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Atomic spectrometry update. Environmental analysis

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This is the twentieth annual review published in JAAS *of the application of atomic spectrometry to the chemical analysis of environmental samples. In the analysis of air, there is ongoing development of instrumentation for continuous emission monitoring and as a means of interrogating the composition of individual airborne particulates. Developments in mass spectrometry applications continue to be an active area of research where the advantages of low detection limits and abilities to perform isotopic measurements are being exploited. There is growing interest in performing speciation measurements in water and this is being aided by the development of hyphenated techniques, most notably* via *the coupling of chromatographic systems to ICP-MS. Dominant themes in the analysis of soils include the optimization of preconcentration and matrix separation techniques, the development of speciation protocols, notably for arsenic, and the increased use of portable XRF systems for* in situ *analysis. In geological analysis, laser ablation as an analytical tool is attracting a wider audience. Multi-collector ICP-MS is increasingly being used in a number of geological facilities to perform high precision isotope ratio measurements.*

1 Air analysis

This section highlights noteworthy areas of research and development in the analysis of aerosols, particulates and gases by atomic spectrometric techniques. A number of *useful reviews* have been published. Dias and Edwards,[1] in a stimulating article, present a summary of the procedures and techniques currently used to distinguish anthropogenic metal sources from natural background sources. They recommend that careful consideration be given to choosing the appropriate sampling methodology that allows sufficient sample to be collected for subsequent analysis. Where possible, complementary analytical techniques should be used to derive as much data as possible, hence the need for a sufficient quantity of sample. They foresee the increased use of sophisticated techniques such as EXAFS and on-line LAMS, which will provide a greater understanding of the chemical makeup of particles. Whilst the authors accept the limitations within various individual receptor models, they believe that by using models in combination, useful data can be extracted for source apportionment studies. Ghosh and Brand[2] summarise the role that stable isotope ratio mass spectrometry can play in measuring slight but discernible

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changes in isotopic ratios of elements such as hydrogen, carbon, nitrogen and oxygen. Such information can be useful in assessing the impact of anthropogenic activities on global climate change. The growing interest in measuring the increased emissions of platinum group elements (PGEs) into the environment is encapsulated in review papers from Belgium[3] and Canada.[4]

1.1 Sampling and sample preparation

Microwave assisted dissolution procedures, under conditions of elevated temperature and pressure, are increasingly being employed as the gold standard in digestion. In a detailed paper, Kulkarni and co-workers[5] optimised a closed vessel digestion procedure for the analysis of airborne particles collected on filters. A goal in their work was to eliminate the direct handling of hydrofluoric acid by its generation *in situ* through the use of sodium fluoride. Recoveries in the range 90–117% were obtained for twenty certified and indicative elements in the NIST CRM 1648 (urban particulate matter) using a mixture of HNO_3 and H_2O_2. The action of generated hydrofluoric acid was, however, required to obtain near acceptable recoveries (typically 75%) for chromium, although it is known that this element exists in a very refractory state within this particular reference material. To extend the lifetime of their digestion vessels, the authors imposed temperature and pressure limits of 200 °C and 200 psi; these are typical operational limits for many commercially available digestion vessels used in laboratories. Unfortunately, it seems that the authors optimised their procedures with only three vessels per digestion run. Nevertheless ICP-MS analysis of digests quantitatively agreed with XRF for As, Cu, Fe, K, Mn, Mo, Pb, Pb and V in fine particulate matter ($<$2.5 μm) sampled on filters, but not for Al, Co, Mg, Ni and Ti. Here, the XRF results were found to be statistically lower. The authors attributed this to difficulties in measuring light elements such as Al and Mg by XRF and the fact that the data for Co were found to be at or below the XRF quantitative detection limit.

