. Paniz and V. L. Dressler, *International Journal of Environmental Analytical Chemistry*, 2009, **89**(2), 129-140.



- 195 A. Detcheva and K. H. Grobecker, *Environmental Chemistry Letters*, 2008, **6**(3), 183-187.
- 196 A. S. Lopes and M. A. Z. Arruda, *Microchimica Acta*, 2009, **164**(3-4), 445-451.
- 197 O. V. Shuuaeva, M. A. Gustaytis and G. N. Anoshin, *Anal. Chim. Acta*, 2008, **621**(2), 148-154.
- 198 L. Husakova, J. Sramkova, T. Cernohorsky and I. Urbanova-Dolezalova, *Talanta*, 2009, **77**(4), 1504-1509.
- 199 A. K. Gilmudinov and K. Y. Nagulin, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2009, **64**(1), 42-47.
- 200 Y. L. Zhang and S. B. Adeloju, *Talanta*, 2008, **76**(4), 724-730.
- 201 J. F. Liang, X. Zhang, Y. Q. Zhou and Q. F. Hu, *Asian J. Chem.*, 2008, **20**(1), 599-607.
- 202 L. Kozak, P. Niedzielski and W. Szczucinski, *International Journal of Environmental Analytical Chemistry*, 2008, **88**(14), 989-1003.
- 203 H. W. Sun and R. Suo, *Int. J. Environ. Anal. Chem.*, 2008, **88**(11), 791-801.
- 204 M. Almeida, M. A. Segundo, J. Lima and A. Rangel, *Journal of Analytical Atomic Spectrometry*, 2009, **24**(3), 340-346.
- 205 A. Matsumoto, S. Osaki, T. Kobata, Y. Ohshita, T. Yamamoto, B. Hashimoto and H. Uchihara, *Bunseki Kagaku*, 2009, **58**(5), 393-397.
- 206 G. M. Gao, H. F. Zou, D. R. Liu, L. N. Miao, S. C. Gan, B. C. An, J. J. Xu and G. H. Li, *Fuel*, 2009, **88**(7), 1223-1227.
- 207 L. W. Liu, Q. Zhou, C. B. Zheng, X. D. Hou and L. Wu, *Atomic Spectroscopy*, 2009, **30**(2), 59-64.
- 208 T. Frentiu, E. Darvasi, M. Senila, M. Ponta and E. Cordos, *Talanta*, 2008, **76**(5), 1170-1176.
- 209 J. S. Becker, R. C. Dietrich, A. Matusch, D. Pozebon and V. L. Dressier, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2008, **63**(11), 1248-1252.
- 210 B. Wu, Y. X. Chen and J. S. Becker, *Analytica Chimica Acta*, 2009, **633**(2), 165-172.
- 211 B. Wu, M. Zoriy, Y. X. Chen and J. S. Becker, *Talanta*, 2009, **78**(1), 132-137.
- 212 J. S. Becker, M. Zoriy, B. Wu and A. Matusch, *J. Anal. At. Spectrom.*, 2008, **23**(9), 1275-1280.
- 213 D. Monticelli, A. Di Iorio, E. Ciceri, A. Castelletti and C. Dossi, *Microchimica Acta*, 2009, **164**(1-2), 139-148.
- 214 L. Arroyo, T. Trejos, P. R. Gardinali and J. R. Almirall, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2009, **64**(1), 16-25.
- 215 N. S. Lloyd, R. R. Parrish, M. S. A. Horstwood and S. R. N. Chenery, *Journal of Analytical Atomic Spectrometry*, 2009, **24**(6), 752-758.
- 216 B. Fernandez, F. Claverie, C. Pecheyran, J. Alexis and O. F. X. Donard, *Anal. Chem.*, 2008, **80**(18), 6981-6994.
- 217 E. Engstrom, I. Rodushkin, B. Ohlander, J. Ingri and D. C. Baxter, *Chemical Geology*, 2008, **257**(3-4), 250-259.
- 218 M. E. Kylander, D. J. Weiss and B. Kober, *Science of the Total Environment*, 2009, **407**(5), 1644-1657.
- 219 P. Galler, A. Limbeck, M. Uveges and T. Prohaska, *J. Anal. At. Spectrom.*, 2008, **23**(10), 1388-1391.
- 220 Z. L. Chen, W. X. He, M. Beer, M. Megharaj and R. Naidu, *Talanta*, 2009, **78**(3), 852-856.

- 221 B. Krasnodebska-Ostrega, M. Asztemborska, J. Golimowski and K. Strusinska, *Journal of Analytical Atomic Spectrometry*, 2008, **23**(12), 1632-1635.
