

# 2014 Atomic Spectrometry Update – A review of advances in environmental analysis

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*This is the 30th annual review of the application of atomic spectrometry to the chemical analysis of environmental samples. This Update refers to papers published approximately between August 2013 and July 2014 and continues the series of Atomic Spectrometry Updates (ASUs) in Environmental Analysis<sup>1</sup> that should be read in conjunction with other related ASUs in the series, namely: clinical and biological materials, foods and beverages<sup>2</sup>; advances in atomic spectrometry and related techniques<sup>3</sup>; elemental speciation<sup>4</sup>; X-ray spectrometry<sup>5</sup> and metals, chemicals and functional materials<sup>6</sup>.*

*In the field of air analysis, highlights within this review period included: the use of 3D printing technology for the rapid prototyping of new air sampler components; single particle ICP-MS studies; use of a new triple-quadrupole ICP-MS for the analysis of radioactive species and the use of FEG-SEM and IBA for the analysis of gun-shot residues.*

*In the field of water analysis, methods continue to be developed: for the extraction and preconcentration of elements; speciation of As, Cr, Hg and Sb forms and determination of elemental constituents in colloidal and NP fractions. Instrumental developments reported included the use of MC-ICP-MS for isotopic tracer studies and a review of XRF techniques and associated preconcentration procedures for trace element analysis.*

*Many articles featuring the analysis of plants and soils appeared but, as usual, most focused on environmental applications rather than the advancement of atomic spectrometry. There have, however, been interesting developments, such as the almost bewildering increase in types of microextraction for analyte preconcentration and the resurgence of CS-AAS.*

*Clearly LIBS is maturing rapidly, with soil analysis becoming more routine in nature. Also notable was the way the accident at the Fukushima-Daiichi nuclear power plant triggered development of analytical methods for assessment of contamination in the surrounding area.*

*Recent research indicates that geological applications still drives many of the instrumental and methodological advances in LA-ICP-MS. Fundamental studies continued to shed light on the processes involved and hence ways of improving the analysis of laser-produced aerosols. The preparation of NP powders for the production of matrix-matched RMs for microanalytical techniques such as LA-ICP-MS and SIMS showed great promise for addressing one of the major issues when analysing geological materials by these techniques. Steady advances in MC-ICP-MS methodology is feeding through to applications in isotope geochemistry, while new SIMS instrumentation is being directed towards probing fine growth structures in biogenic carbonates and inferring past climate conditions from their geochemistry.*

*Feedback on this review is most welcome and the review coordinator can be contacted using the email address provided.*

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## 1 Air analysis

### 1.1 Review papers

A series of *review papers* was published as part of a wider initiative to design the next generation of air quality indicators. Current monitoring techniques and modelling approaches were included in an introductory overview<sup>7</sup> (39 references), a review of suspended particulate matter<sup>8</sup> (50 references) and a review of Hg and its compounds in air<sup>9</sup> (141 references). Vehicular emissions have received increased attention over the last few years and information regarding the sampling and measurement of tailpipe particulate emissions has now been tabulated<sup>10</sup> (310 references). Reviews of techniques for the determination of individual pollutants in air are most welcome: organomercury compounds in environmental samples<sup>11</sup> (176 references); elemental, equivalent black and refractory black carbon aerosol particles<sup>12</sup> (267 references) and <sup>129</sup>I in air<sup>13</sup> (104 references). An overview on the key role of atomic spectrometry in radiation protection was also published<sup>14</sup> (292 references).

### 1.2 Sampling techniques

The development of *personal air samplers* to monitor workers' exposure to airborne NPs is of growing interest. A new sampler consisted of a pre-cyclone for to collect respirable particles, micro-orifice impactor stages with an acceleration nozzle to size NPs and a backup filter to collect residual particles<sup>15</sup>. The cyclone and impactor stages had  $d_{50}$  cut-off diameters of 3.95  $\mu\text{m}$  and 94.7 nm respectively, thus meeting the desired design specifications. A new personal sampler utilised thermophoretic force to collect NPs onto a standard TEM grid<sup>16</sup>. A test aerosol consisting of saline particles in the range 20-600 nm was generated using a collision nebuliser and particle numbers and size were continuously monitored with a SMPS. Particles subsequently collected with this new sampler were examined by electron microscopy. By using both sets of data, sampler inlet losses and collection efficiencies could be determined. These experimental results, together with a theoretical understanding of thermophoretic velocities, were used to formulate a transfer function that related the properties of the collected particles to the properties of the sampled aerosol. This function used a normalisation factor that was greater than one for very small particles but which approached unity for particles larger than *ca.* 70 nm. The ongoing debate about the best NP metric for exposure assessment, be it mass, number or surface area, has led researchers to propose an alternative but interesting metric<sup>17</sup>. A new quasi-real-time sampler-detector, called the Catalytic Activity Aerosol Monitor, exploited the use of specific catalytical reactions

between test gases and engineered NPs collected on a filter. Laboratory studies demonstrated that Ni catalyzed the oxidation of CO to CO<sub>2</sub> and that Pd and Pt catalysed the hydrogenation of ethene to ethane. Such gas-phase conversions were monitored using an IR detector. The linear relationships between mass-on-filter and the detector output meant that this prototype monitor could provide a means of quantifying certain metallic NPs in workplace air. More research is obviously required to assess the viability of this approach.

*Alternative approaches for assessing worker exposure* included the use of ICP-MS to measure the concentration of metals such as Fe and Mn in exhaled particles from welders<sup>18-20</sup>. Exhaled breath was collected through a sampling inlet, reminiscent of an alcohol breathalyser, into a Peltier-cooled collection vial. Challenges included measuring ultratrace levels, relating measured elemental concentration to dose and minimising the potential from cross contamination with non-inhaled particles such as those deposited on the lips.

*New ambient air samplers* continue to be developed. A high volume aerosol-into-liquid sampler was developed to preconcentrate fine particulate matter into a slurry sample<sup>21</sup>. A laboratory study indicated that collection efficiencies were >90% over the particle size range 0.01-2 µm whilst field tests indicated that the system was capable of continuous and unattended operation over 2-3 days at a nominal flow rate of 200 L min<sup>-1</sup>. A multistage sampler, designed to mimic deposition of aerosol in different parts of the human respiratory system, employed foam and nylon mesh to act as both particle size selectors and collection substrates<sup>22</sup>. These substrates were not amenable to gravimetric (mass) analysis due to effects of humidity on weighing but were suitable for chemical analysis. Collecting a defined particle fraction is often required and studies evaluating new sampler inlet designs continue to be reported. The majority of airborne measurements of aerosols employ forward-facing inlets with near isokinetic sampling but these inlets have limitations when sampling in clouds due to artifact formation when liquid or ice cloud particles collide with inlet surfaces. To alleviate this problem a new perpendicular inlet<sup>23</sup> was successfully developed to allow small particles (< 1 µm) to be sampled to the exclusion of cloud particles (>1 µm) with no discernible artifact response. A streamlined, high-volume particle impactor<sup>24</sup> employed a single round jet designed to operate at a flow rate of 1000 L min<sup>-1</sup>. The novelty of this study was not necessarily the design of this new impactor but the combination of computational fluid dynamic tools with rapid prototyping using 3D printer technology. This reviewer is aware of other research groups working in this field who are also exploiting this new powerful 3D printer technology.

Urban air quality can be severely affected by *traffic-derived particulate matter*. Sources of particles include tail-pipe emissions, brake pad and tyre wear and resuspension of road dust by vehicular motion or wind. Techniques involving resuspension of settled road dust in a laboratory setting are not entirely satisfactory as they may not mimic street conditions. A mobile road dust sampler<sup>25</sup>, which consisted of an air sampler mounted on a motorised laboratory trolley, induced resuspension and collected particles directly from road surfaces, and had the ability to collect particles in two size ranges, PM<sub>1-10</sub> and PM<sub>1</sub>. A garden leaf blower was used to resuspend particles under a road surface sampling hood, attached to the front of the trolley and connected via tubing to the air sampler. The authors suggested that this new approach may offer a better method for unbiased sample collection. Continuing the theme of using components designed for other uses, air filters in car engines have been advocated<sup>26,27</sup> as potentially useful urban air samplers. Filters from taxis were used as mobile high-volume air samplers and provided city-wide integrated air concentrations at street level. Approximate air volumes sampled were derived from consideration of the fuel consumption or the engine volume and the associated rpm data. Measured values for a range of elemental species and PAHs were comparable with those derived from more conventional TSP air samplers. Satellite navigation technology could also be employed in logging the itineraries of the vehicles and thus assisting in the future development of urban pollution maps.

The recent UNEP convention binding countries to reduce *mercury emissions* will require developments in air sampling technologies. New Cl and I-impregnated activated carbon traps were evaluated<sup>28</sup> as a means of preconcentrating air samples in order to meet the challenge of collecting sufficient sample for Hg stable isotope research. The low level blank, *ca.* 0.3 ng Hg per g of sorbent, in preconditioned traps equated to <3% of the Hg collected in a typical sample. Recoveries were calculated using a Hg vapour spike of known isotopic composition. No induced isotopic artifacts occurred when recoveries were >81% but a positive mass dependent fractionation bias was observed when recoveries were <81%. Mercury emissions arising from spontaneous combustion within landfill sites represent an anthropogenic source that historically has been overlooked in many Hg inventory estimates. New real-time Hg measurements conducted at a large urban landfill site<sup>29</sup> were made using a field-deployable analyser integrated with a newly developed relaxed eddy accumulation (REA) approach. This REA technique is a micro-metrological method that allows measurement of spatially averaged air-surface exchange Hg fluxes over a much larger area (*ca.* 1 ha) than the few m<sup>2</sup> typically sampled by enclosure systems. Ambient air concentrations above the landfill site increased from a baseline of 43±20 to 396±114 ng m<sup>-3</sup>

following one such combustion event. In light of this work, the authors suggested that data for spontaneous combustion of refuse in landfill sites should be included in future Hg emissions inventory estimates.

### 1.3 Reference materials and calibrants

Filter *reference materials* containing sulfur for XRF calibration<sup>30</sup> were prepared by using a desolvating nebuliser in a test chamber and collecting the particles generated on filters. A typical dust-on-filter deposition pattern at appropriate sample filter mass loading was reproduced by using the same air sampler and filter media combination used for real air samples. These RMs matched real air samples more closely and further work is being undertaken to develop and characterise other multielement calibration filters. Reference materials such as NIST SRM 1649a (urban dust) and NIST SRM 2584 (indoor dust) are widely used in laboratories conducting air quality measurements. Further characterisation<sup>31</sup> of these materials was undertaken using EPMA, SEM, TEM, XANES and XRD techniques in order to provide information on the speciation of Cr, Mn and Pb. The development of NIST SRM 2951-2958 (respirable alpha-quartz on filters) and NIST SRM 2961-2967 (respirable cristobalite on filters) covering the mass range of 5-1000 µg per filter was summarised<sup>32</sup>. These SRMs were prepared by suspending bulk crystalline SRMs in water and spiking an aliquot of the resultant slurry suspensions onto filters. Total Si was determined by ICP-AES as a surrogate marker for batch homogeneity assessment because XRD or FTIR methods were insufficiently sensitive. Representative filter samples were dissolved in HF and neutralised using TMAH prior to sample nebulisation and analysis. Certified values and their associated uncertainties were derived from the ICP-AES data, together with consideration of the purity and crystallinity of the starting bulk SRM materials and the spike volume. Work undertaken at IRMM on the development of CRMs and associated reference methods for nuclear safeguards and security has been summarised<sup>33</sup>.

### 1.4 Sample preparation

The well-worn path of assessing *sample dissolution* procedures continues to be trodden. An assessment<sup>34</sup> of the performance of 5 digestion methods involved both hotplate and microwave-assisted procedures. Acid mixtures containing variable amounts of HF, HCl, HClO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> with HNO<sub>3</sub> were used to digest test aliquots of NIST SRM 1648a (urban particulate matter). Elemental recoveries using a HNO<sub>3</sub>-HF acid reflux procedure were typically >80% except for Cr for which mean recoveries were 46%. However, it is known



that Cr in this particular SRM exists in a refractory chromite phase. A study<sup>35</sup> on the solubility of traffic-related metal(loid)s associated with airborne particulate matter employed a physiologically-based extraction test with two simulated lung fluids, artificial lysosomal fluid (ALF) and Gamble's solution. Airborne dust samples, size fractionated in PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub>, were collected onto filters using a high volume air sampler. Following extraction of the soluble fraction, residues were dissolved in acid using a high pressure asher. Arsenic, Cu, Sb and V in the PM<sub>10</sub> fraction had the highest bioaccessibility. A method<sup>36</sup> was proposed to fractionate atmospheric particulate matter into three components: the water-soluble fraction; the insoluble non-nanometric fraction; and the fraction containing insoluble NPs. The procedure simply involved the ultrasonication of aliquots of either bulk SRM NIST 1649a (urban dust) or filter samples, in water, to leach the soluble phase followed by centrifugation to separate the insoluble non-nanometric fraction from the insoluble NP phase which remained in suspension. The alkaline and alkaline earth metals were typically found in the water-soluble phase and many elements typically emitted from combustion sources (As, Cd, Pb, Sb, Sn and V) were present in airborne matter as insoluble NPs.

*Technique-specific sample preparation* procedures have been advocated. Sample pretreatment strategies<sup>37</sup> for TXRF analysis of particulates included *in-situ* microdigestion, slurry preparation, acid digestion and other extraction procedures. To undertake high precision Hg stable isotope measurements sufficient amounts of Hg (>10 ng) are required but the acid digestion of natural samples with low Hg concentrations (<1–10 ng g<sup>-1</sup>), such as pulverised coal and fly ash, is challenging. An elegant solution<sup>38</sup> lay in the use of combustion to liberate Hg from solid matrices, reduction to Hg<sup>0</sup> and trapping in acidic solution. Solution aliquots were then introduced into a MC-ICP-MS instrument using a CV technique. Provided that Hg recoveries were within 80-120%, no systematic dependence of Hg isotopic composition on the % recovery was observed, echoing findings reported earlier in this review. The limited transfer of residual sample matrix into the acid solution was beneficial as it minimised the potential for matrix interference on the CV reductant step. Peak area measurements in conjunction with a standard addition calibration protocol was proposed<sup>39</sup> to minimise this matrix effect observed when Hg in impinger samples, derived from stack emissions, were analysed using CV-AFS.

## **1.5 Instrumental analysis**

### **1.5.1 Atomic absorption spectrometry**

Three review papers<sup>40-42</sup> considered the development of the *HR-CS-ETAAS* technique. Welz *et al.*<sup>40</sup> (174 references) highlighted the advantage of systems equipped with a CCD detector which adds the wavelength as a third dimension to the conventional display of absorbance over time. The ability to measure elements such as the halogen elements, P and S using molecular absorption spectrometry<sup>41,42</sup> (98 and 108 references respectively) was highlighted. A method<sup>43</sup> for the determination of S in coal and ash slurry samples achieved a LOD of 0.01%, an RSD of 6% and recoveries within the certified values given for NIST 1632b (trace elements in coal) and NIST 1633b (coal fly ash). Although S is normally determined using an elemental analyser, this new AAS method allowed S to be determined together with a range of other elements. The LOD and LOQ values for both Mo and Sb in street dust<sup>44</sup> measured by solid sampling HR-CS-ETAAS were 15 and 50  $\mu\text{g g}^{-1}$ , respectively. The characteristic mass was 28 pg at the Mo 313.259 nm line and 38 pg at the Sb 217.582 nm line. The recoveries from the three CRMs, BCR CRM 176R (fly ash), NIST SRM 1648 (urban particulate matter) and NIST SRM 1649a (urban dust), overlapped the certified ranges. The elegance of the SS-HR-CS-ETAAS technique was thus demonstrated for the determination of trace elements in dust samples that can be difficult to digest with conventional acid digestions. However it must be recognised that well-homogenised powdered samples are required to generate precise results on account of the small sample masses involved.

On-line *AAS techniques for process monitoring* have been evaluated. A CVAAS technique<sup>45</sup> for determining Hg in fuel gases involved the use of a cyclic combustion pretreatment unit which consisted of an electrically heated quartz tube reactor filled with an oxygen source (NiO) dispersed onto quartz sand. Gas samples were fed into the heated reactor and combusted and a condenser used to separate H<sub>2</sub>O from the CO<sub>2</sub> produced, allowing Hg<sup>0</sup> to be determined. To complete the cycle, the reduced Ni surface was subsequently regenerated by oxidation in air. By operating two reactors in parallel so that one could be in operation while the other was being regenerated, it was possible to make continuous Hg measurements. The feasibility of determining Hg in naphtha and petroleum condensate by PVG has been investigated<sup>46</sup>. Samples were presented as a micro emulsion in propan-1-ol mixed with a small amount of water. Additional agents for promoting the generation of volatile Hg compounds were unnecessary. The LOD for a 1 mL micro emulsion test aliquot was 0.6  $\mu\text{g L}^{-1}$ , the spike recoveries were 92–113% and the sample throughput was 6 samples h<sup>-1</sup>. No Hg was found in the naphtha samples tested although concentrations of 76–105  $\mu\text{g L}^{-1}$  were obtained for the petroleum condensate samples examined.

## 1.5.2 Atomic emission spectrometry

Consolidation of information regarding developments of *LIBS* can be found in three reviews<sup>47-49</sup>. Radziemski and Cremers<sup>47</sup> (59 references) sketched out the historical development and advances in the methodologies and instrumentation over the last 50 years culminating with a synopsis of the LIBS 2012 conference. Another review<sup>48</sup> (21 references) focused on industrial applications of this technique including the analysis of coals, slags and dusts whilst a third review<sup>49</sup> (61 references) not only covered environmental pollution but also applications in biomedicine, botany, metallurgy and space exploration. In a study of a new low-pressure laser-induced plasma technique<sup>50</sup> intended for the determination of Hg in power plant emissions, it was noted that black-body-like emissions from the plasma itself and other concomitant atomic and molecular emissions decreased significantly under low pressure conditions. At a pressure of 700 Pa, a LOD of 0.3 ppm was achievable. Ongoing work will assess the feasibility of this approach in real applications.

## 1.5.3 Mass spectrometry

**1.5.3.1 Inductively coupled plasma mass spectrometry.** A new *triple-quadrupole ICP-MS* configuration was exploited to measure radioactive fall-out from the recent Fukushima nuclear incident. In the study of radioactive Cs in rainwater<sup>51</sup>, N<sub>2</sub>O was used as reaction gas to lessen the isobaric interference of <sup>134</sup>Ba, <sup>135</sup>Ba and <sup>137</sup>Ba, on <sup>134</sup>Cs, <sup>135</sup>Cs and <sup>137</sup>Cs respectively, by converting the atomic species to oxide and hydroxide species thus increasing their masses and shifting them away from the analyte masses. The additional quadrupole in front of the reaction cell was tuned to reject entry of Sb and Sn ions that would otherwise have resulted in additional unwanted isobaric interferences from SbO and SnO. Measured <sup>134</sup>Cs/<sup>137</sup>Cs values were consistent with those determined using a more conventional but slower radiochemical method. In another paper, <sup>129</sup>I washout from rainwater was measured in soils<sup>52</sup>. The iodine fractions were extracted from the soils by pyrohydrolysis and purified by solvent extraction. The background intensity at *m/z* 129 arising from <sup>129</sup>Xe impurities in the argon plasma gas was reduced by converting it from an ionic to a non-detectable neutral species using O<sub>2</sub> as a reaction gas. An off-set correction approach corrected for residual isobaric interferences such as <sup>127</sup>IH<sub>2</sub><sup>+</sup> and <sup>127</sup>ID<sup>+</sup> on <sup>129</sup>I by assuming a production ratio of 5 x 10<sup>-9</sup>. The measured <sup>129</sup>/<sup>127</sup>I ratio in NIST SRM 3231 (iodine isotopic standard-level II) was within analytical error of the certified value thereby demonstrating the effectiveness of the

proposed approach. Values determined in soils samples were also consistent with values determined by AMS, further proving the viability of this new ICP-MS approach.

*Analysis of atmospheric particles by ICP-MS* is a fertile research topic. A new aerosol sampler interface<sup>53</sup> consisted of five components: an aerosol inlet; a desolvating nebuliser to provide a calibrant aerosol; an enrichment system to grow small particles through saturation and condensation; a round virtual impactor to preconcentrate aerosols and a membrane drier. This interface gave a BEC for <sup>238</sup>U particles of *ca.* 1 pg m<sup>-3</sup>. A more conventional ETV-ICP-MS approach<sup>54</sup> involving slurry sampling was used to determine Au, Pd, Pt and Ru in road dust samples. Suspensions at a nominal 5% (m/v) were prepared, 2% (m/v) APDC was added as a modifier to enhance the ion count and a standard addition calibration strategy was employed. The LOD was 0.4–0.9 ng g<sup>-1</sup>. An analytical method<sup>55</sup> which combined thermal analysis with ID-CV-ICP-MS for studying Hg in airborne particulate matter was used to quantify Hg<sub>p</sub> in airborne particulate matter. Method validation was carried out through the analysis of NIST SRM 1633b (mercury in fly ash) for which the measured concentration of 0.139±0.009 µg g<sup>-1</sup> was in good agreement with the certified value of 0.141±0.019 µg g<sup>-1</sup> obtained with a microwave-assisted acid digestion and CV-AFS. For air samples, more Hg<sub>p</sub> was collected on undenuded filters than on filters that employed a KCl-coated denuder to remove co-sampled gaseous Hg species. This excess Hg was thought to be most likely due to reactive gaseous Hg partitioning to particulates during sampling.

The *characterisation of single particles by ICP-MS* is an even more fertile area of research. Improvements suggested included: optimisation<sup>56</sup> of the dwell time to minimise the occurrence of more than one particle being measured concurrently; a signal deconvolution method<sup>57</sup> to discriminate between NPs <30 nm in size; determining analyte partitioning during nebulisation to improve accuracy of size distribution and number concentration measurements<sup>58</sup>; online coupling<sup>59</sup> of IEC to remove soluble components so that the discrete signal from individual NPs could be discriminated more easily from the continuous signal derived from dissolved NPs; and the evaluation<sup>60</sup> of helium-assisted evaporation of NP-containing microdroplets.

The use of *ICP-MS for isotopic measurements* continues to be investigated. The Dumarey equation has been the dominant mathematic relationship for calculating the mass concentration of saturated Hg<sup>0</sup> vapour in air within a closed system at a defined temperature for over 25 years and is widely used for calibrating Hg-in-air analysers. However the origin of the equation and validation data supporting its accuracy has never been fully published thus presenting difficulties for regulatory Hg measurements that require traceability to the SI.

A novel ID-ICP-MS measurement procedure<sup>61</sup> mixed Hg air samples with liquid samples that contained an enriched Hg isotope spike and demonstrated that the saturated Hg mass concentration at room temperature (*ca.* 21 °C) was on average 5.8 % higher than that calculated from the Dumarey equation. This procedure provided results traceable to the SI and further measurements at defined temperatures are anticipated once this system has been thermostated. Use of a total consumption nebuliser<sup>62</sup> operating at a flow rate of 20  $\mu\text{L min}^{-1}$  allowed  $^{208}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios to be determined accurately by DRC ICP-MS with an internal precision of 0.12-0.13% and 0.17-0.18% ( $n = 10$ , 10s integration time and a test solution of 10  $\mu\text{g L}^{-1}$  Pb) respectively. Collisional dampening in the DRC cell which was pressurised with  $\text{NH}_3$  improved the precision. The total sample consumption was 200  $\mu\text{L}$ . This new approach was applied to the analysis of atmospheric particles, snow, suspended marine particles and sediments. In the nuclear sector, a new method<sup>63</sup> was based upon the use of a *fs* laser operated at 10 kHz and quadrupole ICP-MS for the analysis of  $\mu\text{m}$ -sized U particles. By optimising the experimental conditions, it was possible to measure  $^{235}\text{U}/^{238}\text{U}$  with an accuracy and reproducibility of <4% when using short transient signals of only 15s and masses of 10–200 pg U. A LOD ( $3\sigma$ ) of 350 ag was achieved suggesting that this system is a promising alternative to more conventional SIMS and FTA-TIMS techniques.