Interest in reconstructing *atmospheric metal deposition* patterns through the analysis of core samples (ice, peat, sediment samples) remains high. Previous Updates have highlighted the care and attention required to take representative ice core samples free from contamination. It is therefore timely to highlight a paper by Givelet *et al.*,[6] suggesting a protocol for the collection, handling and preparation of peat core samples for subsequent chemical, mineralogical and isotopic analysis. This paper draws heavily upon the experiences of Professor Shotyk, a noted expert in this field, and his collaborators. According to the authors, the protocol is both time consuming and expensive. To alleviate unnecessary cost and effort, they suggest that preliminary chemical investigations should be carried out in the field to select suitable core specimens. They also recommend the use of a non-destructive and relatively inexpensive XRF screen on powdered peat samples to generate initial geochemical data prior to embarking on costly wet chemical analysis. This paper makes illuminating reading for analysts working in the wider analytical community.

There is growing evidence that the *bioavailabilty of metals* from fine particulate matter ($<$2.5 μm particles) is more directly linked to health effects than total metal concentrations. Increasing numbers of epidemiological studies are now being carried out where exposures of individuals are being measured, typically by using low flow personal air samplers (PAS). Such samplers usually operate at flow rates around 2 l min^{-1}, in contrast to the more normal 15–25 l min^{-1} flow rates in static samplers used within ambient air-sampling networks. Air samples collected in this way in non-occupational settings provide filters with low mass samples, typically $<$50 μg. The bio-available metal component, typically a defined water soluble fraction, is only a fraction of the total metal mass. Couple this with the small mass of material typically collected and it quickly becomes apparent that measurements, even with sensitive techniques such EDXRF, INAA and ICP-MS, can be challenging. Researchers in the United States[7] studied factors that can impact upon quantification limits, *e.g.*, contributions from filter blanks and the potential for contamination during sample pre-treatment. The authors suggest that a possible standardised protocol could include XRF/INAA measurements for total metals and the measurement of 'soluble' species by ICP-MS. They conclude that elements such as Br, Ca, Cl, Fe, K, S, Si and Zn can be routinely quantified with acceptable precision using XRF on indoor PAS samples. ICP-MS can be used for Al, Ba, Cd, Ce, Co, Cu, La, Mg, Mn, Ni, Pb, Rb, Sb, Sr, Ti and Zn and INAA can be used to measure Ag, Al, Ca, Ce, Cl, Co, Cr, Cs, Cu, Fe, K, La, Lu, Mn, Na, Sc, Se, Th, Ti, V, W and Zn.

1.2 Instrumental techniques for bulk analysis

Combustion processes are important sources of metals in the atmosphere. The determination of *volatile metallic species* in such systems is not easy. Boylan *et al.*[8] used US EPA Method 7473 (determination of Hg by thermal decomposition, amalgamation AAS) to measure Hg in input coal and associated output combustion by-products, *i.e.*, fly ash, bottom ash and flue gas desulfurisation material. They estimated the quantity of Hg emitted into the stack gas stream by difference, using a partial mass balance approach, and investigated the fate of Hg within three coal-fired power plants, each with a different gas scrubbing system. They argue that this approach is a preferable alternative given that there can be safety issues associated with stack sampling and that uncertainties still exist in the measurement of Hg even with standardised wet chemistry procedures. They acknowledge, however, that their approach does require sufficient representative samples to be analysed; instruments that can perform measurements to Method 7473 are typically limited to a sample size of about 0.5 g. Sampling also relies on the expertise of the plant operators in obtaining samples from the correct locations within the process. Initial validation work suggests that estimated yearly stack emissions of Hg with this new approach are within 20% of those calculated using a more conventional method of determining Hg in input coal by bomb combustion—ASTM method D-3684—coupled with measurements made in-stack by EPA 29, EPA 101a or Ontario Hydro methods. The authors conclude that further validation work is required and that it needs to be extended to power plants with different configurations.