- 222 S. E. Afton and J. A. Caruso, *Journal of Analytical Atomic Spectrometry*, 2009, **24**(6), 759-766.
- 223 S. Afton, K. Kubachka, B. Catron and J. A. Caruso, *Journal of Chromatography A*, 2008, **1208**(1-2), 156-163.
- 224 K. Bluemlein, A. Raab and J. Feldmann, *Analytical and Bioanalytical Chemistry*, 2009, **393**(1), 357-366.
- 225 Z. L. Chen, G. Owen, M. Megharaj and R. Naidu, *Rapid Communications in Mass Spectrometry*, 2009, **23**(3), 419-424.
- 226 J. Feuerstein, S. F. Boulyga, P. Galler, G. Stingeder and T. Prohaska, *Journal of Environmental Radioactivity*, 2008, **99**(11), 1764-1769.
- 227 S. Dubascoux, I. Le Hecho, M. P. Gautier and G. Lespes, *Talanta*, 2008, **77**(1), 60-65.
- 228 X. L. Hou, V. Hansen, A. Aldahan, G. Possnert, O. C. Lind and G. Lujanienė, *Analytica Chimica Acta*, 2009, **632**(2), 181-196.
- 229 E. D. S. E, G. Hang and T. Ba, *Spectroscopy and Spectral Analysis*, 2008, **28**(11), 2679-2683.
- 230 A. Shayesteh, V. V. Lavrov, G. K. Koyanagi and D. K. Bohme, *Journal of Physical Chemistry A*, 2009, **113**(19), 5602-5611.
- 231 M. A. Gondal, T. Hussain, Z. H. Yamani and M. A. Baig, *Journal of Hazardous Materials*, 2009, **163**(2-3), 1265-1271.
- 232 J. Cunat, F. J. Fortes and J. J. Laserna, *Analytica Chimica Acta*, 2009, **633**(1), 38-42.
- 233 S. Pandhija and A. K. Rai, *Environmental Monitoring and Assessment*, 2009, **148**(1-4), 437-447.
- 234 M. J. C. Pontes, J. Cortez, R. K. H. Galvao, C. Pasquini, M. C. U. Araujo, R. M. Coelho, M. K. Chiba, M. F. de Abreu and B. E. Madari, *Analytica Chimica Acta*, 2009, **642**(1-2), 12-18.
- 235 V. Motto-Ros, A. S. Koujelev, G. R. Osinski and A. E. Dudelzak, *Journal of the European Optical Society-Rapid Publications*, 2008, **3**.
- 236 T. Ohta, M. Ito, T. Kotani and T. Hattori, *Applied Spectroscopy*, 2009, **63**(5), 555-558.
- 237 M. Galiova, J. Kaiser, K. Novotny, J. Novotny, T. Vaculovic, M. Liska, R. Malina, K. Stejskal, V. Adam and R. Kizek, *Applied Physics a-Materials Science & Processing*, 2008, **93**(4), 917-922.
- 238 L. C. Trevizan, D. Santos, R. E. Samad, N. D. Vieira, L. C. Nunes, I. A. Rufini and F. J. Krug, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2009, **64**(5), 369-377.
- 239 V. Juve, R. Portelli, M. Boueri, M. Baudalet and J. Yu, presented at 4th Euro Mediterranean Symposium on Laser Induced Breakdown Spectroscopy, Paris, FRANCE, Sep 11-13, 2007
- 240 R. M. da Silva, D. Milori, E. C. Ferreira, E. J. Ferreira, F. J. Krug and L. Martin-Neto, presented at 4th Euro Mediterranean Symposium on Laser Induced Breakdown Spectroscopy, Paris, FRANCE, Sep 11-13, 2007
- 241 B. Bousquet, G. Travaille, A. Ismael, L. Canioni, K. M. L. Pierres, E. Bresseur, S. Roy, I. le Hecho, M. Larregieu, S. Tellier, M. Potin-Gauder, T. Boriachon, P. Wazen, A. Diard and S. Belbeze, presented at 4th Euro

- Mediterranean Symposium on Laser Induced Breakdown Spectroscopy, Paris, FRANCE, Sep 11-13, 2007
- 242 E. C. Ferreira, D. Milori, E. J. Ferreira, R. M. Da Silva and L. Martin-Neto, presented at 4th Euro Mediterranean Symposium on Laser Induced Breakdown Spectroscopy, Paris, FRANCE, Sep 11-13, 2007
- 243 M. Hassan, M. Sighicelli, A. Lai, F. Colao, A. H. H. Ahmed, R. Fantoni and M. A. Harith, presented at 4th Euro Mediterranean Symposium on Laser Induced Breakdown Spectroscopy, Paris, FRANCE, Sep 11-13, 2007
- 244 I. Rauschenbach, V. Lazic, S. G. Pavlov, H. W. Hubers and E. K. Jessberger, presented at 4th Euro Mediterranean Symposium on Laser Induced Breakdown Spectroscopy, Paris, FRANCE, Sep 11-13, 2007
- 245 J. F. W. Mosselmans, P. D. Quinn, J. R. Rosell, K. D. Atkinson, A. J. Dent, S. I. Cavill, M. E. Hodson, C. A. Kirk and P. F. Schofield, *Mineralogical Magazine*, 2008, **72**(1), 197-200.