**1.5.3.2 Other mass spectrometry techniques.** A review<sup>64</sup> (142 references) of instrumental developments in *AMS* highlighted the increased use of this technique, due to the ongoing reduction in size and complexity of instruments. A companion review<sup>65</sup> (268 references) considered the ultra-sensitive detection of long-lived radionuclides and their applications in the study of the seven domains of the environment: atmosphere, biosphere, cosmosphere, cryosphere, hydrosphere, lithosphere and technosphere.

Improvements in techniques for the *isotopic analysis of gaseous species* have been published. High-precision He isotope measurements<sup>66</sup> were made possible by purifying a large quantity of air at the start of measurement cycle, controlling the amount of He in each measured aliquot to minimise pressure effects and by employing a standard-sample-standard bracketing protocol. Long-term reproducibility over several months was 0.0033%. The single and triple measurement precisions were 0.2-0.3% ( $2\sigma$ ) and <0.1% respectively. The authors suggested that measurement precision is now at the level required to undertake research to assess temporal variations in atmospheric He isotopes. A sensitive RIMS<sup>67</sup> for monitoring Kr and Xe isotope ratios in gases potentially emitted in a nuclear reactor incident had an error of <3% at a nuclide concentration of 7 ppt when measured over a period of 40 minutes. A

system<sup>68</sup> for measuring  $\delta^{13}\text{C}$  ratios in organic aerosols captured on filters linked a TD oven to an IRMS instrument via a combustion interface. For the aerosol samples examined, the reproducibilities were  $< \pm 0.3\%$  and  $< \pm 0.5\%$  for desorption temperatures of  $< 200\text{ }^\circ\text{C}$  and  $> 200\text{ }^\circ\text{C}$  respectively.

*Characterisation of U in particles* released from facilities can be a useful tool for nuclear safeguarding purposes. A methodology<sup>69</sup> employed SIMS to detect and analyse particles that contain both F and U so as to provide information on their origin and an insight into the U purification, conversion and enrichment steps employed. An improved FTA-TIMS method<sup>70</sup> addressed the problem of particle losses during manipulation of samples by suspending U-particles in a solution of cellulose nitrate co-mixed with isoamyl acetate, spreading onto a glass surface and drying to form a transparent film. After irradiation and etching, particles were located under a microscope, cut out and transferred to a filament for analysis. Non-elemental techniques can be used to derive complimentary analytical data. A sorptive extraction method<sup>71</sup> was developed for the analysis of non-volatile organic ligands in an attempt to identify characteristics of the purification process by which U is separated from its ores. Organic components were extracted from aqueous media by stir-bar technology and analysed directly within the inlet of a GC-MS system.

#### **1.5.4 X-ray spectrometry**

A review<sup>72</sup> (6 references) of the application of  $\mu\text{XRF}$  techniques for the characterisation of nuclear materials highlighted the unique capability of this non-destructive technique to image Pu residues and other elements deposited on large surface wipes.

Analysis of *airborne particles* on filters by EDXRF spectrometry employed a FP calibration protocol<sup>73</sup>. For airborne concentrations of  $> 100\text{ ng m}^{-3}$  the EDXRF results agreed with those obtained by ICP-MS for Ni, Pb and S and by ICP-AES for Ca, Cu, Fe, Mn Ti and Zn. Divergences noted for Mn, Ni and Pb at lower concentrations were attributed to spectral overlaps that compromised FP calculations and to the presence of Ni in blank filters. Trace levels of P were determined<sup>74</sup> in marine aerosols by SRXRF to study the atmospheric transfer of nutrients to the oceans and their role in marine plankton growth. Phosphorous was present in the range  $2\text{-}180\text{ ng m}^{-3}$  and the method LOD was *ca.*  $0.2\text{ ng m}^{-3}$ . The release from fabrics of Ag NPs, added to consumer products because of their antimicrobial properties, was studied using a TXRF method<sup>75</sup>. The sample cell was purged with  $\text{N}_2$  to eliminate interferent Ar peaks and an LOD of  $0.2\text{ ng Ag}$  was achieved. The Ag NPs were typically released attached to fibrous material in the particle size range  $0.13\text{-}2\text{ }\mu\text{m}$ . Crystalline silica collected on filters

is typically determined by XRD spectrometry. The linearity of X-ray response with sample mass is not affected if the dust layer remains thin but as the filter loading increases, attenuation of the X-ray beam can result in a breakdown of this linear relationship. The critical sample mass<sup>76</sup> for a dust sample collected with a commonly used 25-mm diameter filter/cyclonic sampler combination was *ca.* 0.9 mg if a deviation of no more 10 % from linearity was acceptable.

*Speciation of airborne particles by X-ray techniques* continues to be investigated. Use of the XANES technique showed<sup>77</sup> that coarse aerosol particles consisted of  $\text{PbC}_2\text{O}_4$ ,  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  and  $\text{Pb}(\text{NO}_3)_2$  present whereas fine particles consisted of  $\text{PbC}_2\text{O}_4$ ,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{PbSO}_4$ . This suggested that the sources of Pb were different for the two size fractions. Atmospheric soluble Fe particles can be a significant source of nutrition for phytoplankton in oceans but factors affecting the availability of this bioaccessible fraction are not fully understood. Fitting of XAFS spectra coupled with  $\mu\text{XRF}$  analysis showed<sup>78</sup> the main Fe species in aerosol samples collected to be illite, ferrhydrite, hornblende and  $\text{Fe}^{\text{III}}$  sulfate. The soluble Fe fraction in samples determined by leach tests correlated with the  $\text{Fe}^{\text{III}}$  sulfate content determined by XANES suggesting that this species was the dominant soluble Fe species in oceans. An XPS study<sup>79</sup> of size-fractionated urban aerosols identified C as the dominant species on the surfaces of all particles studied regardless of size. However, higher concentrations were noted on the surfaces of particles in the 0.056-0.32  $\mu\text{m}$  size range than on the surfaces of the other size fractions. The concentrations of Ca, N, O and Si were higher on the surface of 3.2-10  $\mu\text{m}$  particles than on the surfaces of smaller particles whereas S was found mainly on the surface of 0.32-1.8  $\mu\text{m}$  particles. A study<sup>80</sup> to ascertain whether XPS was capable of discriminating between elemental and organic carbon found that: aliphatic and aromatic species adsorbed on particle surfaces; higher concentrations of elemental carbon were present in the bulk than on the surface of particles; comparable levels of sulphate species were found on the surface and in the bulk; nitrogen species appeared to be concentrated on the surface of particles and the presence of a signal attributed to the presence of organo-S compounds was noted.

Optimisation of a new FEG-SEM system for *GSR analysis* was described<sup>81</sup> in detail so as to allow other potential users of this technique to follow the protocol. Use of the latest heavy metal-free (HMF) primers requires new forensic solutions to be developed. A comparison<sup>82</sup> of elemental spectra obtained by both SEM-EDS and IBA-PIXE spectrometry showed that the latter was much more sensitive at mid-high energies. In summary, this integrated approach incorporating IBA had, according to the authors, unprecedented

characterisation and discriminatory potential for future GSR studies. More prosaic but nevertheless a serious and under-researched issue, the potential for secondary transfer of GSR via contact between a shooter and a second (innocent) person was examined<sup>83</sup> using a series of simulation exercises that involved SEM-EDS analysis.

### 1.5.5 Other spectrometric techniques

Two useful *review* papers on the analysis of carbonaceous particles covered techniques(267 references)<sup>12</sup> for the characterisation of elemental, equivalent and refractory black carbon aerosol particles and the application<sup>84</sup> (89 references)of <sup>14</sup>C analyses to the source apportionment of atmospheric particulate matter.

Measuring *carbonaceous particles* in wet deposition samples is critical for a more complete understanding of the global circulation, lifetime and radiative forcing of such aerosols but there is currently no accepted standard analytical method for measuring such particles in rain or snow samples. Two papers addressed this issue. In the first<sup>85</sup>, a USN was used to disperse sample water into  $\mu\text{m}$ -sized droplets which were then dried to release black carbon particles for analysing using a single particle soot photometer (SP2) which was connected to the outlet of this nebuliser. Laboratory studies showed that the transfer efficiency for particles in the size range 200-500 nm was *ca.* 10 %. The accuracy and reproducibility of the measured mass concentration of black carbon in sample water after long term storage was  $\pm 25$  % and  $\pm 35$  % respectively. In the second paper<sup>86</sup> techniques including TOA, SP2, UV/VIS and TOC determination were evaluated and their strengths and limitations tabulated. Based upon findings presented, either SP2 or TOA with a filtration step combined with TOC analysis for measurement of dissolved organic carbon held promise for the future analysis of carbonaceous aerosol in rainwater.

The *aethalometer*, an instrument which collects airborne particulate matter onto a filter while continuously measuring its light transmission, has been widely deployed to measure black carbon. Underpinning the use of this technique in a quantification mode is the mass absorption efficiency (MAE), also known as the mass absorption cross section, which varies depending upon the source of the carbonaceous particles. The utility of this technique to reliably measure woodsmoke concentrations has been called into question<sup>87</sup> on account of concern over variability in MAE values. In a detailed study<sup>88</sup>, MAE values of 3.1, 6.6, 9.5 and  $7.9 \text{ m}^2 \text{ g}^{-1}$  were determined in smoke samples from residential wood burning, straw burning, biomass pellet and coal combustion respectively. A novel approach<sup>89</sup> for the direct and continuous measurement of black carbon mass size distribution involved coupling a



differential mobility analyser to an aethalometer. The performance of the new pocket-size MicroAeth<sup>®</sup> for fixed-site monitoring was compared<sup>90</sup> to that of its bigger brother, a rack-mounted system usually deployed at the kerb-side, and it was found that the black carbon results were *ca.* 14 % higher with this new variant. The authors concluded that differences in results may be due to differences in aerosol deposition velocities, sample spot sizes, filter media and attenuation cross-section parameters between the two instruments. In contrast, good agreement between the variants was noted where a near 1:1 correlation was reported<sup>91</sup>.

A novel *colorimetric-based technology*<sup>92</sup> applied a “lab on a chip” approach to measure elements in welding fume collected on a filter. This emerging technology, known as microfluidic paper-based analytical device ( $\mu$ PAD), employed hydrophobic barriers printed onto paper to define fluidic circuits that control liquid (sample) transport and which were chemically modifiable to allow customisation of the colorimetric endpoint for assaying a particular metal e.g. Fe as the reddish ferrioxalate complex after complexation with 1,10 phenanthroline. In this reported study, 10-mm filter punches were taken and subjected to a microwave-assisted digestion to dissolve the sampled welding fume. The digestate was then applied to a  $\mu$ PAD which was moved to the detector zone for the resultant coloured spot to be scanned using a desk-based office scanner. Quantification was achievable by subjecting metal solutions of a known concentration to the same process. Separate welding fume filter punches were subjected to a conventional ICP-AES analysis for comparison. For acid-extractable Cr, Cu, Fe and Ni, 20 of the 28 paired measurements were not statistically different at a 95 % CI. The differences for the remaining 8 pairs were <20%. The authors concluded that  $\mu$ PAD-based technology offered the potential to bring a low cost measurement approach to the field although the sampling costs associated with taking air samples would also need addressing. Future work will focus on  $\mu$ PAD modifications to improve sensitivity, quantitative range and functionality in addition to extending the method to other elements.

In the framework of nuclear safeguards,  *$\mu$ Raman* spectroscopy was coupled<sup>93</sup> to SEM for the first time to analyse  $\mu$ m-sized U oxides particles deposited on carbon disks. This allowed *in-situ* Raman analysis to be performed on particles located by SEM. The reduction in sample manipulation was deemed to outweigh the reduction in instrumental sensitivity when using a coupled system over a more sensitive but stand-alone Raman instrument. A method<sup>94</sup> for the determination of Ni<sup>II</sup> compounds in size-resolved airborne particles employed a derivatisation reaction with DMG to form a complex with strong characteristic stretches at 1352 and 1510  $\text{cm}^{-1}$ . Validation was undertaken using  $\mu$ m-sized aerosols generated by the atomisation of individual NiCO<sub>3</sub>, Ni(OH)<sub>2</sub>, NiO and NiSO<sub>4</sub> species as well

as NiSO<sub>4</sub> mixed with ammonium sulfate, humic and oxalic acids which did not interfere with the detection of Ni<sup>II</sup>. Raman microspectroscopy was also used to determine the chemical composition and mixing state of marine aerosols<sup>95</sup> and to characterise soot and mineral phases in urban aerosols<sup>96</sup>.

## 1.6 Method intercomparisons

*Comparative testing* of methods or techniques is always useful. The need to evaluate personal exposure to urban aerosols instead of simply measuring outdoor concentrations at fixed locations is now evident. Cascade impactor samplers (CISs) employing gravimetric analysis and optical particle counters (OPCs) are likely to be used, on account of their size, weight and low cost. In a field setting, results obtained using both CIS and OPC devices were compared<sup>97</sup> to those obtained from standardised gravimetric methods for PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> that employed EU approved air samplers. Particulate concentrations measured using OPCs were biased low on days when air concentrations were low and biased high when air concentrations were high. In contrast, gravimetric data were generally comparable irrespective of whether the CIS or approved EU sampler were used. Similarly, two performance testing studies<sup>98,99</sup> highlighted the differences that can be obtained when personal measurements are made with different samplers in a workplace setting. A collaborative trial<sup>100</sup> which generated method performance data for a new US EPA ICP-MS method for the determination of Pb in air particles included a comparison with the established reference method employing FAAS. The characterisation of engineered NPs for environmental impact assessment purposes requires analytical methods for quantification of both the absolute mass concentration and the dissolved fraction. Test suspensions of Ag, Ce, Ti and Zn NPs were analysed<sup>101</sup> by ICP-MS either: directly; or following acidification or following a microwave-assisted digestion. Of five fractionation methods (centrifugation, CPE, dialysis, TFF and UF) compared with an ISE method for the determination of the dissolved fraction, UF with microwave digestion was identified as best practice on the basis of applicability, economics and precision.

## 2 Water analysis.

### 2.1 Sample preconcentration and extraction

The *review articles* published recently looked at specific aspects of preconcentration for various matrices including waters. One review<sup>102</sup> (160 references) discussed the state-of-the-art in the use of microbacterial-based solid sorbents. The targeted extraction of individual analytes or groups of analytes<sup>103</sup> (240 references) by modifying the surface properties of NPs, CNTs, bioabsorbents or ion imprinting polymers was considered in a review covering the period 2007-2012. Of particular interest was a review<sup>104</sup> (79 references) on the use of SPE for the speciation and preconcentration of inorganic Se in water samples. Tables 1 and 2 summarise the most significant developments in analyte preconcentration for water analysis.

### 2.2 Speciation and fractionation analysis

The *determination of arsenic species without chromatography* remains of interest. In a simple method<sup>105</sup> using stacked SPE disks, diphenylarsinic acid was trapped from a 200 mL sample at pH 3 on the upper Empore SDB-XD disk, phenylarsonic acid on the middle activated-carbon disk and inorganic acid on the bottom Cation-SR disk loaded with Ca and Zr. The trapping flow rate was 15 mL min<sup>-1</sup>. Diphenylarsinic acid was eluted with 10 mL of ethanol containing 0.5M ammonia, phenylarsonic acid with 20 mL 1.0M ammonia and inorganic arsenic with 20 mL 6M HCl. The ETAAS LOD for As of 0.13-0.16 µg L<sup>-1</sup> was dependent on the enrichment factor. The spike recoveries ranged from 96.1 to 101.6% for a spike concentration of 10 µg L<sup>-1</sup> which was chosen as it is the quality standard for drinking water in Japan. A simple DLLME method<sup>106</sup> for the extraction of As<sup>III</sup> involved acidification of a 5 mL sample with 0.1 mL of 5M HNO<sub>3</sub> and rapid injection of a 400 µL aliquot of a methanolic solution of 0.1 mg L<sup>-1</sup> APDC containing 50 µL of carbon tetrachloride. The organic phase was separated, evaporated to dryness at room temperature and redissolved into 100 µL of 0.1M HNO<sub>3</sub> for ICP-MS analysis using a 90 µL FI sample loop. The total As concentration was determined following reduction with 0.2M sodium thiosulfate and the As<sup>V</sup> concentration obtained from the difference between total As and As<sup>III</sup> concentrations. The method LOD was 0.0031 µg L<sup>-1</sup> (As<sup>III</sup>) and the spike recoveries were in the range 94-106% for As<sup>III</sup> and 92-98% for As<sup>V</sup>.

In a comparison of the microextraction techniques HF-LPME and DLLME for the determination of *antimony species* by TXRF<sup>107</sup>, DLLME was preferred as sample extraction

occurred within 5 minutes. A further advantage for DLLME was that up to 20  $\mu\text{L}$  of extract could be deposited onto the preheated quartz sample carrier whereas HF-LPME was limited to 5  $\mu\text{L}$ . The only disadvantage of DLLME was that it could accept no more than 5 mL of sample, compared to 25 mL possible for HF-LPME. The LODs of 1.1 and 0.09  $\mu\text{g L}^{-1}$  for HP-LPME and DLLME, respectively were therefore very similar. Both methods gave good spike recoveries of 98-100% for  $\text{Sb}^{\text{III}}$  and  $\text{Sb}^{\text{V}}$  from spiked mineral, sea and river waters.

For the *speciation analysis of Cr* in waters, a 30  $\mu\text{L}$  microcolumn was packed<sup>108</sup> with the nanomaterial  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ , which was synthesised by reacting sodium phosphotungstate ( $\text{HNa}_2\text{PW}_{12}\text{O}_{40}$ ) with caesium chloride. The polyoxoanion cluster nanostructure was specific for the retention of  $\text{Cr}^{\text{III}}$  within a pH range 2 to 7. The stationary phase degraded above pH 8. The retained  $\text{Cr}^{\text{III}}$  was eluted with 1M  $\text{HNO}_3$ . The ICP-MS LOD for  $\text{Cr}^{\text{III}}$  was 0.3  $\mu\text{g L}^{-1}$  for a 20  $\mu\text{L}$  sample. Spike recoveries from tap water ranged from 101% (5  $\mu\text{g L}^{-1}$  spike) to 96% (2.5  $\mu\text{g L}^{-1}$  spike). There was no mention of the time required to clean the instrument before it could be used again for Cs or W determination. The analytical uncertainty budget for the HPLC-ICP-MS determination of  $\text{Cr}^{\text{III}}$  and  $\text{Cr}^{\text{VI}}$  in water has been calculated<sup>109</sup> using either a modelled approach i.e. bottom-up approach or by using analytical data obtained from method validation studies i.e. top-down approach. The calculated expanded uncertainties ( $k=2$ ) of the final results were 4.4% and 4.2% for  $\text{Cr}^{\text{III}}$  and  $\text{Cr}^{\text{VI}}$  using the bottom-up approach against values of 7.8% and 7.9% determined using the top-down approach. The authors conclude that the former approach was useful in identifying sources of uncertainty in new methods but that all relevant components of the uncertainty may not have been taken into account. The latter approach using method validation data was advantageous in so far that data generated encompasses both trueness and precision components.

The use of two SCX guard columns in tandem provided a rapid method for the *speciation analysis of Hg* in seawater and marine fish<sup>110</sup>. The advantage of using two 12.5 mm long guard columns was that complete separation of  $\text{Hg}^{2+}$ ,  $\text{CH}_3\text{Hg}^+$ ,  $\text{CH}_3\text{CH}_2\text{Hg}^+$  and phenyl mercury could be obtained in less than 2.5 min. Using a mobile phase of 2.0mM L-cysteine at pH 2.0 at a flow rate of 1.5  $\text{mL min}^{-1}$  and a 5  $\mu\text{L}$  sample loop for ICP-MS detection, LODs of the different species ranged from 0.019  $\mu\text{g L}^{-1}$  ( $\text{Hg}^{2+}$ ) to 0.027  $\mu\text{g L}^{-1}$  ( $\text{CH}_3\text{Hg}^+$ ). The sum of the species concentrations measured for NRCCRM GBW (E) 080042 (seawater) agreed well with the certified total value of  $1.02\pm 0.02 \mu\text{g L}^{-1}$ . The recoveries for a 1.0  $\mu\text{g L}^{-1}$  spike solution ranged from 101 to 96%. It should be noted that these spike levels were much higher than the concentrations found in real seawater samples and probably

resulted in contamination of the instrument. The sensitivity problems highlighted in this paper mean that preconcentration is often required. A new DGT probe<sup>111</sup> for the determination of MeHg in aquatic systems used agarose gel as the diffusive hydrogel and a 3-mercaptopropyl functionalised silica resin gel as the accumulation phase. The advantages of this probe were that the agarose gel had a low affinity for MeHg and that an acid extraction could be used for the accumulation resin meaning that ethylation of MeHg by tetraethylborate was possible for HS-GC-AFS detection. The fact that the diffusion coefficient for MeHg of  $5.1 \pm 0.20 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  in this probe was similar to that in seawater at 20 °C ( $5.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ) meant that diffusion had not been affected. The utility of DGT devices is dependent on there being linear relationships between the amount of analyte (MeHg) accumulated, deployment time and gel thickness. These were all demonstrated for this device.

A rapid (<1.5 min) method<sup>112</sup> for the *determination of V species in water* used RP ultra-HPLC both to separate vanadyl and vanadate ions and minimise the presence of chloride. Subsequently, SF-ICP-MS in medium resolution mode resolved the isobaric interference from residual  $\text{ClO}^+$ . The method used a  $\text{C}_{18}$  column (1.7  $\mu\text{m}$  particle size, 2.1 mm internal diameter x 50 mm long) with an aqueous mobile phase (0.6  $\text{mL min}^{-1}$  flow rate, 20  $\mu\text{L}$  loop) of 18mM EDTA, 0.5mM tetrabutylammonium hydroxide and 20mM phosphoric acid. The LODs were 0.008 (vanadyl) and 0.013 (vanadate)  $\mu\text{g L}^{-1}$  with total peak area RSDs (n=7) of 1.13 and 1.51%, respectively. Recoveries of a 5  $\mu\text{g L}^{-1}$  spike were >95%.

The *binding of trace elements to macromolecules* is of importance as it largely determines the bioavailability of the element in the environment. A study<sup>113</sup> to assess whether metals were bound to proteins in the same size fractions in both seawater and marine plankton used two-stage ultrafiltration, 2D PAGE separation and LA-ICP-MS analysis of the resulting gels. In seawater, Cd, Cr, Cu and Zn were associated with 5 protein fractions with similar molecular weights (10-14 kDa) but with isoelectric points that varied between 5.8 and 7.3. In contrast, in the plankton samples Cd was associated with proteins with different molecular weights (9, 13 and 22 kDa) and isoelectric points of 4.5, 5.2, 5.5 and 10, whereas Cr, Cu and Zn were bound to lower molecular weight fractions with variable isoelectric points. Tangential flow ultrafiltration combined with SEC and AEC was used to isolate marine DOM fractions<sup>114</sup>, the metals associated with this material being identified by ICP-MS. The 3 and 10 kDa fractions contained Mn, Ni, Sr and Zn and eluted close to the SEC UV absorption maximum. Measured signals were significant only for Cu and Mo in the 3 kDa fraction. There were no signals for Al, As, Ba, Cd, Fe, Pb and V. Mass balance experiments

showed that the percentages of metals bound to DOM were very low and ranged from  $4.1 \times 10^{-4}\%$  for Sr to 0.77% for Zn.

The increasing use of *NPs and colloids* means that they have become environmental species in their own right but their impact has yet to be determined. Following on-site filtration ( $<2.0 \mu\text{m}$ ) of swimming pool water and dechlorination with sodium thiosulfate, a preparative-scale tangential-flow filtration system was used<sup>115</sup> to fractionate Ti NPs into a “dissolved phase” ( $<1 \text{ kDa}$ ) and a concentrated microparticulate phase ( $1 \text{ kDa}$  to  $2.0 \mu\text{m}$ ). The fractions were preserved by adding  $\text{HNO}_3$  to obtain a pH of  $<2$  and  $50 \mu\text{L}$  of  $\text{HF}$  was added prior to analysis by ICP-MS. Total Ti concentrations in swimming pool water varied between  $21$  to  $60 \mu\text{g L}^{-1}$ , the major part of which (82-98%) was found in the dissolved phase. The authors proposed sunscreen as the major source with the particulate phase being removed rapidly by the pool filtration system. The dissolved phase was particularly high in pools in which the filtration system was not back flushed regularly. Asymmetric flow FFF was coupled<sup>116</sup> to ICP-MS, UV spectrometry and multi-angle light scattering to study Cu colloids in the runoff from vineyards. Under the optimum conditions of  $5 \mu\text{L}$  injection volumes, a mobile phase of  $1 \times 10^{-3} \text{M NH}_4\text{NO}_3$  at a main flow rate of  $0.6 \text{ mL min}^{-1}$  and a cross flow rate of  $0.6 \text{ mL min}^{-1}$  and a channel thickness of  $250 \mu\text{m}$ , a LOD of  $0.6 \mu\text{g L}^{-1}$  for Cu was achieved.