Along similar lines, Spanish researchers[9] used conventional impinger sampling, as described in the Ontario Hydro method, and wet chemistry techniques, *i.e.*, closed vessel microwave-assisted digestions and cold vapour/hydride generation AAS, to determine the fate of As, Hg and Se in a coal-fired power plant. Samples of coal, fly ash, bottom ash, flue gas (gaseous and particulate phases) were collected and analysed. Mass balance figures for As, Hg and Se were 60–80%; 113–115% and 63–73%, respectively. They found that the gas phase accounted for 24% of As, over 99% of Hg and 90% of Se leaving the stack. However, they noted that the Ontario Hydro method, designed originally to differentiate Hg^0 and Hg^{II} species and used here for this purpose, was not efficient in collecting gas phase Se species. This they attributed to the low solubility of Se species in the potassium chloride trapping solution used, which helps to explain the mass balance result obtained for this element.

In an attempt to elucidate *partitioning of metal species in a combustion process*, Pavageau and co-workers[10] describe their experiments in burning metal enriched fuel oil in a 40 kW domestic boiler. Flue stack measurements of gaseous and particulate phases were carried out isokinetically in accordance with standardised French AFNOR procedures. Mass balance experiments showed that, as expected, elements such as Hg and Se were predominantly found in the gas phase. At least 60% by weight of Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Sn, Tl, V and Zn in the enriched fuel was recovered in the flue particulate matter, while a minimal quantity was collected in the gaseous phase. However, they noted a mass balance deficit of some 20–40% for elements such as Co, Cr, Cu, Mn, Ni, Sn and V. They attributed some of these losses to particulate retention in the system, although it is not reported whether they sampled and analysed retained matter within the boiler and the combustion chamber itself. They admit that, since hydrofluoric acid was not used, incomplete recoveries for elements such as Cr can occur and could also explain results obtained for refractory elements such as Ni and V. Data from the analysis of fly ash reference materials would have been useful here. Further evidence for losses was noted when it was found that quantities of elements such as Cu, Cr and Sn were found in the backup impingers used to trap gaseous species; impinger samplers are usually set up in series to study potential breakthrough in the sampling system. This indicates that incomplete trapping of volatile species is occurring. It may also indicate that ultrafine particulate matter has broken through the prefilter and subsequently has not been quantitatively trapped in the impinger samplers. This reviewer notes that the standard sampling protocol employed a routine nitric acid–hydrogen peroxide mixture as the trapping solution, so analytical results could potentially be biased low. Refractory elements such as Cr, Ni and V, in an ultrafine particulate phase and trapped in these solutions, may require a subsequent laboratory digestion to be recovered fully. The chemistry of metalloid species such as Sb and Sn is such that hydrochloric acid is required to dissolve and retain species in solution. The paper goes on to describe experiments with a cryogenic sampling system for the collection of volatile species for subsequent analysis by ICP-MS. Solid state speciation using XPS was also attempted to examine possible chemical forms of elements in the particulate phase. In summary, the above papers add to our knowledge of metal partitioning within combustion systems but also highlight the need for further work in this area. They also highlight deficiencies and limitations in certain standardised measurement methodologies that will need reviewing when procedures are updated.

There is ongoing interest in *measuring platinum group elements (PGEs) in the urban environment*, most notably arising from abrasion of particles from automobile catalysts. It is good to see that the majority of papers now being published report data obtained on the analysis of the BCR CRM 723 (PGE in road dust). This CRM is also known as CW8, a working title given to it during its certification stage; furthermore, a similar but not identical pre-production prototype known as CW7 also exists in a number of laboratories. Reporting such data allows a comparative assessment to be made of the different published procedures. Closed vessel microwave-assisted digestion, coupled with ICP-MS, has become the method of choice for the analysis of PGEs in samples of road dust, soils and air filters. It appears that the measurement of Pt has now become relatively straightforward. Isobaric interferences from hafnium oxide can be successfully corrected mathematically.[11,12] Optimising the instrument to reduce oxide levels or augmenting instrumental performance by desolvating the aerosol stream[13] also assists in reducing this potential interference. Based on results reported for BCR CRM 723, it seems that an *aqua regia* based digestion is sufficient to release Pt from road dust samples. However, hydrofluoric acid may well be required to release Pt from soil samples. Alternative strategies for this element in the matrices cited above, such as using instruments equipped with a dynamic reaction cell[14] or using cleanup procedures involving an ion exchange step or a precipitation step,[15] although effective, would seem to be unnecessarily complicated for routine monitoring purposes.