- 246 S. G. Eeckhout, O. V. Safonova, G. Smolentsev, M. Biasioli, V. A. Safonov, L. N. Vykhodtseva, M. Sikora and P. Glatzel, *Journal of Analytical Atomic Spectrometry*, 2009, **24**(2), 215-223.
- 247 V. Orescanin, I. L. Mikelic, L. Mikelic and S. Lulic, *X-Ray Spectrom.*, 2008, **37**(5), 508-511.
- 248 M. C. Lagunas-Solar, P. U. Cecilia, C. Solis and A. Mireles, *Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms*, 2008, **266**(10), 2391-2395.
- 249 A. Mireles, C. Solis, M. C. Lagunas-Solar, C. Pina, R. G. Flocchini, A. Sotelo and M. Navarrete, *J. Radioanal. Nucl. Chem.*, 2008, **277**(2), 441-449.
- 250 A. G. Kachenko, R. Siegele, N. P. Bhatia, B. Singh and M. Ionescu, *Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms*, 2008, **266**(8), 1598-1604.
- 251 T. Awane, S. Fukuoka, K. Nakamachi and K. Tsuji, *Analytical Chemistry*, 2009, **81**(9), 3356-3364.
- 252 S. J. Naftel, R. R. Martin, S. M. Macfie, F. Courchesne and V. Seguin, *Canadian Journal of Analytical Sciences and Spectroscopy*, 2007, **52**(1), 18-24.
- 253 P. A. Olsson, E. C. Hammer, H. Wallander and J. Pallon, *Applied and Environmental Microbiology*, 2008, **74**(13), 4144-4148.
- 254 M. Marmiroli, G. Visioli, G. Antonioli, E. Maestri and N. Marmiroli, *Biochimie*, 2009, **91**(2), 180-191.
- 255 R. Struis, C. Ludwig, T. Barrelet, U. Krahenbuhl and H. Rennenberg, *Sci. Total Environ.*, 2008, **403**(1-3), 196-206.
- 256 M. Necemer, P. Kump, J. Scancar, R. Jadmovic, J. Simcic, P. Pelicon, M. Budnar, Z. Jeran, P. Pongrac, M. Regvar and K. Vogel-Mikus, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2008, **63**(11), 1240-1247.
- 257 N. Szoboszlai, Z. Polgari, V. G. Mihucz and G. Zaray, *Analytica Chimica Acta*, 2009, **633**(1), 1-18.
- 258 E. Margui, I. Queralt and M. Hidalgo, *Trac-Trends in Analytical Chemistry*, 2009, **28**(3), 362-372.
- 259 S. J. Nagourney, S. A. Wilson, B. Buckley, H. M. S. Kingston, S. Y. Yang and S. E. Long, *Journal of Analytical Atomic Spectrometry*, 2008, **23**(11), 1550-1554.
- 260 Y. Shibata, J. Suyama, A. Himamoto, N. Yoshihara, S. Tsuruta, K. Nakano and T. Nakamura, *Bunseki Kagaku*, 2008, **57**(6), 477-483.

- 261 Y. F. Yang, S. R. Chen, H. Ni and X. Q. Ye, *Journal of Zhejiang University-Science B*, 2008, **9**(12), 977-981.
- 262 S. Alves, M. M. dos Santos and M. A. Trancoso, *Accreditation and Quality Assurance*, 2009, **14**(2), 87-93.
- 263 Y. Wong, D. Sin, Y. Yip, L. Valiente, A. Toerveyeni, J. Wang, G. Labarraque, P. Gupta, D. Soni, Surmadi, E. Hwang, C. Yafa, O. Cankur, E. Uysal, G. Turk and R. Huertas, *Accreditation and Quality Assurance*, 2009, **14**(3), 151-158.