## 2.3 Instrumental Analysis

### 2.3.1 Inductively Coupled Plasma Mass Spectrometry.

Most of the innovation in the ICP-MS analysis of waters is in the *sample introduction systems* employed. The lanthanides were measured<sup>117</sup> directly in Ca-rich waters using a commercially available system which featured a cyclonic spray chamber heated to  $140^\circ\text{C}$ , a condenser at  $2^\circ\text{C}$  and the option of adding a membrane desolvation unit to reduce oxide formation further. Use of this system increased sensitivity by 5-8 times compared to use of a Scott-type spray chamber and reduced the  $\text{BaO}^+$  interference from 0.10% to 0.005%. Use of the additional membrane system for a  $10 \text{ ng g}^{-1}$  solution eliminated  $\text{BaO}^+$  and reduced  $\text{BaOH}^+$  to 0.02%, thereby resulting in LODs of  $30\text{-}500 \text{ fg g}^{-1}$  for all analytes with a signal RSD of 10% at the  $1 \text{ pg g}^{-1}$  level. Analysis of two natural water reference materials LNEG SERMIN1 (low salt spring water) and LNEG VIDAC18 (sodium carbonate ground water) gave excellent agreement with previously published values. Dual-mode systems for simultaneously introducing both gas phase samples and nebulised aerosols into instruments

have been reported many times for ICP-AES but rarely for ICP-MS. A dual inlet torch was used<sup>118</sup> that could accept both aerosol and vapour streams simultaneously so that an internal standard could be used during CV-ICP-MS. However, this necessitated compromises in the gas flows such as an untypically low nebuliser gas flow of 0.4 L min<sup>-1</sup> and a CV flow of 0.5 L min<sup>-1</sup> to give an optimal total gas flow of 0.9 L min<sup>-1</sup> to maximise the Hg intensity and minimise the CeO:Ce ratio to <2%. Using Bi, Pt and Tl as internal standards, this system adequately corrected for thermal drift over 100 minutes but suffered from a 35% reduction in the Hg signal compared to CV introduction alone. The dual mode LOD for Hg was 0.2 ng L<sup>-1</sup> using external calibration and 0.09 ng L<sup>-1</sup> with ID. The precision and accuracy were confirmed using the IRMM ERM-CA615 (groundwater) which has a certified value of 37 ± 4 ng L<sup>-1</sup>. Three replicate analyses without internal standard correction gave a result of 38.3 ± 0.5 ng L<sup>-1</sup>; internal standard correction gave a result of 38.2 ± 0.7 ng L<sup>-1</sup> showing that dual mode did not improve the accuracy. The long term precision for a 10 ng L<sup>-1</sup> solution (n=5) was improved 3-fold to 3% by using Bi internal standardisation. Use of a low-uptake sample introduction system<sup>62</sup> allowed Pb isotope ratios to be measured in very small samples such as freeze-dried Antarctic snow by quadrupole ICP-MS. By careful optimisation of the gas flows and the reaction cell conditions, it was possible to measure <sup>208/207</sup>Pb and <sup>206/207</sup>Pb with a SD of ±0.003 to 0.008 at Pb concentrations of 18 to 30 pg g<sup>-1</sup> and with a sample uptake rate of 20 μL min<sup>-1</sup>.

Method development for *isotopic analysis of waters* continues to attract interest. The isotopic composition of dissolved Cu in seawater was determined<sup>119</sup> by MC-ICP-MS after a series of preconcentration steps from 20 L of bulk seawater using a Nobias-chelate PA-1 column followed by an AG MP-1 anion-exchange column. The Nobias-chelate PA-1 resin has both imminodiacetic and ethylenediaminetriacetic acid functional groups so retains Cu at low pH but not the alkali and alkali earth elements. Good accuracy for the isotope measurements was demonstrated by spiking seawater with the NIST SRM 976 (Cu isotopic standard) and for concentration measurements by analysis of NRCC CRM CASS-5 and NASS-6 (seawaters). The isotopic analysis of the NRCC CRMs provided new δ<sup>65</sup>Cu data of 0.46 ± 0.006‰ (n=3) and 0.40 ± 0.01‰ (n=2), respectively. A very similar purification method<sup>120</sup> was demonstrated to be suitable for the determination of the stable isotopes of Cd, Fe and Zn in seawater. The same chelating and anion exchange columns were used as in the previous paper but only 1 L of seawater was necessary. Double spike MC-ICP-MS had the advantage of correcting for instrumental bias and any fractionation in the separation procedure as well as allowing IDA of the sample. The 1 σ internal precisions of 0.02-0.7‰,

0.01-0.2‰ and 0.01-0.2‰ for  $\delta^{114}\text{Cd}$ ,  $\delta^{56}\text{Fe}$  and  $\delta^{66}\text{Zn}$ , respectively, were significantly lower than the expected variability in seawater of 2-3‰.

The feasibility of using ID-ICP-MS to determine *Ca concentrations* was demonstrated by the analysis of seawater<sup>121</sup>. A 10  $\mu\text{L}$  sample of seawater was spiked with 10 mg of a 10  $\mu\text{g g}^{-1}$   $^{43}\text{Ca}$  solution and was then diluted to 2.5 g in 5% v/v  $\text{HNO}_3$ . The samples were sonicated for 30 minutes and left overnight to ensure complete equilibration of the spike prior to ID-ICP-MS determination. The OSIL IAPSO (seawater) reference material was used as a bracketing standard to correct for mass discrimination and ratio drift every 5 samples. The accuracy, precision and reproducibility were evaluated by repeat analysis of the seawater standard. The ID-ICP-MS result of  $10255 \pm 10 \mu\text{mol kg}^{-1}$  (SD, n=15, RSD = 0.1%) measured over a 4-month period was in good agreement with the standard EGTA titration method of  $10260 \pm 6 \mu\text{mol kg}^{-1}$ . However, there seems little advantage in using the ID-ICP-MS method when the reduction in analytical time is only from 5 to 3 min and the titration method is more suitable for use on board ships. Although ICP-AES would be a more suitable technique for seawater analysis, the new method has greater potential for smaller samples such as foraminifera.

### 2.3.2 Vapour generation.

The *automation of hydride and cold vapour generation* is still of interest. The miniaturisation achieved<sup>122</sup> by using a lab-in-a-syringe for vapour generation followed by gas-liquid separation for the AAS determination of Hg gave reduced reagent consumption, good precision and a high sample throughput. The LOD was  $0.03 \mu\text{g L}^{-1}$  for Hg in water for a 3 mL sample, the sample throughput  $27 \text{ h}^{-1}$  and the precision 3.1% (n=10) at  $2.0 \mu\text{g L}^{-1}$ . The same research group also used the device for the determination of As in water<sup>123</sup>. For a 3 mL sample and sampling frequency of  $11 \text{ h}^{-1}$ , the LOD was  $0.15 \mu\text{g L}^{-1}$  and the precision 3.2% (n=10) at  $2.0 \mu\text{g L}^{-1}$ .

Selective HG for *arsenic speciation* is commonly used, often coupled with AAS methods. A sensitive method coupling cryotrapping and HG<sup>124</sup> to ICP-MS detection gave LODs ranging from  $3.4 \text{ ng L}^{-1}$  (total As) to  $0.040 \text{ ng L}^{-1}$  (methyl As<sup>III</sup>). The As<sup>III</sup> concentration was determined without reduction whereas the total As concentration was measured after reduction with L-cysteine. Methylated species were separated by thermal desorption after trapping of all hydrides at  $-196^\circ\text{C}$  on Chromosorb. The method gave good results for As species measured in the NRCC CRMs CASS-4 and CASS-5 (near shore seawaters), NASS-5 (seawater) and SLRS-4 and -5 (river waters).



*Multielemental vapour generation methods* seem to be moving away from finding compromise conditions for simultaneous measurement towards fast sequential analysis in which the elements are trapped on microcolumns in complex injection manifolds and then eluted and detected sequentially. One such method for Cd, Hg and Pb<sup>125</sup> in sea and lake waters used two chelating columns packed with the chelate 1,5-bis(di-2-pyridyl)methylene thiocarbamide immobilised on silica gel. For test samples, the LODs were 0.031 (Pb) to 0.064 Cd  $\mu\text{g L}^{-1}$ , enrichment factors 16.4 (Pb) to 27.3 (Hg) and precisions (n=9) 2.5% (Pb) to 2.9% (Hg) at a concentration of 0.5  $\mu\text{g L}^{-1}$ . Results for the NWRI CRMs TMDA-54.4 (fortified lake water), LG6016 (estuarine water) and NRCC CASS-5 (near shore seawater) were in good agreement with the certified values. Recoveries from spiked seawater samples from Malaga Bay were 94% (Cd) to 108% (Pb).

**2.3.3 X-ray spectrometry.** *A review* of trace and ultratrace analysis of liquid samples by XRF<sup>126</sup> (67 references) covered microextraction procedures, nanomaterials, filters and activated thin layers using various types of instrumentation ranging from large scale to hand held systems.

In the determination of *halides* by TXRF<sup>127</sup>, losses during the drying phase were reduced through the use of halide potassium salts dissolved in an aqueous solution of the tetraamine copper(II) nitrate complex  $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$  which resulted in improved recoveries and RSDs for the standards over a concentration range of 1 to 200  $\text{mg L}^{-1}$ . It was noted that Br and Cl recoveries were between 98-123% for standards  $\geq 10 \text{ mg L}^{-1}$ ; below this concentration the recoveries were significantly higher than 100% suggesting possible spectral or contamination problems. The authors reported LODs of 0.002  $\text{mg L}^{-1}$  for Br and 1  $\text{mg L}^{-1}$  for Cl.

**2.3.4 Plasma-cavity ringdown spectrometry.** *The progress of plasma-cavity ringdown spectrometry* as an atomic spectrometry technique was reviewed<sup>128</sup> (91 references). Cavity ringdown spectrometry is an absorption method, but unlike AAS and UV-VIS it possesses the capacity for absolute measurement and the detection of very weak absorption coefficients due to its extremely long path length. Initially ICPs were used as the plasma source, but MIPs are now preferred due to their lower gas flows and their ability to form tubular plasma discharges which are more suitable for use with a collimated light source such as a laser.

**Table 1 Preconcentration methods using solid phase extraction for the analysis of water**

Analyte(s)	Matrix	Substrate	Coating or modifying agent	Detector	Figures of merit ( $\mu\text{g L}^{-1}$ unless otherwise stated)	Method validation	Reference
Cd <sup>II</sup> and Pb <sup>II</sup>	Water and biological samples	TiO <sub>2</sub> NPs	Alizarin red S	FAAS	LODs 0.11 (Cd) and 0.30 (Pb), 200 mL sample	Comparison with ETAAS of NIST SRM 1643e (Trace elements in water)	<sup>129</sup>
Cd, Co, Cr, Cu, Fe, Ga, Mn, Ni, Pb, Se, V, and Zn	Water	MWCNT		ED-XRF, WD-XRF and polarised-ED-XRF	LODs 0.06 (Zn, polarised-ED-XRF) 16.7 (Cd, ED-XRF), 100 mL sample		<sup>130</sup>
Co <sup>II</sup> , Cu <sup>II</sup> , Ni <sup>II</sup> , Pb <sup>II</sup> , and Zn <sup>II</sup>	Water	Graphene oxide	None	ED-XRF	LODs 0.5 (Co) to 1.8 (Zn), 50 mL sample	Spike recovery (94-106%) and comparison with ICP-AES results	<sup>131</sup>
Hg	Water	CNT	Ag and Fe <sub>3</sub> O <sub>4</sub>	AFS	LODs 0.03, 200 mL sample.	NRCCRM GBW07310 (stream sediment) and spike recovery (84-120%)	<sup>132</sup>
Hf, lanthanides, Y and Zr	Seawater	Coprecipitation on Fe <sub>2</sub> O <sub>3</sub>	None	ICP-MS	LODs 2.1 (Ho) to 408.3 (La) ng L <sup>-1</sup> , 1 litre sample volume	Spike recovery, authors report values for NRCC NASS-6 (Seawater)	<sup>133</sup>
Ho, Nd, Tb	Water	TiO <sub>2</sub> nanotubes	None	ICP-MS	LODs (Tb) 0.018 to 0.093 (Nd) ng L <sup>-1</sup> , 100 fold enrichment factor.	Spike recovery (93-104%)	<sup>134</sup>
Pb isotopes	Seawater	AF-Chelate 650 M <sup>®</sup> resin	None	ICP-MS	Analysis precision <sup>206</sup> Pb/ <sup>207</sup> Pb 0.6 ‰, 500 mL sample	NIST SRM-981 (Common lead), comparison with previous methods	<sup>135</sup>
Pu isotopes	Seawater	Coprecipitation with Fe(OH) <sub>3</sub> followed by 2-stage separation on Dowex 1X8 SAX resin	none	SF-ICP-MS	LODs 0.08 ( <sup>240</sup> Pu) to 0.11 ( <sup>239</sup> Pu) fg mL <sup>-1</sup> .	NBS-947 (Plutonium isotopic standard), IAEA-381 and IAEA-443 (seawater)	<sup>136</sup>

REE	Seawater	Chromosorb <sup>®</sup> 106	4-(2-thiazolylazo)resorcinol	ICP-MS	LODs (Pr) 0.06 to (Ce) 0.31 ng L <sup>-1</sup> , 5 mL sample	NRCC CASS-4 (Nearshore seawater)	<sup>137</sup>
Se <sup>IV</sup>	Water	Porous carbon electrode	Au	ETAAS	LOD 0.1, 10 mL sample	NIST SRM 1643e (Trace elements in water), HPS Primary Drinking Water Metals check standard	<sup>138</sup>

**Table 2 Preconcentration methods using liquid phase extraction for the analysis of water**

Analyte(s)	Matrix	Method	Reagent(s)	Detector	Figures of merit (LOD $\mu\text{g L}^{-1}$ unless otherwise stated)	Method validation	Reference
Ag and Cu	Food and water	Ultrasound IL-ME	Dithizone and 1-Hexyl-3-methylimidazolium hexafluorophosphate	FAAS	1.2 (Ag) and 2.0 (Cu), 25 mL sample volume	Spike recovery	<sup>139</sup>
B	Water and plants	Headspace liquid phase microsublimation	NaOH	ICP-AES	8.0 for 0.1 mL of sample	Spike recovery	<sup>140</sup>
CuO nanoparticles	Water	CPE followed by microwave digestion	Triton X-114	ICP-MS and ETAAS	0.02 (ICP-MS) and 0.06 (ETAAS), 10 mL sample	Spike recovery	<sup>141</sup>
Cu and Zn	Water	DLLME	2-(5-bromo-2-pyridylazo)-5-diethyl-phenol, carbon tetrachloride and methanol	ED-XRF	1.8 (Cu) to 1.7 (Zn) $\text{ng L}^{-1}$ , 5 mL sample.	Spike recovery (91 to 95%) and comparison with ICP-AES	<sup>142</sup>
$\text{CH}_3\text{Hg}^+$	Humic rich water	$\text{N}_2$ distillation followed by purge and trap	Sodium tetraethylborate (purge and trap stage)	ID-GC-ICP-MS	0.05 $\text{ng L}^{-1}$ 20 mL of sample	Comparison with US EPA 1630 method	<sup>143</sup>

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

#### **3.1 Review papers**

In a review<sup>144</sup> (84 references) on the *advantages and limitations of different approaches for imaging element distribution and speciation in plant cells*, future trends and challenges – notably the need to improve spatial resolution – were identified and discussed.

Reviews of *analytical methods for the determination of specific analytes* included two articles on the determination of Hg in environmental samples. The first<sup>145</sup> (144 references) covered articles published in 2010-2011 and the second<sup>146</sup> was an update featuring 35 references from 2012. Approaches for the determination of As species were discussed by Rajakovic *et al.*<sup>147</sup> (110 references) with particular emphasis on factors that affected analyte stability during sample collection, storage, preservation and extraction. A detailed evaluation<sup>148</sup> (206 references) of methods for the determination of halogens in biological samples, including plants, featured AAS, ICP-AES, ICP-MS, NAA and XRF spectrometry. A useful summary of biological CRMs with certified halogen concentrations was also provided. Analytical techniques for the measurement of the long-lived radionuclide <sup>129</sup>I were summarised<sup>149</sup> (84 references) and compared critically.

The *contribution of atomic spectrometry to radiation protection* was highlighted in a review<sup>14</sup> by Zheng *et al* (292 references). The article included comparative assessment of analytical techniques; a historical review of radio-ecological applications from the 1940s to the Fukushima Daichi accident; and a critical summary of the current state-of-the-art and future research needs.

A book chapter<sup>150</sup> (142 references) in Elsevier's Advances in Agronomy series provided a useful overview of *the use of nanoSIMS to investigate soil processes*.

#### **3.2 Sample preparation**

##### **3.2.1 Sample dissolution and extraction**

A *review of sample preparation* for arsenic speciation in terrestrial plants<sup>151</sup> (103 references) highlighted the need to minimise the time between extraction and analysis to avoid species interconversion. Another<sup>152</sup> (51 references) compared strategies for preparation of tea for multi-elemental analysis.

Numerous *comparisons of sample digestion protocols* were published but the maturity of the field meant that findings could sometimes be anticipated. For example, Chand and

Prasad<sup>153</sup> compared microwave-assisted *aqua regia* digestion and alkaline fusion for the determination of Al, As, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in marine sediments by ICP-AES. Unsurprisingly, volatile As was lost in the fusion process but retained in the closed vessels used in the microwave process, whereas the recovery of Al – an element likely to be associated to a significant extent with refractory silicates accessible only to HF – was lower with the pseudo total digestion. Other workers<sup>154</sup> reported that, as expected, recoveries of Cd, Cu, Hg, Ni, Pb and Zn from Brazilian soils generally decreased in the order: USEPA Method 3052 (closed vessel microwave assisted digestion with HNO<sub>3</sub> and HF); Method 3051A (closed vessel microwave assisted digestion with HNO<sub>3</sub> and HCl); Method 3050B (open vessel digestion with HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and HCl). A more novel study was a comparison<sup>155</sup> of six procedures for extracting As<sup>III</sup>, As<sup>V</sup>, DMA and MMA from plants for analysis by HPLC-ICP-MS. These procedures were: 2 % v/v HNO<sub>3</sub> at 90 °C (90 min); 2 % v/v HNO<sub>3</sub> at 37 °C (90 min); water at 37 °C (16 h) followed by sonication at room temperature (20 min); water with microwave-assistance (80 °C); 1+1 water–methanol at 37 °C (16 h) followed by sonication at room temperature (20 min); and 1+3 water–methanol at 37 °C (16 h) followed by sonication at room temperature (20 min). The first method gave highest recoveries (*ca.* 90%) but with some interconversion of As<sup>III</sup> to As<sup>V</sup>.

*Improvements in sample digestion apparatus* included an easily automated closed-vessel conductively heated system<sup>156</sup> that, under optimised conditions (200 mg powdered plant sample + 1.5 mL HNO<sub>3</sub> + 1.4 mL 30% H<sub>2</sub>O<sub>2</sub>) could process 38 samples in 80 min. Results were similar to those obtained by microwave-assisted digestion for a variety of plant materials. Recoveries for five NIST plant SRMs were 75-114% of certified values. A novel sample digestion device<sup>157</sup> focussed short-wavelength IR radiation directly onto soil samples held in a customised quartz vessel. Recoveries of 11 elements from SCP EnviroMAT SS-1 (soil standard) measured by ICP-AES were in the range 91-108%, with RSDs 0.7-3.6% (n = 4).

Amongst the *developments involving microwaves* was the extension of a microwave-induced combustion method<sup>158</sup>, previously demonstrated for the determination of Hg, to the measurement of As, Cd and Pb in soils. Samples (300 mg) were mixed with 300 mg microcrystalline cellulose, pressed into pellets and combusted in O<sub>2</sub> (20 bar) in closed quartz vessels. Volatilised analytes were trapped in 2M HNO<sub>3</sub> + 2M HCl (6 mL) for analysis by ICP-MS or ICP-AES. Results were in agreement with certified values for NIST SRM 2709 (San Joaquin soil) and NWRI CRM SUD-1 (Sudbury sediment). A microwave-assisted micellar extraction method<sup>159</sup> used the biodegradable surfactants SDS and Triton X-100 to

isolate Cd, Cr, Cu, Ni and Pb from *Posidonia oceanica* (seagrass) for ETAAS analysis. A miniaturised microwave-assisted EDTA extraction method<sup>160</sup> for grassland plants gave results similar to macro-scale HNO<sub>3</sub> digestion for the measurement of Cd, Co, Cu, Mn, Ni, Pb and Zn by ICP-AES.

In the field of *ultrasound-assisted extraction*, researchers in Vigo<sup>161</sup> used a high intensity ultrasonic probe (50 W) and cup-horn sonoreactor (200 W) to reduce the time required to perform soil extractions. The conventional BCR 1 h EDTA extraction could be completed in 2 min with the probe or 10 min with the sonoreactor and the 16 h acetic acid extraction in 6 min with the probe or 30 min with the sonoreactor. Other workers<sup>162</sup> recommended using a vacuum pump to generate bubbles, thereby improving contact between sample and extractant to reduce extraction time from 2 h to only 2 min for the ultrasound-assisted HCl extraction of Co, Cu, Fe, Mn, Pb and Zn from soil. Focussed sonication<sup>163</sup> at 500 W in 1% formic acid in an ice bath extracted As from kelp in just 30 s. The recovery was 95% of that obtained by microwave-assisted HNO<sub>3</sub> digestion. Although recovery from cultures of *Chlorella vulgaris* (a single-cell green algae) was lower (71%), the rapidity of the procedure allowed the detection of unstable As phytochelatin and glutathione species in algal cells that had been exposed to As<sup>III</sup> solution. These As species were not found in cultures exposed to As<sup>V</sup> thereby providing a new insight into As metabolism.

*Single-step soil extraction methods* have been refined to yield improved information on potential trace element mobility and toxicity. Reis *et al.*<sup>164</sup> showed that the soil:water ratio did not affect the recovery of water-soluble Hg in the range studied (1.5:100 to 20:100). However, it took 24 hours for the extraction to reach equilibrium, considerably longer than is recommended in most extraction protocols in the literature. After comparing numerous reagents for measurement of absorbed B in soils, Goldberg and Suarez<sup>165</sup> selected 0.2M sorbitol as the most efficient and recommended a 24-hour extraction at a suspension density of 100 g L<sup>-1</sup>. After using SSIDMS to study species interconversion during extraction of exchangeable Cr<sup>VI</sup> from soil, Zuliani *et al.*<sup>166</sup> chose ultrasound-assisted extraction in 0.1M K<sub>2</sub>HPO<sub>4</sub> to minimise the effects. Five consecutive 30 min extractions were required for quantitative analyte recovery.

Pyrophosphate was selected over NaCl and NaHCO<sub>3</sub> as *the optimal extractant for the study of iron (hydr)oxide nanoparticles in soil* by asymmetric FFF-HR-ICP-MS<sup>167</sup>. Its superior performance was attributed to its ability to disaggregate organo-mineral assemblages.

A paper<sup>168</sup> describing a *fractionation scheme involving parallel extractions* to identify forms of Mn in spinach leaves was soon followed by a similar paper<sup>169</sup> by the same authors on the speciation of Cu. In both cases 0.01 g freeze-dried samples were treated with water, acetone, chloroform, diethyl ether, ethanol, n-hexane and methanol, with analyte determination by ICP-MS.

