Atomic spectrometry update. Environmental analysis

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This is the twenty-third annual review published in JAAS of the application of atomic spectrometry to the chemical analysis of environmental samples. This update refers to papers published approximately between September 2006 and August 2007. In the analysis of air, there has been an increased awareness of the need to collect and characterise ultrafines, i.e. particles below 100 nm in size, and such work is being facilitated by the development of real-time aerosol mass spectrometric techniques. In the analysis of plant and water matrices, elemental speciation protocols for elements such as As, Cr Hg, Sb, Se and Sn continue to receive considerable attention with particular interest in the speciation of Se compounds in plant matrices. Laser ablation continues continues to go from strength to strength in being adopted as a solid sampling tool in geochemical analysis. Such work is being underpinned by increased knowledge of the ablation process and resultant transport and plasma effects coupled with developments in *fs* UV laser technology. This technique, in conjunction with multi-collector ICP-MS technology, is increasingly being used for the in situ determination of isotope ratios in geological samples. Feedback on this review is most welcome and the lead author can be contacted using the email address provided. Alternatively, readers are welcome to complete the on-line questionnaire at http://www.asureviews.org.

1 Air analysis

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This section highlights noteworthy areas of research and development in the analysis of aerosols, particulates and gases by atomic spectrometric techniques that have been reported since the last Update1.

1.1 Sampling

A recurring theme in aerosol measurements is the need to collect sufficient sample for analysis. High volume air sampling techniques are often employed to sample air at rates typically up to 1000 l min-1 and above, thus allowing highly time resolved-samples to be collected, i.e. resolutions of hours rather than days as is common with low volume air samplers operating typically less than 25 l min-1. There is growing impetus to evaluate the effect on human health of inhaled airborne particulate matter arising from sporadic air pollution episodes whose duration is often only a matter of a few hours. Sampling methods are therefore increasingly being required to support detailed chemical and toxicological studies of particulate matter from such specific pollution events. Dillner and coworkers2 describe their use of the Thermo ChemVol Model 2400TM high volume cascade impactor sampler to collect size segregated particulate matter at a 4-hourly frequency, for subsequent analysis by ICP-MS. This sampling system operates at a nominal 760 l min-1. Particulate matter is collected on polyurethane foam (PUF) substrates and segregated on six stages: < 0.1 µm, 0.1 – 0.5 µm, 0.5 – 1.0 µm, 1.0 – 2.5 µm, 2.5 – 10.0 µm and > 10 µm. Detailed protocols were developed to preclean the PUF substrate in order to minimise its contribution to the blank. The substrate material was digested in 50 mg aliquots using a mixture of HCl and HF in a microwave oven after first being digested in an open vessel for 30 hours using a mixture of HNO3 and H2O2 to wet ash the foam matrix. Samples were then capped and placed within the microwave oven. The authors noted that high Pt and Sn values in the PUF substrate material, arising from the use of these elements in its manufacture, precluded any useful data for these elements. Likewise, Cr data were not reported due to high blank levels subsequently traced to one of the PUF cleaning agents used. The authors reported interferences on As by ICP-MS but this was probably due to carbon loading effects in the plasma when attempting to analysis such elements with high ionisation potential. Impressive method detection limits (3 σ) were obtained which were typically 1 ng m-3 for 4-hour sampling periods. Although the production of this particular high volume cascade impactor sampler has now ceased, a number of similar high volume PUF samplers are commercially available although only with a single size selective inlet, i.e. PM2.5 inlet.

Danish researchers have developed a high volume electrostatic precipitator sampler3. It is based upon a commercially available office air cleaner and consists of an initial prefilter followed by electrostatic collection plates operating at 2.7 kV. The collection efficiency of this sampler reached a maximum of 60 – 70 % for particles in the size range 0.2 – 0.8 µm, dropping to approximately 25 % for particles of 30 nm and 2.5 µm in size. In field sampling tests, at an urban site, the amount of particles collected corresponded to approximately 12 mg day-1 in situations where the ambient PM10 particulate load was around 24 µg m-3 as measured using a nearby real-time tapered element oscillating microbalance (TEOM) sampler. The ozone generating capacity of the corona discharge was measured at around 10 ppbv in the exhaust of the sampler and a PAH degradation test, using benzo(a)pyrene as a marker, showed that approximately 85 % was degraded after 24 hours. However, similar results were obtained when the corona discharge was switched off! The collection plates were coated with silver paint and, not unsurprisingly, oxidised silver particles were found in bulk dust samples collected. Through the analysis of 16 dusts samples, it was shown that this silver concentration was between 0.2 and 1.9 % (m/m). Data yet to be published from bacterial mutagenicity, mammalian genotoxicity and inflammatory marker tests suggest that the 'activity' of such samples is not altered by this silver contamination. The authors are however proposing to develop more inert coatings for the collection plates. This sampler could be a relatively low cost alternative approach to filter-based systems for the collection of milligram quantities of airborne particulate matter for subsequent chemical and toxicological testing.

High volume filter-based air sampling techniques are often employed to ensure that sufficient sample mass is collected for subsequent laboratory analysis and to enable lower MDL to be achieved. The size of the filters, usually in excess of 250 cm2, is such that sub-sampling is required to present suitably sized test samples for analysis. An Argentine study, cited in last year's review1, showed that variability in elemental loading between filter aliquots punched out from a high volume air filter was in the order of 5 – 10 %. Gehrig and coworkers4 employed a similar approach using a high volume sampler in conjunction with WDXRF analysis to ascertain the contribution of railway traffic to local PM10 concentrations at urban sites in Zurich. From 15-cm diameter filters, 4-cm filter punches were taken for analysis. Replicate punches from the same filter suggested that the relative differences in elemental concentrations between punches were typically < 10 % but that filter deposition inhomogeneity was the largest single contribution to the overall measurement uncertainty of 10 % (95 % confidence level).

The CARIBIC project (Civil Aircraft for Regular Investigation of the Atmosphere Based upon an Instrumention Container) was initiated in 1999 to gain increased knowledge of the chemistry and composition of gases and particulates in the troposphere. The project involves the deployment of a laboratory mounted in an airfreight container that can be loaded onto civilian passenger flights. A change in the cooperating airline presented an opportunity for Swedish researchers to design and calibrate a new multi-channel aerosol sampler for in-flight use5. Work carried out to determine the collection efficiency of this sampler is described. The sampler consists of 16 flow channels with impaction surfaces for collection of particles. Solenoid valves facilitate switching between these channels allowing sequential sampling on both outward and inbound flights. An inlet cyclone limits collection of particles to those below 2 µm; laboratory calibration data showed that collection efficiencies were high: 97 %, for particles in excess of 0.2 µm with a 50 % cut-off at a nominal 0.08 µm. The system has been so designed that bulk particle analysis can be performed by PIXE, and single particle analysis by SEM-EDAX and TEM techniques. Based upon a 1.5-hour sampling period, minimum detectable concentrations by PIXE were typically better than 0.1 ng m-3 for elements heavier than vanadium and in the range 0.1 – 40 ng m-3 for elements lighter than vanadium.

Malcolm and Keeler6 have highlighted a potential sampling artefact arising from the sampling of particulate-phase mercury in the marine environment. Inconsistent results were obtained for Hg measured in PM10 (HgP) samples from 12-hour sampling periods versus results from aggregated 4-hour sampling periods. Over seven days of sampling, the mean HgP concentration of 22.5 pg m-3 was significantly higher for the 4-hour samples than the mean value of 8.4 pg m-3 obtained from the 12-hour samples. The day-to-day differences range from minus one to to 29 pg m-3. Understanding the root cause is difficult due to multiple sampling artefacts and the low concentration of airborne Hg encountered in the marine environment. It was proposed that there is loss of HgP due to on-filter chemical reactions that increases with time. A suggested mechanism is one involving reduction of Hg(II)aq to Hg(0)aq which is subsequently lost from the filter as elemental Hg vapour. This mechanism involves loss of co-sampled chloride-containing species from filter samples through reaction with acidic sulphur and nitrogen-containing species thereby shifting the Hg(II) speciation to more readily reducible sulphur species. The development of an aqueous aerosol film on filter samples collected in a moist marine environment also facilitates increased particle-particle interaction. The authors suggest caution in sampling Hg species and call for research to ascertain whether this artefact is seen in other sampling environments. They recommend that denuder sampling systems should be placed in-line before filters to remove both reactive gaseous mercury species and acidic gases if particulate Hg sampling is contemplated. Samples of different duration should be collected to evaluate the potential for sampling artefacts. They also suggest that sampling for gaseous Hg species downwind of the filter could be useful in identifying the magnitude of losses of Hg species from filters.

1.2 Sample preparation

Evaluation and optimization of closed vessel microwave-assisted digestion protocols for the dissolution of suspended particulate matter collected on air filter samples continues to attract attention. As a reviewer, it has been helpful that several researchers make use of the NIST SRM 1648 (urban particulate matter reference material) thus allowing comparisons between work to be made. Sysalova and Szakova7 used a concentrated HNO3/HF/H2O2 (5+1+1) mixture on 20 mg quantities of this SRM in PTFE vessels which were subjected to a focused microwave attack. Instrumental conditions were not tabulated but a PlazmatronikaTM digestion system from Poland was used. Digests were subsequently evaporated on a hotplate to incipient dryness and reconstituted in 5 % (v/v) nitric acid prior to analysis by ICP-AES. Recoveries for As, Cd, Cr, Mn, Ni, Pb and Zn were found to be complete. The mean RSD of six replicate samples was less than 5 % indicating the good microhomogeneity of this SRM, because the recommended test aliquot size is 100 mg. Of interest is the complete recovery of Cr at 398 ± 10 µg g-1 against a certified value of 403 ± 12 µg g-1. Chromium in this SRM is known to be highly refractory, i.e. present as chromite, with many cited analytical recoveries below 50 %. In this reviewer's laboratory, recoveries are typically around 70-80 % when applying a microwave assisted HF procedure (EN method 14902). The digestion procedure adopted by Japanese workers involved the use of a HNO3/HClO4/HF mixture (10 ml volume; 5+3+2) on 10 mg quantities of the SRM8. Pressure rated PFA lined digestion vessels were used in conjunction with a domestic microwave oven. Perchloric acid is a powerful oxidising acid when hot and its use in a microwave oven, particularly a domestic system, should be approached with extreme caution. Preferably, all digestions involving hot and corrosive mineral acids should be performed in dedicated laboratory microwave oven systems with use of appropriate pressure rated digestion vessels. Quantities of perchloric acid, if used, should be minimised and in any case should be diluted with a large excess of nitric acid. Again, these researchers subsequently evaporated the digests on a hotplate to incipient dryness and reconstituted the samples in 1 M HNO3 prior to analysis by ICP-AES/MS. Recoveries for 48 elements were typically within 10 % of the certified and indicative values. Precision, expressed as a RSD on five replicates, was typically determined to be below 5 %. The authors report results for a number of elements not included on the

SRM certificate but, alas, no chromium value was reported! The validated procedure was used to analyse suspended particulate matter (PM10) collected on quartz fibre filters commonly used with high volume air samplers. An initial open vessel digestion involving HF was used to dissolve the filter matrix. Quartz fibre filters are generally regarded as being quite clean but, even so, it proved impossible to measure a number of trace elements because filter blanks were high, representing 20 – 150 % of the airborne concentrations being measured. Researchers at the National University of Singapore used a mixture of HNO3/H2O2/HF to dissolve their filter samples9. Following initial experiments, an optimal ratio of 20+10+1 was found to be sufficient to obtain recoveries in the range 85 % - 110 % for As, Co, Cu, Cd, Fe, Mn, Ni, V and Zn in the NIST SRM. Lead recoveries were surprisingly low at 77 ± 3 %. Digestion experiments were carried out on 10 mg test aliquots using 6 ml of the acid mixture. Interestingly, the final digestion temperature was set at a relatively modest 130 °C. This can be compared to the 220 °C cited in the EN standard 14902. Chromium recoveries were 82 ± 7 % but perusal of the ICP-MS instrumental conditions cited suggests that the ArC polyatomic interference on the measured 52Cr isotope could have been an issue leading to a positive bias in actual recoveries.

In the United States, the concentrations of As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb and Se arising from coal burning emissions are regulated under their Clean Air Act amendment of 1990. Similar regulation is in force in Europe and elsewhere. Fly ash samples, extracted onto filters from chimney stack emission plumes, are commonly analysed by ICP techniques. This assay is not easy as that of coal because the fly ash fractions are refractory. Validated digestion methods have been published, e.g. EN standard 14385:2004 but it is good to see further sample digestion studies incorporating developments in microwave-assisted digestion technology. Iwashite and coworkers10 provide a detailed examination of a microwave-assisted digestion procedure suitable for both coal and related ash products. Satisfactory recoveries (90 – 110 %) were obtained for the above elements using a two-stage digestion procedure on four coal SRM and four coal fly ash SRM. The first stage involved either a HNO3/H2O2 mixture (5+3) or a HNO3/HF/H2O2 mixture (5+1+2) for elements bound up within the silicate matrix. Reference samples, 100-200 mg aliquot sizes, were heated for 37 minutes at temperatures estimated to be around 200 ˚C based on tabulated temperature readings of 130 ˚C obtained using remote IR sensors at the surface of the digestion vessels. The second stage involved, after cooling and venting, the addition of a further aliquot of the HNO3/H2O2 mixture and reheating samples for a further 30 minutes. An on-line vacuum evaporation unit was used to remove the concentrated acids and the test aliquots were subsequently diluted using 1.3 M nitric acid. A radial detection ICP-AES system was used to determine Co, Cr, Mn, Ni and Pb as well as matrix elements, ETAAS to measure trace Be and Cd and HG-AAS to measure As, Sb and Se.

1.3 Instrumental techniques for bulk analysis of particles and gases

Atomic spectrometric methods such as AAS and ICP are now well established for the measurement of elemental species in aerosol samples. The focus lies in the evaluation and development of suitable digestion procedures as described in Section 1.2. Direct analysis of filter samples is possible with laser ablation sampling but it is evident that progress with this technique is being hampered by the lack of suitable calibrants. Ideally, real-world, airborne particulate matter collected on filter samples and characterised at the microscopic level (mm2) would be useful. Electrothermal vaporization techniques offer another potential route for the direct analysis of airborne particulate matter collected on filter samples. Zhang and coworkers11 have explored the use of ETV-ICP-AES and ETV-ICP-MS techniques for the determination of refractory elements in atmospheric particles. Clever use was made of polyvinylidene difluoride (PVDF) filters to sample airborne particulate matter. This filter type was found to be readily soluble in solvents such as dimethylformamide and dimethyl sulfoxide, allowing slurry-sampling protocols to be applied. Furthermore, the thermal degradation of PVDF allows HF to be generated in situ, thus providing a useful chemical modifier source. Fluoride species of refractory metals are more volatile than corresponding carbide/oxide species, giving a sharper vaporisation profile. The method was optimised with slurries of NIST SRM 1633a (coal fly ash) and NIES SRM 8 (vehicle exhaust particulate matter). Solution-based calibration standards were prepared and matrix matched by the addition of small quantities of PVDF powder. Recoveries for elements such as Cr, Mo, Ti, V and Zr were found to be quantitative. Absolute detection limits (3σ) for ETV-ICP-MS based upon analysis of blank solutions were typically less than one pg. The technique was used to determine these refractory elements in an urban air environment where levels were found to be in the range 1 – 5 ng m-3, based upon the collection of 12 m3 sample volumes. In this reviewer's opinion, the potential for this technique lies in the analysis of small mass, size-segregated, airborne particulate samples such as those collected on impaction substrates, i.e. low pressure impactor samplers.

Voltammetry is an alternative to atomic spectrometric techniques for the determination of trace metals in environmental samples. Modern systems can be fully automated, provide multi-element analysis and are relatively cheap compared to say ICP-MS instruments. Buzica and coworkers12 at the EC JRC in Ispra have developed an electrochemical technique for the determination of heavy metals in PM10 airborne particulate matter. They used anodic stripping procedures to determine As, Cd, Cu, Pb and Zn, whilst an adsorptive stripping procedure was developed for the determination of Ni. NIST SRM 1648 was used for method validation and test solutions were prepared using the microwave digestion procedure specified in EN standard 14902. The new method was shown to meet analytical specifications set out in this EN standard, which was specifically developed for use with the ETAAS and ICP-MS techniques. Statistically equivalent results were obtained on two PM10 air filter samples, which, after digestion, were analysed concurrently by both the voltammetric procedures and by ICP-MS. The authors conclude that the technique offers an attractive alternative for laboratories undertaking ambient air monitoring programmes especially those where the cost of an ICP-MS is prohibitive or where argon gas is unavailable. Voltammetric techniques can be very portable. Herman and coworkers13 used a commercially available blood lead analyser, whose operation is based upon a differential pulse anodic stripping voltammetric technique, for in situ measurements of workers in lead handling factories. A portable XRF system was concurrently deployed to undertake dust wipe sampling and soil surveys to ascertain the level of Pb contamination in the wider environment. It is a fact of life that, in developing countries, potential health hazards due to lead poisoning persist and the authors suggest that portable instrumentation could play a valuable measurement role as such countries implement internationally accepted exposure standards.

Elemental analysis of airborne particulate matter based upon x-ray fluorescence techniques are now well established. Polarised energy dispersive XRF (P-EDXRF) instruments are now commercially available and offer the potential for direct analysis of elemental species collected on filter samples. Certain measurement problems still need addressing: the lack of availability of suitable 'particle on filter' standards; particle size and depth effects; and homogeneity of particle deposits on filters. The area of the XRF beam on such systems is typically less than 20 mm in diameter equating to an irradiation area of less than 4 cm2. A 47 mm diameter filter, typically used in air monitoring programs, has an active surface of around 16 cm2. It is therefore necessary to investigate whether particle deposition onto such filters is uniform. Owoade and coworkers14 cut into quadrants 47 mm diameter filters loaded with airborne particulate matter, collected using a 'Ghent-type' sampler, and analysed them by P-EDXRF. Elements in the range Na – U were measured. Reassuringly, data obtained suggested that, at least with this sampler type, the measurement precision for the elements determined were less than 5 % for those elements where the filter loadings were well in excess of their respective quantification values. Further work to investigate the filter deposition patterns on other types of commonly used PM10/2.5 sampler systems would be useful. An alternative approach to assessing the beam profile in a P-EDXRF system has been published by Zhan and co-workers from the National Research Centre for Geoanalysis in Beijing15. They manufactured a small solder disc, consisting mainly of lead and tin, with a diameter of about 3 mm. They utilised it to manually scan an area of approximately 3 cm2 over which they anticipated the excitation beam would reach. The scan was carried out by repetitively moving this solder button under the x-ray beam in a grid-line fashion. Results suggested that the effective target area was over 2 cm2 with the three secondary targets tested: highly oriented Al2O3, pyrolytic graphite and Mo. However, it was noted that, with both the Al2O3 and graphite targets, a sharp beam distribution pattern was obtained wherein 50 % of the intensity was centralised upon a 7 mm x 7 mm spot size. The implications are clear: that the production of future calibrant filters for XRF analysis will have to be spatially characterised at the microscopic level (mm2) and this may well be a function of the sampler used.

Streli and coworkers16 describe the setup of a new SR-TXRF facility at the HASYLAB Beamline L synchrotron facility in Hamburg. This setup is equipped with a new 50 mm2 silicon drift detector which enables the processing of count rates up to 100 kcps at acceptable peak resolutions (FWHM of 160 eV). Initial experiments suggest very low detection limits are possible. Using 17 keV monochromatic excitation radiation, detection limits of 8 fg were obtained based upon the measurement of a test solution containing 100 pg of nickel that had been subsequently dried on an silicon wafer target. Work is ongoing to develop a 12-stage Berner impactor sampler for size selective sampling of air particulate matter using similar silicon wafers as sample impactor plates. Further improvements are required with respect to instrument calibration and aspects of this work are reviewed below. .

The chemical composition of a yellowish rainfall arising from an Asian dust storm event has been measured using both PIXE and μ-PIXE techniques17. Bulk rainwater samples were collected using a simple funnel and flask system. A soluble phase, material passing through a 0.2 μm polycarbonate filter and subsequently dried, and an insoluble phase, material collected on this 0.2 μm filter, were collected. Samples were subsequently analysed by PIXE. Instrument calibration was performed using single element filter standards prepared using a vacuum deposition technique. Individual raindrops were sampled onto a viscous collodion solution mounted on a 10 μm Mylar film. Upon evaporation of this alcohol/ether solution, a thin film containing the imprint of the individual raindrops was left on the Mylar film. This method of collection had been verified for droplets up to approximately 2 mm in diameter. Using a μ-PIXE setup it was found possible to scan across such imprints with a spatial resolution of a few micrometers and absolute elemental detection limits in the order of 10-15 – 10-16 g. The major components in rainwater were determined to be of soil origin, i.e. elements such as Ca, Fe, K, Si and Ti. It was possible also to analyse the insoluble particles retained in individual raindrops and nearly all such particles were found to coexist as a mixed elemental state consisting of the above soil marker elements, sea salt and sulphur, indicating that such dust storm events, originating in continental Asia, pass over marine environments. It is thought that μ-PIXE will be useful in future studies that are planned to elucidate the precipitation scavenging mechanism, i.e. washout of particles.

An Italian expedition collected size-selected aerosol samples on silicon wafers using a 7-stage May cascade impactor at their Antarctic bases located near Terra Nova Bay (Ross Sea) in 200318. In particular, the aims of the study were to demonstrate the capabilities of x-ray microanalytical techniques such as TXRF, TXRF-NEXAFS and low-Z particle EMPA for the characterisation of size-selected aerosols and to compare ammonium/nitrate ratios and light element composition of Antarctic aerosols collected under different meteorological conditions. The May impactor used has, at a nominal 20 l min-1 sampling flow rate, aerodynamic cut-off diameters of 16, 8, 4, 2, 1, 0.5 and 0.25 μm for the seven impaction stages. Typical sampling volumes employed, to ensure optimal particle loadings for the various instrumental techniques, were in the range 0.2 – 2 m3. Interestingly, such volumes were much smaller than the 30 m3 commonly sampled by the same researchers to determine ammonium/nitrate ratios by more conventional IC techniques. Reduced sampling volumes, and hence sampling times, offer the potential for temporal studies of greater resolution to be undertaken. For Antarctic aerosols, in the 0.25 – 0.5 µm size range, nitrogen was observed to be predominately as the ammonium species. Analysis of particles, in size ranges up to 2 µm, showed a decrease in ammonical nitrogen and a corresponding increase in the nitrate content of particles. Single particle EMPA measurements of 160 individual particles supported the measurements by TXRF-NEXAFS that both ammonium-rich and nitrate-rich particles exist in the 1-2 µm size range. However, no pure ammonium nitrate particles were encountered in the particles examined. The stoichiometry of the main chemical component containing nitrogen and sulphur as major elements was determined to be NH4HSO4.