- 264 Y. C. Yip, J. C. W. Lam and W. F. Tong, *Trac-Trends in Analytical Chemistry*, 2009, **28**(2), 214-236.
- 265 V. A. Lemos, M. S. Santos, G. T. David, M. V. Maciel and M. D. Bezerra, *Journal of Hazardous Materials*, 2008, **159**(2-3), 245-251.
- 266 V. A. Lemos, P. X. Baliza, A. L. de Carvalho, R. V. Oliveira, L. S. G. Teixeira and M. A. Bezerra, *Talanta*, 2008, **77**(1), 388-393.
- 267 M. Tuzen, D. Citak, D. Mendil and M. Soylak, *Talanta*, 2009, **78**(1), 52-56.
- 268 U. Sahin, S. Kartal and A. Ulgen, *Anal. Sci.*, 2008, **24**(6), 751-757.
- 269 M. Tuzen and M. Soylak, *Journal of Hazardous Materials*, 2009, **162**(2-3), 724-729.
- 270 V. N. Buluta, D. Ozdes, C. Bekircan, A. Gundogdu, C. Duran and M. Soylak, *Analytica Chimica Acta*, 2009, **632**(1), 35-41.
- 271 C. Duran, V. N. Bulut, D. Ozdes, A. Gundogdu and M. Soylak, *Journal of Aoac International*, 2009, **92**(1), 257-262.
- 272 M. Tuzen, D. Citak and M. Soylak, *Journal of Hazardous Materials*, 2008, **158**(1), 137-141.
- 273 S. Kagaya, Y. Araki, K. Kakehashi, N. Hirai, K. Sakai and K. Tohda, *Analytical Sciences*, 2008, **24**(12), 1643-1646.
- 274 L. Y. Zhu, K. Z. Li, S. P. Zhou, Q. F. Hu, G. Y. Yang, Z. J. Huang and J. Chen, *Asian J. Chem.*, 2008, **20**(6), 4433-4442.
- 275 G. Y. Yang, W. B. Fen, C. Lei, W. L. Xiao and H. D. Sun, *Journal of Hazardous Materials*, 2009, **162**(1), 44-49.
- 276 M. Tuzen and M. Soylak, *Journal of Hazardous Materials*, 2009, **164**(2-3), 1428-1432.
- 277 A. Safavi, S. Momeni and N. Saghir, *Journal of Hazardous Materials*, 2009, **162**(1), 333-337.
- 278 M. B. Luo, H. Wu, J. Zhang, D. X. Shen and S. P. Bi, *Separation Science and Technology*, 2008, **43**(8), 2225-2241.
- 279 M. Tuzen, K. O. Saygi and M. Soylak, *Journal of Hazardous Materials*, 2008, **156**(1-3), 591-595.
- 280 Y. M. Cui, X. J. Chang, X. B. Zhu and X. J. Zou, *Int. J. Environ. Anal. Chem.*, 2008, **88**(12), 857-868.
- 281 C. Duran, H. B. Senturk, L. Elci, M. Soylak and M. Tufekci, *Journal of Hazardous Materials*, 2009, **162**(1), 292-299.
- 282 D. Kara, A. Fisher and S. J. Hill, *Journal of Hazardous Materials*, 2009, **165**(1-3), 1165-1169.
- 283 S. Walorczyk, *Rapid Communications in Mass Spectrometry*, 2008, **22**(23), 3791-3801.
- 284 N. Burham, S. M. Abdel-Azeem and F. El-Shahat, *Int. J. Environ. Anal. Chem.*, 2008, **88**(11), 775-789.
- 285 Y. Furusho, M. Ono, M. Yamada, T. Kitade and S. Motomizu, *Bunseki Kagaku*, 2009, **58**(3), 147-152.

- 286 T. Shamspur, A. Mostafavi and I. Sheikhshoaie, *Journal of Aoac International*, 2008, **91**(4), 865-870.
- 287 M. Tuzen, E. Melek and M. Soylak, *Journal of Hazardous Materials*, 2008, **159**(2-3), 335-341.
- 288 M. Tuzen, M. Soylak, D. Citak, H. S. Ferreira, M. G. A. Korn and M. A. Bezerra, *Journal of Hazardous Materials*, 2009, **162**(2-3), 1041-1045.
- 289 V. N. Tirtom, S. Goulding and E. Henden, *Talanta*, 2008, **76**(5), 1212-1217.
- 290 H. Zheng, T. M. Geng and L. M. Hu, *Chemia Analityczna*, 2008, **53**(5), 673-687.