Interest has continued in *sequential extraction schemes*. Undeterred by the fact that sequential extraction is an operationally defined approach and so established protocols should be applied exactly as prescribed, workers have applied ultrasound-assisted ‘variants’ on the BCR scheme to soil<sup>170</sup>, sediment<sup>171</sup> and even herbal tea<sup>172</sup>! A ten-step sequential extraction<sup>173</sup> was proposed for As fractionation in sediments that could differentiate some of the species grouped together in the residual fraction by other procedures. The use of Cl-containing reagents was avoided to reduce polyatomic ion interference in ICP-MS. The development of the first dedicated sequential extraction procedure<sup>174</sup> for fractionation of Si in soil was based on study of specific minerals and well-characterised soil samples. The reagents selected were: CaCl<sub>2</sub> (step 1); acetic acid (step 2); H<sub>2</sub>O<sub>2</sub> at 85 °C (step 3); and ammonium oxalate under UV light (step 4). Test portions were then subjected either to bio-optical separation with sodium polytungstate followed by extraction with NaOH (step 5) and finally a lithium-based fusion (step 7); or to extraction with NaOH without bio-optical separation (step 6). Sequential extraction procedures are often criticised for being lengthy, but the 1-week NaOH extraction recommended here must surely be a record! A new scheme<sup>175</sup> for sequential extraction of carboplatin, cisplatin and inorganic Pt<sup>VI</sup> in soil followed by CPE and CS-ETAAS potentially allowed inputs from catalytical converter emissions and cancer hospital wastes to be distinguished.

### 3.2.2 Preconcentration procedures

*Authoritative reviews* have been published covering recent developments in liquid phase microextraction<sup>176</sup> with emphasis on SDME, HF-LPME and DLLME; and in the use of microbacteria<sup>102</sup> as sorbents for SPE.

*Numerous preconcentration procedures for specific analytes* continue to be reported. Methods for the analysis of soils, plants or related materials, or those developed for other sample matrices that used soil or plant CRMs for validation, are summarised in Tables 3, 4 and 5.



**Table 3 Preconcentration methods involving liquid-phase microextraction used in the analysis of soils, plants and related materials**

Analyte(s)	Matrix	Method	Reagent(s)	Detector	Figures of merit (LOD $\mu\text{g L}^{-1}$ unless otherwise stated)	Method validation	Reference
B	Plant, water	HS-LPMS	NaOH	ICP-AES	8.0		<sup>140</sup>
Bi, In, Pb	Plant	USAEME	Calix <sub>4</sub> pyrrole + tetrachloroethylene	ICP-AES	0.57 for Bi, 0.76 for In, 0.84 for Pb		<sup>177</sup>
Cd	Hair, vegetables	IL-UA-DMME	1-butyl-3-methylimidazolium hexafluorophosphate extraction of Cd-4-(2-thiazolylazo)-resorcinol complex then MNP	FAAS	0.40	NWRI TMDA-54 (fortified lake water), SPS-WW2 (waste water), NIST SRM 1570a (spinach leaves)	<sup>178</sup>
Cu	Cereals, vegetables	DLLME	2,9-dimethyl-1,10-phenanthroline, N-phenylbenzimidoyl thiourea	FAAS	0.05	NCS ZC85006 (tomato)	<sup>179</sup>
Cu	Water	IL-DLLME	1-hexyl-3-methylimidazolium bis((trifluoromethyl) sulfonyl)imide	ETAAS	0.004	NIST SRM 2709 (San Joaquin soil), NBS SRM 2701 (Buffalo River sediment), NRCC DOLT-2 (dogfish liver), NIST SRM 1643e (trace element in water)	<sup>180</sup>
Cu	Plant, soil, water	DLLME	4-phenyl-3-thiosemicarbazide	FAAS	0.69	HPS QCS-19 (high purity standard), LGC 6156 (harbour sediment), NIST SRM 1572 (citrus leaves)	<sup>181</sup>
Mo	Corn	VAE-SFODME	8-hydroxyquinoline + 1-undecanol	FAAS	4.9	NIST SRM 1568a (rice flour), IRMM BCR 679 (white cabbage)	<sup>182</sup>
Pb	Hair, plants, water	IL-DMME	1-butyl-3-methylimidazolium hexafluorophosphate extraction of Pb-pyrrolidine-dithiocarbamate then MNPs	FAAS	0.57	NCS ZC 81002b (human hair), NWRI TMDA-54.4 (water), TMDA-70 (Ontario lake water), TMDA-64.2 (water),	<sup>183</sup>

						SPS-WW2 (waste water)	
Pu	Sediment, soil, synthetic urine, water	CPE	P,P'-di(2-ethylhexyl) methanediphosphonic acid	ICP-MS (or $\alpha$ -spectrometry)	15-200 $\text{pg L}^{-1}$	IAEA-384 (lagoon sediment) and spike recovery	<sup>184</sup>
REEs	Water	SFODME	1-(2-pyridylazo)-2-naphthol	ETV-ICP-MS	0.65 – 2.1 $\text{ng L}^{-1}$	NRCCRM GBW 07603 (branch and leaf), NRCCRM GBW 07601 (human hair)	<sup>185</sup>
REEs	Sediment, water	SPE + DLLME	Chelex 100 (SPE sorbent) then 1-phenyl-3-methyl-4-benzoylpyrazolone + Tris (DLLME reagents)	ETV-ICP-MS	0.003 – 0.073 $\text{ng L}^{-1}$	NRCCRM GBW 07301a (stream sediment)	<sup>186</sup>
Sb	Soil, water	USE-SFODME	Sodium diethyldithiocarbamate + 1-undecanol*	ETAAS	0.01	IERM GSB 07-1376-2001, NRCCRM GBW 07441	<sup>187</sup>
Se	Rice	CPE	Cyclohexane	ETAAS	0.08	NRCCRM GBW 08502 (rice meal)	<sup>188</sup>
Ti	Plants, water	CPE	Morin (2',3,4',5,7-pentahydroxyflavone) + Triton X-114	FAAS	2.9		<sup>189</sup>
Zr	Soil, water	DLLME	2-(5-bromo-2-pyridylazo)-5-diethylaminophenol	FAAS	44	Spike recovery	<sup>190</sup>

\*  $\text{Sb}^{\text{III}}$  determined, then reduction, determination of total Sb, and estimation of  $\text{Sb}^{\text{V}}$  by difference

**Table 4** Preconcentration methods involving coprecipitation used in the analysis of soils, plants and related materials

Analyte(s)	Matrix	Carrier	Detector	Figures of merit (LOD $\mu\text{g L}^{-1}$ unless otherwise stated )	Method validation	References
Au	Anodic slime, ore, soil, water	N-benzyl-2-(3-methyl-4-(2-morpholine-4-ylethyl)-5-oxo)-4,5 acetylhydrazinecarboxamide	FAAS	0.36 $\mu\text{g L}^{-1}$	Spike recovery	<sup>191</sup>
Cd, Cu, Ni, Pb, Zn	Fruit, vegetables	Lanthanum 8-hydroxyquinoline	ICP-AES	0.31 – 3.2	NCS ZC 85006 (tomato)	<sup>192</sup>
Co, Cu, Ni	Pepper, peppermint, water	2-(4-(2-(1H-indol-3-yl)ethyl)-3-(4-methylbenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl)-N'-(pyridine-2-yl methylidene)acetohydrazide	FAAS	0.40 for Co, 0.16 for Cu, 0.17 for Ni	HPS CRM-SA-C Sandy Soil C	<sup>193</sup>

**Table 5 Preconcentration methods involving solid phase extraction used in the analysis of soils, plants and related materials**

Analyte(s)	Matrix	Substrate	Substrate coating or modifying agents	Detector	Figures of merit (LOD $\mu\text{g L}^{-1}$ unless otherwise stated)	Method validation	Reference
Ag	Biological samples	Titanium dioxide nanotubes	none	ICP-MS	0.021	NRCCRM GBW 07604 (poplar leaves)	<sup>194</sup>
Ag, Cd, Cu, Hg, Pb	Rice, tea, tuna	MNPs	3-(trimethoxysilyl)-1-propanethiol modified with ethylene glycol bis-mercaptoacetate	ICP-AES except CV-AAS for Hg	0.01-0.09	Spike recovery	<sup>195</sup>
Al, Pb	Various vegetables	Amberlite XAD-4	<i>Agaricus arvensis</i>	ICP-AES	0.03 for Al, 0.10 for Pb	NRCCRM GBW 07604 (poplar leaves)	<sup>196</sup>
Au	Anodic slime, ore, soil, water	Amberlite XAD-4	Sorbed as the Au <sup>III</sup> -2-pyridin-5-(4-tolyl)-1,3,4-oxadiazole	FAAS	1.03	Spike recovery	<sup>197</sup>
Au, Pd	Fish, shrimp, soil, water	MWCNTs	Polypropylene amine dendrimers	FAAS	0.08 for Au, 0.12 for Pd	NCS DC 73323 (soil)	<sup>198</sup>
Bi	Plant, water	Bi <sup>III</sup> ion imprinted polymer	Prepared by formation of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol complex	ETAAS	0.0086		<sup>199</sup>
Cd	Blood, cigarettes, soil	Alumina	Sodium dodecylsulfate modified with dithizone	FAAS	3	Spike recovery	<sup>200</sup>
Cd	Herbs, rice, water	MWCNTs	Diphenylcarbazine	FAAS	0.05	NCS DC 73323 (soil)	<sup>201</sup>
Cd	Water	Polyurethane foam	Procaine hydrochloride	ICP-AES	0.01	IAEA Soil-7, NWRI CRM-TMDW (drinking water)	<sup>202</sup>
Cd	Soil, water	MNPs	Coated with silica then functionalised	FAAS	0.11	Spike recovery	<sup>203</sup>

			with amine then Schiff's base				
Cd, Ni, Pb	Fish, sediment, soil, water	MWCNTs	8-aminoquinoline	FAAS	0.09 for Cd, 0.72 for Ni, 1.0 for Pb	CANMET LKSD-4 (lake sediment)	<sup>204</sup>
Cd, Ni, Pb, Zn	Fish, sediment, soil, water	Magnetic metal-organic framework	Prepared from dithizone-modified MNP and a Cu-(benzene-1,3,5-tricarboxylate) metal-organic framework.	FAAS	0.12 – 1.2	CANMET LKSD-4 (lake sediment)	<sup>205</sup>
Cd, Pb	Soil, water	MNPs	Triton X-114	FAAS	0.15 for Cd, 0.74 for Pb	NRCCRM GBW 07425 (soil), NWRI TMDA 53.3 (fortified water)	<sup>206</sup>
Co, Cu, Ni	Plants, water	MNPs	none	FAAS	0.9 for Co, 0.3 for Cu, 0.7 for Ni	NIES No.1 (pepperbush), NIES No.7 (tea leaves)	<sup>207</sup>
Cr	Soil, water	MNPs	Alumina modified with Triton X-114. Sorbed as the Cr <sup>III</sup> -1-(2-pyridilazo)-2-naphtol complex *	FAAS	1.4 – 3.6	Spike recovery	<sup>208</sup>
Cr	Tea leaves	Titanium dioxide nanotubes	none *	ICP-MS	0.0075	NRCCRM GBW 07605 (tea leaves)	<sup>209</sup>
Cu, Fe, Mn	Parsley, spinach, water	Polyurethane foam	Dithiocarbamate	FAAS		Spike recovery	<sup>210</sup>
Cu, Fe, Pb	Kiwi, water, wheat	Graphene-based cobalt nanocomposite	none	FAAS	0.81	NIST RM 8704 (Buffalo River sediment), SRM 1568a (rice flower), SPS-WW1 batch 111 (wastewater)	<sup>211</sup>
Cu, Fe, Pb	Fertiliser, water	MWCNTs	Sorbed as the pyrocatechol violet chelates	FAAS		NIST SRM 1570a (spinach leaves),	<sup>212</sup>

						NWRI TMDA 70 (fortified lake water)	
Cu, Pb	Food, water	Polyhydroxybutyrate-b-polydimethylsiloxane copolymer	Sorbed as the Sudan III chelates	FAAS		NWRI TMDA 54.4 (fortified lake water), NIST SRM 1515 (apple leaves)	<sup>213</sup>
Cu, Pb	Baby food, coffee, tea, water	Polyhydroxybutyrate-b-polyethyleneglycol	none	FAAS	0.32 for Cu, 1.82 for Pb	NIST SRM 1515 (apple leaves), IAEA 336 (lichen), NRCCRM GBW 07675 (tea)	<sup>214</sup>
Hg	Soil	PTFE tube	Ionic liquid methyltrioctylammonium thiosalicylate	CVAAS	0.04	NIST SRM 2709 (San Joaquin soil), NIST SRM 2711 (Montana soil), SRM 2704 (Buffalo River sediment)	<sup>215</sup>
Mn	Food, sediment, water	Poly(protoporphyrin-co-vinylpyridine)	none	FAAS	0.34		<sup>216</sup>
Ni	Peas, soil, water	Walnut sawdust microparticles	SDS coating modified with dimethylglyoxim	FAAS	0.55	NWRI CRM TMDW-500 (drinking water)	<sup>217</sup>
Ni	Effluent, soil, textile	Alumina	SDS coating modified with dithizone	FAAS	0.54	Spiked recovery	<sup>218</sup>
Ni, Pb	Water	Polystyrene-glycidylmethacrylate copolymer resin	none	FAAS	0.92 for Ni, 1.44 for Pb	NRCCRM GBW 08301 (river sediment)	<sup>219</sup>
Pb	Barley, cauliflower,	Ultra layered cobalt oxide	none	FAAS	0.72	NIST RM 8704 (Buffalo River)	<sup>220</sup>

	street sediment, tobacco, water					sediment), IRMM BCR 482 (lichen), SPS-WW1 batch 111 (waste water)	
Pb	Water	Expanded polystyrene foam waste	N,N-alpha-benzoin oxime	FAAS	0.033	IRMM BCR 403 (seawater), IRMM BCR 715 (waste water), NCS DC-78302 (Tibet soil)	<sup>221</sup>
Pd	Tea leaves, water	Nanoclay	5-(4-dimethylaminobenzylidene)rhodanine	ETAAS	0.0026	NIST SRM 2556 (used auto catalyst)	<sup>222</sup>
Pd	Soil, water	MWCNTs	1-butyl 3-methylimidazolium hexafluorophosphate	FAAS	0.41		<sup>223</sup>
REE	Water	Titanium dioxide nanotube	none	ICP-MS	0.19 – 1.2 ng L <sup>-1</sup>	NRCCRM GBW 07605 (tea leaves)	<sup>224</sup>
REE	Tea leaves, water	Fe <sub>2</sub> O <sub>3</sub> @SiO <sub>2</sub> @poly aniline-graphene oxide composite	None	ICP-MS	0.004 – 1.5 ng L <sup>-1</sup>	NRCCRM GBW 07605 (tea leaves)	<sup>225</sup>
V	Chicken, coffee, fruit, tea, vegetables	MWCNTs	Sorbed as the 8-hydroxyquinoline chelate	ETAAS	0.012	NIST SRM 1515 (apple leaves), SRM 1570a (spinach leaves), NRCCRM GBW 07605 (tea leaves)	<sup>226</sup>
Zn	Water	Ion imprinted poly(vinylimidazole)	none	FAAS	1.5	NIST SRM 1515 (apple leaves), SRM 1570a (spinach leaves)	<sup>227</sup>

(\*) Cr<sup>III</sup> determined, then reduction, determination of total Cr, and estimation of Cr<sup>VI</sup> by difference

### 3.3 Instrumental analysis

#### 3.3.1 Atomic absorption spectrometry

Two *new methods based on thermospray flame furnace AAS* have been described. The fast sequential approach of Miranda and Pereira-Filho<sup>228</sup> accurately quantified Cd, Cu and Pb in leaf slurries in just 69 s (23 s per analyte) with LODs of 0.05, 2.1 and 0.68 mg kg<sup>-1</sup>, respectively. Galazzi and Arrida<sup>229</sup> claimed the first determination of Sn by HG-MF-AAS, a variant on TS-FF-AAS in which analyte hydrides are introduced by means of a ceramic tube to a metallic furnace (with holes on the underside to allow partial flame penetration) mounted on the burner of a FAAS instrument. The LOD of the optimised method was 7.1 µg L<sup>-1</sup>. Excellent accuracy (recoveries 101-104 % of expected concentrations) was obtained for analysis of NIST SRM 1643e (trace element in water) but recovery of Sn from NRCC PACS-2 (marine sediment) proved variable (76-121%).

A review<sup>230</sup> (89 references) of *permanent chemical modifiers in ETAAS* included information on reagents applicable in the analysis of organic solutions, suspensions and solid samples, acid digests and waters. A slurry sampling method<sup>231</sup> in which the graphite tube was modified with 0.3 µg Ir + 0.04 µg Nb allowed determination of V in soil and sediments without interference effects, as demonstrated by the successful analysis of four CRMs.

*High speed self-reversal background correction*<sup>232</sup> was effective for the removal of spectral interference from Fe in the ETAAS determination of Cd in soil extracts. Use of a high-intensity boosted-discharge HCL modulated at 100 Hz eliminated the influence of emission noise. Accurate analyte measurements were obtained at Fe/Cd ratios of 100,000 in 0.11M acetic acid and of 10,000 in 0.5M hydroxylammonium chloride.

Reports of *analytical methods based on HR-CS-AAS* have become more numerous as the technique has gained acceptance and become more widely available. Cadmium, Cu, Ni and Pb<sup>233</sup> were determined by HR-CS-ETAAS in acid digests of black tea from Saudi Arabia. Slurry sample introduction<sup>234</sup> proved successful in the measurement of As, Cd, Cr, Cu, Fe, Mn and Pb by HR-CS-ETAAS in NIST SRMs 1570 (spinach leaves) and 1573 (tomato leaves) and in multivitamin dietary supplements from Poland. Direct solid sample introduction HR-CS-ETAAS was used to measure Fe and Ni in plants and lichens from Spain<sup>235</sup>; Sb and Mo in dust from Egypt<sup>44</sup>; and Se in soils from Brazil<sup>236</sup>. A CVG-HR-CS-AAS method<sup>237</sup> with quartz tube atomisation for the determination of Au had a LOD of 2.6 ng mL<sup>-1</sup> and was successfully applied to alloy, soil and water samples.



Also gaining wider acceptance is *the use of commercial total Hg analysers for the speciation of Hg in solid samples by TD-AAS*. The desorption temperature profiles of inorganic Hg compounds –  $\text{Hg}^0$ ,  $\text{HgCl}_2$ ,  $\text{HgO}$ ,  $\text{HgSO}_4$ , humic-bound Hg and  $\text{HgS}$  – were used<sup>238</sup> to study interactions between Hg species and soil. Organic-Hg was determined<sup>239</sup> by TD-AAS following digestion of 0.5 g soil samples in 5 mL of 0.3M  $\text{CuBr}_2$  solution in 5% v/v HCl and selective extraction into 10 mL DCM.

A *deep-UV LED photoreactor* was evaluated by Sturgeon and Luong<sup>240</sup> for the reduction of inorganic and MeHg prior to their determination by PVG-AAS. The device contained a set of 0.3 mW UV LEDs (245-260 nm peak output) and the reaction was carried out in 2% formic acid. Performance was compared with that obtained using a set of 0.3 mW 360 nm output LEDs, and with that of a thermal reactor at 85 °C to assess the effects of wavelength and temperature. Because room temperature irradiation at 350 nm produced no signal, the authors suggested that previous studies at this wavelength which detected a response may have been influenced by unnoticed thermal effects. A 9-min irradiation period quantitatively reduced both Hg species. The LOD of 0.68 ng was similar to that obtained by CV-AAS. A blank-corrected total Hg concentration of  $3.12 \pm 0.15 \text{ mg kg}^{-1}$  was obtained for NRCC PACS-2 (marine sediment), the certified value of which is  $3.02 \pm 0.02 \text{ mg kg}^{-1}$ . Unfortunately, no irradiation conditions could be found that yielded selective response from individual Hg species.

### 3.3.2 Atomic emission spectrometry

Various spectral lines of Ar, Ga, In and Y were evaluated<sup>241</sup> as *internal standards for the axially viewed ICP-AES determination* of Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, V and Zn in plant digests, using NIST SRM 1575 (tomato leaves) as a test sample. Analyte recoveries without internal standard were often <50% of certified values but accurate results could be obtained for Cd and Pb using In (at 230.606 nm) and for the other analytes using Y (371.029 nm) or Ga (417.206 nm) as internal standards. Use of Ar spectral lines proved to be ineffective.

Addition of 0.15% cetyltrimethylammoniumchloride surfactant resulted in an *enhanced signal intensity in the determination of Cd, Cr, Hg and Pb by solution cathode-GD-AES*<sup>242</sup>, and improved LODs to 1, 42, 7 and 2  $\mu\text{g L}^{-1}$ , respectively. Results for stream sediment CRMs NRCCRM GBW 07310 and 07311 were close to target values, except for Hg for which concentrations fell below the LOD.

A solid sampling ETV-ICP-AES method for the measurement of Pt, Pd and Rh in *Brassica Napus* (rapeseed)<sup>243</sup> gave LODs of 0.38, 0.14 and 0.15  $\mu\text{g g}^{-1}$ , respectively, and RSDs of 4.7-7.1% (n=7) for a sample mass of 5 mg. Calibration with aqueous standards dried onto paper filter strips overcame the memory effects observed for Pt when liquid standards were introduced to the furnace.

New methods for Hg determination by CV-AES included a rapid CV-ICP-AES procedure<sup>244</sup> for plants and soils with a LOD of 3  $\mu\text{g kg}^{-1}$  and a miniaturised (micro-torch) CV-CCP-AES approach<sup>245</sup> for soils with a LOD of 4.8  $\mu\text{g kg}^{-1}$ . The latter procedure gave good agreement with certified values for measurement of Hg in six soil and sediment CRMs. Application of the Bland and Altman test to 31 soils from an industrial town in NW Romania showed no significant statistical difference at the 95% confidence interval between results of the proposed method and those obtained using CV-AFS.

### 3.3.3 Atomic fluorescence spectrometry

Researchers in China<sup>246</sup> reported (in Chinese) an *optimised method for determination of methylmercury* in soil by purge-and-trap GC-AFS that yielded a recovery of  $104 \pm 15\%$  when applied to IRMM ERM-CC580 (estuarine sediment) and a LOD of 0.8  $\mu\text{g kg}^{-1}$ . Other workers<sup>247</sup> preferred a headspace trap GC-AFS approach. They obtained results in good agreement with certified values for analysis of CRMs IAEA-405 (estuarine sediment) and IAEA-433 (marine sediment).

In the determination of arsenic in soil by HG-AFS, online multichannel ultrasonic extraction with sequential injection slurry sampling<sup>248</sup> enhanced sample throughput, reduced sample and reagent consumption and minimised potential contamination and analyte loss. A 20-min sonication was used to extract As from 1.0 mL of aqueous sample slurry mixed with 1.5 mL of 6M HCl. The mixture was then flushed into a pre-reduction reactor where the  $\text{As}^{\text{V}}$  species were converted to the  $\text{As}^{\text{III}}$  species using 1% *m/v* thiourea and 0.5% *m/v* ascorbic acid. Finally  $\text{AsH}_3$  was generated using 2.0 %  $\text{KBH}_4$  and flushed to a gas-liquid separator. The LODs were in the range 30-70  $\mu\text{g kg}^{-1}$  and the RSDs <2.0% (n=6).

### 3.3.4 Inductively coupled plasma mass spectrometry

The high sensitivity of SF-ICP-MS was key in the development of a method<sup>249</sup> for *measurement of Te in plants and soil without analyte preconcentration*. Using a conical concentric nebuliser with sample uptake rate of 0.1 mL min<sup>-1</sup>, the LODs were 0.17 and 0.02 µg kg<sup>-1</sup> for soil and plant samples, respectively.