For a greater understanding of the global Hg geochemical cycle, improved procedures for the speciation of mercury are required and this has been assisted by the availability of real-time automatic Hg speciation analysers. Cobbet and Heyst19 have published their research on the sampling and measurement of gaseous elemental mercury (GEM) and other Hg species above agricultural land amended with biosolids from a wastewater treatment plant. GEM measurements were made with a Tekran 2537ATM Hg analyser. Reactive gaseous mercury (RGM) and Hgp were measured on a second Tekran instrument that had Tekran 1130TM and 1135TM speciation modules attached. The basis of the Tekran instrument is a gold trap – AFS system whereby Hg species are determined as elemental Hg. Species collected on gold traps (elemental mercury), KCl-denuders (reactive gaseous species) and quartz fibre filters (HgP species) are thermally released and subsequently reduced to elemental Hg prior to analysis. Average airborne concentrations (mean ± standard deviation) were: GEM 1.8 ± 0.2 ng m-3; RGM 2.3 ± 3.0 pg m-3 and HgP 3.0 ± 6.2 pg m-3 which remained relatively constant throughout this five-week study period. The average GEM flux was 0.1 ± 0.2 ng m-2 hr-1 with flux maxima coinciding with peak solar radiation. The application of biosolids in nearby fields and harvesting activities produced large increases in Hgp and RGM species when samples downwind of such events were analysed. Liu and coworkers20 measured the temporal variability of mercury species in an urban air shed at a site in Detroit using identical instrumentation. Here the average airborne concentrations, again expressed as a mean ± standard deviation, were found to be: GEM 2.2 ± 1.3 ng m-3 ; RGM 17.7 ± 28.9 pg m-3; and HgP 20.8 ± 30.0 pg m-3. Seasonality differences were observed in the results where GEM and RGM concentrations were greater in warmer seasons but HgP concentrations were greater in cold seasons. Clear diurnal trends were observed and were particularly evident during the summer months. Here, RGM concentrations were found to be higher during the day than at night. TGM and HgP species showed similar diurnal patterns but which were found to be inversely correlated with RGM. Further speciated measurements are required and indeed such studies will be facilitated by the ongoing use of automated measurement instrumentation at sampling sites.

Current atmospheric iodine models suggest that iodate is the only stable iodine sink species in the troposphere. However, German researchers, having analysed rain and snow precipitation samples using a coupled IC-ICP-MS procedure, concluded that actually iodate species could be the least abundant iodine containing species in the atmosphere21. Iodine and bromine species in precipitation samples were separated using a Dionex AS16 anion exchange column employing a 35 mmol NaOH eluent. The flow rate used was a nominal 0.9 ml min-1 which is compatible with nebuliser flow rate requirements for ICP-MS analysis. The LOD for iodine species was around 0.2 nmol l-1. Both iodide and iodate peaks were identified in the chromatograms but, in contrast to current atmospheric iodine models, iodide species were four times more abundant than iodate species. Organo-I compounds, identified from their chromatographic peaks, were found to be the dominant species in all the precipitation samples analysed, but their structure could not be ascertained from just the coupled technique employed. At least one of these unidentified species was considered to be ubiquitous because a peak with similar retention time was seen in all chromatograms. The authors suggest that this work has implications for iodine atmosphere models in so far as iodine's ozone destruction potential may be somewhat less than previously thought because of the formation of stable C-I bonds in these, as yet, unidentified organo-I species.

Elemental speciation in atmospheric particles is important for understanding their formation, assessing their origins and evaluating their resultant toxicity. XAFS is an extremely powerful technique for elucidating the in situ speciation of particles collected on filter samples. Chinese researchers22 have evaluated the technique in examining the speciation of iron in airborne particulate matter. Test EXAFS spectra were generated using a series of mixed reference samples containing varying portions of Fe2O3, Fe3O4 and Fe2(SO4)3 – the dominant Fe species predicted in airborne particles. Air samples, both PM10 and PM2.5 size-selected samples, were collected in Shanghai in the vicinity of an iron and steel plant, at a downtown urban location and at a rural site outside the city. These three Fe species were indeed found to be the dominant species at all sampling locations. The relative concentration of Fe3O4 to the other two Fe species was higher in air samples from around the iron and steel plant compared to the other two sites. This was not suprising, as Fe3O4 is used as a raw material in this industry. At the other two sampling sites, the relative concentration of Fe2(SO4)3 was noticeably higher than the other Fe species, suggesting the formation of ferric sulphate species through the interaction of fine iron-containing PM2.5 particulate matter with sulphur dioxide.

1.4 Instrumental techniques for analysis of individual particles

Researchers at the University of Antwerp have demonstrated the usefulness of combining Raman microscopic and EMPA techniques thus allowing information to be gathered on the morphology, size, elemental and molecular composition, as well as the molecular structure of individual particles with a diameter as small as 500 nm23. Collected particles were transferred from the impaction surfaces of a Batelle-type impactor to each of the two separate techniques using a nano-manipulation device employing fine glass capillary tips situated within the working confines of an environmental SEM. Three piezo-driven motors allowed the glass needle attached to the manipulators to be moved in one longitudinal and two rotational directions. Initial work focused on selection of a particle collection substrate suitable for both techniques. It was found that TEM grids with an ultra-thin carbon layer 3 – 4 nm deep and supported by a Cu mesh gave the best results. This decision was based upon the best compromise between the two techniques with respect to acceptable spatial and spectra resolution as well as maintaining useful S/N ratios. The use of an EMPA system equipped with ultra-thin atmospheric window, coupled with a liquid nitrogen cooled sample stage, enabled both qualitative and quantitative determination of often volatile low-Z elements such as C, N and O, as well as higher Z-elements. Initial examination of particles sampled from a museum environment showed a fair correlation between mass concentrations by the thin-window-EDX-EMPA technique and the molecular structure obtained by the micro-Raman technique

Chinese researchers successfully applied pattern recognition to micro-PIXE spectra generated from single airborne particles collected to study the origins of PM10 in the atmosphere above industrialised zones of Shanghai24. The results showed that the predominant sources of particles included metallurgical industries, coal combustion and resuspended soil dust. Particles from vehicular exhausts were also prominent, most notably those from motorcycle exhausts, a popular means of transport in urban China, which contributed approximately 10 % to the PM10 burden. Interestingly, these researchers were unable to procure a suitable commercial particle mounting substrate that was both sufficiently thin and clean. They resorted to producing in-house nylon films by dropping a heated solution of nylon powder dissolved in isobutyl alcohol onto the surface of deionised water. Environmental air samples were collected on nitrocellulose filters using a commercially available PM10 sampler; they were subsequently dried in desiccators for several days. Particles from such filters were removed by vibration and allowed to drop onto the solidifying nylon film.

Research into the development of single particle mass spectrometric techniques for the real-time measurement of particles in air is being driven by the need to better characterise ultrafine particles and their potential effect on human health. An example, in this expanding field, is the work by Spencer and Prather25 who describe how they used an ultrafine aerosol time-of-flight mass spectrometer (UF-ATOFMS) to determine OC/EC mass fractions in airborne particles. Initial laboratory work focused on developing a calibration for the instrument by generating carbon-containing particles. Elemental carbon particles were produced using a spark discharge across graphite rods and the diluted EC particle stream was pulled through a differential mobility analyser (DMA) to select particles with a desired electrical mobility equivalent diameter. Selected particles were then passed through the headspace of a vessel containing unleaded petrol, heated to a set temperature, in order to coat EC particles with OC. Coated particles were then passed through a second DMA in order to provide electrical mobility size distributions. An attached CPC was used to provide particle count information. Finally these size-selected coated and uncoated aerosols, depending on whether or not the unleaded petrol coating vessel was used, were sampled by the UF-ATOFMS for aerodynamic size and chemical analysis. The OC/EC mass fractions were determined using two separate approaches. The first used assumptions about the shape and density of particles based upon literature values, and the second involved calculating the effective densities of particles using measured vacuum aerodynamic and electric mobility diameters from UF-ATOFMS and SMPS measurements. From the two estimation methods, the OC/EC mass fractions, as a function of particle size, were determined. A calibration curve was created by plotting OC/EC ion intensity ratios, from UF-ATOFMS measurements, against the calculated mass fractions of OC estimated from the two methods. Good correlations were obtained from the assumed material density approach (R2 = 0.99) and measured effective densities (R2=0.98) and both correlations were found to be within the range of uncertainties of each other. It was subsequently shown that these laboratory generated particles showed similar OC/EC ion intensity ratios to ambient and source particles sampled by the same UF-ATOFMS system, suggesting that the laboratory generated particles are similar in nature to environmental ones. Ambient particles were sampled at a Freeway in San Diego and urban locations in Atlanta and Boston. Source particles originated from two vehicle dynamometer studies involving both gasoline and diesel powered vehicles. In these cases, the UF-ATOFMS system was operated down stream of a MOULDI impactor sampler, which removed over 50 % of particles greater than 450 nm of aerodynamic size. Using this calibration approach it was found that ambient OC mass fractions were within ~ 20 % of those simultaneously measured in the field using a traditional TOT filter-based method. Further work is planned in the laboratory comparing calibration curves generated using EC particles coated with different classes of organic species that can be present in the ambient air.

1.5 Online and (near) real time measurement techniques

Scattering of solar radiation by constituents in man-made aerosols leads to cooling of the climate via the aerosol radiative forcing effect, thus mitigating, somewhat, the effects of global warning. It is understood that sulphate-containing sub-µm particles are the dominant light-scattering component of aerosols, but it is also suspected that nitrate species in similar sized particles may also contribute to this radiative forcing effect. However, information on the size distribution of such aerosol components is scarce. It is therefore interesting to note the development of a new semi-continuous monitoring system for the measurement of the size distribution of ammonium, chloride, nitrate and sulphate ionic species in aerosol samples26. Novel to this instrument is its size classification inlet system, which consists of four impactors placed in parallel. The cut-off diameters of the impactors are nominally 0.18, 0.32, 0.56 and 1.0 µm. Aerosols smaller than the associated cut-off size pass through the respective impactor and are subsequently analysed. This sampling manifold contains two additional sampling lines: one an open line and one containing a filter that removes all aerosols. This filtered line offers the potential to determine system blanks. The airflow can be switched automatically between sampling lines by means of wide-bore ball valves, thus providing a measurement system that can sequentially interrogate particles of different size fractions. Downstream of this separator system is a wet denuder that can remove gaseous species such as ammonia and nitric acid, not only from the original aerosol sample, but also any arising from revolatilisation from particles trapped on the impactor plates. A steam condensation system is then used to grow the aerosols, i.e. to form a hydration shell around the particles, which are subsequently collected in a cyclone. Droplets drain out from the bottom of this cyclone into the on-line wet chemical analysis system (not described but presumably based upon colorimetric and/or IC techniques). Liquid from the wet denuders can also be collected and provides a means of concurrently measuring gaseous species. The instrument, called MARGA (Measuring AeRosol and GAses), was used to measure aerosol species at a sampling location in Holland situated on a 200 metre tower. The high location was so chosen to minimise the influence of surface emissions of ammonia. In a two-month summertime sampling campaign, the mass concentration of sub-µm nitrate was 2.0 µg m-3, of which some 46% was in particles smaller than 0.32 µm. The concentration of sub-µm sulphate was found to be similar: 53% was found in sizes less than 0.32 µm. The ion balance showed that the compounds were present as the fully neutralised salts.

Scientific and media attention on nutrient loading in aquatic systems has prompted further research into the role and mechanism of ammonia and ammonium (NHX) species in episodes of eutrophication. Myles and co-workers27 deployed a real-time ion mobility spectrometer to measure ambient air ammonia concentrations. They used a commercially available IMS system, which has three distinct sections:

the sample introduction system, the drift tube and the detector. A non-porous dimethylsilicone membrane was used to filter out most of the water vapour in the air sample, and it also inhibited potential positive interferences from ammonium-containing particulate species. The air sample, once across this semi-permeable membrane, was merged into a stream of carrier gas (instrument air) produced by an oil-free compressor. A dopant, dimethyl methanphosphonate (DMMP), was added to this air stream to act as an ionic buffer. This reagent has an electron affinity slightly lower than that of ammonia but it is sufficient to absorb charges from the 63Ni beta-energy source to suppress ionisation of other gaseous molecules in the sample stream. The system has an operational detection limit of 0.10 ppbv with a measurement range 0 – 100 ppbv ammonia. The on-board calibration system produces zero calibration standards using instrument air. A 50 ppbv gas standard was delivered using an internal permeation tube system and the instrument was found to be consistently within ± 6% of the certified value. Field studies showed that the system could detect increases in airborne ammonia concentrations, which, from wind rose data, suggested the presence of point emission sources such as fertiliser manufacturing industries. The authors conclude that IMS is a viable atmospheric research tool that could, in their opinion, be optimised for the measurement of other gaseous species.

1.6 Isotopic analysis

Lead is a much-studied environmental pollutant and is a powerful geochemical tracer of natural and anthropogenic dust sources. Kylander and coworkers28 present Pb isotope data obtained by LA-ICP-MS from airborne particles trapped in sedimentary peat samples and lichens. Samples were initially homogenised and dry-ashed overnight in a muffle furnace at 450 °C. The resultant ash was pressed into a 7 mm diameter pellet without any binder and presented to both LA-MC-ICP-MS and LA-Q-ICP-MS instruments. Comparative analysis was carried out by solution-based MC-ICP-MS and TIMS following acid dissolution of ashed samples in a closed vessel microwave-assisted digestion system. In-house Canadian peat reference samples, previously characterised by TIMS, and BCR CRM 482 lichen were used to evaluate the method. Internal (within run) and external (between runs) precisions for LA-MC-ICP-MS were found to be <1.1% and <0.3% respectively for both 207Pb/206Pb and 208Pb/206Pb ratios. As expected, ratios obtained by LA-Q-ICP-MS had poorer precisions of <14.3% within run and 2.9% between runs. The accuracy of the LA-MC-ICP-MS approach was found to be within 1% of comparative analysis by TIMS whilst LA-Q-ICP-MS results were within 3.1% of those obtained by solution-based MC-ICP-MS analysis. A sample-standard bracketing protocol was used to correct for mass bias. An alternative protocol, using a double Tl spike to correct for mass bias, was found to be unsuccessful. Possible reasons for this failure were thought to be inhomogeneity of the Tl spike within the pellets, differences in the Pb and Tl vaporisation rates and limitations in the precision of the Tl measurements due to the relatively short detector times spent acquiring Tl data.

Australian researchers have investigated the potential of using Pb isotopic ratio measurements in dust particles as a means of assessing the impact of wind blown dust from a uranium mine29. Dust on the leaves of an indigenous tree species was collected for analysis. Leaves were dissected and leached in low molarity nitric acid, the solutions evaporated on a hotplate and redissolved with 0.4M HBr. The samples were then loaded onto Dowex anion-exchange columns and Pb was eluted with 1 M nitric acid; this procedure was repeated not only to preconcentrate Pb but also to remove matrix elements. A 205Pb spike was added so that both the isotopic composition and the Pb concentration could be determined in the same measurement cycle. A few microlitres of sample were loaded onto rhenium filaments for analysis by TIMS. Dusts collected on Teflon air filter samples were similarly processed. Procedural blanks for filters amounted to approximately 280 pg Pb and were, on average, less than 4% of the total Pb measured in the samples collected. Procedural blanks for leaf samples were found to be smaller and amounted to 20 – 60 pg for samples containing between 200 pg and 100 ng total Pb. Seasonal measurements showed that the annual average contribution from this mine to airborne Pb concentrations in a small town situated 2.5 km NW was approximately 13%, although there were variations between the dry and wet seasons. In the dry season, the relative contribution from the mine dropped to less than 1% at a distance of 12.5 km along the major wind direction. Based on isotopic data in this study, an effective radiation dose arising from the potential of inhaling mine dust particles was calculated to be approximately 2 µSv year-1. The authors suggest that high volume air sampling protocols, combined with rapid Pb isotope ratio measurements by ICP-MS, could provide a quick and reliable method of dose apportionment around similar uranium mining operations.

Although Pb isotope measurements are often carried out on aerosol samples from urban environments to assist in source apportionment studies, measurements in more pristine maritime environments are rarer. Thus it is good see a paper by Witt et al.30 describing the sampling for heavy metals they carried out on cruises from the UK to the Falkland Islands and from South Africa to Australia. Aerosol TSP samples were collected on acid-washed cellulose ester filters at a flow rate of 1 m3 min-1 for 24 hours whilst steaming in the Indian Ocean. For the Southern Atlantic cruise, an alternative sampler was employed and particles were separated into two size fractions, namely >1 µm and <1 µm. Portions of each filter were leached in 0.1 M trace metal grade HNO3 and Pb isotopes measured by MC-ICP-MS. A Tl spike was used to monitor mass bias and NIST SRM 981 lead isotope standard was used to verify the quality of the data. Normalised blank-corrected beam intensities were used to calculate the lead isotope ratio of the sample filters. Clear differences were noted in the isotope ratios of samples collected on either side of the Indian Ocean, with the signature of Australian lead ore dominating over much of the eastern and mid-southern Indian Ocean. Samples collected over the western Indian Ocean, and parts of the Atlantic Ocean under the influence of airstreams from South Africa, suggest that the isotope ratios are now dominated by mining and coal burning activities from this region. The northern Atlantic Ocean was found to have isotopic compositions similar to those reported for European aerosol samples but differences in isotopic compositions between onshore and offshore winds suggest mixing of European and American lead sources.

Korean researchers used high volume air sampling techniques (details of size selective inlet system not given) to collect aerosol samples for the subsequent determination of Pu and its isotopes31. Cellulose ester filter samples were digested in concentrated nitric acid after spiking each sample with ~ 80 fg of 242Pu for subsequent quantification using an ID procedure. Initially, all Pu species in these digests were reduced to PuIV with sodium nitrite. Then 100 mg of TEVA resin (100-200 mesh, EIChrom Ltd) was added to each digest so that Pu species could be preconcentrated. Initial washing of this resin with 20 ml of 2 M nitric acid and 10 ml of 9 M hydrochloric acid removed U and Th species. Finally, Pu was eluted with 1 ml of 0.05 M ammonium oxalate. A MC-ICP-MS system equipped with a desolvating micro-concentric nebuliser was used for the subsequent analysis. A 233U/236U mixed spike was added prior to analysis to correct for mass bias. Interferences on

239Pu arising from peak tailing from 238U and the formation of 238U1H was minimised by the chemical separation procedure employed and optimisation of the spike concentration used. Residual overlaps were corrected using factors previously determined in conjunction with concurrent 238U measurements. Figures of merit included LOD of 0.61 fg ml-1 for 239Pu and 0.56 fg ml-1 for 240Pu; this equates to 0.004 μBq m-3 and 0.012 μBq m-3 for 239Pu and 240Pu respectively based on a nominal 350 m3 air sample. The precision of the Pu isotope ratio measurements was better than 2% for sample quantities greater than 20 fg of 239Pu. Dust from mainland Asia was sampled between June 2001 and April 2002 and peak concentrations of 0.58 μBq m-3 for 239Pu and 0.40 μBq m-3 for240Pu were determined in springtime samples. Mean 240Pu/239Pu ratios were calculated to be 0.191 ± 0.013, close to regional averages determined previously.

Winterholler and coworkers32 describe preliminary studies they carried out using a new commercially available NanoSIMS instrument to measure sulphur isotope ratios in μm-size airborne particulate matter collected on nucleopore filters. Initial results suggest that the instrument is capable analysing individual particles with an internal volume down to 0.5 μm3 at a precision of 3 – 10‰ (2σ) for δ34S.

Spanish workers describe a procedure for the measurement of 129I in aerosol samples by AMS33. Very high volume sampling was employed (~450 m3 hr-1) to collect weekly samples that were subsequently batched to provide monthly-integrated samples. Filter samples were leached in an extraction solution consisting of 0.05 M sodium hydroxide and 0.025 M sodium hydrogen sulphate. The solution was then extracted into a chloroform phase and back extracted into 0.1 M sodium hydrogen sulphate. Sulphates were removed by centrifugation after the addition of barium nitrate and iodine species were subsequently extracted as silver iodide by the addition of silver nitrate. This precipitate was washed and dried and finally mixed with pure silver before pressing into a target pellet. The isotopic ratio 129I/127I was subsequently measured for air samples collected in Seville during 2001-2002. However, no short-term correlations with gaseous 129I emissions from nuclear reprocessing plants at Sellafield and La Harve could be deduced. Results were also compared with those determined previously in Seville for gaseous and rainwater samples. The aerosol samples collected in the current work showed higher isotopic ratios than those determined in the gaseous samples and are at odds with the known decline in gaseous 129I emissions from these nuclear reprocessing facilities in the intervening time period. The higher isotopic ratios in the aerosol samples could suggest that the 129I is mainly released in an aerosol form or maybe initially as a gaseous form, which subsequently associates itself with aerosol species. The similarity between isotope ratios measured in rainwater samples and in the aerosol samples suggests that washout from airborne particulates more readily occurs than washout from gaseous phase iodine.

Ridley and Stetson34 reviewed the current status of Hg isotopic measurements and included an overview of the capabilities of the current generation of MC-ICP-MS systems. They suggest that it is possible to measure the Hg isotopic ratios with sufficient precision (<0.2‰) to evaluate natural fractionation processes. Studies to date suggest that these processes produce a spread of δ202 Hg values of ca. ±7‰. They suggest that it is vital to establish a reference material, with precisely known values for Hg isotope ratios, to facilitate future inter-laboratory comparisons. In conclusion, they suggest that Hg isotope systematics may be an important addition to the geochemical toolbox in economic geology and environment studies.