- 291 J. J. Guo, J. B. Cai and Q. D. Su, *Journal of Rare Earths*, 2009, **27**(1), 22-27.
- 292 X. B. Zhu, Y. M. Cui, X. J. Chang, X. J. Zou and Z. H. Li, *Microchimica Acta*, 2009, **164**(1-2), 125-132.
- 293 K. P. Jochum and U. Nohl, *Chem. Geol.*, 2008, **253**(1-2), 50-53.
- 294 S. P. Verma, L. Diaz-Gonzalez and R. Gonzalez-Ramirez, *Geostandards and Geoanalytical Research*, 2009, **33**(1), 29-49.
- 295 M. Constantin, *Geostandards and Geoanalytical Research*, 2009, **33**(1), 115-132.
- 296 N. K. Roy and S. S. Bose, *Geostand. Geoanal. Res.*, 2008, **32**(3), 331-335.
- 297 Z. C. Hu, S. Gao, Y. S. Liu, J. Xu, S. H. Hu and H. H. Chen, *Geostand. Geoanal. Res.*, 2008, **32**(3), 347-360.
- 298 M. A. V. Logan and M. A. Wise, *Geostandards and Geoanalytical Research*, 2009, **33**(1), 85-93.
- 299 G. L. Luvizotto, T. Zack, H. P. Meyer, T. Ludwig, S. Triebold, A. Kronz, C. Munker, D. F. Stockli, S. Prowatke, S. Klemme, D. E. Jacob and H. von Eynatten, *Chemical Geology*, 2009, **261**(3-4), 346-369.
- 300 K. P. Jochum and S. M. Brueckner, *Geostandards and Geoanalytical Research*, 2008, **32**(4), 405-452.
- 301 J. Blichert-Toft, *Chem. Geol.*, 2008, **253**(3-4), 252-257.
- 302 M. L. A. Morel, O. Nebel, Y. J. Nebel-Jacobsen, J. S. Miller and P. Z. Vroon, *Chemical Geology*, 2008, **255**(1-2), 231-235.
- 303 L. Nasdala, W. G. Hofmeister, N. Norberg, J. M. Mattinson, F. Corfu, W. Dorr, S. L. Kamo, A. K. Kennedy, A. Kronz, P. W. Reiners, D. Frei, J. Kosler, Y. S. Wan, J. Gotze, T. Hager, A. Kroner and J. W. Valley, *Geostand. Geoanal. Res.*, 2008, **32**(3), 247-265.
- 304 S. Richter, A. Alonso, Y. Aregbe, R. Eykens, F. Kehoe, H. Kuhn, N. Kivel, A. Verbruggen, R. Wellum and P. D. P. Taylor, *International Journal of Mass Spectrometry*, 2009, **281**(3), 115-125.
- 305 J. Aggarwal, F. Bohm, G. Foster, S. Halas, B. Honisch, S. Y. Jiang, J. Kosler, A. Liba, I. Rodushkin, T. Sheehan, J. J. S. Shen, S. Tonarini, Q. L. Xie, C. F. You, Z. Q. Zhao and E. Zuleger, *Journal of Analytical Atomic Spectrometry*, 2009, **24**(6), 825-831.
- 306 K. Gotan, S. Nakai and H. Matsuzaki, *Geochemical Journal*, 2008, **42**(3), 305-308.
- 307 J. L. Mann, R. D. Vocke and W. R. Kelly, *Rapid Communications in Mass Spectrometry*, 2009, **23**(8), 1116-1124.
- 308 A. Heuser and A. Eisenhauer, *Geostand. Geoanal. Res.*, 2008, **32**(3), 311-315.
- 309 P. J. Sylvester, *Geostandards and Geoanalytical Research*, 2008, **32**(4), 469-488.
- 310 C. C. Garcia, H. Lindner and K. Niemax, *Journal of Analytical Atomic Spectrometry*, 2009, **24**(1), 14-26.

- 311 M. Walle, J. Koch, L. Flamigni, S. Heiroth, T. Lippert, W. Hartung and D. Gunther, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2009, **64**(1), 109-112.
- 312 Z. C. Hu, Y. S. Liu, S. Gao, S. H. Hu, R. Dietiker and D. Gunther, *J. Anal. At. Spectrom.*, 2008, **23**(9), 1192-1203.
- 313 M. Shaheen, J. E. Gagnon, Z. P. Yang and B. J. Fryer, *Journal of Analytical Atomic Spectrometry*, 2008, **23**(12), 1610-1621.
- 314 K. Ikehata, K. Notsu and T. Hirata, *J. Anal. At. Spectrom.*, 2008, **23**(7), 1003-1008.