The accident at the *Fukushima Daiichi nuclear power plant* in March 2011 provided considerable impetus for analytical method development. Ohno *et al.*<sup>52</sup> successfully used a triple quadrupole ICP-MS instrument to measure <sup>129</sup>I in soil. In previous studies that used O<sub>2</sub> to overcome the interference from <sup>129</sup>Xe<sup>+</sup> (an impurity in Ar plasma gas), the formation of <sup>127</sup>IH<sub>2</sub><sup>+</sup> from <sup>127</sup>I<sup>+</sup> in the reaction cell limited the LOD achievable. With the new instrument, most <sup>127</sup>I<sup>+</sup> ions were excluded from entering the reaction cell by the first quadrupole and residual interference could be corrected by subtraction, assuming a production ratio in the plasma of 5 x 10<sup>-9</sup> for (<sup>127</sup>IH<sub>2</sub><sup>+</sup> + <sup>127</sup>ID<sup>+</sup>)/<sup>127</sup>I<sup>+</sup>. The results were consistent with those obtained by AMS, even for soils with <sup>129</sup>I activities as low as 2 mBq kg<sup>-1</sup>. Zheng *et al.*<sup>250</sup>, who used the same type of instrument with N<sub>2</sub>O as the reaction cell gas to measure <sup>135</sup>Cs/<sup>137</sup>Cs isotope ratios in forest litter, lichen and soil, concluded that the radiocaesium had been mainly released from the Unit 2 reactor. In contrast, Takagi *et al.*<sup>251</sup> specifically opted for quadrupole ICP-MS for measurement of <sup>90</sup>Sr in soil in order to ensure that the method was widely accessible. Online chelate column separation was used to preconcentrate Sr from soil digests. The use of ultrapure oxygen as the reaction gas in the DRC overcame isobaric interference from <sup>90</sup>Zr. The LOD of 3.9 Bq kg<sup>-1</sup> was sufficient to measure <sup>90</sup>Sr in samples collected up to 20 km from the power plant.

*Isotope ratio measurement methods* were reported for Pb<sup>62</sup> in various matrices including sediment by quadrupole ICP-MS; for Os<sup>252</sup> in biological samples by SF-ICP-MS; and for Se<sup>253</sup> in soils by HPLC-ICP-MS.

Use of *ultrasonic slurry sampling* obviates the need for sample digestion and is suitable for use with ETV-ICP-MS. A procedure<sup>54</sup> for determination of Au, Pd, Pt and Rh involved sonicating samples of road dust with APDC to produce a mixture containing 0.5% *m/v* dust and 2% *m/v* of the chemical modifier. Analysis by standard additions gave results similar to certified values for Pd, Pt and Rh in IRMM BCR 723 (road dust) with LODs of 0.4 to 0.9 µg kg<sup>-1</sup>. A method<sup>254</sup> which used 1% *m/v* 8-hydroxyquinoline as chemical modifier in the determination of As, Cd, Hg and Pb in herbs achieved LODs of 0.1-0.3 µg kg<sup>-1</sup>.

*Applications of LA-ICP-MS to geological samples* such as rocks and soils have been reviewed<sup>255</sup> (179 references). An innovative (and thrifty) approach<sup>256</sup> to obtain information

on sources of Pu in the environment involved measurement of  $^{239}\text{Pu}/^{240}\text{Pu}$  ratios in archived  $\alpha$ -spectrometry sources that had been prepared from Russian sediment samples in the mid-1990s. Low S/N proved to be a limitation, but it was still possible to distinguish between weapons-grade, civilian grade and global fallout Pu.

Efforts continue to improve *the homogeneity of targets used in LA-ICP-MS* because this is key to accurate quantification. Malherbe *et al.*<sup>257</sup> mixed powdered samples of soil and sediment SRMs with lithium borate, added isotopically enriched spike solutions and then fused the mixtures into glass before measuring Ba, Cr, Pb, Sr and Zn by ID-MS. Fusion led to a more homogeneous distribution of elements than possible with traditional pelletisation and the dilution of the sample in the flux gave a relatively standard target matrix for ablation. Horner and Beachemin<sup>258</sup> compared silicon- and zirconium-based xerogels containing 8-hydroxyquinoline complexes of analytes as standards for soil analysis by LA-ICP-MS. Zirconium-based gels were preferred because they were more homogeneous, gave slightly more accurate results for analysis of NIST SRM 2711 (Montana soil) and SCP EnviroMAT SS-2 (soil standard) and were easier to form into pellets.

A useful development for *LA-ICP-MS analysis of plants* was a new Peltier-cooled LA cell<sup>259</sup> that measured the sample temperature directly, allowing faster mitigation of thermal effects caused by the laser and thus ensuring thermal stability of the sample during ablation. The cell was successfully used in the elemental mapping of Cu and I in fresh leaves of *Solanum lycopersicum* (tomato plant). In contrast, mapping<sup>260</sup> of Hg in root cross sections of *Zea mays* (maize) initially proved problematic due to memory effects caused by sorption of the analyte inside the ablation chamber. These effects were overcome by performing spot analysis using a 10 s delay and washout between spots.

The development and use of *hyphenated techniques with chromatographic or electrophoretic separation coupled to ICP-MS* is now widespread. Recent examples included a species-specific ID-GC-ICP-MS method<sup>261</sup> for the determination of MeHg in water, sediments and biological tissue; a procedure<sup>262</sup> for speciation of Zn in plants that used SEC-ICP-MS and IC-ICP-MS in sequence; and a CE-ICP-MS instrument<sup>263</sup> for As speciation in water, plants and animal tissue that had a novel high-efficiency sprayer interface adapted from CE-ESI-MS. Speciation methods based on HPLC-ICP-MS were reported for P in transgenic plants<sup>264</sup>, for Sb in soil<sup>265</sup> and for Se in *Brassica chinensis* (pakchoi)<sup>266</sup>.

### 3.3.5 Laser induced breakdown spectroscopy

A detailed and authoritative *review*<sup>267</sup> (216 references) described the fundamental principles and attributes of LIBS and provided a comprehensive overview of applications to natural materials, including soils and sediments. Khater<sup>268</sup> included soil in his review (98 references) of the use of LIBS to determine the elements B, Be, C, Cl, F, Li, P and S. The technique was also the subject of a review<sup>269</sup> (100 references) of potential applications concerning the determination of glycemic elements in medicinal plants.

*Improvements in LIBS for the analysis of soil* included the addition of a planar mirror<sup>270</sup> positioned vertically on the sample surface 10 mm from the plasma axis. This increased the signals obtained for Al, Ba, Fe and Mg from NRCCRM GBW 07411 (Chinese soil) approximately two-fold and improved S/N. Matrix effects in the determination of Cd were reduced<sup>271</sup> through use of a combined calibration curve derived from the individual calibrations for neutral and singly ionised species. New criteria<sup>272</sup>, proposed for selection of a suitable reference line to serve as internal standard in LIBS analysis, were based on correlation criteria rather than similarity in excitation potentials between analytical and reference line. The measurement of Pb in soils was given as an example. Kriging interpolation<sup>273</sup> and use of a database of spectra from nine spiked artificial soils containing different proportions of sand, kaolin and goethite showed promise for the quantitative determination of Zn.

The *application of chemometrics* to whole LIBS spectra, or selected wavelength regions thereof, is becoming a powerful tool for sample classification. Mukhono *et al.*<sup>274</sup> showed that PCA and SIMCA could distinguish soil and rocks derived from: high background radiation areas with geothermal influence; high background radiation areas without geothermal influence; and normal background radiation areas with geothermal influence. Researchers based in Korea<sup>275</sup> used PCA to categorise soil as either contaminated with metals, contaminated with oil or clean. Meanwhile, two groups in the USA<sup>276, 277</sup> demonstrated the utility of PLS for differentiating inorganic and organic soil C.

Improved calibration<sup>278</sup> in *the analysis of plants by LIBS* was achieved by creating a set of matrix-matched calibration standards that allowed results statistically similar to ICP-AES data (at 95% confidence interval) to be obtained for the determination of Ca, Cu, K, Mg, Mn, P and Zn in sugar cane. A blank (or low concentration) standard, prepared by extraction of ground sugar cane leaves with 0.2M HNO<sub>3</sub>, was mixed with various aliquots of the original ground leaves and pressed into pellets to produce the calibrants. The latest in a series of similar papers reporting the determination of specific analytes in Gannan navel oranges focussed on the determination of Cd<sup>279</sup> and Cr<sup>280</sup>. The studies were successful in that

they yielded similar results to AAS analysis, but only the outer surface of the fruit was analysed so the relevance of the measurement in terms of food contamination assessment is questionable.

A rapid LIBS method<sup>281</sup> for *identification of P-containing proteins* separated by gel electrophoresis used an extract of *Brassica napus* (canola, a cultivar of rapeseed) as test substrate. The prominent band observed at 45 kDa was excised, digested and identified by MALDI-MS as ribulose-1,5-biphosphate carboxylase/oxygenase, the primary plant enzyme in carbon fixation.

### 3.3.6 X-ray spectrometry

A critical review<sup>282</sup> (145 references) of *metal(loid) speciation in environmental samples by XAS* provided an excellent introduction to the field. It explained the underlying principles of EXAFS and XANES spectrometries, provided example applications, and highlighted emerging trends and research needs.

The use of 1600 rather than 400 kN in a *new high pressure sample preparation apparatus*, as described in a Chinese language article<sup>283</sup> (with English abstract), improved sensitivity and hence LOD by reducing particle size. The apparatus produced dense, flat, smooth and crack-free pellets from soil and sediment samples suitable for XRF analysis without the addition of binder.

As in LIBS, increased *use of chemometric tools* has proved beneficial in XRF analysis. Akbulut<sup>284</sup> successfully used PLS and principal component regression calibration models to predict concentrations of As, Ba, Co, Cu, Mn, Ni, Pb, Rb, Sr, V and Zn in a suit of CRMs, including soils and sediments, analysed by EDXRF spectrometry. Ghasemi *et al.*<sup>285</sup> employed PLS, principal component regression and support vector machine algorithms to overcome overlap between the Na ( $K_{\alpha}$ ) and Zn ( $L_{\alpha}$ ) lines in analysis of soil by WDXRF spectrometry.

In *the analysis of plants*, the first use<sup>286</sup> of  $\mu$ -EDXRF spectrometry for quantitative determination of macro- and micro-nutrients and silicon in plant materials (specifically sugar cane) was reported. A  $\mu$ -PIXE method<sup>287</sup> for analysis of frozen-hydrated sections of biological materials such as plants, mentioned in a previous Update<sup>288</sup>, was improved to allow the handling of thinner samples (20-50  $\mu$ m thickness).

Improvements in the LODs achievable with *field portable XRF spectrometry* are allowing established uses such as the screening of highly contaminated soils, *e.g.* from

abandoned mines<sup>289</sup>, to be supplemented by more novel applications, *e.g.* analysis of plant litter<sup>290</sup>, peatland samples<sup>291</sup> and agricultural soil<sup>292</sup>. However, as demonstrated in a study<sup>293</sup> of As in French soils, care is still required to optimise analytical parameters and to correct for factors that can affect results, especially the sample moisture content, which can affect the XRF signal. It should be noted that this moisture need not be in the liquid state. Wiendorf *et al.*<sup>294</sup> showed that results for *in situ* analysis of frozen Alaskan soils, laboratory analysis of refrozen soils and laboratory analysis of melted soils were all less than results for oven dry soils, using Ba, Ca, Cr, Fe, K, Mn, Pb, Rb, Sr, Ti, Zn and Zr as test analytes.

## 4 Analysis of geological materials

### 4.1 Reference materials and data quality

It is not always widely appreciated that proficiency testing schemes and inter-laboratory comparisons (sometimes referred to as ‘round robins’) are designed to serve different purposes. Participation in a *proficiency testing scheme* forms part of a laboratory’s routine QC procedures to enable it to detect unsuspected errors in its analytical systems, and take appropriate action, thus providing an independent demonstration of its data quality. An assessment<sup>295</sup> of data submitted in the period 2001-2011 to the GeoPT proficiency testing scheme for geochemical laboratories run by the International Association of Geoanalysts (IAG), identified elements and concentration ranges over which routine analytical performance could be considered satisfactory. This study, in itself, is a marker of the overall data quality generated by geochemical laboratories. Some suggestions were made for the causes of unsatisfactory performance, such as incomplete digestion of resistant minerals or unsuspected interferences, which may deserve more detailed investigation.

In contrast, *inter-laboratory comparisons* provide a snapshot of the state-of-the-art rather than feedback on performance to individual laboratories. Measurements<sup>296</sup> of Sr/Ca in coral from 21 laboratories involved in an international collaboration reconstructing past seawater temperatures showed that inter-laboratory bias could be significant. Of the many potential sources of bias, traces of Sr in Ca standards and uncertainties in reference solution composition accounted for half of the combined uncertainty. During this exercise the GSJ RM JCp-1 (*Porites* coral) was sufficiently well characterised to be accorded a ‘certified’ Sr/Ca value of  $8.838 \pm 0.089 \text{ mmol mol}^{-1}$ , according to IAG guidelines. An inter-laboratory comparison<sup>297</sup> of measurements of B isotopes in a range of marine biogenic carbonates (coral,

foraminifera, brachiopods) deliberately involved just four laboratories, each using a different analytical technique. No significant inter-laboratory biases were observed for boric acid or seawater, a common in-house RM, but the carbonate samples had a pooled 2 SD of 1.46‰ for  $\delta^{11}\text{B}$ , which was larger than the measurement uncertainty reported by each laboratory. Overall sample size, in terms of total B available, and B/Ca ratio in each sample were significant factors contributing to the overall uncertainty, although the exact mechanisms were uncertain. Despite the encouraging agreement, the results demonstrated the need for a suite of well-characterised marine carbonate RMs for B isotope determinations.

An inter-laboratory comparison<sup>298</sup> of *U-Pb dating of synthetic detrital zircons* by LA-ICP-MS and SIMS, involving 10 laboratories that routinely perform this type of analysis, reported a level of bias mostly within 2% of the ID-TIMS U-Pb age. Variable rates of Pb-U laser-induced elemental fractionation resulting from differences between the zircon matrix of the samples and RMs used for calibration was thought to be the main cause of this bias. The precision of individual zircon age determinations was mainly influenced by the procedures used for data reduction and measurement propagation, and was largely independent of instrumentation, analytical technique and RMs. Most laboratories underestimated the true uncertainty of their measurements, resulting in reported values with confidence limits outside the uncertainty of the age predicted by ID-TIMS data. All laboratories showed a bias towards selecting larger grains for analysis and it was recommended that grain selection should be randomised.

Several new potential *RMs for U-Pb dating* have been characterised. SoriZ93 zircon<sup>299</sup>, obtained from the residual mineral fraction after the preparation of the SORI93 biotite RM from a Japanese granodiorite, was analysed using a SHRIMP. Cathodoluminescence imaging revealed a fine oscillatory zoning, typical of zircons with no xenocrystic core from granitic rocks. Although some mineral inclusions were present, it was possible to select an inclusion-free zone 30  $\mu\text{m}$  wide necessary for analysis by the microbeam technique. With a recommended  $^{206}\text{Pb}/^{238}\text{U}$  age of  $93.9 \pm 0.6$  Ma (95% confidence limit), the SoriZ93 zircon was proposed as a suitable RM for dating Late Cretaceous zircons. Qinghu zircon grains<sup>300</sup>, from the Qinghu quartz monzonite from SE China, were considered to be sufficiently homogeneous at the 20 to 60  $\mu\text{m}$  scale to be proposed as a working RM for U-Pb age ( $159.5 \pm 0.2$  Ma) and Hf and O isotope determinations. Careful selection of suitable areas for microanalysis with the aid of a photomicrograph and cathodoluminescence imaging was recommended as some of the grains contained opaque mineral inclusions and a few grains had high U and Th contents. In response to the general lack of sufficiently abundant and high



quality rutile RMs for *in situ* U-Pb geochronology, two new rutile samples<sup>301</sup> from granulite facies metasedimentary rocks in the Canadian Shield were chosen as candidate RMs (Sugluk-4 and PCA-S207). Characterisation of these materials showed that their U-Pb compositions, including any common Pb, were much more homogeneous than those of existing rutile RMs. The new RMs were used to develop a U-Pb normalisation procedure that did not rely on a correction for common Pb, resulting in a long-term reproducibility of 2-4% (2 RSD) for  $^{206}\text{Pb}/^{238}\text{U}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$ , which was only slightly worse than that for long-term data for zircon RMs. Using a 50  $\mu\text{m}$  LA spot size, the sensitivity of the LA-MC-ICP-MS set-up employed allowed dating of *ca.* 90% of rutiles within a sediment containing rutile as young as 10-20 Ma, and eliminated the need to pre-screen the samples for low U concentrations.

Exciting developments in the preparation of *nanoparticulate powders with a prescribed composition* have opened up new possibilities for the production of true matrix-matched RMs for the calibration and validation of microanalytical techniques such as LA-ICP-MS, EPMA, SIMS and SR-XRF. The flame spray technique was used to produce a nanomaterial<sup>302</sup> with a matrix composition similar to that of NIST SRM 610 glass plus a selection of REEs, precious metals and Pb at concentrations of 400-500  $\text{mg kg}^{-1}$ . The liquid precursor mixture was sprayed and collected as a nanopowder, pressed to form pellets (without a binder) and analysed by solution ICP-MS, LA-ICP-MS and EPMA. The material synthesised was homogeneous for major elements and REEs at a scale similar to that for the NIST 610 glass, i.e. <5% RSD, whereas the spatial variation of the PGEs was larger at <7.5% RSD. In addition, contamination during production resulted in heterogeneous distributions of Ag and Pb. The major advantage of this technique is that the composition can be tailored to the specific requirements of the application and up to several 100 g can be prepared in a single batch. In an alternative approach, Garbe-Schönberg and Müller<sup>303</sup> prepared NPs powders with a typical grain size of  $d_{50} < 1.5 \mu\text{m}$  by wet-milling in aqueous suspension using a high power planetary ball mill and agate tools. Pressed powder tablets produced from this NP material without the incorporation of any binder had excellent cohesion, homogeneity and mechanical stability. A selection of geochemical CRMs covering a wide range of natural rock types, prepared by this procedure and analysed by LA-ICP-MS gave precisions of 2-5% RSD. The preferred values could be reproduced for most of the 38 trace elements determined. These figures of merit were similar to those obtained from LA of glasses and were significantly better than data reported from the analysis of pressed powders in many previous studies. As no binder was required, LODs in the low ppb range were achieved and volatile elements were quantitatively retained. A few elements, such as Mo, Sb, Sn, W and Zn, did

not satisfy the precision and accuracy criteria required. One source of contamination was thought to be the anvil and dies in the tablet press, made of alloyed steel or tungsten carbide.

Chinese reference glasses<sup>304</sup> with the compositions of basalt, syenite, andesite and soil were evaluated for *U-series measurements* by MC-TIMS and MC-ICP-MS. The Th-U concentration and isotopic data obtained by the two techniques agreed within estimated errors. The value of these glasses to the community comes from the large  $^{238}\text{U}$ - $^{234}\text{U}$ - $^{230}\text{Th}$  disequilibria observed, combined with the wide range in Th/U ratios; the long-term aim is to develop them as microanalytical RMs. Given the routine use of the NIST SRM 61x series of glasses for calibrating microanalytical techniques, there are surprisingly few data available on their U isotopic composition. This has now been rectified to some extent with the publication<sup>305</sup> of atom percent and U isotope ratios for all four glasses determined by fs LA-MC-ICP-MS. Results for NIST SRM 610 were in excellent agreement with literature values but the atom percent  $^{235}\text{U}$  measured did not match the certificate values. Large corrections required for  $\text{PtAr}^+$  interferences on the U minor isotopes, as a result of platinum introduced from the crucible during the preparation of the glass, may have contributed to these discrepancies. Thorium and U concentrations in four marine sediment CRMs (NIST 1646a and NRCC HISS-1, MESS-3 and PACS-2) were re-evaluated<sup>306</sup> using ID-MC-ICP-MS. The new ID data were consistently lower than the informative values on the original certificates and also there were heterogeneities in the distributions of these elements in 100 mg subsamples of the CRMs.

*Molybdenum isotope variations* are increasingly being used to investigate the oxygenation of the Earth's ocean and atmosphere. Despite attempts to establish NIST SRM 3134 (Mo standard solution) as the delta zero, there is still no internationally accepted RM for Mo isotope composition in studies of mass-dependent isotope fractionation. Nagler *et al.*<sup>307</sup> proposed that  $\delta^{98}\text{Mo}/^{95}\text{Mo}$  in NIST SRM 3134 now be defined as +0.25‰, rather than zero. They argued that this would facilitate the comparison of previous  $\delta^{98}\text{Mo}/^{95}\text{Mo}$  data obtained using other RMs, which had  $\delta^{98}\text{Mo}/^{95}\text{Mo}$  values in the relatively narrow range of -0.16 to 0.37‰ relative to NIST SRM 3134. They also recommended the use of open ocean seawater, of which there are limitless supplies, as a secondary RM with a defined  $\delta^{98}\text{Mo}/^{95}\text{Mo}$  of  $+2.34 \pm 0.10$ ‰. Meanwhile Mayer and Wieser<sup>308</sup> determined the absolute isotopic composition and atomic weight of Mo in SRM 3134 by MC-ICP-MS using a  $^{92}\text{Mo}$ - $^{98}\text{Mo}$  double-spike to correct for instrumental mass bias. These data should go a long way to establishing SRM 3134 as the international standard for Mo isotope measurements.

## 4.2 Solid sample introduction

### 4.2.1 Laser ablation inductively coupled plasma mass spectrometry

Although *LA sample introduction* is in widespread use in many scientific disciplines, geological applications still drive many developments in LA-(MC)-ICP-MS<sup>309</sup>. This was exemplified in an authoritative review<sup>310</sup> (50 references) of recent instrumental and methodological advances in ICP-MS and LA-ICP-MS analysis. A more basic review<sup>255</sup> (179 references) highlighted the factors affecting accurate elemental analysis of geological materials by LA-ICP-MS.

Now that modern instrumentation permits high spatial resolution measurements at the  $\mu\text{m}$ -scale over a very wide range of concentrations, there is increasing interest in *elemental imaging or mapping* of geological materials by LA-ICP-MS. This application has necessitated further developments such as optimised ablation cell designs for rapid wash-out, reduction in cross-contamination when rastering across a sample and the development of appropriate data processing software to produce the images<sup>311</sup>. Recent examples included the mapping of trace elements in biogenic and inorganic carbonates with complex internal geometries<sup>312</sup>. An in-line signal smoothing device provided much more stable signals and less noise in the data. Pre-ablation cleaning was found necessary for accurate determination of some trace elements, particularly Al and Zn. Multielement maps of element distributions in a Late Archean impact spherule layer were acquired<sup>313</sup> by LA-ICP-MS at a lateral resolution of 15  $\mu\text{m}$ . A teardrop ablation cell (volume 2.9  $\text{cm}^3$ ) had better performance characteristics than a larger standard circular cell (volume 33  $\text{cm}^3$ ) for this application. Helium was preferred over argon as the transport gas to prevent redeposition of ablated particles on the sample surface. Significant matrix effects were observed<sup>314</sup> during the production of elemental maps of iron meteorites when ablating the different iron phases with a 213 nm laser system. Careful application of a matrix-matched external standard and proper internal standardisation were essential to correct for these matrix effects. The potential for a combination of LA-ICP-MS and LIBS to provide expanded elemental coverage for simultaneous 3D imaging was demonstrated using a rare earth ore sample<sup>315</sup>. Following data acquisition, the signals from the two techniques were integrated and reassigned to xyz spatial coordinates to produce layer-by-layer 2D elemental maps. Basic principles of computed tomography were adopted to visualise multiple elemental and isotopic distributions in 3D.

*Investigations into fundamental aspects of LA-ICP-MS* provided a better understanding of some of the complex processes involved. The sensitivity of a HR MC-ICP-

MS instrument was improved<sup>316</sup> *ca.* 2-fold through a series of modifications to the geometry of the sampler and skimmer cones, the interface pumping configuration and source lens. This enabled micro-sampling at a higher spatial resolution with no loss in accuracy. In another study, signal enhancement was achieved<sup>317</sup> by the addition of water and/or ethanol vapour to laser-ablated dry aerosols, using a custom-made introduction system that provided long-term stability. For most of the 60 elements studied, the addition of small amounts of water and/or 1-4% (v/v) ethanol vapour, in combination with a shielded torch, improved the sensitivity of LA-ICP-MS measurements by a factor of 2.5–3.0. Spatial profiling of analyte and background species in the ICP provided insights into some of the mechanisms for this enhancement. Further investigations<sup>318</sup> into the effect of carrier gas humidity on the vaporisation of laser-produced aerosols in ICPs utilised an ICP-AES instrument with a Czerny-Turner monochromator operating in 2D imaging mode to obtain axial profiles of the ICP. Under dry conditions, the profiles for Ca and Na in the ICP were separated by several mm. However, by introducing precise amounts of water *via* a micro-droplet dispenser, the two axial profiles were superimposed over a range of humidities. These observations supported the hypothesis that, under these conditions, the two elements vaporised at the same position in the plasma. These operating conditions were then used for quantitative analysis of silicate glass by LA-ICP-MS, resulting in a significant improvement in the accuracy as well as lower LODs, with only a moderate increase in oxide formation. The performance of LA sampling in air was compared<sup>319</sup> to that of conventional LA in a closed cell for the determination of isotope ratios by MC-ICP-MS using a fs laser. Samples of galena, zircon and brass were ablated in air and the aerosol generated aspirated into a gas exchange device, in which the air was replaced with argon before transfer to the ICP. Comparable precisions and accuracies were obtained making the system suitable for isotope determinations of materials too large to fit into an ablation cell. However, the signal intensities from the atmospheric sampling method were lower by up to a factor of five. Further modifications, such as more stable gas flows and improved sampling efficiency, were recommended for fast and spatially resolved determinations using scanning mode LA.