1.7 Calibration standards, reference materials and inter comparison studies

The lack of suitable calibration standards, i.e. standard filters carrying particles of known chemical composition, continues to hinder the quality of aerosol measurements. Filter standards for XRF techniques remain scarce and analysts often have to prepare such standards in-house. The approach used by Gehrig et al.4 was to collect natural samples on filters and to analyse them initially by WDXRF. Subsequently, the filters were subjected to acid dissolution and elemental analysis by ICP-AES and ICP-MS. The ICP data was then entered into the XRF instrument software to complete the calibration loop. The advantage of this approach is that real rather than artificial samples are used for calibration and the data are traceable to primary standards via the use of the ICP multi-element standards. However, this only holds true if the dissolution step employed is quantitative. The main disadvantage with this approach lies in the fact that it may not be possible to collect sufficient material on filters to provide extended calibration ranges. An alternative approach sometimes used to produce standard filters for XRF calibrations is to prepare artificial filter standards using a desolvating nebuliser to generate a stream of dry metallic particles from multi-element solutions. A novel variation developed by European collaborators was to produce potential calibration standards for SR-TXRF by modifying inkjet printers so that they deposited picolitre quantities of standard solutions reproducibly onto TXRF targets35. Depending on the type of printer cartridge used, droplets generated by such printers were found to be between 50 and 200 µm in size. The precision of the amount deposited, based upon the replicate SR-TXRF analysis of a nominal 2.5 ng cobalt sample, was found to be of the order of 12%. The researchers suggest that it would be technically feasible to ‘print’ a given deposition pattern using widely available printing software packages, thereby mimicking the deposition pattern of airborne particles collected in impactor samplers.

Elemental carbon is a major component of soot produced from burning of fossil fuel and from biomass fires. There is ongoing concern regarding its role in the degradation of air quality and the public health effects from exposure to carbon- containing dusts such as diesel fumes. That said, its measurement remains problematic. There are difficulties with thermally based instrumental methods in so far as their ability to distinguish and quantify elemental and organic carbon species depends inherently upon the instrumental conditions employed. The viability of the alternative aethalometer technique, based on the difference in light transmitted through a clean quartz sampling filter compared to a particle loaded filter, has also been questioned. The assumption that there is a linear response between black carbon content and light attenuation, and that the attention coefficient is constant, is being debated. The potential for light scattering within the detector cell to falsely enhance the signal has also been raised. Despite numerous intercomparisons and the development of a NIST RM filter, differences between procedures can be seen but not easily explained. Kirchstetter and co-workers36 suggest that what is required is the development of a reproducible means of producing well characterised ‘elemental carbon on filter’ RMs. They developed a procedure whereby elemental carbon aerosols are reliably produced by an inverted methane–air diffusion flame. It was possible to generate test aerosols over a period of ten hours, at µg m-3 levels, with a precision of 2.8%. Shorter-term precisions of test atmospheres generated at mg m-3 levels were around 1%. They suggest that future work could investigate the co-mixing of inorganic components such as metals and organic carbon components into this elemental carbon plume to produce aerosols that would mimic natural carbonaceous aerosols more closely.

Lee and co-workers37, with a similar aim but a different approach, used a spray-drying approach to generate simulated submicron carbonaceous particles. These particles were produced by nebulising elemental carbon (EC) in the form of a carbon black hydrosol and potassium hydrogen phthalate (KHP) as a source of organic carbon (OC). The latter was chosen because it has a relatively low solubility in water and a high melting point, making it suitable for use with a desolvating ultrasonic nebuliser. The resultant aerosols were sampled onto quartz fibre filters. These reference filters were analysed by TOA methods based upon both the IMPROVE and NIOSH 5040 analytical protocols. Results were compared to concentrations derived from gravimetric measurements. Total carbon measurements, i.e. the sum of EC and OC species, by both protocols were found to be in good agreement with gravimetric data. However, discrepancies were noted in EC and OC measurements arising from problems in measuring accurately the quantity of pseudo EC generated pyrolytically from the combustion of OC species. These two approaches of generating reference filters with predetermined EC/OC ratios, as well as the spark source generation system mentioned in section 1.4, will be invaluable in the future development, evaluation and optimisation of TOA methods, aethalometer-based techniques and other emerging mass spectrometric methods.

The NIST SRM 1648 urban particulate matter, is a reference material that has been widely used to validate digestion procedures. The stock of this material is now exhausted and it is welcome news that NIST is in the process of producing a new batch38. Homogeneity has been improved through the use of an advanced jet-milling process and it is anticipated that this replacement RM will be certified using 1 – 10 mg sample aliquots, thus equating more closely to the mass of particulate material typically collected on air filter samples. It is understood by the reviewer that similar airborne particulate CRM are in production by other organisations such as IRMM and NIES and it is interesting to note that the new generation SS-AAS instruments will play a vital role in future characterisation studies involving powdered candidate materials. These developments are most welcome in a measurement arena where there is a paucity of suitable CRMs.

Another CRM widely used, specifically for the determination of PGE in airborne particulate matter, is BCR CRM 723. In a detailed paper, Sutherland39 provides a comprehensive statistical re-examination of the certification data supplied with this material. He observed statistically significant differences between data sets supplied by certification laboratories for Pd, Pt and Rh that used similar measurement procedures. Differences were also noted between data sets derived using different instrumental techniques. Interestingly, statistically significant differences were also noted between laboratories using ID-ICP-MS procedures. Some caution has to be exercised regarding the acceptance of ID as a gold standard technique, as the effectiveness of the initial digest of solid materials prior to the addition of the enriched isotope spike, in a liquid form, may well be a critical source of bias. Sutherland also cites statistical evidence for a bi-modal distribution in the Pd results and recommends the development of a new CRM with a more representative mix of PGEs and significantly higher Pd concentrations to mimic more closely the composition of particles analysed nowadays.

Because reference filter standards for EC/OC, such as those described above, are not widely available, evaluation of TOA protocols has had to rely on intercomparison studies. Bae et al.40 describe results from the field-testing of two Sunset Laboratory semi-continuous TOA instruments, which have similar PM2.5 cyclonic inlet and denuder systems. These denuder systems contain replaceable charcoal impregnated filter strips to remove gaseous organic compounds that could otherwise absorb on the quartz fibre filter. The difference between the two systems is the number of ramp steps and the hold temperatures in the heating programmes employed. There was considerable scatter in the correlation plot of OC determinations by the two instruments (slope 0.97 ± 0.07, R2 of 0.37), no doubt influenced by the differences in the thermal programmes used. Better correlation between the two instruments was demonstrated for EC measurements (slope 1.05 ± 0.15, R2 of 0.98). Black carbon (BC) was also measured in parallel but the correlation slope between EC and BC varied between 1.23 and 1.61, suggesting a possible variation in the BC attenuation coefficient.

An intercomparison of real time ammonium measurements at both urban and rural locations in New York has been undertaken41. Three real time semi- continuous measurement systems were deployed. The first instrument, a particle-into-liquid sampler plus IC system, involved mixing the particles with saturated water vapour to produce droplets easily collected by inertial techniques. These droplets are collected into a small stream of high purity water for subsequent analysis by IC. They were analysed concurrently for anions and cations at a rate of 4 samples per hour. A PM2.5 cyclonic inlet system was used in conjunction with a denuder system to remove coarse particles, gaseous ammonia, nitric acid, sulphur dioxide and organic vapour species. The second system, the wet-scrubbing long path absorption photometer, works by using a gas-liquid separator to scrub atmospheric ammonia and ammonium species collected on glass frit impactors. Dissolved gaseous species are then derivatized to form a highly light-absorbing indophenol within an in-line reaction coil for subsequent analysis using a long path absorption spectrometer. A twin channel system was used: channel one measured total NHX species (gas plus aerosol) whilst channel two measured aerosol ammonium only, as gaseous ammonia was removed by a citric acid coated denuder system upstream of the glass frit impactor. The sampling resolution of this instrument was 4 minutes. The third system evaluated was an aerosol quadrupole mass spectrometer. Aerosol particles are focused into the instrument using an aerodynamic lens, which efficiently focuses particles in the 60-600 nm size range. These particles then strike a heated surface (500-700 °C) where volatile and semi-volatile components evaporate. The resultant vapour is ionised by electron impact and the ions generated are analysed by quadrupole MS. A collection efficiency factor was required to correct data for incomplete detection of PM2.5 particles due to particle losses within the system. Results obtained from these three instruments were compared against 24-hour integrated samples collected using the US EPA speciation trends network (STN) protocol. STN samplers employ the PM2.5 size selective inlets. In this protocol, a nylon filter is used to collect particles from pumped air samples, which are subsequently leached in water and analysed by IC for ammonium ion and other ionic species. Paired instrument correlation slopes between 0.71 and 1.04 were obtained indicating a consistency of performance between instruments (R2 > 0.82). Although the number of STN filter measurements was small, results indicated that the semi-continuous measurement technique and the filter-based technique tracked each other fairly well (R2 = 0.90-0.99). Divergences between results could be explained on the basis of differences in particle size collection efficiencies, inlet transport losses and both positive and negative sampling artefacts arising from the use of different denuder-based gaseous scrubbing systems.

2 Water analysis

This section highlights new developments and improved analytical methods using atomic spectroscopy for the determination of trace metal(loid)s and their associated elemental species in environmental water samples reported since the last Update1. As with previous Updates in this series, elemental speciation and the use of sample preconcentration methods have featured strongly. Tables summarizing the preconcentration and extraction procedures of interest have been included. These will be of particular interest to analysts without access to the most sensitive instrumentation such as ICP-MS.

2.1 Sample preparation.

2.1.1 Sample collection, preservation and filtration. Serious sample contamination resulting from the bottles used for sample storage is not unknown. High-density polyethylene (HDPE) bottles are felt to be the best choice of sample container for trace metal analysis. However, a recent study has highlighted high blank values for Ag, Ba, Sr, V, Zn and Zr and the values for Ba and Zn were about ten times above the concentrations that would be expected in natural water samples42. Laboratory studies showed that the source of the contamination was the HDPE bottles themselves and even simple acid washing prior to use did not solve the problem. This emphasizes the need to regularly check the bottles used for water samples and include provision for establishing blank values within the experimental design used for sampling.

The effect of oxic and anoxic filtration on the methylmercury concentration of pore waters from pulp fibre sediments severely contaminated with Hg has been investigated by Drott et al.43 using species-specific isotope dilution GC-ICP-MS. The analyte levels measured after anoxic filtration were greater than those after oxic filtration and also varied dramatically between samples. The main mechanism for the loss of methylmercury from the samples was proposed to be adsorption onto newly formed Fe/Mn oxy/hydroxide surfaces in samples with an intermediate redox potential and containing a mixture of oxidation-sensitive minerals. This type of study, using highly reliable analytical measurements, is crucial for identifying specific steps in the analytical protocol that can be the source of systematic errors and should be a particular focus of attention during method development.

On-site measurements are important for water analysis, particularly for screening samples to be taken for further investigation, or when dealing with sites located in remote areas. The USEPA evaluated seven field test kits designed to detect AsIII, AsV and a combination of As-containing species44. Only 2 of the 7 kits tested met criteria for accuracy, precision, linearity, expense, and ease of use. The authors concluded that, given the variable performance among the kits, users should be cautious in choosing field test kits for regulatory purposes.

2.1.2 Pre-concentration, extraction and separation procedures. Two main approaches for preconcentration of trace elements from water have dominated the literature during this review period: cloud point extraction (CPE) and SPE using columns packed with chemical or biological adsorbents. These methods will be of interest to workers who require low LOD but do not have access to the most sensitive instrumentation. Details are given in Table 1, which describes the SPE applications, and Table 2, which details CPE.

Analytes	Sample Matrix	Substrate Coating	Column Substrate	Detector	Comment	Ref
Ag, Cd, Co, Ni, Pb, U, Y	Natural water samples	1-phenyl-3-methyl-4-benzoylpyrazol-5-one	PTFE knotted reactor	FI-USN-ICP-TOF-MS	LOD (ngl-1) 0.3 for Y to 15.2 for Ni. Elution with 1% HNO3. Enrichment factor 3 to 14.	45
Ag, Au, Ga, In, Nb, Pd	Natural water	3-(8-quinolinylazo)-4-hydroxybenzoic acid	Nanometer-sized alumina	FI-ICP-OES	LOD (μg l-1): 0.12 for Ag; 0.27 for Au; 0.19 for Ga.; 0.54 for In; 0.18 for Nb; 0.44 for Pd. Enrichment factor 10.	46
Ag, Cu, Zn	Natural water	Salen 2,2’-(3-aza-1,5-pentanedyle bis(nitrilomethylidyne)) bis-phenol	Surfactant-coated alumina	ETAAS	LOD (μg l-1): 0.8 for Ag; 0.3 for Cu; 0.47 for Zn. Enrichment factors: 125 for Ag; 166 for Cu; 210 for Zn.	47
Ag	Waste water	2-mercaptophenylimino)methyl] phenol	Octadecyl silica membrane disk	FAAS	LOD 8.0 ng l-1.	48
Ag	Natural water	n/a	Multiwalled carbon nanotubes	FAAS	LOD 0.6 μg l-1. Elution with 1M HNO3.	49

AsIII	**Natural water**	**Pyrrolidine dithiocarbamate**	**PTFE turnings**	**HGAAS**	**LOD 20 ng l-1. Elution with 2M HCl.**	**50**
Be, Cd, Cr, Cu, Pb	**Natural water**	**n/a**	**Iminodiacetate chelating resin**	**ICP-AES**	**LOD between 0.001 – 0.18 6 µg l-1. Enrichment factor 19. NRCC SLRS-4 riverine water.**	**51**
Cd, Cu, Ga, In, Ni, Pb, REE, Sc, Th, U	**River water**	**Serine diacetic acid**	**Chitosan**	**ICP-AES**	**LOD <1 µg l-1. Elution with 1M HNO3. NRCC SLRS-4 riverine water.**	**52**
Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn	**Tap and stream water**	**n/a**	**Amberlite XAD-2000**	**FAAS**	**LOD between 0.3 – 2.2 µg l-1. Enrichment factor 100. 8-hydroxyquinoline complexes adsorbed onto resin.**	**53**

Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	**Natural water**	**Chromotropic acid**	**Alumina**	**ICP-AES**	**LOD (μg l-1): 0.14 for Cd; 0.62 for Cr; 0.22 for Cu.; 0.54 for Fe; 0.27 for Mn; 0.28 for Ni; 0.53 for Pb; 0.38 for Zn. Enrichment factor 50 – 100.**	**54**
Cd, Fe, Mn, Ni, Sb	**Waste waters**	**Trioctyl phosphine oxide**	**Bentonite**	**FAAS**	**LOD (μg l-1): 0.25 for Cd; 0.12 for Fe; 0.19 for Mn.; 0.17 for Ni; 2.3 for Sb. Elution with 1M HNO3.**	**55**
Cd, Co, Cu, Ni, Pb	**Pond, tap and drinking waters**	**Aminothioamidoanthraquinone**	**Silica gel**	**FAAS**	**LOD (μg l-1): 1.1 for Cd; 0.95 for Co; 1.0 for Cu.; 2.9 for Ni; 22.5 for Pb. Elution with 1% HNO3.**	**56**
Cd, Co, Cu, Zn	**Natural water**	**2,6-dihydroxyphenyl-diazoaminoazobenzene**	**Amberlite XAD-4**	**FAAS**	**LOD (μg l-1): 0.1 for Cd; 0.5 for Co; 0.3 for Cu; 0.2 for Zn. Elution with 0.5M HCl. Enrichment factors): 42 for Cd; 33 for Co; 28 for Cu; 31 for Zn. 2,6-dihydroxyphenyl-**	**57**

					diazoaminoazobenzene complexes adsorbed onto resin.	
Cd, Co, Cu	Tap and river water	2,4-dinitrophenyldiazoaminoazobenzene	Amberlite XAD-2	FAAS	LOD (μg l-1): 0.06 for Cd; 0.08 for Co; 0.06 for Cu.	58
Cd, Cu, Zn	Dam, lake and tap waters	Saccharomyces carlsbergensis immobilized on support	Silica gel 60	FAAS	LOD (μg l-1): 1.5 for Cd; 1.7 for Cu; 1.1 for Zn. Validated with spiked samples.	59
Cd, Co, Ni	Natural water	Mesoporous alumina coating	Capillary fibre	ICP-MS	LOD (ng l-1): 1.4 for Cd; 0.33 for Co; 1.5 for Ni. Enrichment factor 10 for each element.	60
Cd, Pb	Drinking water	n/a	Dowex Optipore V-493	FAAS	LOD (μg l-1): 0.43 for Cd; 0.65 for Pb. LGC 6010 hard drinking water. Dibenzyldithiocarbamate complexes adsorbed onto resin.	61
Cd	Drinking water	4-(2-Pyridylazo)-resorcinol	Polyurethane foam	FAAS	LOD 20 ng l-1. NIST SRM 1643d trace elements in natural water.	62
Cd	River and lake	Chlorella vulgaris and Saccharomyces	Silica beads	ETAAS	LOD 1.0 ng l-1. Elution with HNO3. Enrichment factor 37.	63

	water	cerevisiae immobilized on support			1000 mL sample vol.	
Co, Cu, Fe, Ni, Pb, Zn	Natural water	Aspergillus fumigatus immobilized on support.	Dialon HP-2MG	FAAS	LOD (μg l-1): 0.7 for Co; 0.3 for Cu; 0.3 for Fe; 0.6 for Ni; 0.5 for Pb; 0.4 for Zn. NRCC SLRS-4 riverine water.	64
Co, Cu, Fe, Pb	River water	Bacillus sphaericus immobilized on support.	Diaion SP-850	FAAS	LOD 0.2 – 0.8 μg l-1. Elution with 1M HCl. NRCC SLRS-4 riverine water.	65
Co, Cr, Fe, Pb	Tap and stream water	4-(2-Pyridylazo)-resorcinol	Amberlite XAD-1180	FAAS	LOD (μg l-1): 3.3 for Co; 3.0 for Cr; 1.3 for Fe; 7.2 for Pb. Elution with 3M HNO3. Enrichment factors: 50 for Co; 75 for Cr; 125 for Fe; 75 for Pb.	66
Co, Ni	Natural water	5-(6-methoxy-2-benzothiazoleazo)-8-aminoquinoline	C18 silica extraction disks	ICP-AES	LOD (μg l-1): 0.08 for Co; 0.06 for Ni. Elution with 0.01M HNO3. Enrichment factor 100.	67
Co, Mn	River water	2-hydroxyacetophenone-3-thiosemicarbazone	Amberlite XAD-2	ICP-AES	LOD (μg l-1): 0.82 for Co; 0.60 for Mn. Elution with 2M HNO3.	68
Cr, Cu,	Natural	Tributyl phosphate	Montmorillonite	FAAS	LOD (μg l-1): 0.19 for Cr; 0.16	69

Fe, Mn	**water**				**for Cu; 0.09 for Fe; 0.23 for Mn.**	
Cr, Cu, V	**Lake water**	**Mesoporous titania**	**Fused-silica capillary fibre**	**ETV-ICP-MS**	**LOD (ng l-1): 3.3 for Cr; 6.3 for Cu; 1.1 for V. Elution with 1M HNO3. Enrichment factor 33.**	**70**
CrVI, Pb	**Natural water**	**n/a**	**Polychlorotrifluoroethylene beads**	**FAAS**	**LOD (µg l-1): 0.4 for CrVI; 1.2 for Pb. Elution with IBMK. Enrichment factor 94 for CrVI and 220 for Pb. NIST SRM 1643d trace elements in natural water. Ammonium pyrrolidine dithiocarbamate complexes adsorbed onto beads.**	**71**
Cr	**Sea water**	**2-amino-benzenethiol**	**Dowex 50W-X8**	**ICP-AES**	**LOD 0.3 µgl-1.**	**72**
Cu , Pb	**Natural water**	**n/a**	**Polychlorotri-fluoroethylene beads**	**FAAS**	**LOD (µg l-1): 0.07 for Cu; 2.7 for Pb. Elution with IBMK. Enrichment factor 250. Diethyldithiophosphate complexes adsorbed onto beads.**	**73**

Cu, Pb	**Natural water**	**1,2-Bis(salicylidenamino) ethane**	**SDS coated alumina**	**ETAAS**	**LOD (ng l-1) 2.7 for Cu; Pb for 8.6. Elution with 4M HNO3. Enrichment factor 100.**	**74**
FeIII	**Natural water**	**2,3-dihydroxy benzoic acid**	**Amberlite XAD-4**	**FAAS**	**LOD 6nM. Elution with 0.5M H3PO4. Enrichment factor 100.**	**75**
FeIII	**Natural water**	**n/a**	**Surface-imprinted (Fe) amino-functionalized silica gel**	**ICP-AES**	**LOD 0.34 µg l-1.**	**76**
Hf, Nb, Ta, W, Zr	**Seawater**	**8-hydroxyquinoline**	**TSK resin**	**ICP-MS**	**LOD 0.009 - 0.15 pM kg-1. Resin stable to 5M HF. Enrichment factor 50.**	**77**
Hg	**Natural water**	**4-(2-Pyridylazo)-resorcinol**	**Nanometer SiO2**	**CVAAS**	**LOD 0.43 µg l-1. Elution with 6M HCl. Enrichment factor 50.**	**78**
HgII	**Natural water**	**n/a**	**Multi-walled carbon nanotubes**	**CV-AFS**	**LOD 1.2 ng l-1. Enrichment factor 39.**	**79**
HgII	**Lake and well water**	**n/a**	**Cyanex 923**	**CVAAS**	**LOD 0.2 ng l-1. Elution with 10% HNO3. Reduction with NaBH4. Selective for HgII over MeHg.**	**80**

Ni	**Natural water**	**n/a**	**Surface-imprinted (Ni) amino-functionalized silica gel**	**ICP-AES**	**LOD 0.16 μgl-1.**	**81**
Pb	**Seawater**	**1,5-Bis(2-pyridyl)-3-sulpophenyl methylene thiocarbonohydrazide**	**Aminopropyl-controlled pore glass in autosampler tip**	**ETAAS W-Rh coated tube**	**LOD 12 ng l-1. Elution with 10% HNO3. Enrichment factor 20.5.**	**82**
Pb	**River water**	**n/a**	**Analig Pb-01**	**ICP-AES**	**LOD 70 ng l-1. Elution with nitrilotriacetic acid. Enrichment factor 19. NRCC SLRS-4 riverine water.**	**83**
Pb	**Tap, mineral and synthetic seawater**	**n/a**	**Multi-walled carbon nanotubes**	**FAAS**	**LOD 2.6 μg l-1. Elution with 1M HNO3. Enrichment factor 44.**	**84**
Pb	**Lake water**	**Dithizone**	**Amberlite XAD-2**	**FI-FAAS**	**LOD 79 ng l-1. On-site preconcentration. Enrichment factor 384 (50 ml sample vol.).**	**85**

					GBW 08608 metals in water.	
Pd	Natural water	n/a	Surface-imprinted (Pd) amino-functionalized silica gel	ICP-AES	LOD 0.36 µg l-1.	86
Pd	Lake and seawater	3-chloro-1,2-epoxypropane	Chitosan	ETAAS	LOD 0.14 µg l-1.	87
REE	Seawater	Maleic acid	Polytetrafluoro-ethylene fiber	ICP-MS	LOD in the range 1 – 20 pg l-1. Elution with 0.9M HNO3. Enrichment factors 69 – 97.	88
REE	Lake water	n/a	Anthracene-cetyltrimethyl ammonium bromide	ICP-AES	LOD in the range 11 – 304 ng l-1. Elution with HCl. Enrichment factor 25 for each of 16 REEs. Retention of REE pyrocatechol violet complexes.	89
Sb	River water	Saccharomyces cerevisiae immobilized on support.	Polyurethane foam	HG-ICP-AES	LOD (µg l-1): 0.8 for Sb; 0.15 for SbIII. Total Sb determined after reduction with thiourea.	90
SeIV, SeVI	Drinking water	Methionine	Controlled-pore glass	FI-HG-ICP-	LOD 11 ng l-1. Elution with 10% HCl. Enrichment factor 90.	91

				AES	**SeVI selectively retained at pH 3, speciation by difference.**	
UVI	**Natural water**	**Salicylaldehyde**	**Mesoporous silica**	**ICP-AES**	**LOD 0.5 μg l-1. Enrichment factor 100. Adsorption at pH 5.0.**	**92**
Zn	**Natural water**	**n/a**	**Surface-imprinted (Zn) amino-functionalized silica gel**	**ICP-AES**	**LOD 0.29 μg l-1.**	**[, ,28/0121**

Table 1: The SPE applications used for sample preconcentration.

n/a – not applicable.