- 315 M. Walle, J. Koch and D. Gunther, *J. Anal. At. Spectrom.*, 2008, **23**(9), 1285-1289.
- 316 J. E. Gagnon, B. J. Fryer, I. M. Samson and A. E. Williams-Jones, *Journal of Analytical Atomic Spectrometry*, 2008, **23**(11), 1529-1537.
- 317 E. T. Tipper, P. Louvat, F. Capmas, A. Galy and J. Gaillardet, *Chemical Geology*, 2008, **257**(1-2), 65-75.
- 318 M. Resano, E. Garcia-Ruiz, K. S. McIntosh and F. Vanhaecke, *Journal of Analytical Atomic Spectrometry*, 2008, **23**(12), 1599-1609.
- 319 A. Muller, M. Wiedenbeck, B. Flem and H. Schiellerup, *Geostand. Geoanal. Res.*, 2008, **32**(3), 361-376.
- 320 Z. C. Hu, S. Gao, Y. S. Liu, H. H. Chen and S. H. Hu, *Spectroscopy Letters*, 2008, **41**(5), 228-236.
- 321 M. Guillong, C. Latkoczy, J. H. Seo, D. Gunther and C. A. Heinrich, *Journal of Analytical Atomic Spectrometry*, 2008, **23**(12), 1581-1589.
- 322 G. Lambrecht, L. W. Diamond and T. Pettke, *American Mineralogist*, 2008, **93**(7), 1187-1190.
- 323 S. Y. O'Reilly, W. L. Griffin, N. J. Pearson, S. E. Jackson, E. A. Belousova, O. Alard and A. Saeed, *Australian Journal of Earth Sciences*, 2008, **55**(6-7), 983-995.
- 324 M. Girod, T. N. T. Phan and L. Charles, *Rapid Communications in Mass Spectrometry*, 2008, **22**(23), 3767-3775.
- 325 S. Johnston, G. Gehrels, V. Valencia and J. Ruiz, *Chemical Geology*, 2009, **259**(3-4), 218-229.
- 326 D. Frei and A. Gerdes, *Chemical Geology*, 2009, **261**(3-4), 261-270.
- 327 A. I. S. Kemp, G. L. Foster, A. Schersten, M. J. Whitehouse, J. Darling and C. Storey, *Chemical Geology*, 2009, **261**(3-4), 244-260.
- 328 A. J. R. Kent, *J. Anal. At. Spectrom.*, 2008, **23**(7), 968-975.
- 329 P. R. Craddock, O. J. Rouxel, L. A. Ball and W. Bach, *Chem. Geol.*, 2008, **253**(3-4), 102-113.
- 330 D. L. Death, A. P. Cunningham and L. J. Pollard, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2008, **63**(7), 763-769.
- 331 J. Cunat, F. J. Fortes, L. M. Cabalin, F. Carrasco, M. D. Simon and J. J. Laserna, *Applied Spectroscopy*, 2008, **62**(11), 1250-1255.
- 332 J. Namiesnik and P. Szefer, *Ecological Chemistry and Engineering S-Chemia I Inzynieria Ekologiczna S*, 2008, **15**(2), 167-244.
- 333 M. Al-Harashsheh, S. Kingman, C. Somerfield and F. Ababneh, *Analytica Chimica Acta*, 2009, **638**(1), 101-105.
- 334 D. Nna-Mvondo, M. P. Martin-Redondo and J. Martinez-Frias, *Analytica Chimica Acta*, 2008, **628**(2), 133-142.
- 335 L. Qi and M. F. Zhou, *Geostand. Geoanal. Res.*, 2008, **32**(3), 377-387.

- 336 V. A. Lemos, L. S. G. Teixeira, M. D. Bezerra, A. C. S. Costa, J. T. Castro, L. A. M. Cardoso, D. S. de Jesus, E. S. Santos, P. X. Baliza and L. N. Santosi, *Applied Spectroscopy Reviews*, 2008, **43**(4), 303-334.
- 337 N. Vajda, A. Torvenyi, G. Kis-Benedek and C. K. Kim, *Radiochimica Acta*, 2009, **97**(1), 9-16.
- 338 Y. L. Sun and M. Sun, *Journal of Analytical Atomic Spectrometry*, 2009, **24**(2), 232-236.
- 339 V. Balaram, *Journal of the Geological Society of India*, 2008, **72**(5), 661-677.
- 340 A. J. Fitzpatrick, T. K. Kyser and D. Chipley, *Geochemistry-Exploration Environment Analysis*, 2009, **9**, 93-100.