The *makeup of catalysts is, however, changing, with greater use being made of palladium and rhodium* in contrast to the earlier generation of catalysts which were predominantly platinum based. Measurement, by ICP-MS, of these two elements can be more problematical as a number of severe isobaric interferences exist. Here the use of cleanup procedures is mandatory. Fritsche and Meisel[16] used a novel online chromatographic procedure coupled to ICP-MS to determine Pd, Pt and Rh as well as Ir, Re and Ru in roadside soil samples. They used enriched PGE isotopes for isotope dilution calibration, but monoisotopic Rh was determined using the other PGE elements as comparative calibrants. Osmium was also measured in the microwave-assisted digested solutions by sparging volatile osmium tetroxide into the ICP-MS. Satisfactory recoveries were obtained for Pd, Pt and Rh in BCR 723 and in CANMET geological reference materials TDB-1 (basalt) and WGB-1 (gabbro). The authors also provide useful indicative values for Ir, Os, Re and Ru in BCR 723. Whiteley and Murray[17] used an off-line ion exchange procedure with the strong cation exchanger Dowex AG50W-X8 to cleanup samples prior to determining Pd, Pt and Rh in roadside soils and dusts by ICP-MS. The cleanup step was initially checked with synthetic solutions and the performance subsequently confirmed by analysing BCR 723. Other instrumental techniques can be used. Zereini *et al.*[18] used TXRF to determine Pd in air filter samples after a cleanup/enrichment step involving a mercury based reductive co-precipitation procedure. They determined Rh and Pt in digested samples by voltammetry. No quality control data is given in the paper but the authors state that the procedures had been used successfully during the certification of BCR 723. Using a similar co-precipitation protocol, Lesniewska and co-workers[15] compared the performance of TXRF against HRICP-MS for measuring Pd in road and tunnel dust samples. Initial findings were that the ICP-MS results were 30–45% higher than the TXRF results. Further comparative testing is expected in an attempt to narrow such discrepancies. It would be interesting to see whether procedures involving ICP-MS systems equipped with collision or reaction cells could attenuate these interferences without the need to resort to laborious sample pre-treatment protocols.

1.3 Instrumental techniques for analysis of individual particles

There is growing interest in developing new techniques for *measuring the chemical composition of individual airborne particles* in order to understand aerosol processes and possible health effects associated with airborne particles. Spolnik and Tsuji,[19] working in association with Van Grieken's group at the University of Antwerp, applied the recently developed technique of grazing-exit EMPA (GE-EMPA) for the determination of light elements in several types of individual particles. Some of these had been prepared artificially in the laboratory by pipetting suspensions onto a silicon substrate, and some collected from the atmosphere using a Berner-type impactor. This GE-EMPA technique extends the capabilities of conventional EMPA to the measurement of low-Z elements such as carbon, nitrogen and oxygen. The authors suggest that the technique can also be used to measure the surface layers of single particles with minimal influence from the core and the collection substrate. Further developments are keenly awaited. Work is under way to develop an 'expert' computer programme to interrogate the typically large data sets generated by techniques such as EMPA.[20] The software runs under MS Excel™ using a MS Visual Basic™ interpreter. Currently, the knowledge database has been built using thirteen data sets from two Asian dust and four urban and seven marine aerosol samples, amounting overall to data from approximately 20 000 particles. To validate this prototype system, the authors analysed 333 particles prepared from seventeen classes of chemically pure standard particles (approximately twenty particles per class). The performance was encouraging and the system initially identified correctly 292 particles. A further 23 particles were subsequently correctly identified as ammonium nitrate once the database was upgraded with information about particles containing only nitrogen and oxygen. The system was subsequently applied to a dust sample collected in Korea. As the database already included information on two similar Asian dusts, a high identification rate of 94.7% was achieved. From the 1100 particles measured, 145 different particle classes were identified and the most abundant particle group detected was that classified as 'aluminosilicates'. It took approximately only one hour to classify the particle data from this sample using a modern PC.