Analyte	Matrix	Surfactant	Chelator	Detector	Comment	Ref.
Ag, Co, Cr, Cu, Fe, Mn, Ni, Pb	**Natural and sea water**	**Triton X-114**	**Ammonium pyrrolidine dithiocarbamate**	**ETAAS**	**LOD (µg l-1): 0.003 for Ag; 0.008 for Co; 0.003 for Cr; 0.006 for Cu; 0.015 for Fe; 0.002 for Mn; 0.009 for Ni; 0.01 for Pb. Enrichment factor 200. NRCC CASS-4 and NASS-5 seawater, NIST 1640 natural water.**	**93**
Ag	**Natural water**	**Triton X-114**	**2-mercaptobenzothiazole**	**FAAS**	**LOD 2.2 µg l-1.**	**94**
Ag	**Natural water**	**Triton X-114**	**Diethyl dithiophosphate**	**ETAAS**	**LOD 7.8 ng l-1. Enrichment factor 35.**	**95**
Cd	**Tap, waste and sea water**	**Triton X-114**	**None**	**FAAS**	**LOD 1.0 µg l-1. Iodide media required for extraction.**	**96**
Cd	**Natural water**	**Triton X-114**	**Ammonium pyrrolidine dithiocarbamate**	**F-QF-AAS**	**LOD 0.04 µg l-1.**	**97**
Cd	**Natural**	**Triton X-114**	**2-(5-bromo-2-pyridylazo)-**	**ETAAS**	**LOD 0.04 µg l-1. Enrichment**	**98**

	water		5(diethylamino)-phenol		factor 21.	
Cd	**Natural water**	**Polyethyleneglycol mono-p-nonylphrnylether**	**None**	**CVAAS**	**LOD 0.56 ng l-1. Enrichment factor 62.**	**99**
CeIV	**Natural water**	**Triton X-114**	**n-p-tolylbenzohydroxamic acid**	**ICP-AES**	**LOD 0.4 µg l-1. Enrichment factor 13.8.**	**100**
Co, Ni	**Natural water**	**Triton X-114**	**2-(6-methyl-benzothiazolylazo)-4-bromophenol**	**FAAS**	**LOD 0.9 µg l-1 for Co and 1.1 µg l-1 for Ni.**	**101**
Cu, Ni	**Natural water**	**Triton X-114**	**2-hydroxyimino-1-methylpropylidene amino-1-naphthyl imino-2-butanone oxime**	**FAAS**	**LOD 0.14 µg l-1 for Cu and 0.2 µg l-1 for Ni. Enrichment factors 65 for Cu and 59 for Ni.**	**102**
Cu	**Drinking, tap and sea water**	**Triton X-114**	**1-(2-pyridylazo)-2-naphthol**	**ETAAS**	**LOD 5.0 ng l-1.**	**103**
Cu	**Natural and drinking**	**Triton X-114**	**6-(2'-(6'-methyl-benzothiazolylazo))-1,2-dihydroxy-3,5-benzene**	**FAAS**	**LOD 1.5 µg l-1. Enrichment factor 14.**	**104**

	water		disulfonic acid			
FeIII, Mn	**Natural water**	**Triton X-100**	**1-phenyl-3-methyl-4-benzoyl-5-pyrazolone**	**ETAAS**	**LOD 0.08 μg l-1 for FeIII and 0.02 μg l-1 for Ni. Enrichment factors 25 for FeIII and 31 for Mn.**	**105**
HgII	**Natural water**	**Triton X-114**	**None**	**CVAAS**	**LOD 0.1 μg l-1. Iodide media required for extraction.**	**106**
MnII, MnVII	**Natural water**	**Triton X-114**	**1-phenyl-3-methyl-4-benzoylpyrazol-5-one**	**ETAAS**	**LOD 0.02 μg l-1. MnII separated from MnVII by affinity to complexing agent**	**107**
Mn	**Natural water**	**Triton X-100**	**1-phenyl-3-methyl-4-benzoyl-5-pyrazolone**	**FAAS**	**LOD 1.45 μg l-1. Enrichment factor 20.**	**108**
Ni	**Natural water**	**Triton X-100**	**1-phenyl-3-methyl-4-benzoyl-5-pyrazolone**	**ETAAS**	**LOD 0.12 μg l-1. Enrichment factor 27.**	**109**
Pb	**Natural water**	**Triton X-114**	**Brillant cresyl blue**	**FAAS**	**LOD 7.5 μg l-1.**	**110**
Rh	**Natural water**	**Triton X-114**	**2-propylpiperidine-1-carbodithioate**	**FAAS**	**LOD 0.052 μg l-1. Enrichment factor 50.**	**111**
Se	**Natural waters**	**Triton X-114**	**Pyrrolidine dithiocarbamate**	**ETV-ICP-MS**	**LOD 8.0 ng l-1. Enrichment factor 39. SeIV separated from**	**112**

SeVI by affinity to complexing agent.

Table 2: The cloud point extraction applications used for sample preconcentration.

2.2 Speciation.

The determination of elemental speciation in waters has continued to figure strongly in the literature. New approaches to the measurement of As, Sn and halide-containing compounds have been reported, mainly involving the use of HPLC-ICP-MS, with less of a focus on molecular MS methods compared to last year.

Review papers dealing with chemical speciation of different elements in water samples have been published. A review of the speciation of Hg in the aquatic environment considers methods with low LOD that can be applied to real samples, including water113. It pays particular attention to the necessity for clean sampling procedures, proper sample storage and the performance of different separation techniques, including LC, HPLC and on-line and off-line GC. The speciation of Al in natural water has been reviewed114. The toxicity of Al is strongly influenced by its speciation but, because of its propensity to form unstable complexes and severe contamination issues, analytical measurement is difficult. This review highlights the most important analytical methodologies of the last 10 years and charts new trends in Al speciation.

The interest in unusual As-containing species has continued from last year with further reports on the particular As species found in sulfidic waters and the degradation products of Second World War chemical warfare agents. Wada et al.115 have developed a method based on molecular MS for the simultaneous determination of a range of As-containing chemical warfare degradation products in natural water samples. Eight compounds: 2-chlorovinylarsonic acid, phenylarsonic acid, phenylmethylarsinic acid, 2-chlorovinylarsine oxide, phenylarsine oxide, diphenylarsenic acid, bis(2-chlorovinyl)arsinous acid and bis(diphenylarsine) oxide, were determined by LC-MS/MS with LOD between 0.1 and 500 □g l-1. The As-S species present in synthetic geochemical water solutions have been investigated116. By using a method based on anion-exchange chromatography coupled to ICP-MS detection, the major species present in arsenite-sulfide simulated anoxic solutions were shown to be the four (oxy)thioarsenate species: mono-, di-, tri- and tetra-thioarsenate. The method was also applicable to the determination of AsIII, AsV and MMA, but not DMA. The sulfur content of the thio-arsenate peaks was measured as SO+ and provided a LOD of 0.1 □M l-1, whereas that for As was 0.1 nM l-1. The identity of the (oxy)thioarsenates present in the synthetic solutions was confirmed by the use of ESI-MS/MS, however it was not possible to generate spectra for natural water samples due to matrix effects.

The speciation of halogen-containing compounds has been an active area of interest recently. The determination of I and Br speciation in snow by IC coupled to ICP-MS has been reported117. Samples were collected from the northern Black Forest area over an altitude profile of 84 m. The results showed that organically bound iodine is the dominant species in snow (60 – 75%), followed by iodide, whereas iodate was only found in 2 samples despite a detection limit of 0.3 nM l-1. Two unknown species were observed at levels of 2 – 10 % of the total I and these were most likely anionic organo-I species. The majority of the Br was inorganic bromide with a maximum proportion of 32% organo-Br. A method based on anion-exchange coupled to ICP-MS detection has been reported for the determination of bromate and bromide in water containing high chloride levels118. An ammonium-containing mobile phase at pH 5.8 enabled resolution of the two species in 7 mins with limited clogging of the sample cone due to the volatile nature of the eluent. The detection limits for both species ranged from 2.0 to 3.0 □g l-1 for a 50 □l injection and the method was applied to the analysis of bromate and bromide in seawater. Bruchert et al.119 have developed a new approach to I speciation which uses species-specific ID and was employed to measure iodide and iodate in marine aerosols. Gel electrophoresis was coupled on-line to ICP-MS and species-specific ID using 129I enriched iodide and iodate corrected for the impact of the matrix on the electrophoretic migration and detection sensitivity of the ICP-MS. Iodide and iodate were shown to be present at the ng m-3 and sub-ng m-3 levels respectively in the aerosol samples. A further I-containing species, probably triiodide, was also observed in the samples, but it was unclear whether this was an artifact or not.

The speciation of organotin compounds in environmental waters continues to be addressed. Isotopically enriched butyltin compounds have been used for the routine quantitative and semi-quantitative determination of all the alkyltin species in landfill leachates120. After derivatization with tetrapropylborate all of the methylated, ethylated and butylated tin compounds were determined by GC-ICP-MS. The analytical procedure was optimized to take into account the variety of analytes and the high organic content of the samples and encompassed three major steps: nitric acid digestion under microwave heating; derivatization using sodium tetrapropylborate; and chromatographic separation. The level of butyltin compounds in the Southern hemisphere has been investigated121. Twelve organotin compounds were determined by GC-ICP-MS in the waters of Suruga Bay, Japan, with total organotins ranging from 0.8 to 19.7 ng l-1. In contrast, only three organotin compounds were detected in the Southern Ocean 1000 km from Antarctica, with the total concentration ranging from undetectable to 0.3 ng l-1.

2.3 *Instrumental analysis*

2.3.1 Atomic emission spectrometry. A novel method has been developed for the determination of dissolved inorganic, organic and total carbon in natural waters by IC-ICP-AES122. Dissolved inorganic carbon (DIC) was measured in untreated samples using IC with post-column addition of 0.1 M HNO3, to enhance CO2 removal in the nebuliser, followed by ICP-AES detection. Total dissolved carbon (TDC) was measured after on-line mixing with 0.1 M NaOH followed by ICP-AES detection. The dissolved organic carbon (DOC) was determined as the difference between DIC and TDC. The LOD were 0.5 mM for DIC and 0.1 mM for DOC.

2.3.2 Vapour generation methods. Two reviews on vapour generation methods have been published. Analytical methods for the determination of Hg using CV generation coupled to atomic spectrometry have been reviewed123. This focused on the use of three reductants, SnCl2, KBH4 and HCOOH and provided information on LOD and tolerance to interferences. Based on sensitivity, “greenness” and freedom from interference, the best choice for measurement of ultratrace Hg was UV-CV-ICP-MS with HCOOH as the reductant. Kumar and Riyazuddin124 have published a more comprehensive review of the literature on non-chromatographic HG atomic spectrometric techniques for the speciation analysis of As, Sb, Se and Te in waters. They cover HG coupled with AAS, ICP-AES and AFS for these elements and deal specifically with how careful control of experimental conditions, offline and online sample pretreatment methods and cryogenic trapping can be used for speciation analysis without the use of chromatographic separation. The other approaches that can be used include solvent extraction, ion exchange and selective retention by micro-organisms.

A number of new methods for vapour generation have been developed. Tyson's group at the University of Massachusetts have extended the use of the tetrahydroborate-form anion-exchange material developed by them for other hydride-forming elements, to the determination of antimony in water125. The FI-QT-AAS system includes tetrahydroborate immobilized on a strong anion-exchange resin (Amberlite IRA-400), packed in a column. The methodology was trialed on spiked sea and well waters and provided a detection limit of 0.55 μg l-1. Interferences from transition metals and signal suppression due to high ionic strength solutions were eliminated by the addition of L-cysteine or thiourea. A new CV-AAS approach for the determination of total Hg in water samples employs high-intensity ultrasonication to generate the cold vapour126. Chemical reduction of HgII to Hg0 is not required as this is facilitated by gases formed during sonication, which also aids transport of Hg0 from the solution as a result of the cavitation process. Addition of low MW organic acids such as formic acid favours the reduction process, giving an LOD of 0.1 μg l-1. Counter anions such as chloride favoured stabilization of HgII in solution, thus limiting full recovery. The same authors have also used the system coupled to a ETAAS detector for the determination of Hg in natural water samples127. After in situ trapping of Hg0 for 10 min onto a metal-pretreated platform (Pd, Pt or Rh) inserted into a graphite tube, a 10 ml sample generated an LOD of 0.03 μg l-1. Menemenlioglu et al.128 have developed a miniature quartz trap coupled to an electrochemical HG for the determination of Sb in drinking water. A portion of the inlet arm of a conventional quartz tube atomizer was used as an integrated trap for the on-line preconcentration of the generated hydride. A specially constructed thin layer electrochemical cell was used to generate stibine and the overall method gave an LOD of 0.053 μg l-1 for a sample size of 6 ml and trapping for 2 min. This represented an 18-fold sensitivity improvement compared to electrochemical HG alone. A novel and simple hydride generator has been developed to couple CE to ICP-AES129. The device eliminates the nebulisation step and overcomes the common problem of suction flow due to the nebulisation gas, which can affect CE separations. The system was applied to the speciation of Se oxidation states in tap and river water, providing LOD of 2.1 for SeIV μg l-1 and 2.3 μg l-1 for SeVI.

2.3.3 X-ray spectrometry. An important X-ray absorption fine-structure (XAFS) application for investigating the kinetics of chemical reactions at solid-liquid interfaces has been developed130. The methodology was applied to investigate the oxidation reaction of AsIII by manganese oxide using a column reactor. The work is of considerable importance in relation to leaching from fluvial sediments containing high concentrations of As, such as occurs in Bangladesh and SE Asia.

The determination of halogens in waters by different X-ray techniques has been described. Total reflection XRF has been used for the selective determination of bromate in drinking water131. Various membranes containing a few micrograms of different complexing agents in a PVC matrix were produced on the surface of quartz glass reflectors and immersed in the sample solution. After equilibrium, the reflectors were dried and then analysed by TXRF. An LOD equivalent to 0.9 ng l-1 was obtained with a PVC-aliquat-336 membrane and o-dianisidin as complexing agent. XANES has been used for the quantification of total organic and inorganic Cl concentrations in natural water samples132. The XANES spectra reflect contributions from all Cl-containing species present and therefore provide data on the total Cl content. Spectral features near the Cl K-absorption edge provide detailed information about the bonding state, whereas the absolute fluorescence intensity of the spectra is directly proportional to total Cl, thus allowing simultaneous determination of speciation and total Cl in the sample. Using this synchrotron-based technique, the Cl concentration could be determined down to the 5-10 mg l-1 level. It was possible to distinguish between inorganic chloride and organochlorine, as well as between aliphatic and aromatic organochlorine, by using the characteristic near-edge features of Cl in various model compounds.

2.3.4 Inductively coupled plasma mass spectrometry. A number of sample introduction systems for ICP-MS analysis have been compared and characterized. Asfaw and Wibetoe133 have developed and optimized a dual mode sample introduction system for ICP-MS, enabling the simultaneous analysis of HG vapour and liquid aerosol. The system was used for the determination of As, Bi, Cd, Co, Cu, Ni, Pb, Sb and Zn. The sensitivity increased significantly compared to conventional pneumatic nebulization, with enhancements of 77, 33 and 56 for As, Bi and Sb respectively. No significant change was apparent for the other elements that can form volatile species with NaBH4. A number of CRMs were used to verify the accuracy of the methodology, including NIST SRM 1643e (trace elements in water). Research workers at NRCC134 have compared solution nebulisation (SN), electrothermal vaporization (ETV) and laser ablation (LA) for the analysis of radionuclides in sea and river waters. LA is not a technique normally associated with such analyses, but was applied in this context to dried micro-droplets. The authors summarized the unique advantages and disadvantages of each system: ETV accommodates samples with a higher content of dissolved solids, whereas SN and LA require additional dilution by 50- and 10-fold respectively; ETV and LA achieved similar sensitivities and LOD, the latter ranging from 0.017 to 0.029 ng l-1; and although SN provides the best precision, 2% RSD versus 7% for ETV and 8% for LA, the formation of UH+ can be reduced at least 100-fold using LA. Accuracy was validated by the determination of Th and U in the NRC CRMs CASS-4 nearshore seawater and SLRS-4 riverine water and spike recoveries for Pu.

Methods utilizing collision or reaction cell instrumentation to reduce interferences have been reported. Taylor et al.135 used a tunable bandpass DRC, with O2 as the reaction gas, for the determination of 90Sr in natural water samples. The isobaric interference from the stable isotope 90Zr was efficiently removed by the reaction cell and the developed protocol provided an LOD of 3 pg l-1. The results were in good agreement with values determined by the Cerenkov counting technique for beta-emitters. The authors make the point that, whilst analysis by ICP-MS does not yet rival the LOD achieved by radiometric counting, this approach requires long analysis times whereas ICP-MS enables same-day preparation and determination. The analysis of 129I in groundwater samples136 at concentrations below the US maximum contaminant level of 5.7 ng l-1, without the requirement for sample pre-concentration, has utilized a reaction cell instrument with O2 as the reaction gas. By using minimal sample dilution the estimated quantification limit achieved was 5.1 ngl-1. This is a cost-effective, high-throughput technique for the direct quantitative analysis of 129I in groundwater samples at environmentally relevant concentrations. Another method for the analysis of groundwater has focused on the measurement of Ru isotope ratios137. In this study, Ru fission-product isotopes were used as analogues to characterize the mobility of mono-isotopic 99Tc in sub-surface environments. Precise Ru isotopic ratio measurements were achieved using a low-flow Meinhard type nebuliser and a long acquisition time. Interferences from 96Mo and 96Zr were reduced by more than 99.7 % using an O2 filled reaction cell.

The development of isotope ratio methods based on ICP-MS measurements have been used for the investigation of isotopic fractionation processes in natural systems. A double-spike ID method for the measurement of Ge isotope fractionation in geothermal fluids used a MC-ICP-MS instrument138. The procedure employed a 73Ge - 70Ge double spike to correct any analytical fractionation, in combination with HG to extract Ge from the sample matrix. Natural environmental fractionation was evaluated using the 74Ge/72Ge isotope ratio. The method showed an excellent external standard reproducibility of 0.4 0/00 over the course of several months and a LOQ of 2 ng of Ge. A similar approach has been used for the determination of Cd isotope fractionation in seawater by double spike MC-ICP-MS139. In this case a 110Cd/111Cd double spike, along with a column clean-up step, gave the most precise measurements with the lowest sample consumption. The results revealed small but discernible Cd isotope fractionations in seawater. A fully validated method for the determination of □34S measurements in mineral waters by MC-ICP-MS140, included calculation of a full uncertainty budget. The effect of large concentrations of Na and Ca salts on the □34S was negligible when operating the instrument in the medium resolution mode. Consistent compensation for instrumental mass bias on the 34S/32S isotopic pair was achieved by using the mass bias observed for the 30Si/28Si isotope amount ratio, in conjunction with the Russell correction equation.

2.3.5 Laser-induced breakdown spectroscopy. Some fundamental LIBS research for the in situ analysis of bulk aqueous solutions at oceanic pressures has been reported141, 142. LIBS is a promising technique for use in oceanographic studies but, being in its infancy, requires laboratory-based validation studies. This has been addressed in these two papers which focus on the detection of dissolved Ca, K, Li, Mn and Na at pressures up to 2.76 x 107 Pa. Pressure had no effect on the emission intensity for Ca and Na, but an increase was observed for Mn at increased pressure. The presence of NaCl enhanced the emission intensity for Ca, but had no effect on peak intensity of Mn or K. Overall, increased pressure, the addition of NaCl to the solution and temperature did not inhibit detection of analytes in solution and in some instances enhanced analyte detectability. The results suggest that LIBS is a viable chemical sensing method for in situ analyte detection in high-pressure environments such as the deep ocean.

2.4 Metrology and data quality.

The analysis of different water reference materials has been described. The National Metrology Institute of Japan, which has been producing matrix certified reference materials since 2001, has recently described the certification process for trace elements in river water by ID-MS analysis143. The National Geophysical Research Institute, Hyderabad has presented the results from an interlaboratory determination of Al, Cd, Co, Cu, Mn, Pb, V and Zn in rainwater by ICP-MS144. All of the reported values were within the Z-score range $-2 < Z < 2$, indicating good agreement to the reference values. The Pu isotopic composition of the IAEA-381 Irish Sea water RM has been determined by SF-ICP-MS analysis145. The methodology involved a two-stage chromatographic separation and purification step and provided 239Pu, 240Pu concentration and 240Pu/239Pu ratio data in agreement with the certified values.