- 341 A. Makishima, B. N. Nath and E. Nakamura, *Geochemical Journal*, 2008, **42**(3), 237-246.
- 342 A. Makishima and E. Nakamura, *Geochemical Journal*, 2008, **42**(2), 199-206.
- 343 M. Staniszewska, B. Radke, J. Namiesnik and J. Bolalek, *Int. J. Environ. Anal. Chem.*, 2008, **88**(11), 747-774.
- 344 C. Lemini and E. Canchola, *Physiology & Behavior*, 2009, **96**(4-5), 662-666.
- 345 S. Bangkedphol, H. E. Keenan, C. Davidson, A. Sakultantimetha and A. Songsasen, *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering*, 2008, **43**(14), 1744-1751.
- 346 J. Pacheco-Arjona, P. Rodriguez-Gonzalez, M. Valiente, D. Barclay and O. F. X. Donard, *Int. J. Environ. Anal. Chem.*, 2008, **88**(13), 923-932.
- 347 E. L. Gao, G. B. Jiang, B. He, Y. G. Yin and J. B. Shi, *J. Anal. At. Spectrom.*, 2008, **23**(10), 1397-1400.
- 348 L. P. Bedard, *Geostandards and Geoanalytical Research*, 2008, **32**(4), 399-403.
- 349 G. D. Matos and M. A. Z. Arruda, *Talanta*, 2008, **76**(2), 475-478.
- 350 C. Zhang, Y. Li, X. Y. Cui, Y. Jiang and X. P. Yan, *J. Anal. At. Spectrom.*, 2008, **23**(10), 1372-1377.
- 351 K. L. Linge, *Geostandards and Geoanalytical Research*, 2008, **32**(4), 453-468.
- 352 E. H. Evans, J. A. Day, C. D. Palmer and C. M. M. Smith, *Journal of Analytical Atomic Spectrometry*, 2009, **24**(6), 711-733.
- 353 V. Padmasubashini and D. S. R. Murty, *Atomic Spectroscopy*, 2009, **30**(1), 32-40.
- 354 P. Liang, E. Zhao and R. Liu, *Geostandards and Geoanalytical Research*, 2009, **33**(1), 63-69.
- 355 M. A. Amberger, N. H. Bings, P. Pohl and J. A. C. Broekaert, *Int. J. Environ. Anal. Chem.*, 2008, **88**(9), 625-636.
- 356 J. Wills, S. McSheehy, T. Oki, M. Hamester and B. Spence, *Spectroscopy*, 2008, 28-+.
- 357 S. G. de Madinabeitia, M. E. S. Lorda and J. I. G. Ibarguchi, *Anal. Chim. Acta*, 2008, **625**(2), 117-130.
- 358 I. V. Nikolaeva, S. V. Paleskii, O. A. Koz'menko and G. N. Anoshin, *Geochemistry International*, 2008, **46**(10), 1016-1022.
- 359 G. Bayon, J. A. Barrat, J. Etoubleau, M. Benoit, C. Bollinger and S. Revillon, *Geostandards and Geoanalytical Research*, 2009, **33**(1), 51-62.
- 360 K. Nagaishi and T. Ishikawa, *Geochemical Journal*, 2009, **43**(2), 133-141.
- 361 J. D. Woodhead, *Geostandards and Geoanalytical Research*, 2008, **32**(4), 495-507.

- 362 M. Feineman, S. Penniston-Dorland, F. Poitrasson and S. Weyer, *Chemical Geology*, 2009, **258**(1-2), 1-4.
- 363 J. Aggarwal, J. Habicht-Mauche and C. Juarez, *Applied Geochemistry*, 2008, **23**(9), 2658-2666.
- 364 A. J. W. Gleadow and J. F. Lovering, *Australian Journal of Earth Sciences*, 2008, **55**(6-7), 753-767.
- 365 J. Barling and D. Weis, *J. Anal. At. Spectrom.*, 2008, **23**(7), 1017-1025.
- 366 H. Q. Liao, J. Zheng, F. C. Wu, M. Yamada, M. G. Tan and J. M. Chen, *Applied Radiation and Isotopes*, 2008, **66**(8), 1138-1145.
- 367 C. Negre, A. L. Thomas, J. L. Mas, J. Garcia-Orellana, G. M. Henderson, P. Masque and R. Zahn, *Analytical Chemistry*, 2009, **81**(5), 1914-1919.
- 368 J. Zheng and M. Yamada, *Journal of Oceanography*, 2008, **64**(4), 541-550.