Although it has been established that, in general, short pulse *fs* LA *sample introduction* provides better accuracy and precision than the use of long pulse ns lasers, the fundamental ablation mechanisms of fs lasers are still being evaluated. Particles<sup>320</sup> produced by ablating magnetite, siderite, pyrrhotite and pyrite with a UV fs laser were collected with a cascade impactor and the various size fractions analysed by solution MC-ICP-MS for their Fe isotope composition. Despite the isotopic variations observed across the aerosol size

fractions, the composition of the total aerosol, as calculated from a mass balance, was stoichiometric in terms of its Fe isotope content for all the minerals ablated. As well as providing insights into the behaviour of condensates from laser-induced plasmas, the study demonstrated the importance of quantitative transport of the laser aerosol to the ICP. Data<sup>321</sup> obtained for Cu isotopes in cubanite by LA-MC-ICP-MS using two fs laser systems operating at 260 nm and 780 nm showed better precision for the UV fs system (<0.10%, 2 SE). At both laser wavelengths, matrix-matched standards were still required for reliable Cu isotope data. An IR ( $\lambda=1030$  nm) fs LA system was used to sample micrometre-sized U-containing particles to determine  $^{235}\text{U}/^{238}\text{U}$  by quadrupole ICP-MS<sup>63</sup>. The particles were first fixed on a transparent polycarbonate disk and then located either by observing fission tracks after irradiation or by SEM using EDXRF. Laser repetition rate was a major factor affecting the isotopic measurements whereas plasma humidity had no significant effect. Accuracy and reproducibility were typically <4% for a 15 s transient signal, in which between 10 and 200 pg U was sampled. No isotopic fractionation was detected and the technique was capable of analysing about 100 particles a day. In a study<sup>322</sup> of the ablation characteristics of brass and NIST 612 glass using a 1030 nm fs laser, higher laser repetition rates and larger spot sizes (>70  $\mu\text{m}$ ) resulted in better estimation of elemental ratios. Additional work was required to separate fractionation effects at the ablation site from those in the ICP.

A review<sup>323</sup> of *fluid and melt inclusion studies* showed how these reflect developments in analytical techniques over the years (111 references). Directions for future research may include: age measurements of inclusion fluids; the use of biomarkers, noble gas isotopes and halogens to trace the source of inclusions; and the study of micro-organisms in fluid inclusions. The current state-of-the-art was assessed<sup>324</sup> using a highly sensitive SF-ICP-MS instrument coupled to a 193 nm excimer laser to analyse an assemblage of fluid inclusions (from a few to *ca.* 200  $\mu\text{m}$  in size) with identical salinities of  $4.0 \pm 0.1$  wt % NaCl equivalent. For 21 elements covering the mass range from Li to Pb, the LODs were 10 times lower than those determined by quadrupole ICP-MS using the same laser system, while the cycle time was only 20% longer for such a suite of elements. The absolute LOD for Au was 1 fg ( $10^{-15}$  g). Albrecht *et al.*<sup>325</sup> employed a 194 nm fs laser coupled to a fast scanning SF-ICP-MS instrument with SEM and Faraday detectors to determine B, Bi, Cd, K, Pb, Te and Tl at a concentration of 53  $\mu\text{g g}^{-1}$  in NaCl-H<sub>2</sub>O synthetic fluid inclusions in quartz. To gain the best advantage from the low heat transfer properties of the fs laser, the ablations were performed at temperatures of around  $-40$  °C using a modified heating-freezing stage as the ablation cell. As a result, frozen fluid inclusions (8 to 25  $\mu\text{m}$  in diameter) down to a depth of 50  $\mu\text{m}$  below

the surface, could be opened very precisely, thereby giving LODs varying between  $0.1 \mu\text{g g}^{-1}$  for  $^{209}\text{Bi}$  to  $10 \mu\text{g g}^{-1}$  for  $^{39}\text{K}$ . Typical analytical uncertainties were 15 to 30% (1 RSD), a significant improvement in precision compared to earlier studies for samples with relatively low analyte concentrations. Although various methods for synthesising reference fluid inclusions have been published previously, the details given have often been insufficient to replicate the procedure. For this reason, the preparation<sup>326</sup> of liquid-vapour inclusions in the  $\text{H}_2\text{O}-\text{CH}_4-\text{NaCl}$  system were described in great detail. The method used pre-existing microcavities in polished quartz chips, which were decrepitated and rinsed before being treated with a NaCl solution of known composition in an autoclave at a fixed temperature and pressure for up to four weeks to synthesize the new inclusions. Advantages of this procedure included quicker healing of the microfractures at lower temperatures, choice of larger inclusions, simple quartz sample preparation, the ability to control the composition of the fluid inclusions, and the use of commercial autoclaves. A summary of methods used to analyse acid saline fluid inclusions<sup>327</sup> noted the difficulties of employing LA-ICP-MS for this purpose due to the extreme chemistry of these inclusions, often located in halite and gypsum matrices.

The ablation characteristics of *sulfide minerals* are complex and vary depending on the mineral being ablated. This was demonstrated in a recent LA-ICP-MS study<sup>328</sup> in which the amount of S fractionation, relative to Fe, was compared for a range of sulfide minerals using three different LA systems: a 213 nm Nd:YAG, a 193 nm Nd:YAG and a 193 nm excimer. Although significant fractionation occurred in all the sulfides, its extent was dependent on the amount of melting around the ablation crater, which was mainly mineral specific and primarily dependent on its physical properties. Consequently, matrix-matched standards were necessary for accurate S determinations using either the 213 nm or the 193 nm lasers systems. In related work, laser parameters for the determination of S isotopes in sulfide minerals by LA-ICP-MS were investigated<sup>329</sup> using two different 193 nm lasers. Matrix effects were reduced by increasing the laser fluence, but the optimal fluence for each laser system needed to be evaluated as it was dependent on laser wavelength and pulse width. The design and material of the tubing between the ablation cell and the ICP were found to be critical for improving the precision and washout time for S. The isotopic composition and homogeneity of a range of sulfide minerals were characterised for use as potential RMs, including a large isotopically homogeneous pyrite crystal PPP-1 ( $\delta^{34}\text{S} = 5.3 \pm 0.2\%$ ). Because of a paucity of suitable matrix-matched standards, a multi-standard approach<sup>330</sup> was adopted for the LA-ICP-MS analysis of sulfides from a PGE deposit in South Africa. Several

RMs, including a new synthetic in-house standard containing As, Sb, Se and Te, bracketed the unknown samples, and  $^{33}\text{S}$  derived from EPMA measurements was used as the internal standard. A similar approach, involving the measurement of two RMs and a blank before and after every unknown<sup>331</sup>, was adopted in the determination of trace elements in pyrite from a magmatic sulfide Ni-Cu ore deposit in Spain. In this case, internal standardisation was based on  $^{57}\text{Fe}$  obtained from the mean Fe value in each pyrite. In a study<sup>332</sup> of a zoned Ge-rich sphalerite from the main Ge deposit in western Europe, SEM and EPMA were used to define major and minor element distributions. A detailed assessment of isobaric interferences on Ge was carried out before a wide range of trace elements was determined by LA-ICP-MS. In combination with Ge isotopes measured by MC-ICP-MS, S isotopes by SIMS and mineralogical observations, the trace element data were used to discriminate between different ore types and shed light on the genesis of the deposit.

*Zircon* has become the most popular accessory phase for U-Pb age determinations because of its widespread abundance, resistance to abrasion, its ability to retain trace elements over geological time and its low initial content of non-radiogenic Pb (common Pb). New results<sup>333</sup> on young zircons (<1 Ma) demonstrated that LA-ICP-MS can reproduce the precision and accuracy of the SHRIMP, while analysing many more zircons with relative ease. Improvements in the design of the two-volume ablation cell ensured that the cell volume and gas flow remained truly constant while moving the samples in the sample holder. Samples were corrected for initial thorium disequilibrium using a new formula that accounts for disequilibrium in  $^{230}\text{Th}$  decay. The counts on  $^{204}\text{Pb}$  and  $^{207}\text{Pb}$  were too low to correct reliably for common Pb and other strategies were needed to minimise its influence on the dataset. A modified methodology<sup>334</sup> allowed the rapid analysis of large numbers of detrital zircons by LA-ICP-MS without compromising analytical precision or accuracy. Based on generating ages using integrated total counts of Pb and U rather than a series of integrated Pb/U ratios, which require longer counting times, additional refinements in sample preparation, imaging and automation resulted in a sampling rate of *ca.* 180 analyses  $\text{h}^{-1}$ . Consequently, much more statistically robust datasets for 300-1000 detrital zircons could be produced for provenance investigations at an economic cost. Looking to the future, developments in real-time data reduction will be a considerable aid in enabling the analyst to decide when a sufficient number of analyses have been completed.

Detailed investigations<sup>335</sup> of *systematic biases observed for zircon U-Pb ages determined by LA-ICP-MS* with a 193 nm excimer laser, using ID-TIMS as the reference technique, revealed that there were small but significant differences in ablation rate between

reference and sample zircons. Intrinsic optical properties of the zircon matrix and subtle defocusing effects of the laser beam both contributed to variations in ablation rates. Although thermal annealing changed the ablation behaviour of the zircons by reducing the amount of radiation damage, the variation in behaviour between different zircon matrices was not eliminated. A discrete multi-pulse method<sup>336</sup> designed to acquire LA depth profiles when coupled to a quadrupole ICP-MS system was able to resolve variations in U-Pb ages in zircon at the sub- $\mu\text{m}$  scale. Isotopic ratios were calculated by integrating the total counts on a transient signal generated by discrete bursts of 5 laser pulses. Correction for fractionation effects was achieved through iterative smoothing and interpolation of a continuous function, non-parametric 3D surface from which discrete values for any time and sample depth could be calculated. There was a high positive correlation between radiation damage, crystal lattice distortion and ablation pit depths. These data indicated that radiation damage exerted a fundamental control on LA efficiency although the exact process was unknown. Consequently, large differences in the amount of radiation damage suffered by RMs and unknown zircons would result in a degradation of accuracy and precision. Another factor found to influence laser-induced elemental fractionation was the amount of oxygen in the helium carrier gas flushing the ablation cell<sup>337</sup>. Oxygen concentrations in the carrier gas as low as 500 ppm shifted U-Pb ages measured in zircon by as much as 9%, well above the typical analytical uncertainty of zircon dating by LA-ICP-MS. The addition of larger amounts of oxygen increased the instrument sensitivity significantly, as well as promoting Th and U oxide formation, probably as a consequence of improved atomisation and ionisation capabilities of the mixed gas ICP. This study highlighted the importance of maintaining a constant level of oxygen in the ablation cell over an analytical session as a prerequisite for improvements in the precision of such measurements.

Age determinations by LA-ICP-MS of other *U-bearing accessory minerals* such as apatite, allanite, titanite and rutile typically requires the use of matrix-matched standards. These measurements may often be complicated by variable amounts of common (or initial) Pb not only in the unknown samples but in the RMs as well. Chew *et al.*<sup>338</sup> proposed a general approach to correcting for common Pb using a modified version of the VizualAge U-Pb data reduction package for Iolite software. Advantages of this data reduction scheme were that it could incorporate any accessory mineral standard, even if it contained variable amounts of common Pb, and it could be applied to raw data files from the majority of modern ICP-MS instruments. Studies on the optimal conditions for the reliable U-Pb age determinations by LA-ICP-MS for titanite<sup>339</sup>, bastnaesite<sup>340</sup>, allanite<sup>341</sup> and rutile<sup>342</sup> all



emphasised the importance of a matrix-matched RM to correct for laser-induced elemental fractionation and other matrix effects.

Not only are *measurements of Hf isotopes in zircon by LA-MC-ICP-MS* subject to large isobaric interferences but molecular interferences can be significant, depending on the rate of oxide formation. The magnitude<sup>343</sup> of these isobaric and REE oxide interferences were reassessed using a series of natural zircons and synthetic glass beads. Molecular interferences from Gd oxides were found to be more significant than those from Dy oxides. A protocol for correcting for these interferences involved the daily monitoring of the rate of formation of Gd and Hf oxides. Guidelines<sup>344</sup> for reporting *in situ* Hf isotope data stressed the importance of supplying sufficient detail, including the procedure adopted for interference corrections, to enable reviewers and readers to assess the quality of the data presented. Potential pitfalls included assignment of incorrect ages and the difficulty of estimating the uncertainties in the initial Hf composition of zircon. One way of ensuring that correct ages are assigned to the Hf isotope compositions in complex zircons was to use the technique known as LA split stream<sup>345</sup>. By splitting the laser aerosol downstream of the ablation cell, simultaneous measurements<sup>346</sup> of U-Pb ages by single-collector ICP-MS and Hf isotopes by MC-ICP-MS were made with little degradation of precision in the Hf isotope data. The veracity of this approach was demonstrated by analysing 10 reference zircons with well-characterised age and Hf isotopic compositions, using laser spot diameters of 30 and 40  $\mu\text{m}$ .

*Other studies of in situ isotopic determinations by LA-MC-ICP-MS* included an evaluation of matrix effects during the measurement of B isotopes in tourmaline<sup>347</sup>, optimisation of ICP interface conditions for low oxide formation in the determination of Nd isotope ratios in glasses and minerals<sup>348</sup> and use of an enhanced sensitivity mass spectrometer<sup>349</sup> for Pb isotope measurements of silicate rocks and minerals with low Pb contents.

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

An excellent *review*<sup>267</sup> of geochemical and environmental applications of LIBS (216 references) also provided a comprehensive account of the fundamentals of the technique, its versatility in the analysis of a wide range of materials and the various statistical signal processing techniques employed. Lin *et al.*<sup>350</sup> reviewed the development of instrumentation that combines LIBS and Raman spectroscopy (90 references). After a presentation of the basic principles and technological aspects of the combined technique, a variety of

applications were discussed, including the analysis of geological materials and deployment in future planetary missions. The performance of LIBS for the determination of light (low atomic number) elements in non-conducting materials was assessed from previously published studies<sup>268</sup>. Future improvements in sensitivity by combining LIBS employing fs laser pulses with other diagnostic techniques based on probing the plasma via diode lasers were anticipated.

Much of the development of the LIBS technique, including the associated *statistical analysis and interpretation of LIBS data*, has stemmed from its inclusion as an integral component of analytical instrumentation on the NASA Curiosity Mars Science Laboratory. The advantages of using independent component analysis, rather than PCA to classify rocks remotely were demonstrated<sup>351</sup> by modelling LIBS data from the ChemCam instrument on board the Mars rover. In another study, two different multivariate techniques<sup>352</sup>, PLS discriminant analysis and support vector machines (SVMs), were used to correlate LIBS data from 16 Triassic sedimentary rocks (sandstone, limestone and mudstone) acquired with both Czerny-Turner and Echelle spectrometer systems. A combination of the Echelle spectrometer system with SVM statistical analysis provided nearly 100% accurate classification of the sedimentary rocks analysed. In an evaluation<sup>353</sup> of spectral lines for the determination of trace amounts of U in uraninite and NIST 1872 glass RMs by LIBS, low ppm LODs were achieved by careful selection of an appropriate emission line with minimal spectral interferences.

*Isotope ratio measurements by LIBS* are difficult because of collision-induced broadening of spectral lines and the very small isotopic spectral shift characteristic of atomic transitions<sup>267</sup>. Computer simulation was used to evaluate a method<sup>354</sup> for improving the precision of U isotope ratios by monitoring multiple LIBS emission lines. The precision of these measurements depended primarily on the signal-to-background ratio and the net intensity of the emission line, rather than the magnitude of isotopic splitting. In an alternative approach<sup>355</sup>, which took advantage of the fact that molecular isotopic shifts can be significantly greater than the respective atomic isotope shifts, spectral analysis of molecular emissions from laser-induced plasmas were used to determine B isotope ratios in samples of boron carbide.

## **4.3 Sample preparation**

### **4.3.1 Sample dissolution**

Simpler methods developed for the *dissolution of chromite ores* included automated fusion<sup>356</sup> with a flux of Na<sub>2</sub>O<sub>2</sub>-Na<sub>2</sub>CO<sub>3</sub> in a zirconium crucible which provided a quick and cost-effective dissolution method for the analysis of chromite ores, ferrochromes and chromium slags by ICP-AES. A protocol<sup>357</sup> for the decomposition of chromite based on oxidation by bromic acid at room temperature in closed plastic vessels was devised for the measurement of Cr isotope abundance. After treatment with HF to decompose the silicate matrix, two additions of bromic acid over a 15-day period were required because of the acid's limited stability. No statistical difference between Cr isotopic compositions measured on solutions prepared by a conventional alkaline oxidative fusion and by bromic acid decomposition was observed.

Since the report of a *dissolution procedure*<sup>358</sup> employing NH<sub>4</sub>HF<sub>2</sub> in last year's ASU, the use of ammonium fluoride (NH<sub>4</sub>F) has been systematically investigated<sup>359</sup> because it has a higher boiling point (260 °C) and so can be used in open digestion vessels. For complete digestion of refractory minerals, a 6+1 proportion of NH<sub>4</sub>F to sample mass was recommended. The main advantages of this method were that it was performed in screw-top PFA vials rather than high pressure digestion bombs, it did not suffer from the formation of insoluble fluorides and the reagent was removed by taking the sample to dryness before making up to volume for analysis by quadrupole ICP-MS. However, NH<sub>4</sub>F has many of the same safety handling requirements of HF, especially when heated to dryness to remove Si as SiF<sub>4</sub>.

Qi *et al.*<sup>360</sup> produced a *new design of Carius tube* consisting of a main body with 3 mm thick glass, a neck and head with 4 mm thick walls and an efficient screw-thread stopper. These new features reduced the time taken in manipulating the samples compared to the traditional design and allowed the tubes to be reused many times. Low procedural blanks for Os, Re and the PGEs were demonstrated.

A new *microfluorination method*<sup>361</sup> for the determination of δ<sup>18</sup>O values in quartz and silicate microfossils utilised high temperature pyrolysis with continuous flow IRMS. Dehydroxylated samples were mixed with PTFE powder and graphite in silver foil capsules and reacted in a standard thermal conductivity elemental analyser. The graphite provided an additional source of labile carbon, facilitating quantitative formation of CO during pyrolysis at 1450 °C.

### **4.3.2 Sample separation and preconcentration**

Several new *methods for the separation and purification of boron prior to isotopic measurements* have been proposed. In a protocol<sup>362</sup> based on sublimation of B, the silicate samples were first digested with HF and mannitol at 80 °C for 3 days. Doping the rock digests with a concentrated solution of NaCl before micro-sublimation in PFA vials appeared to suppress the evaporation of major elements and improve the B recovery. Artefacts in the B isotope ratios determined by MC-ICP-MS arising from silicon and other matrix elements in the sublimate were estimated to contribute a typical bias of  $<-0.8\text{‰}$   $\delta^{11}\text{B}$ . When combined with the uncertainty of the MC-ICP-MS measurements (better than 0.3‰) and the blank contribution of  $<0.3\text{‰}$ , the total uncertainty of the  $\delta^{11}\text{B}$  measurements was considered to be suitable for many geochemical investigations. In an alternative approach<sup>363</sup>, a B-specific resin, Amberlite IRA 743, was used to separate rock digests prepared by alkaline fusion (or acid dissolution for carbonates). The blanks from the three-column ion-exchange procedure ( $0.50 \pm 0.04$  ng, 2 RSD), were considered to be negligible compared to the sample size. More than 98% B was recovered from each step and the final solution medium was appropriate for analysis by TIMS and MC-ICP-MS. The reader may also wish to consult a recent review of B isotope variations in nature and methods for their determination<sup>364</sup>.

Of interest to isotope geochemists, for whom low analytical blanks are critical, is the development of a *Teflon HPLC system*<sup>365</sup>. Its construction was made possible by the availability of Teflon components used in the semi-conductor industry. Features of the system included a fluid-flow path that is entirely enclosed in Teflon, fully automated elution schemes in which the electronic controls are protected from corrosive fumes, temperature control of the entire system and a modular design that can be adapted to a variety of separation schemes. Using this system, it was possible to separate Ni from Mg using one long column at an elevated temperature, as opposed to up to five passes using traditional column chromatographic schemes. The effective separation of individual REEs could also be achieved using a long column and elevated temperatures. Although some challenges, such as the tailing of the REEs, still remained, this development may have a significant influence on how such analytical studies are conducted in the future.

Persimmon, a fruit rich in tannin and known to contain several polyphenols, was employed as a novel reagent for the *preconcentration of gold* from geological materials<sup>366</sup>. The persimmon was modified by treatment with 4M HNO<sub>3</sub> to promote crosslinking between tannin and polysaccharides and thereby improve its absorption characteristics. The powder was then used as a SPE adsorbent for the separation and preconcentration of Au in 3% *aqua regia* before analysis by ICP-MS. The LOD was 1.32 ng L<sup>-1</sup> (3 $\sigma$ ) and the precision (n=11) at

1.0  $\mu\text{g L}^{-1}$  0.83% (RSD). Another method<sup>191</sup> for the preconcentration of Au from anodic slime, gold ore, soil and waters samples was based on coprecipitation with a 1,2,4-triazole derivative and had a FAAS LOD of 0.36  $\text{pg L}^{-1}$  Au and a RSD of 5.1%.

*Elemental species in rocks* are rarely determined but knowledge of Cr species in phosphate rock is important when the rock is used as a precursor in the production of fertilisers<sup>367</sup>. In order to prevent interconversion of the Cr species, ultrasound digestion in 4 mL of 4M  $\text{HNO}_3$  was used and  $\text{Cr}^{\text{III}}$  was separated at pH 9 on MWCNTs acting as the SPE absorbent. The total Cr concentration was determined by FAAS after reduction of  $\text{Cr}^{\text{V}}$  to  $\text{Cr}^{\text{III}}$ . The LOD for  $\text{Cr}^{\text{III}}$  was 0.288  $\text{mg kg}^{-1}$ . For a full account of recent developments in speciation analysis, the relevant ASU<sup>4</sup> should be consulted.

## 4.4 Instrumental analysis

### 4.4.1 Atomic emission spectrometry

The analysis of *complex geological matrices, such as ores*, by ICP-AES often requires specific methods for optimum results. During the development of a protocol for the ICP-AES determination of 13 major and minor elements in nickeliferous minerals<sup>368</sup>, the most suitable digestion conditions, spectral lines, plasma operating conditions and matrix effects were all assessed experimentally. Matrix-matched calibration solutions with high levels of Fe or Mg were required to achieve accurate results. For the ICP-AES measurement of U in uranium ores<sup>369</sup>, the results at three U emission lines were compared using matrix-matched standards, plasma optimisation or an internal standard (Sm) as alternative ways of compensating for matrix interferences. The main factor influencing precision and accuracy was the U wavelength selected but use of a Sm internal standard improved accuracy at all the lines.

A tutorial review<sup>370</sup> of recent advances in *microwave plasma sources* for optical emission and MS highlighted the great number of different designs of MP cavities available and their future potential. Until recently, the use of MP-AES has mainly been confined to the analysis of gaseous samples, with limited application to liquids. However, this may change with the development of robust, commercially-available MIP-AES instruments offering fast sequential multi-element analysis. The potential of one such instrument for the bulk analysis of geochemical samples<sup>371</sup> and the determination of precious metals in rocks and ores<sup>372</sup> has been assessed. The technique provided LODs that were much superior to those obtained by FAAS (and comparable to ICP-AES LODs for some elements) with longer linear dynamic

ranges, thereby removing the need for time-consuming dilutions often required for FAAS. Data for major and minor elements in a series of geological RMs had good accuracy with a precision of  $\leq 3\%$ . Precious metals could be determined at sub  $\mu\text{g g}^{-1}$  levels after appropriate separation and preconcentration of the analytes. The instrument had the great advantage of low running costs as only nitrogen was required to operate the plasma so making it ideal for use in laboratories in remote locations.