3 Analysis of soils, plants and related materials

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This section highlights noteworthy areas of research and development in the analysis of soils, plants and related materials by atomic spectrometric techniques that have been reported since the last Update1.

3.1 Sample Preparation

3.1.1 Sample dissolution

Ultrasonic extraction has again been used frequently as a sample pre-treatment technique for soils, plants and related materials. Fernandez-Costas et al.146 used ultrasonic extraction, followed by ozonation, before determination of As in a sample of Acacia dealbata and in various CRM's by CF-HG-AFS. The advantage of the technique was the minimisation of the use of corrosive and oxidising acids in sample decomposition. The authors reported LOD of 0.03 to 0.15 µg g-1 As with 2-11% precision at a sample thoughput of 40 samples h-1 with flow injection. The efficiency of ultrasonic-assisted extraction has been shown to be element dependent and increase either linearly or exponentially with decreasing pH147. Ultrasound assisted extraction has also been used for slurry samples of beech and olive leaves148. Here the removal of the analyte, Cd, was achieved from an acid / peroxide solution (1mol l-1 + 16% (v/v) H2O2) using an ultrasound probe for 17 minutes.

Several groups have employed pressurized fluid extraction. A method has been developed for the determination of As, Cd, Cr, Ni, and Pb in sediments and soils149, using 8M acetic acid in a 5.0ml extraction cell at 100oC and 1500psi for 16 minutes. A method focusing on Cd and Zn in plants employed 0.01M 1,2-diaminocyclohexane-N,N,N',N'- tetraacetic acid at pH 4.5, 75oC and 1500psi; recoveries in excess of 90% reported150.

A comparison of open and closed digestion methods for sediments prior to analysis by ICP-MS has been reported by Begum et al151. The study was based on the digestion of six RM's and showed that excellent agreement can be obtained with the certified values using both methods for most elements. However, for Cr, Ni, Pb and Sr the closed method offered better accuracy and precision.

The application of high temperature fusions for major and trace elements in marine sediment trap samples has been reported152. This method consumed only 1 to 2 mg of sample yet facilitated the measurement of 18 elements with an accuracy of > 90% in most cases.

3.1.2 Separation and preconcentration procedures

Since last year's review1 many authors have reported preconcentration / separation techniques for improved analysis of soils, plants and related materials. Wang et al.88 evaluated a new sorbent, maleic acid grafted PTFE fibre, for on-line solid-phase extraction coupled with ICP-MS to determine rare earth elements in soil and sediment samples. The technique was particularly useful in separation of REEs from barium, which produces significant interferences. Detection limits of 1-120 pg l-1 at a throughput of 22 samples h-1 with a precision of 0.5-1.1% was achieved. Pu et al.153 modified nanometre-sized alumina microcolumns with gallic acid to separate and preconcentrate Nb, Ta and V from soil and stream sediment samples prior to measurement by ICP-MS analysis. Respective adsorption capacities of, 8.9, 13.3 and 7.0mg g-1 and respective detection limits of, 0.24, 0.66 and 0.25ng l-1 were recorded and good agreement with certified values in CRM's was reported. A preconcentration factor of 50 with RSD values between 2.9 and 9.8% has been reported for Cd, Co, Cu, Ni and Pb in plant materials using 1,10-phenanthroline complexes on activated carbon154. Cadium and Cu have also been preconcentrated on a new chelating phase prepared by coating 3,3'-diaminobenzidine onto silica gel155. The method offers a preconcentration factor of about 200. Prasad et al.156 studied coprecipitative preconcentration of sequentially extracted Cd and Pb from contaminated Indian soils onto 5,7-dibromoquinoline-8-ol embedded benzophenone (DBQ) prior to determination by FAAS. The DBQ technique allowed enrichment over a wider pH range (6.0-8.0) than previous preconcentration techniques using similar materials. Detection limits of 0.1 µg l-1 for Cd and 2.0 µg l-1 for Pb were reported, 400 times lower than achieved with direct FAAS analysis. Precision (RSD) was 2.2-2.45%, accuracy was confirmed with soil and sediment CRM (IAEA Soil 7 and Canadian National Research Council marine sediment MESS 3).

Commercial resins also continue to be used. AmberlystTM 36 (TM Rohm and Haas Co.) was used to preconcentrate Co from soil and roadside dust prior to analysis by FAAS157. An analytical detection limit of 0.44 µg l-1, precision (RSD) of 1.9% and a resin capacity of 82 mg g-1 was reported. Dowex M-41 has been used to alleviate some of the problems with the production of artefact methylmercury from the BCR sediment reference material CRM-580158. The resin was used to adsorb Hg2+ species which methylate to give the MeHg+ artefact. Although not totally eliminating the problem, better results were obtained.

3.2 Speciation

Most speciation studies have once again concentrated on the determination of a small range of elements, including Cr, Se and V. A particular focus was the determination of selenium species in plant materials.

Several studies have investigated the speciation of Se in Allium sp. Larsen et al.159 used cation exchange and reversed-phase HPLC with ICP-MS to study Se species in garlic (Allium sativum) grown in soils amended with selenate fertiliser and mycorrhizal fungi. The Se was extracted by proteolytic enzymes, ensuring that Se species contained in peptides or proteins were liberated. Two-thirds of the Se was in the form of gamma-glutamyl-Se-methyl-selenocysteine whereas methylselenocysteine, selenomethionine and selenate each amounted to a few percent. Interestingly, mycorrhiza and selenate amendment did not influence the distribution of selenium species in the garlic. Bulska et al.160 investigated Se speciation in hydroponically-grown onion plants (Allium cepa L.) utilising confocal microscopic µXRF and µXANES, which allowed in vivo measurements. The distribution of Se in various oxidation states was obtained with a spatial resolution of a few tens of micrometers within root tips and leaves. The study revealed that the nature of Se transport within the plant depends on the nature of the Se compounds taken up. Kapolna and Fodor161, using HPLC-ICP-MS, showed that the predominant form of Se in the leaves and bulbs of green onions (Allium fistulosum) was Se-methylselenocysteine, although Caruso's group162 have also reported Se containing volatiles of low molecular weight such as MeSeSeSeMe in this species of onion. Kapolna and co-workers163 used another HPLC-ICP-MS to study Se speciation in Allium sp., in this case, Allium schoenoprasum (chives), exposed to SeIV and SeVI. Selenium containing proteins in the plants and two extractions (perchloric acid-ethanol and enzymatic) were investigated using SEC-HPLC. They found that Se distribution among different forms of amino acids strongly depended on the type of Se enrichment employed. Enrichment with SeVI leads to accumulation of selenium in inorganic forms: Methyl-selenocysteine and selenocystine were present in samples enriched with SeIV and SeMet-, respectively.

Studies have also been undertaken on the speciation of Se in other plants. Gergely et al.164 investigated Se speciation in aqueous extracts of alfalfa sprouts (Medicago sativa) by LC-ICP-MS. The extracts were fractionated by SEC in a Superdex Peptide column followed by further purification using either a Shodex Ashaipack column or a reversed phase C-8 column, coupled to ICP-MS with an octapole reaction system. Both separation procedures allowed the detection of Se-methionine and Se-methyl selenocysteine as the main Se species. The authors noted the possible presence of selenocysteine, a derivative of the Se-2-propeny. Similarly, LC-ICP-MS has been used to identify Se species in Se enriched Lens esculenta grown in hyponic culture165. Cankur et al.166 determined Se speciation in leaves, stems and roots of the herb, dill (Anethum graveolens L.) using ion pairing reversed phase and cation exchange HPLC-ICP-MS. The ion pairing agent used was heptafluorobutyric acid (HFBA). Low molecular weight species were extracted with

0.1 M HCl; high molecular weight species were extracted enzymatically. The main species found were Se-methyl-selenoeysteine, throughout the plant, and Se-methyl-selenomethionine, in the roots. Selenomethionine was also detected in small quantities. Freeman et al.167 used microfocused scanning XRF to study Se speciation in the Se hyperaccumulator plants, Astragalus bisulcatus and Stanleya pinnata, which have been known to accumulate Se to up to 1% dry weight. The technique revealed that, in A. bisulcatus, Se was present in leaves as methylselenocysteine, g-glutamyl-methylselenocysteine and, to a lesser extent, as inorganic Se (selenate and selenite). In leaves of S. pinnata, methylselenocysteine and selenocystathionine were determined by LC-MS. The study showed that organic Se species are accumulated in specific areas in the periphery of the plants,e.g. leaf edges. This appears to be a unique property of Se hyperaccumulators and that the high concentration of Se in the plant periphery may contribute to Se tolerance.

Zhao et al.168 reported a procedure for the determination of oxidation states of vanadium species using ion-exchange resin separation, with methylene blue as a chelating agent for VV, and ETAAS. Total V was determined and VIV was calculated by difference. The authors report a detection limit for VV of 0.48 µg l-1 and precision (RSD) of 2.6% (n = 5). Panichev et al.169 determined VV species in soil and plants in the vicinity of a vanidium mine, using ETAAS. The VV species were leached from the soil and plant samples by 0.1 N Na2CO3. The study indicated that approximately 50% of the V in the soil and plant samples was present as VV species.

Tsuno et al.170 used XANES to investigate the oxidation states of Cr in artificially contaminated soils. The results of a 240-day experiment showed that much of the CrVI originally added to the soils was reduced, particularly as a function of soil humidity' and CrV was reduced even in dry conditions. The authors state that added CrVI would be completely reduced to CrIII over a period of five years. Ion chromatography coupled to ICP-MS has been used to determine the mobility of Cr species in compost171. The Cr was mobilised as CrIII bound to humic and fulvic acids and only about 6% was found as CrVI in the solid.

In an interesting study, capillary LC was coupled to ICP-MS to investigate plant protein phosphorylation172. The protein extracts were screened for their P and S content at different stages of plant development. The same technique was used to estimate the efficiency of a novel phosphoprotein enrichment method based on aluminium hydroxide, since the enrichment of phosphorylated species is often an essential step in molecular characterization.

Speciation of a wide range of other elements in soils, plants and related materials was investigated. Elements include: Am and Pu in sediments by SF ICP-MS173; Ni in plant tissue extracts, using hydrophilic interaction HPLC with electrospray Q-TOFMS/MS174, and in elemental mapping exercises of hyperaccumulator plants such as Alyssum lesbiacum175; in soils, using solid-phase extraction with ICP-OES176; I in soils using XANES177; Sb in soils using XAFS and HPLC-ICP-MS178; As in soils using HPLC-ICP-MS179; Cd in plant tissue using SEC-ICP-MS and ESI-TOF-MS180 and XRF and XANES181; Hg in mine wastes using µEXAFS182; Zn in soils using synchrotron-based studies183; and P in soils using synchrotron-based studies184. A detailed study of the extractability of As from the RM Fucus sp. based reference material IAEA-140/TM as also been reported185.

3.3 Instrumental analysis

3.3.1 Atomic absorption spectrometry

Flame atomic absorption spectrometry has been used to determine Cu residues from the control of olive fungal diseases in NE Portugal186. The higher Cu levels in some pesticide formulations lowers the level of total phenols and hence the antioxidant properties.

Flow-injection hydride-generation AAS was used by Hagarova et al.187 for the determination of arsenic in non-contaminated soils and plants. The authors reported recoveries of 103% for closed-vessel decomposition under elevated pressure using HNO3, and measurement in the presence of urea, and 100% recovery for an aqua regia digest. The authors also reported a LOD of 0.015 µg g-1 and RSDs of 2-8% for soils and 4-12% for plants.

Yaman and Akdeniz188 used platform atomisation-ETAAS to determine As in plant samples, including grass, clover and pine needles, as part of a study into matrix modifiers. The most effective modifiers were reported to be nitrate salts of Pd and a mixture of Ca, Mg and Triton-X 100. Similarly, Gonzalez-Nieto et al.189 used various chemical modifiers in the determination of Se in soil CRM (RTC-CRM 023-050 and RTC-CRM 025-050, Resource Technology Corporation, Wyoming, USA) by Zeeman ETAAS. For each modifier, pyrolysis and atomisation curves were obtained and optimal values assessed. Accurate results were obtained for all modifiers and the maximum precision (RSD) value reported was 7.5%. The LoD for Se in soil extracts was 3 µg l-1.

Ultrasonic slurry-sampling ETAAS was used to develop a method for the determination of V in soils190. An LoD of 0.6 µg l-1 was reported for CRM (Montana soil 2711) and the method was applied to the determination of V in several Polish soils. Felipe-Sotelo et al.191 investigated interference effects in the determination of Sb in soils and other solids by slurry-sampling ETAAS. Using experimental designs, based on partial least squares and artificial neural networks, they found that Na and Ca most affected the signal.

Solid sampling ETAAS has been employed for the direct determination of B in plant tissues192. Two pyrolysis steps (up to 2100ºC) were used and the choice of matrix modifier was critical. A combination of citric acid with W, added as a permanent modifier, worked well. Resano et al.193 investigated the use of ETAAS as a fast method for the determination of Ag in soils and other solid samples. They developed a procedure for determining a large range (40 ng g-1 to 350 µg g-1) of Ag concentrations, using a sample mass of 0.1 g. They emphasised the importance of optimising the temperature programme, the use of chemical modifiers and appropriate argon flow and sample mass selection. A throughput of 15 min sample-1 (for 5 replicate samples), a low LOD (2 ng g-1) and good precision (<10% RSD) were reported.

3.3.2 Atomic emission spectrometry

Hayson and Ostatek-Boczynski194 developed a simplified procedure, based on analysis by ICP-AES analysis, for the determination of Si in plant samples. According to the authors, whilst such analyses are being requested increasingly frequently in agricultural laboratories, conventional analysis (e.g. HF digestion) is protracted, particularly where no XRF facility is available, and a simpler and faster procedure is required. The plant sample was digested in nitric acid / peroxide and the hydrated silica released was dissolved in NaOH; low pressure microwave digestion was used for both steps. The results were linearly correlated with considerably slower conventional techniques. Masson et al.195 used ICP-AES to analyse maize and oak leaves for As by HG. No interference effects were observed from elements present at high concentrations in the plant and from transition metals. A mixture of KI and ascorbic acid was recommended for improved recovery, as poorer recoveries were observed when KI alone was used for reduction of AsV to AsIII. An LOD of 0.1 µg l-1 was reported. P was determined by ICP-AES in an investigation of soil tests for extractable and plant-available P196. The results allowed effective prediction of P fertiliser application rates and the authors noted the potential of the tests for protecting water quality, by identifying areas where P fertilisation is and is not required. Masson197 highlighted the inherent difficulties of using ET as a form of sample introduction for ICP-AES for the analysis of plant materials but they reported agreement with the certified values for three reference materials when using cellulose in the calibration procedure.

Allium cepa L. has proved a popular matrix this year for a range of studies. It has been the subject of a geographical origin study using ICP-AES in conjunction with ICP-MS and FAAS to monitor 14 elements in 309 samples198. The study aimed to separate the onions grown in the primary growing areas in Japan, from those grow elsewhere. Similar studies have been performed on Welsh onions Allium fistulosum L.199, marijuana samples from Brazil200, and cultivars of Cuban mango201.

A dual mode sample introduction system for MIP-AES has been used to determine simultaneously a range of hydride and non-hydride forming elements in biological and environmental202. The system employed a reaction / nebulisation device for use with slurry samples (agitated using an ultrasonic probe) and could handle volatile and non volatile species without changes to the instrumental settings. The RSD values obtained were ca 10%.

3.3.3 Atomic fluorescence spectrometry

There have been few novel applications of the use of AFS this year. Arsenic and Sb in tobacco plants have been determined by a novel HG-AFS technique where the sample and borohydride solutions are sprayed oppositely each other in the generator to react in the nebuliser phase203. Detection limits of 6.3ng l-1 for As and 19.2 ng l-1 for Sb were obtained with rsd values (10 replicates of 1ug l-1) of 3.2% and 1.8% respectively. AFS has been directly coupled to LC and HG to assess the distribution of As species in soils polluted by mining {28/1642].

3.3.4 Mass spectrometry

3.3.4.1 Inductively coupled plasma mass spectrometry

Li et al.204 described the development of a novel procedure, based on ICP-MS, for the simultaneous determination of Pd, Pt and Rh in soils and other environmental materials. The method utilised a rapid-column HPLC with on-line enrichment. The elements were derivatized with 5-(2.4-dihydroxyphenylazo)-rhodanine and the chelates adsorbed onto the front end of a Zorbax enrichment column before being then sent to the analytical column and back-flushed using a 0.05 mol l-1 H3PO4 solution as the mobile phase. The chelates were completedly separated from matrix elements within 2 mins, using a 54% aqueous solution of acetonitrile containing 0.05 mol l-1 of H3PO4 and 0.1% of triton X-100 as the mobile phase. An enrichment factor of 100 was achieved and LOD of 1.4 ng l-1, 1.6 ng l-1 and 2.0 ng l-1 were reported for Pd, Pt and Rh, respectively. The same elements were determined in a study of their spatial distribution along a major highway in Germany205. The results showed an increase in concentration of about 2 fold for Pt and Rh and 15 fold for Pd indicating an accumulation in the environment with time.

Mueller-Spitz et al.206 coupled size-exclusion chromatography with on-line ICP-MS in a novel study of the binding of chromium to DNA isolated from microbial communities in Cr-contaminated soils. The isolated DNA was purified using DNA 'clean-up' resins. The DNA / Cr aduct isolated from the studied soils contained 0.5-0.7 μg kg-1 Cr indicating that Cr was bound to the nucleic acids of the isolated DNA.

Pye et al.207 investigated the instrumental measurement precision of a LiBO2 fusion ICP-MS procedure for forensic comparison of soils and other solids. Instrumental measurement precision (repeatability) was better than 2-3% for most elements. However, this increased to 5-6% for many elements when different solutions were prepared from the same sample. CRM (geological materials named as ACE, BEN, GSN and SCo and a marine sediment named as MAG) were analysed in 23 instrument runs over an 18 month period, with the authors reporting a mean CV of 11%. There was a range of variability amongst the elements determined, with W found to be the most variable. Ce, La, Nd, Rb, Sr and a few others generally provided the most reliable basis for inter-sample comparison. The authors concluded that forensic samples should be analysed in the same, or at least sequential, sample runs.

Techniques for the measurement of isotope ratios continue to be popular. Novel applications include U in soil from a military site using 229Th-232Th double spike to correct for mass bias208. This technique was used to report on the presence of enriched amounts of 235U in particles isolated from soils from the area of the nuclear weapons accident in Palomares, Spain209. Stable isotope labelled selenite enriched with 78Se and selenite enriched with 76Se were used to assess the sorption coefficient and isotopically exchangeable concentrations of Se in soils and sediments210. The results suggest that the valid determination of the isotopically exchangeable concentration of Se necessitates that the Se oxyanions are speciated in solution.

Continuous-flow ICP-MS detection has been proposed for detailed investigation into metal mobility and distribution in soils, using the well-known 3-step BCR sequential extraction procedure211. A peristaltic pump was used to achieve alternate directional flow of the extractants to ensure a steady partitioning flow rate of up to 10 ml min-1. A flow injection interface was used to allow the introduction of extracts, at a given dilution, to the detector. The procedure enables, for example, detailed geochemical information, on the kinetics of metal release to be obtained. The authors emphasised the value of this flow-through system for the study of elemental associations in soils.

Barrelet et al.212 used a laser ablation system coupled to HR-ICP-MS to measure S, P and K in annual tree rings (Norway spruce). The technique allowed the measurement of low element concentrations in narrow annual rings. Interestingly, a seasonal pattern was found for P when it had previously been assumed that P distribution remained constant throughout the year.

3.3.4.2 Other mass spectrometric techniques

Chamizo et al.213 used accelerator MS to detect environmental traces of Pu in south east Spain, where Pu was released from thermonuclear bombs in 1966 following an accident involving a B52 bomber (referred to above). Previous efforts, involving measurements of 238 Pu / 239 Pu and 240 Pu ratios, to assess the environmental impacts had not been productive. However, using AMS, they were able to detect ultra-trace levels and report isotope ratios in low-activity samples. Straume et al.214 also used AMS to measure 129I in Belarussian soils contaminated after the Chernobyl accident in 1986. The authors found that 129 I was retained firmly in the top 15-20 cm of the soil and noted that total iodine concentrations in the Belarussian topsoils were low compared with those in other parts of the world which had incidences of radiogenic thyroid cancer.

As in recent years, several groups have reported the use of LIBs for the analysis of soils and sediments.. An interesting study by Lazic et al.215 has investigated the viability of using LIBs directly on sediments underwater. Although several elements, including Ba, Mn and Ti, were detected fluctuations in the plasma made calibration difficult. In addition, the natural and laser induced surface roughness and sample softness caused problems. Rapid determinations were made of Ba, Ca, Fe, K, Mg, Ni, P, and S in greenhouse soil by LIBs and detection limits of 7 – 12 mg kg-1 were achieved216.

3.3.5 X-Ray fluorescence spectrometry

Microchemical imaging is becoming a powerful tool for investigating elemental distribution in plants. Microfocused synchrotron based -XRF can provide good lateral resolution (<1 um) but is not quantitative. Isaure et al.217 have used this approach to look at the Cs distribution in plants and its interaction with K and other essential elements. The use of a micro XRF analyzer with a 100mm resolution and a XRF whole core scanner with a 5mm resolution has been used to produce element maps of wet marine sediment cores218. Discrete subsamples analysed by ICP-AES were used for calibration. Several studies have used XRF to investigate elemental distribution in hyperaccumulator plants which have potential for remediation of contaminated land. Kashiwabara et al.219 examined the distributions of As and K in the roots of the As hyperaccumulator fern, Pteris vittata L. They reported that a wide beam (vertical and horizontal beam sizes of 300 um and 2800 um, respectively) allowed examination of the elemental distribution along the winding shapes of the roots. Arsenic concentrations became higher from the top to the base of the roots, while potassium concentrations were more constant along the root length. Xu et al.220 studied Phytolacca acinosa Roxb., which has been found to hyperaccumulate Mn. Synchrotron radiation XRFwas used to investigate the distributions of Mn and other elements in different parts of the plant, including the roots, stems and leaves. Concentrations were highest in the vascular tissues of the root, stem, petiole and midrib and were higher in leaf epidermis than in the mesophyll, suggesting that Mn sequestration in leaf epidermis might be a detoxification mechanism. Ni localization and storage in tissues of Phyllanthus L. has also been reported following studies using XRF and ICP-AES techniques221.