- 369 K. Iwamoto, H. Nagao and M. Toyoda, *European Journal of Mass Spectrometry*, 2009, **15**(2), 249-260.
- 370 L. Halicz, L. Yang, N. Teplyakov, A. Burg, R. Sturgeon and Y. Kolodny, *Journal of Analytical Atomic Spectrometry*, 2008, **23**(12), 1622-1627.
- 371 S. V. Paleskii, I. V. Nikolaeva, O. A. Koz'menko and G. N. Anoshin, *Journal of Analytical Chemistry*, 2009, **64**(3), 272-276.
- 372 R. Harlou, D. G. Pearson, G. M. Nowell, C. J. Ottley and J. P. Davidson, *Chemical Geology*, 2009, **260**(3-4), 254-268.
- 373 J. Harvey and E. F. Baxter, *Chemical Geology*, 2009, **258**(3-4), 251-257.
- 374 J. S. Scoates and R. M. Friedman, *Economic Geology*, 2008, **103**(3), 465-471.
- 375 J. H. Chen, D. A. Papanastassiou and G. J. Wasserburg, *Geochimica Et Cosmochimica Acta*, 2009, **73**(5), 1461-1471.
- 376 M. Wiedenbeck, *Geostandards and Geoanalytical Research*, 2008, **32**(4), 489-494.
- 377 T. R. Ireland, S. Clement, W. Compston, J. J. Foster, P. Holden, B. Jenkins, P. Lanc, N. Schram and I. S. Williams, *Australian Journal of Earth Sciences*, 2008, **55**(6-7), 937-954.
- 378 P. Mouroulis, B. van Gorp, D. Blaney and R. O. Green, *Applied Spectroscopy*, 2008, **62**(12), 1370-1377.
- 379 M. J. Whitehouse and A. A. Nemchin, *Chemical Geology*, 2009, **261**(1-2), 31-41.
- 380 X. H. Li, Y. Liu, Q. L. Li, C. H. Guo and K. R. Chamberlain, *Geochemistry Geophysics Geosystems*, 2009, **10**.
- 381 S. Hu, P. Zhou, S. Jiang, Q. Fu, M. He, J. Yang and H. Tong, *Bone*, 2009, **44**, 210.
- 382 I. R. Fletcher, M. R. Kilburn and B. Rasmussen, *International Journal of Mass Spectrometry*, 2008, **278**(1), 59-68.
- 383 M. Wiedenbeck, D. Schulze and I. Veksler, *Geostandards and Geoanalytical Research*, 2009, **33**(1), 111-114.
- 384 M. A. W. Marks, R. L. Rudnick, T. Ludwig, H. Marschall, T. Zack, R. Halama, W. F. McDonough, D. Rost, T. Wenzel, E. P. Vicenzi, I. P. Savov, R. Altherr and G. Markl, *Geostand. Geoanal. Res.*, 2008, **32**(3), 295-310.
- 385 P. Sjovall, V. Thiel, S. Siljestrom, C. Heim, T. Hode and J. Lausmaa, *Geostand. Geoanal. Res.*, 2008, **32**(3), 267-277.
- 386 M. Burtscher, *Sleep and Breathing*, 2009, **13**(2), 119-120.
- 387 S. Merchel, R. Braucher, L. Benedetti, O. Grauby and D. L. Bourles, *Quaternary Geochronology*, 2008, **3**(4), 299-307.



- 388 G. Balco and C. W. Rovey, *American Journal of Science*, 2008, **308**(10), 1083-1114.
- 389 B. E. Rosenheim, S. R. Thorrold and M. L. Roberts, *Rapid Communications in Mass Spectrometry*, 2008, **22**(21), 3443-3449.
- 390 H. Z. Shan, S. J. Zhuo, R. X. Shen and C. Sheng, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2008, **63**(5), 612-616.
- 391 N. Zhang, T. Y. Li, Z. C. Meng, C. N. Wang, L. Ke and Y. H. Feng, *Microchemical Journal*, 2009, **91**(1), 59-62.
- 392 M. Loubser and S. Verryyn, *South African Journal of Geology*, 2008, **111**(2-3), 229-238.
- 393 M. F. Gazulla, M. P. Gomez, M. Orduna and M. Rodrigo, *X-Ray Spectrometry*, 2009, **38**(1), 3-8.
- 394 N. A. Kolpakova, A. S. Buinovskii and I. A. Mel'nikova, *Journal of Analytical Chemistry*, 2009, **64**(2), 144-148.
- 395 G. J. Weltje and R. Tjallingii, *Earth and Planetary Science Letters*, 2008, **274**(3-4), 423-438.