#### **4.4.2 Inductively coupled plasma mass spectrometry**

Advances in instrumentation, not least the emergence of MC-ICP-MS, over the last 20 years has revolutionised the *analytical methods and innovations in isotope geochemistry*. In a review<sup>373</sup> (305 references) of recent discoveries and future challenges that still confront isotope geochemists, closer collaborations with chemists and physicists were encouraged because some observations emerging from stable isotope geochemistry have the potential for new insights into the nature of chemical bonds and reactions. Silicon isotope geochemistry is just one field that has grown rapidly since the advent of MC-ICP-MS so a review<sup>374</sup> (156 references) of the latest breakthroughs in high-temperature Si isotope geochemistry, and associated analytical methodologies, was very timely. Chiaradia *et al.*<sup>375</sup> offered basic guidelines to address some fundamental problems that they believed are overlooked in many geochronological studies designed to date magmatic-hydrothermal events in porphyry systems using a combination of U-Pb, Re-Os and  $^{40}\text{Ar}/^{39}\text{Ar}$  methods. A novel teaching exercise<sup>376</sup> designed to introduce the concepts of stable isotope fractionation to geochemistry students may be of interest to those involved in teaching the next generation of geochemists. Participants were asked to read several scientific papers and then develop spreadsheets to test the proposed fractionation models. Although the students found the construction of the spreadsheet the most challenging part of the exercise, many transferable skills were developed during the process.

Many of the recent developments in the *determination of isotope ratios in geological materials by ICP-MS* involve a combination of modifications in sample preparation and measurement procedures. Table 6 summarises this information.

**Table 6      Methods used in the determination of isotope ratios in geological materials by ICP-MS**

Analyte	Matrix	Sample treatment	Detector	Comments	Reference
B	Roman glass	Digested with HF–HNO <sub>3</sub> at 110 °C for 2 days; mannitol added and taken to dryness at 70 °C; <i>aqua regia</i> added and heated at 110 °C for 2 days; mannitol added and taken to dryness at 70 °C; residue redissolved in 0.02 M HCl. Two-step column separation: (a) cation-exchange resin Dowex AG 50W-X8, major cations retained on resin while B eluted with 0.02M HCl; (b) anion-exchange resin AG 1X8 to remove P and S.	MC-ICP-MS	Sample dissolution scheme devised to prevent B fractionation. Separation method fine-tuned to composition of glass samples. NIST SRM 610 (glass) used for validation. Mass bias correction using Li internal standard and sample-standard bracketing. Uncertainty of δ <sup>11</sup> B values was 1.6‰ (k=2).	377
B	Tourmaline and carbonate	Tourmaline: alkaline fusion with K <sub>2</sub> CO <sub>3</sub> and residue dissolved in HCl; dissolution in HCl for carbonate. Three-step column separation: (a) mixed cation-anion resin to remove major cations; (b) B-specific resin Amberlite IRA 743; (c) mixed cation-anion resin to convert acidic solution to neutral (only required for comparison between TIMS and ICP-MS). >98% recovery of B from each column.	MC-ICP-MS and TIMS	Final eluent split into two parts, one for TIMS after addition of CsOH, the other for ICP-MS after adding high purity HNO <sub>3</sub> . B blank 0.50 ± 0.04 ng (2 SD). Using NIST SRM 951 (boric acid solution), <sup>11</sup> B/ <sup>10</sup> B external precision was ±0.09‰ (n=10) for TIMS and 0.11‰ (n=100) for MC-ICP-MS. In latter method, mass bias correction with sample-standard bracketing procedure plus blank correction for B memory.	363
B	Geological RMs	Digested with HF–HNO <sub>3</sub> and mannitol at 80 °C for 3 days; taken to dryness at 65 °C; HNO <sub>3</sub> added and heated at 80 °C for 4 h. Solution centrifuged to separate supernatant, doping with NaCl before B separated using modified micro-sublimation technique.	MC-ICP-MS	B blank ~ 20 ng. Mass bias corrected by sample-standard bracketing procedure plus blank correction for B memory. Using NIST SRM 951 (boric acid solution) <sup>11</sup> B/ <sup>10</sup> B external precision was ±0.3‰ (2SD, N=8).	362
Ba	Geological RMs	Digestion with HClO <sub>4</sub> –HF (1+4), followed by HClO <sub>4</sub> –HCl (1+4), then HCl alone, with final uptake in 2.5 M HCl. Separation by cation-exchange chromatography on AG50W-X8.	MC-ICP-MS	Ba blank <13 pg. Method based on <sup>130</sup> Ba– <sup>135</sup> Ba double-spike, sample-standard bracketing protocol. Instrumental setup for low oxide ratios: BaO/Ba <0.1%. Ba ratio in double spike determined using an iterative calibration method developed in this study. Reproducibilities about 5x better than previous study.	378
Ca	Terrestrial and meteoritic samples	Digested in HF–HNO <sub>3</sub> at 130 °C for 4 days; dried and redissolved in 6N HCl; dried and redissolved in 0.5N HNO <sub>3</sub> and centrifuged. Three-step separation: (a) Ca separated from sample matrix using Eichrom DGA extraction chromatography resin (b) second pass through DGA resin; (c) Ca separated from Sr using Sr-specific resin. Combined Ca yield was >98%.	MC-ICP-MS	Total procedural blanks <1 ng Ca. Ti interferences were too large to obtain precise data for <sup>46</sup> Ca and <sup>48</sup> Ca. Mass bias corrected using sample standard bracketing protocol with NIST SRM 915b (calcium carbonate) and resulting data normalised to SRM 915a.	379
Cu, Fe	Igneous rocks	Digested in HF–HNO <sub>3</sub> at 160 °C; dried residues refluxed with HNO <sub>3</sub> –HCl and dried at 80 °C; refluxed with HNO <sub>3</sub> and dried residues taken up in HCl plus a trace of H <sub>2</sub> O <sub>2</sub> . One-step anion exchange chromatography on Bio-Rad AG-MP-1M used to	MC-ICP-MS	Procedural blanks 1-2 ng Cu and 2-10 ng Fe. Cu isotopes measured in low resolution mode and Fe ratios in high resolution mode using sample standard bracketing. Once issues of incomplete recovery,	380



		separate Cu and Fe, unlike previous methods which required different schemes for the two analytes.		mismatch in acid molarity and concentration between standards and samples, and isobaric interferences from matrix elements had been addressed, long term precision better than 0.05‰ (2 SD) for $\delta^{65}\text{Cu}$ and $\delta^{56}\text{Fe}$ obtained.	
Cu, Sb	Ancient glass	Modified preparation protocol to obtain Cu and Sb from the same digest. HF–HNO <sub>3</sub> at 110 °C for 2 d; dried and redissolved in <i>aqua regia</i> ; dried and redissolved in 0.14M HF and used directly for Sb isotope measurements; an aliquot evaporated and redissolved in 8M HCl for Cu isotope ratios. Various separation protocols based on AG MP-1 anion-exchange resin evaluated for Cu; Sb purified by cation-exchange chromatography.	MC-ICP-MS	Recoveries from anion-exchange 100±5% for Cu and >94% for Sb. Sb A small amount of Co was co-eluted with Cu but did not affect accuracy. Samples analysed using a sample standard bracketing protocol; Zn and In added as internal standards for Cu and Sb respectively. Revised Russell's law used to correct Cu and Sb for instrumental mass fractionation.	381
Hf	Ilmenite and rutile (Ti-rich minerals)	Mixed acid HF initial digestion, then with HCl, take up in HCl with trace of HF. Separation of Hf from high TiO <sub>2</sub> content by 3 column chemistry: (a) Fe and REEs elimination on AG50W-X8 resin; (b) Elimination of most of Ti using AG1-X8 resin; (c) HClO <sub>4</sub> evaporation (3 times) before successful separation of remaining Ti from Hf and Zr on AG50W-X8 cation-exchange resin.	MC-ICP-MS	Hf and Lu concentrations measured by SF-ICP-MS. Corrections for isobaric interferences on <sup>176</sup> Hf made using natural abundances of Lu and Yb isotopes and by measuring <sup>172</sup> Yb and <sup>175</sup> Lu, which were corrected for mass bias using <sup>179</sup> Hf/ <sup>177</sup> Hf. JMC-475 Hf reference solution used to bracket every 2 samples. Modified column chemistry improved yields from 2-5% to 78-100% for ilmenite compared to previous studies.	382
Lu	Rocks and minerals	HF–HNO <sub>3</sub> digestion, then conc HNO <sub>3</sub> (3 times), then 6M HCl before take up in HCl. Separation of Lu in 4 steps using 3 columns: (a) separation of Fe and U using anion-exchange chromatography; (b) separation of heavy REEs on Ln-Spec resin; (c) separation of Lu from Yb using a longer column containing finer-grained Ln-Spec resin; (d) repeat of step (c) to minimise amount of Yb in Lu fraction.	MC-ICP-MS	All standards and samples spiked with W metal and normalised to the nominal W isotopic composition to correct for drift and instability. Mass bias corrected by normalisation to the Ames Lu standard. After correction for isobaric interferences, particularly <sup>176</sup> Yb, precision on <sup>176</sup> Lu/ <sup>175</sup> Lu was close to their target value of 0.1 ‰. Use of NIST 3130a (Lu solution) as bracketing standard was proposed.	383
Nd	Geological RMs	HF–HNO <sub>3</sub> – HClO <sub>4</sub> digestion, residue dissolved in HCl. REEs separated on cation-exchange resin AG50W-X8; no chemical separation of Sm from Nd or addition of enriched isotope spikes. Method may need further validation for geological samples containing significant amounts of refractory minerals.	MC-ICP-MS	Blank <0.1 ng for Sm and Nd. Isobaric interferences on Nd isotopes were reassessed. Sm interference on <sup>144</sup> Nd corrected using the exponential law and selected Sm isotopic compositions. Sm/Nd ratios agreed well with previous values when sample bracketed with matrix-matched secondary standards. Four USGS RMs (2 basalts, an andesite and a rhyolite) used for method validation.	384
Nd	Geological	HF–HNO <sub>3</sub> digestion, then concentrated HNO <sub>3</sub> , and final take	MC-ICP-MS	Careful control of conditions for separation by gave	385

	materials	up in HCl. Separation by two column chromatography: strong cation resin, AG50W-X12, to separate the REEs, then Nd purified on Ln resin treated with HDEHP.		Nd recoveries close to 100%; Sm and Ce removed to the extent that the interferences could be corrected effectively. Precisions comparable and Nd isotope data identical within analytical error to those obtained the double spike method. Validation on range of rock RMs including granites.	
Ni	Geological materials	Initial digestion: silicates HF–HNO <sub>3</sub> (1+3), non-silicates HNO <sub>3</sub> –HCl (1+1); dried and redissolved in HNO <sub>3</sub> –HCl; final takeup in HCl with a trace of H <sub>2</sub> O <sub>2</sub> . Two-step column separation: (a) anion-exchange on AG1-X8, addition of Ni double-spike, then (b) Ni-specific resin.	MC-ICP-MS	Procedural blanks 3-4 ng Ni. Double-spike correction scheme presented. Interference correction for <sup>58</sup> Fe isobar on <sup>58</sup> Ni; Cu isotopes used to correct for instrumental mass bias. Precision of ±0.02 – 0.04‰ (2SE) for δ <sup>56</sup> Ni/ <sup>58</sup> Ni.	<sup>386</sup>
Pb-U	Carbonates	Sample dissolved in HNO <sub>3</sub> , dried and redissolved in acetic acid ready for a new separation protocol based on AG 1-X8 anion-exchange resin. A mobile phase of 90% acetic acid was used to elute the matrix components before Pb, Th and U were eluted with 2% HNO <sub>3</sub> .	MC-ICP-MS	Blanks of 6.4 pg Pb, 1.8 pg Th and 8.4 pg U were attained if the acetic acid was purified prior to use in separations; Pb blank still the major factor limiting the analytical precision. Method sufficiently free of matrix-induced instrumental biases to be appropriate for U-Th-Pb chronology. Method validation by analysis of speleothem.	<sup>387</sup>
Pt	Geological RMs	Addition of <sup>196</sup> Pt- <sup>198</sup> Pt spike prior to digestion by NiS fire assay procedure and separation by anion-exchange chromatography on AG1-X8 resin.	MC-ICP-MS	At least 90-95% Pt recovered from column chemistry. Blanks typically 0.5-2 ng. Precision ±0.040 (2 SD) for δ <sup>198</sup> Pt in solution RM but poorer (e.g. ±0.088, 2 SD) for rock RMs.	<sup>388</sup>
S	Uranium ore concentrates	Sample powders leached with ultra-pure water for 24 h at room temperature to obtain leachable sulfate. Sulfate separated from other anions using anion-exchange resin AG 1-X4.	MC-ICP-MS	CRMs IAEA-S-2, IAEA-S-3, IAEA-S-4 used for method validation. Matching of sample matrix to that of bracketing standard was necessary to obtain accurate results. δ <sup>34</sup> S uncertainty 0.45-1.9‰ (k=2)	<sup>389</sup>
Sb	Roman glass	Digested with HF–HNO <sub>3</sub> at 110 °C for 2 days; taken to dryness at 70 °C; <i>aqua regia</i> added and heated at 110 °C for 2 days; evaporated at 90 °C and residue redissolved in 0.14M HF. Two-step column separation: (a) separation of Sb from major cations using AG50-X8; (b) purification of Sb on weak anion-exchange resin Amberlite IRA 743.	MC-ICP-MS	NIST SRM 610 (glass) used for validation (see ref. <sup>377</sup> ). Better precision obtained when mass bias corrected using “revised Russell’s law” compared to sample standard bracketing procedure. External precision of <sup>123</sup> Sb/ <sup>121</sup> Sb ratio in glass was ca. 0.4ε.	<sup>390</sup>
Se	Organic-rich shales	Digestion with HF–HNO <sub>3</sub> –HClO <sub>4</sub> at 130 °C for 2 days; excess acid evaporated to incipient dryness; 6M HCl added to reduce Se <sup>VI</sup> to Se <sup>IV</sup> ; insoluble fluorides removed by centrifugation. Se purified using thiol-impregnated cotton fibre. <i>Aqua regia</i> treatment after column extraction to reduce Ge content and organic compounds.	Quadrupole ICP-MS	Precision better than 0.2‰ for most Se ratios. Mass bias corrected using sample standard bracketing with NIST SRM 3149 (Se solution). Concentration of Se in standards and samples needed to be matched to within 5% to minimise the impact of isobaric interferences.	<sup>391</sup>

Te	Au-Ag telluride ores	Digestion in <i>aqua regia</i> at 80 °C overnight, evaporated to incipient dryness and dissolved in 2N HCl. Isolation of Te from matrix elements, particularly Ag, by anion-exchange chromatography on AG 1-X8 resin with <i>ca.</i> 96% yield.	MC-ICP-MS	Cadmium used to correct for mass bias. Precision was $\pm 0.10\%$ for $^{130}\text{Te}/^{125}\text{Te}$ under wet plasma conditions.	<sup>392</sup>
Th-U	Carbonates	Dissolution in HNO <sub>3</sub> , addition of $^{229}\text{Th}$ - $^{236}\text{U}$ spike, and UTEVA extraction chromatography to separate Th and U from matrix elements. Up to 24 samples could be processed simultaneously.	MC-ICP-MS	Sample standard bracketing routine plus double spike to correct for instrumental mass bias. Development of open source algorithm to process U and Th data and calculate an accurate age and uncertainty propagation. Technique validated by replicating U-Th ages in speleothem.	<sup>393</sup>

Various methods of *correcting for mass discrimination*<sup>394</sup> were assessed for two target elements, one in the low mass region (B) and one in the medium mass region (Sb). Using synthetic solutions containing Be, Cs, Be+Cs, or Fe, the performance of the correction protocols in the presence of matrix elements was also evaluated. For B, all approaches to mass bias correction produced data of similar quality, with standard-sample bracketing giving slightly better precision, but for Sb common analyte internal standardisation and the revised Russell's law provided better precision and accuracy.

A compilation<sup>395</sup> of *Ca isotope data* in over 70 published studies provided a fascinating insight into our current understanding of the global biogeochemical cycle of Ca and the utility of Ca isotopes as a proxy for examining the Earth's history. It included a description of determining Ca isotope ratios by TIMS and MC-ICP-MS, highlighting the analytical challenges in their measurement and inconsistencies in the way external reproducibilities were reported. When the data were converted to a single reference scale based on NIST SRM 915a (artificial carbonate), a significant difference between  $\delta^{44}\text{Ca}$  in carbonate (0.60‰) and silicate (0.94‰) samples was demonstrated. A new method<sup>379</sup> for determining Ca isotope ratios by MC-ICP-MS with sufficient precision to explore genetic links between Earth and meteorites is included in Table 5.

Accurate measurements of *boron concentrations and isotope ratios by ICP-MS* depend on minimising losses and isotope fractionation during sample digestion and any subsequent manipulation of the samples. Mannitol is often added to an acid digest<sup>362, 377</sup> to complex B but this does not always completely suppress B volatilisation. In an alternative strategy<sup>396</sup> for determining B concentrations by ID quadrupole ICP-MS, rock powders were spiked with  $^{10}\text{B}$ -enriched NIST SRM 952 (enriched boric acid) before dissolution in a slight excess of HF on a hot plate at 65–70 °C for up to 72 h. After centrifugation, the supernatant in *ca.* 0.3M HF was analysed directly using a PFA inert introduction kit to reduce memory effects and contributions to the blank from contact with borosilicate glass. This ID procedure had a very low blank of <0.5 ng B so was particularly suitable for samples with low B contents. An improved procedure<sup>397</sup> for the measurement of B/Ca ratios in foraminifera by HR-ICP-MS had a B/Ca blank of  $2.0 \pm 1.0 \mu\text{mol mol}^{-1}$ , an external precision of  $\leq 4.0\%$  ( $2\sigma$ ) and the capability of analysing 60 samples a day, making it well suited for routine measurements in paleoclimatic studies.

The precisions obtained for *strontium isotope ratios* in geological materials by MC-ICP-MS now rival those achieved by TIMS using a  $^{84}\text{Sr}$ - $^{87}\text{Sr}$  spike, as demonstrated by Ma *et al.*<sup>398</sup> who improved the stability of the instrumental mass discrimination by carefully

controlling carryover on a MC-ICP-MS instrument by using a vigorous in-run washing procedure to reduce memory effects. The reported precision of  $\pm 0.010\text{--}0.014\%$  for  $\delta^{88}\text{Sr}/^{86}\text{Sr}$  was 2-3 times better than previously published data obtained by MC-ICP-MS without spiking. In a study<sup>399</sup> on the effect of high barium concentrations on the accuracy and precision of Sr isotope measurements, the measured Sr isotopic composition became inaccurate when the Ba concentration in the sample solution exceeded 1 ppm. This effect was related to matrix-dependent changes in mass discrimination processes. Consequently, a 125  $\mu\text{L}$  rather than a 1 mL column volume was chosen for extraction chromatography with Eichrom Sr Spec resin. The Ba was washed from the column with 8M  $\text{HNO}_3$  before Sr was collected. The modified method was successfully employed for the measurement of  $^{88}\text{Sr}/^{86}\text{Sr}$  and  $^{88}\text{Sr}/^{87}\text{Sr}$  in barite and seawater. A concentration gradient method<sup>400</sup> for improving the precision of isotope ratio data obtainable by quadrupole ICP-MS was demonstrated for Pb and Sr. In this method, the isotopes of interest were measured, in TRA mode, in a series of sample solutions spiked with different amounts of the analyte, *i.e.* 50, 40, 30, 20, 10 and 0  $\mu\text{g L}^{-1}$ . The sample sequence was designed to ensure a very high repeatability and minimised the number of rinsing steps to achieve the best plasma stability. The resulting signal intensities for each isotope were plotted against each other and the slope of the regression line was, by definition, the isotope ratio. Nine measurements of J P Baker standard solution yielded a mean  $\delta^{87}\text{Sr}/^{86}\text{Sr}$  of  $-3.23\%$  with a measurement uncertainty of  $\pm 0.21\%$ .

*Investigations into interferences* from titanium and chromium species on Cu isotope measurements<sup>401</sup> by MC-ICP-MS showed that artificial solutions designed to mimic the Cr:Cu:Ti ratios of sediment samples after anion-exchange chromatography did not behave in the same manner. For example,  $^{67}\text{Zn}/^{68}\text{Zn}$  proved to be the most appropriate Zn isotope ratio for mass bias corrections in the artificial solutions but caused the largest error in  $\delta^{65}\text{Cu}$  when used for external normalisation in real samples. It also proved difficult to predict formation of Cr and Ti polyatomic species in the plasma as it varied with sample matrix. Consequently, optimal removal of Cr and Ti by a two-step chromatographic purification plus rigorous monitoring of six Zn isotope ratios to verify the absence of spectral interferences were recommended for the determination of accurate Cu isotope ratios in sediments. A study<sup>402</sup> of potential factors affecting the accuracy and precision of Mg isotope ratios by MC-ICP-MS indicated that the presence of matrix elements and mismatches between the Mg concentration and acid strength in samples and standards could result in analytical artefacts that were comparable in size to the total magnitude of the variation of Mg isotope ratios in silicate

rocks. Possible mechanisms for effects observed, which varied considerably for different instruments, were discussed in detail.

The performance characteristics of *tandem quadrupole ICP-MS* with collision-reaction cell technology were demonstrated in the determination of very low  $^{236}\text{U}/^{238}\text{U}$  ratios<sup>403</sup>. Peak tailing of the major  $^{238}\text{U}$  on the  $^{236}\text{U}$  peak was reduced to *ca.*  $10^{-10}$  and the interference of  $^{235}\text{UH}^+$  on  $^{236}\text{U}$  was effectively reduced to a ratio of  $1 \times 10^{-8}$  by reaction of  $^{235}\text{UH}^+$  with oxygen in the collision-reaction cell. The  $^{236}\text{U}/^{238}\text{U}$  ratios, measured as  $^{236}\text{U}^{16}\text{O}^+ / ^{238}\text{U}^{16}\text{O}^+$ , were determined in the range  $10^{-7}$  to  $10^{-9}$  using Tl to correct for mass bias but without correction for spectral interferences. Although the procedure was validated using synthetic solutions and seawater, it is evident that this relatively simple and rapid technique could be applied to various environmental samples for the monitoring of radioactive contamination arising from nuclear waste.

Although ICP-MS offers *multi-element analysis of geological materials* on a routine basis, improved protocols are still sought for some elements, particularly the PGEs. The Se and Te contents of nine RMs and 79 other geological materials, covering a wide range of compositions, were measured to provide a better understanding of the relationship between Se and Te in the geological environment<sup>404</sup>. After acid digestion, thiol cotton fibre was used to separate Se from samples containing high concentrations of interfering elements. The LODs by quadrupole ICP-MS were 0.02 and 0.005  $\mu\text{g g}^{-1}$  for Se and Te, respectively. A single acid digest obtained by high pressure ashing was used<sup>405</sup> to determine both the Ir, Pd, Pt, Re, Ru, S, Se and Te abundances in 18 geological RMs by ID-SF-ICP-MS and the Os isotopes by NTIMS. The PGEs were separated using 50W-X8 cation-exchange resin, a two-step ion-exchange chromatography method being needed to separate S, Se and Te from the matrix elements. Unsurprisingly, the measured PGE concentrations in most RMs were highly variable as the test portions taken were 1 g or less. In contrast, good precisions (<5% RSD) were obtained for S, Se and Te. Another procedure<sup>406</sup> for the measurement of PGEs by ID-ICP-MS and Os-Re isotopes by NTIMS involved an inverse *aqua regia* digest of 1-2 g of sample powder in a Carius tube with  $^{99}\text{Ru}$ ,  $^{105}\text{Pd}$ ,  $^{185}\text{Re}$ ,  $^{190}\text{Os}$ ,  $^{191}\text{Ir}$  and  $^{194}\text{Pt}$  spikes. Osmium was separated by  $\text{CCl}_4$  solvent extraction before a two-stage column separation involving cation-exchange on AG50W-X8 followed by purification of PGE-Re using BPHA extraction resin. Although the PGE-Re concentration and Os isotope data for the four CRMs analysed agreed well with published data, nugget effects were evident in some of the data. The importance of sampling, nugget effects and analytical methodologies were highlighted in a study<sup>407</sup> of siderophile element abundances across the Cretaceous-Paleogene boundary. New

PGE data for 113 samples from 38 sections across this boundary worldwide were obtained by quadrupole ICP-MS after nickel sulfide fire assay.