There were other applications of XRF to the study of plant materials, notably by Uskokovic-Markovic et al.222, who developed a sensitive and fast, energy dispersive XRF measurement of W in plant samples, using the tobacco plant in this case. The authors reported that the procedure requires less dried sample (0.1 g compared to 1 g in conventional XRF measurements) and a LOD of 15 mg kg-1. Overlap of the W and Zn peaks was avoided by spectral deconvolution and the technique was applied to a wide range of concentrations (up to 2000 mg kg-1). The monitoring of environmental pollution by trace element analysis in tree rings using synchrotron radiation TXRF has been reported223. The method employed monitored K/Ca, K/P and Pb/Ca ratios which were found to decrease towards the bark.

Field-portable XRF monitors have again been applied to the analysis of soils in situ. Dixon et al.224 used a field-portable monitor to assess Pb contamination of garden soils, thus facilitating the monitoring of remediation treatments. Similar equipment was used by Herman et al.13 to measure Pb in soil, dust and paint in situ as part of an assessment of human Pb exposure in India.

4 ANALYSIS OF GEOLOGICAL MATERIALS

This section highlights noteworthy areas of research and development in the analysis of geological materials by atomic spectrometric techniques that have been reported since the last Update1.

4.1 Reference Materials

Several reviews have confirmed that recent advances in analytical methodology and their applications have been a significant driver in the continuing development of geochemical and environmental reference materials. In their overview of current issues, Jochum and Willbold225 discussed the development and certification of geochemical RMs for the determination of the PGEs, in situ microanalysis, analysis of zircons and isotope measurements. They observed that there was a notable trend towards further characterisation of existing RMs, especially to provide reliable values for the PGEs. All the analytical data from references cited in their paper are included in GeoReM, the new geochemical database for RMs and isotopic standards that was highlighted in last year's review. Valladon226 compiled his annual review of the usage of relevant RMs based upon citations in papers appearing in major analytical and geological journals in 2005. New additions to NIST's extensive collection of environmental RMs are described by Zeisler et al.38, with particular emphasis on the measurement of inorganic contaminants in a wide range of materials.

New data for the PGEs for existing and proposed chromite RMs have been reported227. The RMs were spiked with enriched isotopes and digested in a mixture of HNO_3 and HCl at 300°C and 125 bar in a high pressure asher. Osmium was determined by sparging the OsO_4 directly into an ICP-MS instrument. After dissolution of the residue, the other PGEs were separated on-line with a simple cation-exchange column coupled to quadrupole ICP-MS. Replicate measurements of aliquots of one of the RMs (0.5 to 4 g) yielded SDs that were much smaller than those obtained in the initial collaborative trial, demonstrating that sample inhomogeneity was not the major problem in the original certification exercise. Sutherland39 re-examined the data used to certify PGEs in an a road tunnel dust CRM BCR-723. He showed that concentrations of Pd and Pt differed significantly depending on detection technique, and between those laboratories using a similar definitive method based on ID-ICP-MS. The author put in a plea for the development of a new CRM with a more representative mix of PGEs and higher levels of Pd, thus supporting the conclusions of Jochum and Willbold225.

Fujitani and Nakamura228 have contributed precise estimates of chlorine concentrations in nine igneous RMs of varying composition, seven from the GSJ and two from the USGS. Samples of about 10 mg were spiked with ^{37}Cl, before decomposition with HF; after neutralisation with calcium hydroxide, the Cl was isolated by precipitation with silver chloride. The precipitate was dissolved in aqueous ammonia before analysis by ID and N-TIMS. The Cl concentrations ranged from 152 to 1008 $\mu g\ g^{-1}$ and agreed partly, but not completely, with recommended values where these were available.

Total digestions are normally used to determine the metal content of marine sediments; however, partial extractions using aqua regia or similar reagents are attractive because they are simple, fast, relatively safe and target the more labile phases. The difficulty of finding an appropriate RM for these circumstances has been addressed by Townsend et al.229. They have characterised marine sediments MESS-3 and PACS-2 (supplied by the NRCC) by SF-ICP-MS following a 1 M HCl extraction. Data acquired over three and five years are presented, along with extraction efficiencies based on the total certified concentrations. For most elements, precisions of better than 15% were achieved.

The drive for RMs with well constrained isotopic data has prompted a two pronged attack, involving the characterisation of RMs with established concentration data and the production of new RMs specifically for isotope ratios. Three in-house RMs with known Li concentrations and isotopic compositions, traceable to primary standards, have been prepared by Carignan et al.230. These Li solutions are available from the authors on request. Chapman et al.231 reported Cu and Zn isotope ratios for five geological CRMs: BCR-027 blende ore; BCR-030 calcined calamine ore; BCR-1 basalt; NOD-P-1 manganese nodule; and SU-1 copper-cobalt ore. High-purity Cu and Zn fractions were obtained by ion-exchange prior to measurement by MC-ICP-MS. The values reported agreed well with the limited data available from other investigations for these materials and long term reproducibility was usually better than ±0.07‰. A systematic study of the Nd, Pb and Sr isotopic content of USGS RMs covering a broad compositional range was carried out using TIMS and MC-ICP-MS232. The results provided a valuable dataset and demonstrated that the RMs were homogeneous for Sr and Nd isotopes but not Pb; this was attributed to contamination during their original production. Recent studies by Irisawa and Hirata233 have provided useful information on the W isotopic composition of three igneous rock RMs (JB-3, JA-3 and JR-1), a sediment (JCh-1) and an ore (JMn-1), all produced by the Geological Survey of Japan. Nebel and Mezger234 investigated variations in data reported for the measurement of Rb/Sr and Sr isotope ratios in the standard K-feldspar NIST SRM-607, which is widely used as a RM for this purpose. They concluded that sample heterogeneity was a major reason for the large inter-laboratory differences, thus limiting its use an RM. However, they argued that it could still be used as a high-precision standard for Rb-Sr calibration if the Rb/Sr and Sr isotope composition were reported relative to a reference isochron for this material.

For radiogenic isotopes, an alternative approach is to use a RM with a known geological age. Amelin and Back235 investigated the possibility of using opal as a U-Pb geochronometer. They concluded that precious opals are not suitable for this purpose because they contain low concentrations of U and high amounts of common Pb. In contrast, non-gem standard opals are enriched in U and contain sufficient amounts of radiogenic Pb to enable precise 206Pb/238U and 207Pb/235U dates to be calculated. Criteria for a better opal U-Pb standard are given. Kraml et al.236 used three independent methods to reassess the date of a phonolitic tephra (Limberg t3) that had been dated previously by the K/Ar method. Fisson track analysis of single apatite crystals and (U-Th)/He measurements on titanite and apatite yielded dates that were in close agreement with Ar/Ar dates on single crystals of sanidine. Because the material had been cooled rapidly on formation, all three thermochronometers provided one single age representing the eruption event. Consequently, it was proposed that this tephra be used as a RM for age determinations by a variety of techniques.

4.2 Solid sample introduction

4.2.1 Laser ablation

Two authoritative reviews on LA-ICP-MS have been published recently. Sylvester237 discusses analytical developments and Earth science applications in 2004-2005, and covers LA research using quadrupole, single-collector and multi-collector ICP-MS instruments as detectors. He highlights an increasing awareness of the need to address matrix effects in LA-ICP-MS for the best accuracy, particularly for isotope ratio measurements. Some of the more fundamental studies cited are concerned with phase transformations at the ablation site, size distribution and composition of the particles produced on ablation, and subsequent agglomeration and transport of the particles. There is a section devoted to RMs and homogeneity testing, which supplements the latest literature discussed in Section 4.1. Košler238 provides an overview of LA-ICP-MS before concentrating on developments in U-Pb dating of zircons and other accessory minerals by LA-ICP-MS. He covers recent applications in fission track and U-series dating before speculating on future developments required for geochronological studies.

It is recognised that ultra-violet femtosecond laser radiation is a promising approach for improving the performance of LA-ICP-MS because of its enhanced ablation characteristics and the potential for matrix-independent sampling. Koch and Gunter239 have produced an excellent summary of the current status of fs-LA-ICP-MS, together with an assessment of the remaining problems and how they might be overcome. Analytical figures of merit for fs-LA-ICP-MS at ~265 and ~200 nm have been provided by Koch et al.240. They studied the elemental ratios of aerosols produced by ablation of silicate glass (SRM NIST 610) under varying fluence conditions, taking into account laser-induced (66Zn/65Cu) and particle size related (238U/232Th) phenomena. Fractionation was not observed when µm-sized particles were absent. Similarly, Gonzalez et al.241 evaluated the repeatability of fs and ns LA-ICP-MS at 266 nm. The improvement in precision with fs sampling was thought to be due to the smaller particle size and tighter particle size distribution. Although the fs LA removed a smaller volume of material, the ICP-MS signal intensity and sampling efficiency (signal/ablated volume) were greater for fs compared to ns LA, resulting in better precision. Hergenröder242 proposed a theoretical model for the generation of small particles under typical conditions for LA-ICP-MS. Using his model, he describes the optimum conditions to minimise laser-induced fractionation. For most materials, these translate to the use of fs lasers at UV wavelengths. The behaviour of the laser-induced aerosol can influence the LA sample chamber design. Computer simulation of the performance of several sample chambers for aerosols produced by ns-pulse lasers, has shown that an optimised design could improve the extraction efficiency over conventional cylindrical chambers by a factor of six243.

Although much effort has been directed at minimising laser-induced fractionation, elemental fractionation in the plasma should not be ignored239. Matrix effects related to the mass loading of laser-generated aerosols in the ICP were studied by Kroslakova and Gunther244. Reference glass NIST 610 was ablated at two laser wavelengths, 266 nm and 193 nm, in order to separate particle effects from matrix effects. Different mass loadings in the ICP were achieved using: different crater diameters; an aerosol dilutor; a tandem ablation setup; and mixing a desolvated single element solution with the laser-generated aerosols. Signal depression caused by high mass loading in the plasma was most severe for elements with low melting points, e.g. Ag, Cd, Cu, Pb and Zn. They commented that internal standardisation, using a single internal standard, was not suitable for correcting matrix effects caused by mass loading of the plasma because it was likely that vaporisation and ion generation of different elements takes place in different zones of the plasma. The authors concluded that accurate quantitative analyses should only be carried out using the same crater diameters and ablation times for standard and sample.

Silicate glasses are often used to assess the performance of different laser systems or analytical techniques. New values and their uncertainties for up to 74 elements in the MPI-DING reference glasses (Max Plank Institute, Germany) have been published245. This compilation includes data for the isotopic compositions of B, Ca, H, Hf, Li, Nd, O, Pb and Sr. These materials appear to be homogeneous if a minimum of 5-20 ng is sampled. By ablating MPI-DING, USGS and NIST reference glasses, Jochum et al.246 showed that the figures of merit for a solid-state 193 nm Nd:YAG laser, in combination with single collector SF-ICP-MS, were superior to those obtained with a 213 nm laser system. Although elemental fractionation using the 193 nm laser was lower than that at 213 nm, there was significant variation in the fractionation factors for some elements, e.g. Rb, T and Pb, in glasses with different major element compositions. Thus, for the best accuracy, calibration with a material of a similar major element composition to the sample is required. Not surprisingly, Kent and Ungererz247 demonstrated that magnetic sector ICP-MS provided superior detection limits to quadrupole ICP-MS for the determination of B, Be and Li in glasses by LA. Accurate measurements of these elements in glasses with a range of compositions were obtained using 43Ca as an internal standard. Comparison of data obtained by LA-ICP-MS and PIXE on fused glasses prepared from RMs from the GSJ showed good agreement, within 10%, for most elements248. Of particular note was an attempt to estimate an uncertainty budget for the multi-elemental analysis of glasses by LA-ICP-MS in accordance with published international guidelines, using the ‘bottom up’ approach249. The system was calibrated using NIST 610, and the uncertainty budgets for Co, La and Th evaluated in other NIST and USGS reference glasses. For some RMs, instrumental drift and uncertainties in the values for analytes in NIST 610 were the major factors, whereas in others the uncertainty contributions from Poisson counting statistics dominated, particularly at low concentrations.

Laser ablation has opened the door to many new geochemical applications. However, little of analytical novelty is included in many papers, reflecting the fact that LA is now considered to be a routine tool for geochemical analysis. In a study of the distribution of Zr in minerals, Bea et al.250 made 4000 LA measurements on 152 thin sections of common crustal rocks; these results had several important implications for processes involved in the formation of zircons in crystallising magmas, as well as for Hf and Zr geochemistry generally. Chemical variations between pyrites in different alterations zones were investigated as potential indicators of the occurrence of gold veins in an ore deposit251. Ohlander et al.252 looked at the possibility of using LA-SF-ICP-MS to quantify the enrichment of trace elements on pyrite surfaces in mine tailings. Although there were many uncertainties in the resulting calculations, they concluded that metals, particularly As and Cu, released by oxidation and weathering of the sulphide minerals, were absorbed onto pyrite surfaces at deeper, unoxidised levels within the tailings. Iron-manganese oxide coatings on pebbles were analysed by LA-ICP-MS to see whether they could be used as indicators in mineral exploration or environmental monitoring because of their absorption properties253. Water samples from the same locations were also analysed and PCA applied to both data sets. Interpretation of the data was complicated by various factors but the authors were able to identify areas of heavy metal pollution and locate geological inputs.

The determination of isotope ratios for geochronological studies by LA coupled to MC-ICP-MS continues to attract much attention. Advances in in situ U-Pb dating of accessory minerals was the subject of a conference presentation by Storey and co-workers254 They reported accurate U-Pb ages in titanite, allanite and rutile, minerals that are not widely used in such determinations, using laser beams as small as 30 μm in diameter and obtained precisions on Pb/U and Pb/Pb ratios between 1 and 3% (2σ). Simonette et al.255 ablated standard petrographic thin sections using small crater volumes at a spatial resolution of 5-40 μm for U-Pb dating of zircon, monazite and titanite. Well-characterised mineral standards, previously dated by ID-TIMS, were employed for calibration and to calculate normalisation factors for 206Pb/238U and 207Pb/235U; during an analytical session, the external reproducibility (2σ) for these ratios was ≤3%. Instrumental mass bias on 207Pb/206Pb was corrected simultaneously by the aspiration of a thallium solution, resulting in a RSD (2σ) of 0.3 to 1%. The accuracy of their analytical protocol was verified on thin sections that had been previously dated by ID-TIMS. Cox and Wilson256 evaluated the potential of LA-ICP-MS for U-Pb dating of the mineral perovskite. This was not straightforward because of the lack of suitable standards together with the large correction required for the presence of common Pb. After careful calibration with zircon RMs, they decided that the most appropriate way to correct the 206Pb/238U ages for common Pb was to use the 207Pb/206Pb ratio to estimate the common Pb fraction. Dates obtained by this method were consistent with published data for the study area in Quebec, Canada. In another study, geochronologial ages obtained from combined U-Pb and Hf isotope measurements of detrital zircons by LA-ICP-MS yielded results that were identical to, but more precise than, those previously obtained by SHRIMP257. This improvement was attributed to the fact that analyses by SHRIMP are more sensitive to common Pb contamination on the surface of the grain mount. Griffin et al.258 have compiled a database of over 600 analyses of Harvard zircon 91500, which is often used as a reference standard for Hf ratio measurements. These data show considerable heterogeneity in the 176Hf/177Hf distribution, which is essentially bimodal, thus limiting the degree to which zircon 91500 can be used as a reference material.

Other isotopic systems investigated using LA-ICP-MS included the measurement of the Mg isotopic compositions of olivines from the Earth, Moon, Mars and a pallasite parent body259; all bodies appear to have been formed from a nebular reservoir that was homogeneous with respect to Mg isotopes. Horn et al.260 demonstrated that by employing UV-fs laser ablation coupled to MC-ICP-MS, a precision of better than 0.1‰ (2σ) could be obtained for in situ measurements of Fe isotope ratio for a variety of matrices, including pure iron metal, magnetite, Fe-meteorites and hydrothermal hematite, siderite and goethite from an old mining area in Germany. These materials were independently analysed in solution by MC-ICP-MS after chromatographic separation of the Fe; the in situ and solution Fe ratios agreed to better than 0.1‰. This precision and accuracy was achievable in both raster and spot ablation modes. Significant Fe zonations revealed in the hydrothermal minerals analysed were explained in terms of primary siderite precipitation from carbonate-rich fluids during the formation of the ore deposit.

4.2.2 Laser-induced breakdown spectroscopy

The utility of LIBS for remote sensing has been extended to some novel applications that are not without their difficulties. The major problems encountered in the in situ analysis of underwater sediments by LIBS were related to the natural and laser-induced surface roughness, and to the soft nature of the sediment surface215. The friable nature of the sample resulted in the formation of particle clouds above the sediment surface, which scattered the laser beam and plasma radiation, and often resulted in the production of the breakdown spectra above the target area. Because of large shot-to-shot fluctuations in the plasma temperature, a data processing procedure was applied that automatically selected only the spectra characterised by similar plasma parameters, which were related to their continuum spectral distribution. This procedure could be used in other situations to improve measurement accuracy. An equally tricky scenario is the concept of using LIBS for landmine detection and discrimination261. Spectra were collected from a suite of landmine casings as well as other materials likely to be present in the soil of a conflict area, including rocks, metals objects, cellulose materials and different types of plastics. Using a linear correlation approach, 'mine/no mine' assessments were correctly made for more than 90% of samples using both laboratory LIBS and a prototype man-portable system. It will be interesting to see whether this research results in a commercial product in the future.

Other applications of LIBS often address specific requirements that cannot be met by other spectroscopic techniques. One such example is the real-time evaluation of phosphate ore rocks in order to separate high silica pebbles from the ore prior to processing262. By monitoring the emission line intensities of P and Si via single LA shots, the P/Si ratio provided a simple and reliable indicator of the quality of the rock. It has also been demonstrated that LIBS can be used to determine the Pb content of different types of lead silicate glasses263. The samples were artificially weathered under neutral, acid and alkaline attack, and the effect of corrosion characterised by comparing successive LIBS spectra recorded for the same area. Anzano et al.264 evaluated matrix effects commonly observed in the analysis of geological materials by LIBS. Synthetic samples were prepared from various iron and aluminium compounds spiked with silica and calcium carbonate, and analysed as a loose powder or a pressed pellet. Matrix effects were observed on ablating the pressed powders but were absent when the samples were presented to the laser as loose powders on a tape. It was concluded that accurate analysis was possible provided the sample particle diameters were greater than about 100 µm.

4.2.3. Slurry sampling

Although slurry sampling is somewhat of a minority interest, two reviews on the current state of the technique have been published recently. Santos and Nobrega265 summarised the preparation of slurries for the analysis of inorganic materials by ICP-AES and ICP-MS. Sample grinding, stabilisation of slurries and calibration strategies were discussed critically, together with advantages and limitations of the analysis of slurries. Vale et al.266 reviewed the literature published between 1995 and 2005 on direct solid sampling for AAS. They observed that, in the 1990s, slurry sampling was considered to be the technique of choice, at least in part because of the availability of a commercial accessory for automated sampling. Now the situation is completely reversed, as the production of this accessory has been discontinued and new devices for direct solid sampling have proved to be rugged and reliable. Direct solid sampling ETAAS has been shown to provide the best LOD of the techniques discussed because of the absence of any dilution and minimal risk of contamination. The introduction of high resolution continuum source AAS appears to provide additional attractive features because optimisation of the furnace programmes is significantly simplified, and the ability to view the spectral environment of the analytical lines at high resolution makes it easy to avoid spectral interferences.

Several applications employing slurry nebulisation and ICP-AES have been effective for materials that are otherwise difficult to dissolve. The determination of Nb and Ta in Nb-Ta minerals was accomplished by introducing the slurried samples into an ICP-AES instrument via a V-groove ceramic nebuliser267. After wet grinding, 90% of the particles were less than 2.32 μm; subsamples were dispersed in aqueous solutions at pH 9 and agitated in an ultrasonic bath for 15 min prior to analysis. Aqueous calibration standards were employed and good agreement with results from a conventional fusion decomposition was obtained. Santos and Nobrega268 evaluated the direct introduction of slurries into an ICP-AES instrument with axial viewing for the analysis of clays and refractory materials. A multivariate extension of the conventional standard additions method was used. Aluminium, Ca, Fe, K, Mg, Na, P, Si and Ti were determined in CRMs prepared as slurries in 10% v/v nitric acid. Although accurate results were obtained at the 95% confidence level, it is not clear how robust this method would be when presented with real samples. Schwarzer et al.269 reported a more unusual application of slurry nebulisation for the analysis of PGEs and Au in precious metal concentrates. After grinding, slurries containing

0.05% m/v sample, 0.5%Triton X-100 and 5% v/v HCl were prepared and analysed using an in-house quality control sample for calibration. Results for Ag, Au, Cu, Fe, Ir, Ni, Pb, Pd, Pt, Rh, Ru and Te were within the 95% confidence limit of those obtained using the Carius tubes technique and in a much shorter time.

4.3 Sample Treatment

4.3.1 Sample dissolution

Fusions are commonly employed when a total decomposition of geological materials is required. Lithium tetraborate is often used as a flux when neither Li or B is determined, such as in the multielemental analysis of material from oceanic sediment traps by high resolution ICP-MS152. Radhamani and co-workers270 described the use of a mixture of sodium dihydrogen orthophosphate and disodium hydrogen orthophosphate as a novel flux for the decomposition of titanium minerals. The melt was dissolved in distilled water and analysed by AAS or ICP-AES; the attraction of this method lies in its simplicity, ease and speed of fusion, and use of environmentally friendly reagents compared to other fusion procedures.

The usual crop of comparisons of acid digestion protocols is evident again in this review period. Open and closed digestion procedures for the determination of trace elements, including the REE, in marine sediment CRMs by ICP-MS were evaluated by researchers in India151. There was little difference in recoveries afforded by the two methods, apart from a few trace elements such as Cr, Ni, Sr and Pb, where the closed digestion method was more effective because of the controlled temperature and pressure maintained for many hours. Care needs to be taken in applying this method to silicate rocks containing HF-resistant minerals as full recovery may not be achieved for all elements. However, this paper does provide data for a wide range of trace elements in GSMS-2, GSMS-3, HISS-1, PACS-2., MESS-1 and MESS-3 (marine sediment CRMs from the USGS and NRCC), including all the REEs. Hassan et al.271 sought to maximise total elemental recoveries via microwave-assisted digestion methods while avoiding the use of HF. They modified the US EPA method 3051 by increasing the temperature and duration of the microwave digestion, varying the ratio of sample mass to acid volume and altering the composition of the acid mixture. The experiments were conducted on various CRMs in two laboratories using different microwave digestion systems and ICP-MS instruments. The authors claim that their modified microwave-assisted nitric acid digestion method improved recoveries for Cu, Fe, Pb, V and Zn to the extent that they approached the values obtained by XRF and INAA as reported on the certificates of analysis. Recoveries for elements such as Cr and Ni compared well with ‘near-total’ recoveries from traditional acid digestion methods. Li et al.272 evaluated three sample digestion methods for the determination of trace Ag and Cd in geological and environmental materials by ICP-MS. They concluded that the simplest system, aqua regia in an open vessel, was preferred because the target analytes were fully recovered whilst there was low extraction of interfering elements, such as Zr.

One of the standard tests for assessing the worst-case scenario for the leaching of metals from landfill stipulates a minimum sample mass of 100 g. George et al.273 tested a procedure for the same protocol on sample masses between 10 and 150 mg, using two CRMs certified for the standard test; the resulting solutions were analysed by ICP-MS for Ag, As, Ba, Cd, Cr, Hg, Pb and Se. For masses greater than 100 mg, the microleaching procedure met the target criteria of an RSD of <20% and a bias of <±10% against the certified values. However, it is debatable whether this sort of performance could be achieved for real samples, which would tend to be much more heterogeneous than the CRMs employed. Silva et al.274 developed a procedure to leach a mini-column of crushed rock with successive 250 µl injections of water and nitric acid at 1%, 10% and 30% v/v, using a microwave heating to speed up the reactions. The mini-column was connected directly to the nebuliser of an ICP-MS instrument so that the release of elements could be monitored continuously. The focused microwave heating system used employed was unable to maintain a constant temperature and therefore the precision was worse than results obtained at room temperature. However, it offered a more rapid analysis, i.e. 15 min instead of 2 h or more per sample and provided real-time data on metal mobilisation.

4.3.2 Separation and preconcentration

A dominant theme arising from the papers under review is the continuing desire to find ways of preconcentrating PGEs, and preferably separating them from the matrix material in order to avoid interferences. Exfoliated graphite packed in micro-columns was used to absorb Pd(II)-diethylammonium dithiocarbamate prepared from an acid digest of a Pd ore275. The Pd was then eluted with acidified methanol and determined by FAAS; from 8 ml of sample, a LOD of 1.0 µg l-1 was achieved. Hydrogels, synthesized by gamma radiation, have been used to recover trace amounts of Ag, Au, Pd and Pt from dissolutions of geological materials276. Selective adsorption of the precious metal ions was facilitated by adjusting the pH of the solution to 0.5; desorption was performed with 0.8 M thiourea in 3 M HCl and provided preconcentration factors of at least 1000. Graphite furnace AAS gave LOD of <10 ng l-1 for all the elements studied. Another solid phase extraction procedure employed naphthalene-methyltrioctyl ammonium chloride, which has an affinity for the chloride complex ions of Au and Pd277. Elution was effected with thioacetamide and FAAS used to provide LOD of 2.3 for Au and 3.5 ng ml-1 for Pd. Hang et al.46 synthesized a novel organic reagent, 3-(8-quinolinylazo)-4-hydroxybenzoic acid, to chemically modify nanometre-sized alumina packed into micro-columns for FI on-line preconcentration of trace elements from geological and environmental samples46. This gave a 10-fold preconcentration factor; measurement by ICP-AES yielded LOD of 0.12, 0.27, 0.19, 0.18 and 0.44 µg l-1 for Ag, Au, Ga, In, Nb and Pd respectively. A novel lead fire assay procedure has been reported for the extraction of Au, Cu, Ir, Ni, Pd, Pt, Rh and Ru from platiniferous ores278. Lead buttons were prepared from large masses, typically 50 g, to ensure they were representative and homogeneous. The procedure involved the separation of the molten lead from the fire assay slag in an inert atmosphere to form rapidly quenched buttons. These were analysed by three solid sampling techniques (spark-OES, LA-ICP-MS and GD-SF-MS), thus avoiding the process of cupellation. Whilst spark-OES provided the greatest sample throughput, its detection limits were not sufficiently low for some analytes. Improved LOD were achieved with mass spectrometry, particularly GD-SF-MS; the importance of having an instrumental configuration capable of dealing with the spectral interferences was highlighted.

Somewhat unusually, Lu et al.279 developed a method based on the coprecipitation of Mo, Sb, Sn and Ti with fluorides to determine B, Hf, Nb, Mo, Sb, Sn, Ta, Ti and Zr in silicate materials by ICP-MS. Known amounts of B, Zr-Hf and Mo-Sn-Sb spikes were added to the samples prior to decomposition with HF and mannitol. The resulting solutions were evaporated and redissolved in 0.5 mol l-1 HF, followed by centrifugation to remove insoluble fluorides. Before analysis, the samples and standards were diluted so that the concentrations of HF and mannitol were similar, to compensate for the matrix effects of these reagents. The method had low blank levels and was effective for analysing small and precious samples such as carbonaceous chondrites. Limits of detection were of the order of µg g-1 for Ti and ng g-1 for B, Hf, Nb, Mo, Sb, Sn, Ta and Zr.

Several modified methods for separating Hf and related elements prior to isotope measurement by MC-ICP-MS have been described. However, a one-column procedure for purifying Hf using anion-exchange chromatography280 and an improved chemical separation for Lu-Hf and Sm-Nd from a single rock dissolution281, may not be readily accessible as they are written in Chinese. Connelly and co-workers282 developed a two stage method to separate Lu and Hf using TODGA resin supplied by Eichrom Industries. The first step employs a 2 ml cation exchange column to separate the HFSEs and REEs from the rock or mineral matrix. Subsequently, a 0.2 ml TODGA column is used to separate Hf-Zr and Yb-Lu from the HFSE-REE concentrate. Boric acid is employed in two roles, firstly to breakdown the fluorides formed when drying down the HF-HNO3 digests and, secondly, it is added to the loading solution at the second step to prevent the formation of Hf-fluorides that would not be retained by the TODGA resin. The authors claim that this method gives sufficiently pure fractions to overcome all atomic and molecular interferences, as well as minimising the detrimental effects of titanium on the mass fractionation Hf during measurement by MC-ICP-MS.

4.3.3 Speciation studies

Compared to previous years, relatively few papers on speciation studies of geological materials have been published in this review period. Reference materials certified for species analysis are rare, so the work carried out by the National Metrological Institute of Japan (NMIJ) to certify a new marine sediment RM, NMIJ CRM 7306-a, for butyltin and phenyltin species is welcomed283. Certification involved three different types of species-specific ID mass spectrometry after the sediment had been spiked with 118Sn-enriched organotin compounds synthesized from 118Sn-enriched metal. Four different extraction methods, mechanical shaking, ultrasonic, microwave-assisted and pressurised liquid extraction, were adopted to avoid possible analytical bias caused by non-quantitative extraction and degradation or inter-conversion of the species during sample preparation. The certified values for TBT, DBT, MBT, TPhT and DPhT are lower than in other sediment CRMs currently available for this type of analysis. Van and co-workers284 compared continuum and line source AAS for the determination of organotin species following GC separation. With background correction, the instrumental LOD were 6-22 pg as Sn for continuum source AAS, while the corresponding values for line source AAS were five to ten times poorer.

A well known problem in the measurement of methyl mercury in sediments is the potential for methylation of Hg2+ during preparation and analysis, giving rise to anomalously high MeHg values. Using two sediment CRMs, Delgado et al.158 studied the conditions that favoured this conversion. The main factor appeared to be the amount of Hg+ available in the sample. They introduced an ion exchange step at the extraction stage to minimise the concentration of Hg+ but a slight positive bias was still evident. Readers should refer to Section 3.2 for commentary on papers related to speciation in soils.

4.4 Instrumental analysis

4.4.1 Atomic absorption spectrometry

Although AAS is still in routine use for geochemical analysis in many laboratories, there is little new to report. Bédard285 has reviewed developments in AAS in relation to the earth sciences for the period 2004-2005. Some development work has focussed on the use of ultrasound in sample preparation. Güngör and Elik286 reported a rapid and inexpensive procedure based on the use of ultrasound to speed up the dissolution of river and pond sediments with a mixture of HNO3-HClO4-HF (2+1+1) prior to the measurement of Cu, Mn, Ni, Pb and Zn by FAAS. A related paper describes the use of phthalate buffers at pHs between 2.2 and 6.0 in ultrasonic leaching experiments to study the release of Cu, Mn, Ni, Pb and Zn under varying pH conditions; the resultant solutions were analysed by FAAS147. With ultrasound assistance, the time required for leaching was reduced from 12 h to 25 min. Depending on the metal and sample type, the amount leached increased linearly or exponentially with decreasing pH.

4.4.2 Atomic emission spectrometry

New developments in the application of ICP-AES for geochemical analysis are scarce compared to those involving ICP-MS. In a review of the literature published on this subject in 2004 and 2005287, one of the reasons proposed for this state of affairs was the lack of novel developments in ICP-AES instrumentation in recent years. Considering ICP-AES is such a mature technique, it was interesting to note the number of references devoted to the investigation of interferences.

Fluorine is not easy to determine in geological materials; total digestion is difficult to achieve because of its volatility and the need to dissolve resistant minerals. Thus, Jankowski et al.288 developed a method for direct introduction of powdered samples into a helium MIP-OES instrument. Calibration standards were prepared by dropping aliquots of an ammonium fluoride solution onto a suitable carrier, such as silica or activated carbon, which was then thoroughly dried and homogenised. A number of soil, coal and fly ash CRMs were used to validate the method. The values obtained were all higher than the certified values but the authors pointed out the certified values were obtained by indirect methods where losses of analyte were possible. The experimental LOD was of the order of 3-6 µg g-1, with an uncertainity of 5-17%.

A comparison of the measurement of Mg/Ca and Sr/Ca ratios in marine carbonates using radially viewed ICP-AES and magnetic sector ICP-MS demonstrated that, after accounting for matrix effects, data generated by either technique were essentially interchangeable289. Both types of instrumentation returned long term precisions of 0.9% for Mg/Ca and 0.6% for Sr/Ca.

4.4.3 Inductively coupled plasma mass spectrometry

The development of new analytical methods based on ICP-MS continue to make a significant contribution to geological and cosmochemical research290. Advances in fundamental studies and ICP-MS instrumentation have been documented recently in a sister Update in this series on atomic mass spectrometry291. This review, and that of Linge287 on geological applications, demonstrate that considerable effort is still being expended on trying to reduce interferences by various means. This is one of the themes that is reflected below.

4.4.3.1 Quadrupole-based instrumentation

Nowadays, the multi-elemental capability of ICP-MS is often employed in environmental and geochemical mapping programmes for the analysis of stream sediment samples. One recent study, based on aqua regia digests analysed by ICP-MS, was able to discriminate between contributions from natural and anthropogenic sources for As, Cd, Cr, Cu, Pb, Hg and Zn in a region of Italy[292]. For total concentrations, fusions are often preferred particularly if the REE and other elements that are associated with refractory minerals as required. Methods involving acid digestion followed by fusion of the insoluble residue have been in use for many years. In contrast, Awaji et al.[293] advocate a method that involves a lithium metaborate fusion followed by treatment with HF-HNO_3-$HClO_4$. The publication of this paper is somewhat surprising since it is the reverse of a procedure, involving an HF mixed acid digest followed by fusing any residual material with NaOH, that has been in use for many decades. It would be interesting to see the results of a comparison between these two approaches.

A number of approaches have been taken to reduce interferences seen in ICP-MS. Cadmium suffers from a number of isobaric overlaps with Mo, Sn and Zr, all of which can be present at high levels in geological matrices. Duan et al.[294] proposed a two-stage separation after an initial HF-mixed acid digestion. After solvent extraction, Cd was left in the aqueous solution while most of the Mo, Sn and Zr was extracted into the organic phase. On-line clean up with an SPE column containing Cyanex 923, a mixture of tertiary octyl and hexyl phosphine oxides, before measurement by ICP-MS resulted in a preconcentration factor of 22 and a LOD of 2 ng g^{-1}. Hu and co-workers[295] used ethanol as a matrix modifer to improve the sensitivity of the measurement of Te by ICP-MS, as well as reduce interferences. The addition of 4% ethanol was found to suppress interferences from Xe by a factor of 6, while enhancing the sensitivity three times over the signal obtained from a conventional solution containing 3% nitric acid. No C-based polyatomic interferences were observed at the masses of the Te isotopes and the LOD for ^{126}Te was 1.5 ng g^{-1}, enabling its accurate determination in various rock CRMs.

Quadrupole ICP-MS continues to contribute fit-for-purpose isotope ratio measurements. Shen and colleagues[296] developed a protocol that enabled them to determine U concentrations and isotope ratios with a precision at the per mil level. They used a ^{233}U-^{236}U double spike to correct for mass fractionation and each sample was bracketed by a U standard to correct for changes in sensitivity. With a signal acquisition of 15-20 min, standards containing 30 ng U produced a within-run precision of better than 3‰ for δ234U (±2RSD) and 2‰ for U concentrations. This technique was applied to the analysis of coral and speleothem materials. Other studies of corals and marine biogenic carbonates looked at ways of making precise measurements of Cd/Ca297, or Mg/Ca and Sr/Ca ratios298. Isotope dilution and gravimetric standards with internal standardisation were used to determine Cd and Ca respectively297; separation of the alkaline earth elements from Cd by IC reduced the TDS while maintaining a strong Cd signal. Repeated Cd/Ca measurements of a coral standard yielded a precision of ±2.2% (1 SD). Shen et al.298 achieved long term precisions of 0.84% for 24Mg/43Ca and 0.49% for 86Sr/43Ca using a quadrupole ICP-MS instrument in cold plasma mode at 650 W and a desolvating nebuliser. The enhanced sensitivity provided by the dry introduction system meant that smaller amounts of sample could be aspirated, resulting in less Ca deposition on the sampling cones, reduced spectral interferences from polyatomic species of H, N, O and Ar and smaller matrix effects. All measurements were made in pulse counting mode. External matrix-matched standards were inserted every 4-5 samples to correct for mass bias and instrumental drift, and a correction made for the influence of doubly charged 86Sr2+ on 43Ca+. These isotope ratios, when determined on samples of planktonic formaminifera and coral, provide estimates of ocean temperatures that are relevant to climate change studies.

Makishima and Nakamura299 developed a method for the determination of major, minor and trace elements in silicate samples by a combination of quadrupole and SF ICP-MS using isotope dilution-internal standardisation (ID-IS) and multi-stage internal standardisation. The sample powders were mixed with an enriched 149Sm spike before decomposition with a mixture of HF and HClO4; after a number of drying steps to decompose fluorides present, the final take up was in 0.5 mol l-1 HNO3. Trace elements were measured by quadrupole ICP-MS, with Sm determined by ID, while the 149Sm signal was used as an internal standard for Ba, Be, Bi, Cs, In, Li, Pb, Rb, REEs, Sr, Tl, Th, Y and U. Major and minor elements were split into several groups for measurement by SF-ICP-MS: Al, Ca, Co, Fe, Mg, Mn, P, Na and V were measured at a medium resolution of ~3000 using Sr obtained by ICP-QMS as the internal standard; Cu, Ga, Ni, K, Sc, Zn were quantified at a high resolution of

~7500, again with Sr obtained by ICP-QMS or Mn by SF-ICP-MS as the internal standard. Some of the merits of this ID-IS method are that accurate dilution of the sample is not necessary and that the LOD are sufficiently low to allow the determination of these trace elements in very small masses of depleted ultramafic rocks. By employing a pseudo-flow injection for the ICP-QMS, they were able apply the procedure to 5 mg of asteroid material to obtain 42 elemental concentrations and have enough solution remaining for the isotopic determinations of Pb, Nd and Sr.

4.4.3.2 Magnetic sector instrumentation

In his review of developments in isotope ratio determinations in the earth sciences during 2004-2005, Woodhead300 observed that there had been a spectacular increase in the availability of MC-ICP-MS instruments and the number of applications papers reported over that period. This trend has continued, with the publication of a bewildering range of geochemical studies in which data provided by MC-ICP-MS have underpinned new theories and interpretations. In contrast, many of the analytical protocols are relatively well-established and any advances are often directed at the determination of non-traditional stable isotopes, as indicated in the recent Update on mass spectrometry301.

Several recent papers have addressed the problem of isobaric interferences when measuring actinide elements. Nygren et al.302 compared the use of 241Pu/241Am and 240Pu/236U ratios to determine the age of Pu, i.e. the time since the last separation of Pu isotopes from their daughter nuclides. Sediment RMs were spiked with a solution containing 243Am, 242Pu and 233U, and decomposed with a lithium borate fusion, before a thorough chemical separation using a solid phase extraction procedure that included the Eichrom UTEVA, TEVA, TRU and Ln resins. During measurement by SF-ICP-MS, instrumental dead time, mass discrimination, 238U1H formation and abundance sensitivity were monitored using solutions containing U of natural isotopic composition. Of the two ratios studied, 241Pu/241Am provided reliable results after correction for any initial 241Am present, whereas inaccuracies could arise from the determination of 236U, because of tailing from 238U+ peak. The results demonstrated the importance of basing Pu age calculations on more than one ratio. Varga303 developed a new separation and preconcentration method for the determination of low level 241Am in various environmental matrices, including sediments, by SF-ICP-MS. This involved the addition of a 243Am spike to the homogenized sample, digestion with concentrated HNO3 and H2O2, and filtration, before co-precipitation with CaF2 to remove most of the matrix elements. The precipitate was then dissolved in a mixture of 3M HNO3 and boric acid before solid phase extraction on TRU™ resin. Measurements by SF-ICP-MS confirmed that 241Pu and other potential interfering elements had been eliminated, enabling low backgrounds and accurate results to be achieved. The absolute LOD of 0.86 fg was comparable to that obtained by alpha spectrometry, demonstrating that the method was suitable for low-level environmental measurements. A procedure for the separation and preconcentration of Pu from marine sediments prior to the determination of Pu isotopes by SF-ICP-MS has been proposed by Donard et al.304. Their method involves microwave digestion with HNO3 and

H_2O_2, filtration, conversion to Pu(IV), purification by ion-exchange chromatography, followed by liquid–liquid extraction and a final column clean up, which also preconcentrated the Pu. A recovery of 42% was achieved reproducibly and allowed the accurate simultaneous determination of 239Pu, 240Pu, 241Pu and 242Pu. As the authors indicate, the method will be greatly improved when the possibility of automating the chemical processing is realised.

Although Si isotope ratios can be measured with high precision by MC-ICP-MS, previous techniques for the extraction and purification of Si from geological materials have been based on the requirements for gas source mass spectrometry, which requires fluorination of the Si. To obtain the very pure solutions required, Georg and co-workers305 developed a method based on fusion with NaOH in silver crucibles, followed by cation-exchange on Dowex 50W-X12 (200-400 mesh) in the H+ form. By avoiding the use of HF, an overall recovery of better than 98% was achieved without any fractionation occurring during the process. The samples analysed in this study were mainly high purity silica and river waters. An alternative procedure, proposed by van den Boorn et al.306, achieved high yields of Si (>97%) from samples ranging from pure silica to basaltic (45-52 %wt. SiO_2). Powdered samples were mixed with NaOH monohydrate in PFA beakers and heated at ~200ºC in a furnace over three days. Some of the silicate rocks produced a residue that required further treatment with HNO_3 and then a second fusion with NaOH monohydrate. Although the procedure was lengthy, and could take up to six days to produce a clear solution, the use of Teflon containers for the fusion facilitated low blanks. The solutions were purified by ion-exchange chromatography on AG50-X8 resin before measurement by MC-ICP-MS in medium resolution mode (~2500) to resolve the polyatomic interferences. Instrumental blanks were reduced to acceptable values with a desolvating nebuliser equipped with PFA spray chamber and PFA micro-concentric nebuliser; this mode of sample introduction also reduced the formation of 28Si1H to a negligible level.

New methods for the determination of non-traditional stable isotopes continue to abound. Leya and co-workers307 developed a procedure for highly precise measurements of Ti isotopes in geological materials using high resolution MC-ICP-MS that overcame interferences observed when TIMS or low resolution MC-ICP-MS are employed. Two data collection protocols at a resolution of about 2000 were necessary because the detector array did not allow the simultaneous measurement of all Ti isotopes, as well as selected isotopes of Ca, Cr and V required to correct for isobaric interferences. Instrumental mass fractionation was internally corrected via 49Ti/47Ti. Quadrupole ICP-MS was used to determine the Mo/Ti and Zr/Ti ratios, which were used to monitor and correct for interferences from Mo2+ and Zr2+. Long-term reproducibilities (2σ) of 0.28ε, 0.34ε and 0.28ε were reported for 50Ti/47Ti, 48Ti/47Ti and 46Ti/47Ti respectively. A novel method for the determination of Fe isotope ratios in dissolved and particulate Fe from various marine environments has been reported by de Jong et al.308. After digestion of the solid materials, i.e.

particulates on filters, sediment, soil or rock, the samples were subjected to a high-yield ion-exchange chromatographic purification procedure; a double pass separation was employed for samples containing low masses of Fe. For the highest sensitivity, the solutions were introduced via a desolvating sample inlet system into a MC-ICP-MS instrument operating in low resolution mode. A combination of standard-sample bracketing and normalisation with 65Cu/63Cu from a Cu spike was used to correct the data. Argon interferences were determined prior to each analysis and automatically subtracted during the run. The sample size varied between 200 and 600 ng Fe per measurement and the procedural blanks were better than 10 ng of Fe. External precisions (1 SD) of ±0.07‰ for δ56Fe and ±0.09 for δ57Fe were reported. Isotopic variations of Ge in igneous rocks and biogenic opal were studied using a new procedure employing a continuous flow HG system coupled to MC-ICP-MS309. After dissolution and separation from any insoluble fluorides, the samples were purified and preconcentrated by anion and cation-exchange. A modified Scott-type spray chamber cooled at 4°C, without the nebuliser in place, was used as the gas-liquid separator and alkaline sodium borohyride employed in the production of gaseous Ge hydrides. The method was sufficiently precise, 0.2‰ (2 SD) for 74Ge/70Ge, for studies of the natural isotopic fractionation of Ge by physicochemical processes.