#### **4.4.3 Other mass spectrometric techniques**

**4.4.3.1 Thermal ionisation mass spectrometry.** Many of the recent developments in *TIMS measurements of isotope ratios in geological materials* have concerned improved methods of purification of the element of interest combined with modifications in the measurement strategy. This information is summarised in Table 7.

**Table 7        Methods used in the determination of isotope ratios in geological materials by TIMS**

Analyte	Matrix	Sample treatment	Detector	Comments	Reference
B	Biogenic carbonates	Dissolution in 1.7N HCL to give <i>ca.</i> 750 ppb B in solution. Separation of B using improved micro-sublimation method at 70-74 °C for 12 h.	NTIMS	Total evaporation method on a Re filament, with a sample size of <1 ng B, with normalisation to NIST SRM 951a (boric acid). Reproducibility better than 1.4‰ (2 SD, n>10) was achieved for standards with a range of B isotope ratios. Analysis of NIST SRM 951 (boric acid) gave a mean value for $^{11}\text{B}/^{10}\text{B} = 4.0328 \pm 0.0054$ (2 SD, n=25).	<sup>408</sup>
B	Foraminifera (and seawater)	Organic materials oxidised before dissolution. Two-step chromatographic separation: (a) Amberlite IRA 743 B-selective resin; (b) mixed ion-exchange resin, followed by micro-sublimation.	TIMS	Static multicollector method using $\text{Cs}_2\text{BO}_2^+$ ions and custom designed arrangement of Faraday collectors, with graphite loading onto Ta filaments. Typical blank <20 pg B. Repeated analyses of 25 ng B of NIST SRM 951 (boric acid) gave a mean value for $^{11}\text{B}/^{10}\text{B} = 4.05229 \pm 0.00028$ (n=36).	<sup>409</sup>
B	Tourmaline and carbonate	Tourmaline: alkaline fusion with $\text{K}_2\text{CO}_3$ and residue dissolved in HCl. Dissolution in HCl for carbonate. Three-step column separation: (a) mixed cation-anion resin to remove major cations; (b) B-specific resin Amberlite IRA 743; (c) mixed cation-anion resin to convert acidic solution to neutral (only required for comparison between TIMS and ICP-MS). >98% recovery of B from each column.	TIMS and MC-ICP-MS	Final eluent split into two parts, one for TIMS after addition of CsOH, the other for ICP-MS after adding high purity $\text{HNO}_3$ . B blank $0.50 \pm 0.04$ ng (2 SD). Using NIST SRM 951 (boric acid solution), $^{11}\text{B}/^{10}\text{B}$ external precision was $\pm 0.09\%$ (n=10) for TIMS and $0.11\%$ (n=100) for MC-ICP-MS. In latter method, mass bias correction with sample-standard bracketing procedure plus blank correction for B memory.	<sup>363</sup>
Nd	Coral	Extensive physical cleaning, digested in 8M $\text{HNO}_3$ , then refluxed in <i>aqua regia</i> to destroy organic compounds. Final solution in $\text{HNO}_3$ spiked with $^{150}\text{Nd}$ . Two-step column chemistry: (a) Eichrom RE resin to separate REEs from sample matrix; (b) Ln resin to separate Nd from rest of REEs. Blanks <5 pg Nd.	TIMS	Nd measured as $\text{NdO}^+$ ; best loading technique for generating high and stable Nd ion beam intensities was to use a micro-loading technique and $\text{TaF}_5$ activator on single W filaments. External reproducibility of $\pm 16$ ppm (2 SD) demonstrated on 10 ng and 30 ng Nd loads isolated from USGS RM BCR-2 (basalt) and an in-house coral RM.	<sup>410</sup>
Nd, Sm	Ultramafic rocks	Digestion with $\text{HF} + \text{HNO}_3 + \text{HClO}_4$ , then $\text{HClO}_4$ at 190-200 °C to digest chromite; $\text{H}_3\text{BO}_3$ dissolution of fluorides. REEs separated using cation-exchange chromatography, Sm and Nd separated on Ln columns.	TIMS	Nd isotopes determined as $\text{NdO}^+$ , Sm isotopes as $\text{Sm}^+$ , both with very high sensitivity using single W filaments with $\text{TaF}_5$ as an ion emitter. Sm/Nd concs as well. No $\text{Fe}(\text{OH})_3$ precipitation step required.	<sup>411</sup>
Os	Geological materials	Method development carried out using two RM solutions; Durham Romil Os Standard (IAGeo Limited) and University of Maryland Johnson Matthey Os standard.	NTIMS	Static collection of $\text{OsO}_3^-$ using Faraday cups and amplifiers fitted with $10^{12}\Omega$ resistors. For sample loads as small as 0.025 ng Os, isotope data with precisions of 0.1% or better were obtained.	<sup>412</sup>
Pb	Baddeleyite ( $\text{ZrO}_2$ )	Selected mineral grains cleaned in 4N $\text{HNO}_3$ . No other preparation required. Procedural blanks <1 pg Pb.	TIMS	Grains were embedded in silica glass on rhenium filaments. Thermal extraction TIMS method employed, with collection of Pb isotope signals in static multi-collector mode when the	<sup>413</sup>



				temperature of the filament was between 1530 and 1580 °C. The accuracy and precision of $^{207}\text{Pb}/^{206}\text{Pb}$ ages obtained were comparable with U-Pb ages obtained by conventional methods.	
Sr	Geological materials	A $^{84}\text{Sr}$ - $^{87}\text{Sr}$ double spike added prior to separation of Sr from major cations in $\text{CaCO}_3$ and silicate samples on Eichrom Sr-specific resin. Total blank <0.2 ng Sr.	TIMS	Double spike calibration routine and algorithm described, together with data reduction method based a user-friendly computer programme developed specifically for Sr double spike. External precision for $\delta^{88}\text{Sr}$ better than 0.02‰ (1 SD). Sr isotope data reported for several carbonate, phosphate and silicate USGS RMs.	<sup>414</sup>
Te	Rocks and carbonaceous chondrites	Dissolution in $\text{HF}+\text{HNO}_3$ , take up in HCl. Three-step column chemistry: (a) AG1-X8 resin to remove major elements; (b) TRU-Spec resin to separate Te from Sn; (c) AG1-X8 resin to remove organic matter derived from TRU-Spec resin. Yield of 98% Te reported.	NTIMS	Optimum analytical conditions for a strong $\text{Te}^-$ ion beam obtained with a zone-refined Re single filament and $\text{Ba}(\text{OH})_2$ activator. Reproducibilities of Te isotope ratios obtained by static multicollection using Faraday cups comparable to those in previous studies by MC-ICP-MS.	<sup>415</sup>

A significant instrumental advance was the development of *new*  $10^{13} \Omega$  resistors<sup>416</sup>, which theoretically have 10-times lower noise levels than the  $10^{11} \Omega$  resistors normally fitted in the feedback loop of Faraday cup amplifiers in TIMS instruments. Their improved performance was demonstrated by measuring Nd and Sr isotope ratios in samples containing 10 and 100 pg of these elements. Variations in the fourth decimal place of  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{87}\text{Sr}/^{88}\text{Sr}$  ratios could be resolved provided the procedural blanks and chemical separation were optimal.

Measurements by TIMS and MC-ICP-MS were both addressed in a review<sup>364</sup> of *methods for the determination of B isotopes* and their application in various branches of geochemistry. In a new approach<sup>408</sup> to the analysis of carbonate materials for B isotopes by total evaporation TIMS, a micro-sublimation device was developed in which 20 samples could be processed simultaneously. Quantitative recovery of B and low blanks, with separation from major elements and organic matter, were achieved without chromatographic separations or treatment with  $\text{H}_2\text{O}_2$ . Boron isotope data for a range of environmental samples, including foraminifera, were measured using a modified TIMS procedure<sup>409</sup> based on static multicollection of  $\text{Cs}_2\text{BO}_2^+$  ions.

Lehn *et al.*<sup>417</sup> discussed their current best practices for *measuring*  $\delta^{44}\text{Ca}/^{40}\text{Ca}$  by MC-TIMS. These included the addition of a  $^{43}\text{Ca}$ - $^{42}\text{Ca}$  double spike to the sample prior to purification and optimising the technique using a Monte Carlo error model. Improvements in their experimental protocol eliminated drift within a measurement session and the resultant external precision for  $\delta^{44}\text{Ca}/^{40}\text{Ca}$  was  $\pm 0.041\%$  (2 SD).

Three different measurement protocols for the TIMS determination of the *absolute abundance of*  $^{40}\text{K}$  were tested<sup>418</sup> on two NIST KCl SRMs (918b and 985). All the results agreed with the terrestrial  $^{40}\text{K}/^{39}\text{K}$  value suggested by IUPAC but had better precisions. An amplifier configuration that used  $10^{10}$ ,  $10^{11}$  and  $10^{12} \Omega$  resistors on the three Faradays cups provided the most accurate results. The new data provided by this study will serve to reduce the uncertainty of K-Ar ages measured on geological materials.

**4.4.3.2 Secondary ion mass spectrometry.** There is much interest currently in the use of SIMS to make *accurate, high precision measurements of oxygen isotopes* in a variety of matrices. For example, it was possible to resolve subtle intragrain variations of  $\delta^{18}\text{O}$  in titanite<sup>419</sup> by SIMS at the 10  $\mu\text{m}$  scale. By careful comparison of microstructural and compositional data, patterns of  $\delta^{18}\text{O}$  zoning were shown to reflect processes such as

diffusion, recrystallisation and crystal growth. Spot-to-spot precision for  $^{18}\text{O}/^{16}\text{O}$  SIMS measurements in Ca-Mg-Fe garnet grains<sup>420</sup> was  $\pm 0.2\%$  (2s) or better, as expected from consideration of shot noise and Faraday detector noise. The uncertainties due to spot-to-spot repeatability were of a similar magnitude to the uncertainties associated with matrix corrections and uncertainties in the RM values which, in some cases, dominated the uncertainty budget.

The high spatial resolution of SIMS makes it suitable for probing fine growth structures in *biogenic carbonates*, such as foraminifera and corals skeletons, and inferring past climate conditions from their geochemistry. Scanning white light interferometry was used to determine the dimensions and volumes of craters produced by SIMS analysis of the skeleton of an aragonitic coral<sup>421</sup> during the measurement of  $\delta^{11}\text{B}$ ,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . Crater widths ranged from *ca.* 17  $\mu\text{m}$  ( $\delta^{13}\text{C}$ ) to *ca.* 36  $\mu\text{m}$  ( $\delta^{11}\text{B}$ ), and their depths from  $\leq 3$   $\mu\text{m}$  ( $\delta^{18}\text{O}$ ) to  $>20$   $\mu\text{m}$  ( $\delta^{11}\text{B}$ ). These dimensions may be significant compared to accretion rates in some biogenic carbonates if the organisms grow slowly. In a comparison<sup>422</sup> of the performance of SIMS and nano-SIMS for the measurement of Mg/Ca, Sr/Ca and Ba/Ca ratios in carbonates, the internal variability of  $<1\%$  on both machines was dominated by counting statistics. However, not all of the nine carbonate RMs examined were homogeneous enough within individual crystals to be used to monitor the accuracy and precision of the data. In general, matching the element:Ca ratios of the standards with those of the sample was not as important as finding homogeneous materials for calibration. It was concluded that independent measurements, *e.g.* by ID-ICP-MS, were required for most of the standards tested, even if they were from the same batch. In a study<sup>423</sup> of C and H stable isotopes in the rare carbonate minerals malachite and stichtite, SIMS data were corrected for instrumental mass fractionation using whole rock compositions determined by traditional stable isotope analysis. It was shown to be a viable strategy for data correction when well characterised RMs were not available for microanalytical calibration.

*Time-of-flight SIMS* has become a very popular technique for obtaining well-resolved 2D and 3D elemental and isotopic maps. It also has the potential to determine parameters that control the surface reactivity of minerals and thus their behaviour during mineral beneficiation by froth flotation. A review<sup>424</sup> of research relevant to this application (73 references) examined the capacity of TOF-SIMS to provide reliable surface chemical data for evaluating factors controlling stream partitioning in various mineral flotation processes. A novel mode of TOF-SIMS operation for improved accuracy and lateral resolution of oxygen

isotope measurements was devised<sup>425, 426</sup> for measuring oxygen diffusion coefficients in industrial oxides; this may become relevant to geochemical applications in the future.

A study<sup>427</sup> of *zircons with high U contents* demonstrated that when zircons with extreme radiation damage were analysed by SIMS, an apparent increase in U-Pb age and a real decrease in  $\delta^{18}\text{O}$  were observed. Potential mechanisms for this behaviour were proposed along with strategies for zircon selection.

**4.4.3.3 Accelerator mass spectrometry.** A noteworthy *review*<sup>428</sup> of major developments in AMS over the last 25 years identified key advances during this period (285 references). One of the most remarkable advances has been the development of small AMS machines and their role in establishing AMS facilities worldwide. The main nuclides used in geological applications,  $^{10}\text{Be}$ ,  $^{14}\text{C}$ ,  $^{26}\text{Al}$  and  $^{36}\text{Cl}$ , were discussed in relation to AMS instrumentation, cosmogenic nuclide production rates, methods of surface exposure dating, measurement of erosion and weathering, burial dating and meteoric  $^{10}\text{Be}$ . A critical comparison<sup>449</sup> of analytical techniques for the determination of  $^{129}\text{I}$  (85 references) concluded that AMS is the most sensitive method available. Because of the significant increase in the number of AMS facilities over the last ten years, combined with the reduction in costs and its superior detection capabilities, AMS replaced NAA as the most popular method for the measurement of  $^{129}\text{I}$  from the year 2000 onwards. Progress in chemical separation and purification of  $^{129}\text{I}$  for its detection at very low concentrations by AMS has been a critical factor in expanding the number of applications of  $^{129}\text{I}$  data in environmental and geological research, including its use in the investigation of radioactive contamination from the Fukushima incident.

For *measurements of  $^{10}\text{Be}$  by AMS*, a carrier solution containing stable  $^9\text{Be}$  is normally added prior to radiochemical separation of  $^{10}\text{Be}$  to enhance the amount of  $^9\text{Be}$  in the final BeO target. Because the levels of  $^{10}\text{Be}$  are too high in commercial  $^9\text{Be}$  solutions, Merchel *et al.*<sup>429</sup> prepared a  $^9\text{Be}$  solution from phenakite ( $\text{Be}_2\text{SiO}_4$ ), containing very low concentrations of  $^{10}\text{Be}$ . In a round-robin exercise to establish an accurate  $^9\text{Be}$  value for this solution, it was evident that even nowadays the determination of  $^9\text{Be}$  can be challenging: the preliminary data reported had a SD of *ca.* 8%! As the accuracy of  $^{10}\text{Be}$  data is dependent on that of the  $^9\text{Be}$  concentration, it was recommended that all AMS laboratories using in-house  $^9\text{Be}$ -carrier solutions should have them analysed by at least one independent laboratory. Regular participation in  $^9\text{Be}$  inter-laboratory comparisons was also advocated.

#### 4.4.4 X-ray techniques

For up-to-date information on *instrumental developments and applications of X-ray techniques*, readers should consult the ASU review on XRF<sup>5</sup> whose sections covering geological and related applications are substantial.

*Synchrotron XRF* microscopy was employed for elemental mapping of carbonaceous chondrites<sup>430</sup>. Data were collected using a 2  $\mu\text{m}$  spot size at very low dwell times (0.1 – 0.5 ms), resulting in maps of entire thin sections in approximately 5 h. The penetration of the X-ray beams and characteristic lines of fluoresced elements enabled structures at depth to be detected and imaged at full resolution. In a study<sup>431</sup> of the properties of argillaceous rocks and their suitability for the disposal of radioactive waste, elemental mapping with synchrotron  $\mu$ -XRF was used to identify the main mineral groups responsible for the uptake of different metal ions by clay-rich rocks. Multivariate methods were found to be efficient tools for extracting information from the elemental maps for the clay matrix and fracture infill regions. By using positive matrix factorisation as a new approach, the factors with higher sorption capacity could be identified and, together with additional mineralogical information, the uptake capacity of different mineral phases could be quantified.

Sulfide- and oxide-bearing RMs were mapped using EDXRF to provide spatial information on the *heterogeneity of RMs*<sup>432</sup>. The RM powders were prepared as XRF pellets and a simple mathematic approach was proposed for characterising their spatial geochemistry and the magnitude of heterogeneities. This approach could be used to estimate the minimum mass that should be taken as an analytical test portion relative to the precision, and would also be useful in the preparation of RMs.

## 5 Glossary of terms

2D	two-dimensional
3D	three-dimensional
AAS	atomic absorption spectrometry
AEC	anion exchange chromatography
AES	atomic emission spectrometry
AFS	atomic fluorescence spectrometry
AMS	accelerator mass spectrometry
APDC	ammonium pyrrolidine dithiocarbamate
ASU	Atomic Spectrometry Update
BCR	Community Bureau of Reference ( <i>of the European Community</i> ) now IRMM
BEC	background equivalent concentration
BPHA	N-benzoyl-N-phenylhydroxylamine
CANMET	National Resources Canada
CCD	charge coupled detector
CCP	capacitively coupled plasma
CE	capillary electrophoresis
CI	confidence interval
CNT	carbon nanotube
CPE	cloud point extraction
CRM	certified reference material
CS	continuum source
CV	cold vapour
CVAAS	cold vapour atomic absorption spectrometry
CVG	chemical vapour generation
DCM	dichloromethane
DGT	diffusion gradient in thin films
DLLME	dispersive liquid liquid microextraction
DMA	dimethylarsenic acid
DMG	dimethylglyoxime
DMME	dual magnetic microextraction

DOM	dissolved organic matter
DRC	dynamic reaction cell
EDS	energy dispersive spectrometry
EDTA	ethyldiaminetetraacetic acid
EDXRF	energy dispersive X-ray fluorescence
EGTA	ethylene glycol tetra-acetic acid
EPA	Environmental Protection Agency (USA)
EPMA	electron probe microanalysis
ERM	European Reference Material
ESI-MS	electrospray ionisation mass spectrometry
ETAAS	electrothermal atomic absorption spectrometry
ETV	electrothermal vapourisation
EU	European Union
EXAFS	extended X-ray absorption fine structure
FAAS	flame atomic absorption spectrometry
FEG	field emission gun
FFF	field flow fractionation
FI	flow injection
FP	fundamental parameter
FTA	fission track analysis
FTIR	Fourier transform infrared
GC	gas chromatography
GD	glow discharge
GSI	Geological Survey of Japan
GSR	gunshot residue
HCL	hollow cathode lamp
HDEHP	di(2-ethylhexyl) orthophosphoric acid
HF-LPME	hollow fibre liquid phase microextraction
HG	hydride generation
Hg <sub>p</sub>	particulate phase mercury
HPLC	high performance liquid chromatography
HPS	High Purity Standards (USA)
HR	high resolution
HS	head space

IAEA	International Atomic Energy Agency
IAG	International Association of Geoanalysts
IBA	ion beam analysis
IC	ion chromatography
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma atomic emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
ID	isotope dilution
IDA	isotope dilution analysis
IEC	ion exchange chromatography
IERM	Institute for Environmental Reference Materials (of Ministry of Environmental Protection, China)
IL	ionic liquid
IL-ME	ionic liquid micro extraction
IR	infrared
IRMM	Institute for Reference Materials and Measurements
IRMS	isotope ratio mass spectrometry
ISE	ion selective electrode
IUPAC	International Union of Pure and Applied Chemistry
LA	laser ablation
LED	light emitting diode
LGC	Laboratory of the Government Chemist (UK)
LIBS	laser induced breakdown spectroscopy
LNEG	National Laboratory of Energy and Geology (Portugal)
LOD	limit of detection
LOQ	limit of quantification
LPMS	liquid phase micro sublimation
MALDI-MS	matrix assisted laser desorption ionization mass spectrometry
MC	multicollector
MF	metallic furnace
MIP	microwave induced plasma
MMA	monomethylarsenic acid
MNP	magnetic nanoparticle
MP	microwave plasma



MS	mass spectrometry
MWCNT	multiwalled carbon nanotube
<i>m/z</i>	mass to charge ratio
NAA	neutron activation analysis
NASA	National Aeronautics and Space Administration (USA)
NBS	National Bureau of Standards (USA) now known as NIST
NCS	China National Analysis Centre for Iron and Steel
Nd:YAG	neodymium doped:yttrium aluminum garnet
NIES	National Institute for Environmental Studies (Japan)
NIST	National Institute of Standards and Technology (USA)
NP	nanoparticle
NRCC	National Research Council of Canada
NRCCRM	National Research Centre for Certified Reference Materials (China)
NTIMS	negative thermal ionisation mass spectrometry
NWRI	National Water Research Institute (Canada)
OSIL	Ocean Scientific International Ltd (UK)
PAGE	polyacrylamide gel electrophoresis
PAH	polyaromatic hydrocarbons
PCA	principal component analysis
PFA	perfluoroalkyl
PGE	platinum group element
PIXE	particle induced X-ray emission
PLS	partial least squares
PM <sub>1</sub>	particulate matter (with an aerodynamic diameter of up to 1 µm)
PM <sub>1-10</sub>	particulate matter (with an aerodynamic diameter of between 1 and 10 µm)
PM <sub>2.5</sub>	particulate matter (with an aerodynamic diameter of up to 2.5 µm)
PM <sub>10</sub>	particulate matter (with an aerodynamic diameter of up to 10 µm)
ppb	part per billion
ppm	part per million
PTFE	poly(tetrafluoroethylene)
PVG	photochemical vapour generation
QC	quality control
REE	rare earth element

RIMS	resonance ionisation mass spectrometry
RM	reference material
RP	reversed phase
rpm	revolutions per minute
RSD	relative standard deviation
s	standard deviation of sample
SCP	SCP Science (Canada)
SCX	strong cation exchange
SD	standard deviation
SDS	sodium dodecyl sulfate
SDME	single drop microextraction
SE	standard error
SEC	size exclusion chromatography
SEM	scanning electron microscopy
SF	sector field
SFODME	solidification of floating organic drop microextraction
SHRIMP	sensitive high resolution ion microprobe
SI	Le <b>S</b> ystème <b>I</b> nternational d' <b>U</b> nités (International System of Units)
SIMCA	soft independent modelling of class analogy
SIMS	secondary ion mass spectrometry
SMPS	scanning mobility particle sizer
S/N	signal-to-noise ratio
SPE	solid phase extraction
SPS	Spectrapure Standards (Norway)
SR	synchrotron radiation
SRM	standard reference material
SRXRF	synchrotron radiation X-ray fluorescence
SS	solid sampling
SSIDMS	species specific isotope dilution mass spectrometry
TD	thermal desorption
TEM	transmission electron microscopy
TFF	tangential flow filtration
TIMS	thermal ionisation mass spectrometry
TMAH	tetramethylammonium hydroxide

TOA	thermal optical analysis
TOC	total organic carbon
TOF	time of flight
TRA	time resolved analysis
TS-FF-AAS	thermospray flame furnace atomic absorption spectrometry
TSP	total suspended particles
TXRF	total reflection X-ray fluorescence
UA	ultrasonic extraction
UF	ultrafiltration
UNEP	United Nations Environment Programme
USAEME	ultrasound assisted emulsification extraction
USGS	United States Geological Survey
USE	ultrasound assisted emulsification
USEPA	United States Environmental Protection Agency
USN	ultrasonic nebuliser
UV	ultra violet
UV-VIS	ultra violet-visible spectrophotometry
VAE	vortex assisted emulsification
WDXRF	wavelength dispersive X-ray fluorescence
XAFS	X-ray absorption fine structure spectrometry
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectrometry
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

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