Nickel isotopes are of special interest in cosmochemistry because they can provide information on nucleosynthetic events that occurred during the formation and early evolution of the solar system. The variations in Ni isotope ratios are often extremely small, in the range of a few parts per thousand, and therefore hard to resolve. Quitté and Oberli310 developed a method involving a two-stage ion-exchange procedure based on the complexation of Ni with dimethylglyoxime before measurement by MC-ICP-MS. This procedure replaced liquid-liquid extraction used in previous methods and provided full recovery of Ni from silicate materials. Corrections for isobaric interferences from Fe and Zn were accurate as long as Fe/Ni was <0.1 and Zn/Ni was <0.0006. Replicate measurements of a standard solution yielded long-term external precisions (2σ) of ±50 ppm for 60Ni/58Ni and ±120 ppm for 60Ni/58Ni after normalisation to 62Ni/58Ni. Parallel studies of nickel isotopes in meteorites by Cook and co-workers311 employed a single-focusing MC-ICP-MS instrument with a hexapole collision cell to remove interfering polyatomic species.

After digestion, a three-step ion-exchange separation procedure provided high yields of Ni. Samples were measured using the standard-sample bracketing technique with NIST SRM 986 as the Ni isotope standard. They reported an external precision of ±15 ppm for 60Ni/58Ni, which compared favourably with other MC-ICP-MS studies. They claim to have achieved the first high precision data by MC-ICP-MS for 64Ni; an external precision of ±1.5ε (2σ) for 64Ni/58Ni was better than previous results obtained by TIMS.

The tungsten isotopic composition of iron meteorites can also shed light on the chronology of the early solar system. A method to determine W isotopes in such materials has been developed by Qin et al.312. After dissolution, a two-step ion-exchange procedure was employed to recover W in solution, with a yield of better than 80%, free from the presence of matrix elements and direct isobars of W. It was crucial to match the W concentration in the samples and standards to within 3% for accurate corrections of mass bias when applying the sample-standard bracketing method. Precisions of better than ±0.1ε on ε182W and ε184W were achieved routinely. Irisawa and Hirata233 introduced a newly developed correction technique for mass discrimination using rhenium when measuring W isotopes in six geochemical RMs by MC-ICP-MS. This allowed them to discriminate between fractionation of W when the rock originally formed and radiogenic growth of 182W from the decay of 182Hf. They achieved external precisions of 0.03‰ for 182W/183W and 184W/183W, which was almost comparable to those obtained by the conventional internal correction technique. No significant level of variation in 182W was found for any of the RMs analysed in this study.

The improvement in the precision afforded by MC-ICP-MS has opened up research centred on Ag isotopes and their application in economic geology and hydrothermal geochemical studies, as well as cosmochemistry. An optimised MC-ICP-MS procedure for the determination of Ag isotopic ratios at high precision in terrestrial samples, including basalts and meteorites with low Pd/Ag ratios, has been reported recently313. A three-stage ion-exchange process was used to separate Ag from matrix elements, including titanium, which was not always removed efficiently by previous protocols developed for iron meteorites. An external reproducibility of ±53 ppm (2 SD) for 107Ag/109Ag was obtained after correcting for mass bias using a palladium standard, which was added to every sample, and sample-standard bracketing. Improved precision was achieved by using a conventional water-cooled glass spray chamber with impact bead, rather than a desolvating system that introduces a relatively dry aerosol into the plasma. It was found that small random differences in the mass bias of Ag and Pd relative to each other were introduced during the desolvation process. These effects disappeared under wet plasma conditions, making the correction for mass bias more reliable.

The development of procedures for the measurement of radiogenic isotopic systems continues to attract attention. Makishima et al.314 reported a double spike procedure, with simple column chemistry, for the determination of Pb isotope ratios by MC-ICP-MS. Instead of using thallium, they added a 207Pb-204Pb double spike that had been calibrated by TIMS. The accuracy and precision of their method was shown to be comparable to those obtained with double spike TIMS. Chai and co-workers315 set up an analytical scheme for determining 235U/238U by MC-ICP-MS on less than 1 ng of U, in order to search for isotopic anomalies caused by the disintegration of 247Cm in meteorites. They reported an improved procedure for purifying U separated from meteorite samples and were able to detect a variation in the 235U/238U ratio of the order of ±4‰. Studies of the U-Th radioactive disequilibrium in carbonate rocks prompted Watanabe and Nakai316 to develop a new procedure for determining Th and U abundances and isotopic composition of these rock types. They demonstrated that it was possible to use a double spike of 230Th and depleted 235U, which were much easier to purchase than alternatives in current use. The elements of interest were purified by Fe-coprecipitation, ion-exchange and U/TEVA resin before measurement by MC-ICP-MS. In-house standard solutions with known U and Th isotope ratios were measured between each sample and used to correct for mass fractionation and the Daly/Faraday gain factors. Memory effects in the mass spectrometer resulted in poor precisions for Th isotope determinations; consequently, the in-house U standard was used to correct the Th data. After this modification, the precisions for U isotopic analysis were better than 0.1% while that for 230Th/232Th was 0.5%.

Producing Hg isotope ratio measurements with sufficiently good accuracy and precision to be meaningful is extremely challenging. Although Blum and Bergquist317 do not document the details of an analytical method, they make a plea for a uniform approach to mass bias correction, standardisation and nomenclature so that data from different laboratories can be easily compared and evaluated. They present measured values for isotope ratios in several Hg standard solutions, which will be of interest to those tackling this emerging field of analysis.

4.4.4 Other mass spectrometric techniques

Recent developments in AMS systems and associated methodology have been reviewed by Bacon et al.301 Although many of the applications relate to radiocarbon analysis, other nuclides of interest to environmental scientists include the measurement of 129I318. After difficulties encountered in setting up an iodine beam line at an AMS facility in Japan had been resolved, an overall precision of 1.1% was achieved for measurements of 129I/127I, with a detection capability of better than 10-13 for this ratio. However, a large memory effect was observed when measuring low level 129I, which was thought to be caused by contamination of the sample surface by other samples in the ion source. This was overcome by deleting the first 30 minutes' worth of data from the TOF spectrum acquired over 40 to 90 min. Desilets and co-workers319 described an innovative approach to 36Cl dating by AMS using isotope dilution. The spike was added to the sample as a solution of NaCl containing 99.66% 35Cl, before an HF-HNO3 mixed acid digestion was performed in a closed bomb to prevent significant loss of Cl as volatile species. After cooling, the Cl was precipitated as AgCl and purified to remove the 36S isobar by barium sulphate extractions followed by rinses with deionised water. The closed bomb method was also applied to carbonate samples by encasing the sample in ice made from deionised water and sealing the bomb very quickly after adding the sample to the nitric acid! However, an open vessel digestion was found to give similar results for carbonates, provided AgNO3 was added prior to digestion to prevent loss of Cl.

Thermal ionisation mass spectrometry (TIMS) is a mature technique that still finds favour over MC-ICP-MS for a variety of applications, particularly those where sample mass is limited285. Charlier and co-workers320 describe methods for taking µg samples from single crystals (mainly feldspar) and purifying them for the determination of Rb and Sr isotopes by TIMS and MC-ICP-MS. Although the procedure of micro-milling, dissolution and chemical separation, followed by analysis by TIMS, is time consuming, the authors considered it to be the best method for obtaining highly accurate and precise Sr data in most geological materials when handling small masses. They achieved long term precisions (2 SD) of 50 ppm for load samples containing as little as 3 ng Sr. Amelin and Davis321 developed a method for measuring Pb isotopes on sub-ng amounts by TIMS using a 202Pb-205Pb spike. This double spike method of correcting for isotopic fractionation was compared with the conventional external normalisation procedure. The improvement in precision and reproducibility varied depending on the amount of Pb analysed. Similarly, Kuritani and co-workers322 developed a method for the simultaneous determination of Pb abundance and isotopic composition on small test portions, using ID coupled with the double spike technique. In their procedure, a 202Pb-205Pb spike was added to the samples prior to the chemical separation, and then the isotopic composition of the spike-sample mixture was determined by TIMS using a 207Pb-204Pb double spike. A more unusual application reported was the determination of Sn in a candidate fly ash RM by ID-TIMS323. The samples were equilibrated with a spike solution prepared from 112Sn-enriched metal, before extraction with 4.5 M HCl. Because of the complex nature of the material, a two-step purification procedure employing ion-exchange chromatography was required prior to measurement of Sn by TIMS. Sample deposition onto a rhenium filament was performed in three steps, using a silica gel-phosphoric acid mixture, and a strict protocol was maintained when heating the filament. Fujitani and Nakamura228 proposed a procedure for determining Cl in silicate rocks by ID and negative TIMS. About 10 mg of sample was spiked and decomposed with HF, neutralised with Ca(OH)2 and the Cl isolated by precipitation of AgCl. An ammonical solution of AgCl was then prepared for analysis. Precisions of 1-2% were obtained. Data for Cl in nine igneous rock RMs were partly, but not completely, in agreement with recommended values where available.

For a rapid introduction to current issues in secondary ion mass spectrometry (SIMS), several recent reviews provide good commentaries. Developments in SIMS instrumentation and fundamental studies are covered in a companion Update301. A more targeted précis of the contribution the technique has made to the geological and material sciences during 2004-2005 is also available324. A personal account of the history of developments in SIMS that resulted in the construction of the Sensitive High Resolution Ion MicroProbe (SHRIMP) is given by Compston and Clement325. They describe the advances in its application to the dating of younger zircons down to ca. 1 Ma by the use of radiogenic 206Pb/238U, and speculate on future developments.

Considerable advances in the study of extraterrestrial materials have been facilitated by the invention of the Cameca nanoSIMS 50 ion microprobe. Hoppe326 provides examples of important breakthroughs in cosmochemistry resulting from the high spatial resolution and sensitivity of this generation of ion microprobe. New estimates of the abundance of heat-producing elements in the mantle of the Moon have been made from SIMS measurements of Sm and Th in lunar pyroclastic glasses using a Cameca ims 4F spectrometer327.

New strategies for quantifying B, F and H in minerals by SIMS have been proposed by Ottolini et al.328. Normally, accurate measurements rely on the availability of well-characterised matrix-matched standards to compensate for matrix effects, and silicon chosen as the reference element for silicates. By using 27Al or 44Ca as the reference element, they found that the ion yields were more stable with time and less sensitive to changes in instrumental conditions. Matrix effects in the determination of H isotopes in silicate glasses by SIMS have also been investigated329.

4.4.5 X-ray techniques

Although many geochemical laboratories employ XRF for routine analysis, developments in instrumentation and applications relevant to the earth sciences abound. An important factor in any XRF analysis is the mathematical model used to correct for matrix interferences. Thus, an authoritative tutorial330 on this subject will be of particular interest to XRF practitioners. The influence of the water content of soft marine sediments on measurements of bulk chemistry made by an XRF core scanner has been investigated331. Lighter elements, such as Al and Si, were particularly affected by variations in the physical properties of the core; chlorine was successfully used as a proxy for seawater content. Sitko332 proposed an empirical model for matrix correction when analysing particulate material on membrane filters by WDXRF. For a comprehensive review of recent advances in these and other aspects of XRF, the Update by West et al.291 is recommended.

Samples are usually presented to XRF instruments as fused beads or pressed powder pellets. Fused beads are not often used for trace element determinations because of the large dilution factor involved in their preparation. Thus a method for making fused beads with a low ratio of sample to borate flux (1+1) is of interest333. Two stages of heating, with cooling to room temperature in between, were required to prepare homogeneous beads, which were analysed for 42 elements, including Cs, Hf, REEs, Sc, Sn and Ta. An optimised procedure for preparing fused beads of chromite ores has been reported334. The most homogeneous beads were obtained using a flux containing a 1+1 mixture of LiBO2 and Li2B4O7, a sample to flux ratio of 1:50, LiI as a releasing agent and fusing for

10 min at 1100°C. Song et al.335 adopted a modified procedure for fusing manganese ores to cope with air bubbles released during fusion of these materials. The addition of nitric acid to the sample destroyed any organic matter and encouraged expulsion of air before the sample was fused at 1000°C.

The REEs are not usually determined by EDXRF because of interferences from major elements and lack of sensitivity. To overcome these difficulties, Orescanin and colleagues336 devised a procedure to separate and preconcentrate the REEs prior to their measurement on thin targets. The REEs were separated using Dowex 50W-X8 resin before preconcentration on ammonium pyrrolidine dithiocarbamate; XRF targets were prepared from the resulting suspension. The authors claim to achieve full recovery for the granite CRM G-2 (USGS), which is somewhat surprising given that the microwave-assisted digestion was achieved with nitric acid only – an unlikely recipe for full dissolution.

Interest in portable XRF instrumentation is still strong. Previous work testing a hand-held EDXRF system has now been extended to the evaluation of a prototype benchtop TXRF spectrometer for on-site analysis of contaminated land337. Samples were ground manually and then mixed with Triton X solution, plus gallium as an internal standard, to form a suspension; 10 µl was dried on a quartz carrier prior to measurement of As, Cd, Cr, Cu, Fe, Pb, Hg, Ni, Sb, Se, V and Zn by TXFS, with a 12 min counting time. Recommendations for improvement included the use of a second excitation source in addition to the primary tungsten anode tube, to overcome interferences on Cd, Ag and Sb, and data acquisition from a larger area of sample to reduce the effects of sample inhomogeneity. Elemental mapping of marine sediment cores has been undertaken by Boning et al.218 using micro-XRF and a whole-core XRF scanner with resolutions of 100 mm and 5 mm respectively. By calibrating the XRF measurements with the results from discrete subsamples analysed by ICP-AES, quantitative profiles of Ca, Fe, K, Sr and Ti were obtained; there was good agreement between the two XRF techniques. The micro-XRF data were used to discriminate between changes in provenance and diagenetic effects in the Fe profile.

An XRF microprobe optimised for the detection of precious metals in geological and biological samples has been developed338. Bragg diffraction from a surface shaped to a log-spiral curve was used to focus X-rays of a particular energy onto a solid-state detector. Enhanced line signals combined with reduced backgrounds resulted in an improvement of an order of magnitude for the LOD for Au. However, the determination of Au at ppm levels in natural samples remained difficult, especially in the presence of interfering elements such as arsenic and tungsten.

5 Appendix: Glossary of terms

Terms include the plural form

AAS	Atomic Absorption Spectrometry
AFS	Atomic Fluorescence Spectrometry

AMS	Accelerator Mass Spectrometry
BCR	Community Bureau of Reference
BP	Before Present
CCA	Copper Chromium Arsenic
CCC	Counter Current Chromatography
CE-UV	Capillary Electrophoresis-Ultraviolet Spectrophotometry
CE-ICP-MS	Capillary Electrophoresis-Inductively Coupled Plasma-Mass Spectrometry
CEM	Continuous Emission Monitoring
CRM	Certified Reference Material
CV-AAS	Cold Vapour Atomic Absorption Spectrometry
CV-AFS	Cold Vapour Atomic Fluorescence Spectrometry
DBT	Dibutyltin
DMA	Dimethyl arsenic acid
DIBK	Disobutyl ketone
DNPH	2,4-dinitrophenylhydrazine
DPhT	Diphenyltin
EC	Elemental Carbon
EDXRF	Energy Dispersive X-ray Fluorescence
EDTA	Ethylenediaminetetraacetic acid
EN	European Committee for Standardisation
EMPA	Electron Microprobe Analyser
ES-MS	Electrospray-Mass Spectrometry
ETAAS	Electrothermal Atomic Absorption Spectrometry
ETV-AAS	Electrothermal Vaporisation- Atomic Absorption Spectrometry
ETV-ICP-MS	Electrothermal Vaporisation-Inductively Coupled Plasma-Mass Spectrometry
EXAFS	Extended X-ray Absorption Fine Structure)
FI	Flow Injection
FI-CV-ICP-MS	Flow injection-Cold Vapour-Inductively Coupled Plasma-Mass Spectrometry
FI-HG-QF-AAS	Flow injection-Hydride Generation-Quartz Furnace- Atomic Absorption Spectrometry
FI-ICP-MS	Flow injection-Inductively Coupled Plasma-Mass Spectrometry

FP	Fundamental Parameter
fs	Femto second
GC	Gas Chromatography
GC-AFS	Gas Chromatography- Atomic Fluorescence Spectrometry
GC-C-IR-MS	Gas Chromatography-Combustion-Isotope Ratio-Mass Spectrometry
GC-ICP-MS	Gas Chromatography-Inductively Coupled Plasma-Mass Spectrometry
GC-IR-MS	Gas Chromatography-Isotope Ratio-Mass Spectrometry
GC-MIP-AES	Gas Chromatography-Microwave Induced Plasma-Atomic Emission Spectrometry
GC-MS	Gas Chromatography-Mass Spectrometry
GF-AAS	Graphite Furnace-Atomic Absorption Spectrometry
GPS	Global Positioning System
GSJ	Geological Survey of Japan
HDPE	High Density Polyethylene
HFA	Hexafluoroarsenate
HG-AAS	Hydride Generation-Atomic absorption Spectrometry
HG-AFS	Hydride Generation-Atomic Fluorescence Spectrometry
HG-ICP-MS	Hydride Generation- Inductively Coupled Plasma-Mass Spectrometry
HG-QT-AAS	Hydride Generation-Quartz Tube- Atomic Absorption Spectrometry
HPLC	High Performance Liquid Chromatography
HPLC-ICP-MS	High Performance Liquid Chromatography- Inductively Coupled Plasma-Mass Spectrometry
HPLC-DF-ICP-MS	High Performance Liquid Chromatography-Double Focusing-Inductively Coupled Plasma-Mass Spectrometry
HPLC-HG-AFS	High Performance Liquid Chromatography- Atomic Fluorescence Spectrometry
IC	Ion Chromatography
IC-HG-AFS	Ion Chromatography-Hydride Generation-Atomic Fluorescence Spectrometry

IC-ICP-MS	Ion Chromatography- Inductively Coupled Plasma-Mass Spectrometry
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICP-TOF-MS	Inductively Coupled Plasma-Time of Flight-Mass Spectrometry
ID	Isotope Dilution
ID-ICP-MS	Isotope Dilution- Inductively Coupled Plasma-Mass Spectrometry
ID-MS	Isotope Dilution-Mass Spectrometry
INAA	Instrumental Neutron Activation Analysis
IRMM	Institute for Reference Materials and Measurements
IRMS	Isotope Ratio Mass Spectrometry
ISO	International Standards Organisation
LA	Laser Ablation
LA-ICP-MS	Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry
LA-MC-ICP-MS	Laser Ablation- Multi Collector- Inductively Coupled Plasma-Mass Spectrometry
LC-HG-AFS	Liquid Chromatography-Hydride Generation-Atomic Fluorescence Spectrometry
LC-ICP-MS	Liquid Chromatography-Inductively Coupled Plasma-Mass Spectrometry
LC-MS	Liquid Chromatography-Mass Spectrometry
LC-MS-MS	Liquid Chromatography-Mass Spectrometry-Mass Spectrometry
LIBS	Laser Induced Breakdown Spectrometry
LoD	Limit of Detection
LoQ	Limit of Quantification
MA	Methylarsonic acid
MBT	Monobutyltin
MC-ICP-MS	Multi Collector- Inductively Coupled Plasma-Mass Spectrometry
MDL	Method Detection Limit

MIP-AES	Microwave Induced Plasma- Atomic Emission Spectrometry
MMA	Monomethyl arsenic
MeHg	Methyl Mercury
Me2Hg	Dimethyl Mercury
MPhT	Monophenyltin
MS/MS	Tandem Mass Spectrometry
NAA	Neutron Activation Analysis
NAAQS	National Ambient Air Quality Standards
Nd:YAG	Neodymium Doped:Yttrium Aluminum Garnet
NEXAFS	Near Edge X-ray Absorption Fine Structure
NIES	National Institute for Environmental Sciences
NIOSH	National Institute of Occupational Safety and Health
NIST	National Institute of Standards and Technology
NRCC	National Research Council of Canada
NTIMS	Negative Thermal Ionisation Mass Spectrometry
OC	Organic Carbon
PGE	Precious Group Element
PIXE	Particle-Induced X-ray Emission
PFA	Perfluoroalkoxy
PLE	Pressurised Liquid Extraction
PTFE	Poly(tetrafluoroethylene)
P-EDXRF	Polarised-Energy Dispersive X-ray Fluorescence
PXRF	Portable X-ray Fluorescence
REE	Rare Earth Element
RM	Reference Material
RSD	Relative Standard Deviation
RTI	Research Triangle Institute
SeCN	Selenocyanate
SEM	Scanning Electron Microscopy
SF-ICP-MS	Sector Field Inductively Coupled Plasma-Mass spectrometry
SHRIMP	Sensitive High mass Resolution Ion Microprobes
SIMS	Secondary Ion Mass Spectrometry
SIRMS	Stable Isotope Ratio Mass Spectrometry
SPE	Solid Phase Extraction

SPME	Solid Phase Microextraction
SRM	Standard Reference Material
SRXRF	Synchrotron Radiation X-ray Fluorescence
STN	Speciation Trends Network
SSID	Species Specific Isotope Dilution
TBT	Tributyltin
TD-GC-ICP-MS	Thermal Desorption-Gas Chromatography-Inductively Coupled Plasma-Mass Spectrometry
TD-GC-IR-MS	Thermal Desorption-Gas Chromatography-Isotope Ratio-Mass Spectrometry
TEM	Transmission Electron Microscopy
TIMS	Thermal Ionisation Mass Spectrometry
TMAO	Trimethylarsine oxide
TMSb	Trimethylantimony dichloride
TOF-SIMS	Time of Flight- Secondary Ion Mass Spectrometry
TOK	Thermal Optical Kinetic
TOT	Thermal Optical Transmission
TPhT	Triphenyltin
TXRF	Transmission X-ray Fluorescence
USGS	United States Geological Survey
UV	Ultra Violet
WDXRF	Wavelength Dispersive X-ray Fluorescence
XAFS	X-ray Absorption Fine Structure Spectrometry
XANES	X-Ray Absorption Near Edge Structure
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
US EPA	United States Environmental Protection Agency
VOC	Volatile Organic Carbon
VG	Vapour Generation
WHO	World Health Organisation
ZAAS	Zeeman Atomic Absorption Spectrometry

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