Real-time single particle spectrometry is another powerful tool that continues to be developed for characterising atmospheric aerosols. Lake *et al.*[21] used an improved spectrometer to characterise particles online. It has a wider dynamic range of measurement of the ion signal and the ability to measure both positive and negative ions simultaneously. Compared to positive ion mode, negative ion detection greatly enhances the ability to measure particulate sulfate, a key constituent in airborne particles. Ambient air is sampled, in a laminar fashion, through an inlet duct and passes into the mass spectrometer *via* a pipe. Moisture is removed from this air stream along the way by passing it through a Nafion drier. The aerosol then enters a multi-position valve, which directs airflow through one of nine flow-limiting orifices that are used to select particles in the 45–1250 nm range. The resultant size-selected aerosol then enters the mass spectrometer *via* four differentially pumped stages into an ionisation/extraction chamber. Here, positive and negative ions are produced *via* laser ablation of individual particles with a 193 nm ArF excimer laser and are analysed after movement through linear drift flight tubes. The system has the ability to nominally resolve adjacent m/z values up to m/z 250. A particle is considered detected and its mass spectra saved whenever the signal intensity exceeds an experimentally determined threshold value. The instrument was operated semi-continuously at the EPA super site in Baltimore over an 8-month period. On average, 2000 particles were analysed daily, which was a trade-off between obtaining sufficient data and the need to maintain long-term instrument uptime. Inlet air was also sampled into a scanning mobility particle sizer (SMPS) and an aerodynamic particle sizer to provide additional information about the particles. Site visits were minimised by interrogating the instrument remotely using a modem link. The researchers found that nitrate, sulfate and elemental and organic carbon species dominated, but that over 10% of the detected particles contained transition or heavy metals. The average size-dependent detection efficiency, defined as the fraction of particles entering the inlet that are subsequently analysed, was determined in conjunction with data obtained from the SMPS. Using these experimentally derived detection efficiencies, it was possible to determine particle number concentrations of specific chemical components in air. This is not an exact science as actual detection efficiency for an individual chemical component can differ somewhat from tabulated averages and so these particle number concentrations can at best regarded as semi-quantitative. Nevertheless, the instrument has potential. For example, the authors noted on occasions a statistically significant particle number spike for particles that contained lead. These spikes were highly correlated with wind direction, thereby indicating a specific point source for this metal.

1.4 Online and (near) real-time measurements

To understand more fully how climatic and industrial processes work, there is a growing requirement to make *measurements at higher temporal resolutions*. As discussed above, a great deal of work is being carried out to understand the fate of metals in combustion systems. Zamzow *et al.*[22] describe their work in developing and validating a real time AA-based continuous emission monitor (CEM) for Hg that has potential use in stack gas monitoring. Their sampling system consisted of an isokinetic sampling probe, a heated transfer line and a sample splitter that draws 1 l min^{-1} of sample into the prototype instrument. The air is passed through a heated pyrolysis tube to convert oxidised Hg species to an elemental form prior to analysis. Elemental Hg is detected only if the air is allowed to by-pass this tube. Therefore, oxidised Hg species can be estimated by difference. The detection system consisted of a pen lamp light source and a laboratory-built echelle spectrometer to provide simultaneous detection between 253 and 579 nm. This allowed online corrections for coexisting SO_2 and NO_2 gas species to be made on the primary Hg line at 253.65 nm. Measurements made at this primary line were normalised against those made at the 546.07 nm Hg line, where absorption does not occur, enabling fluctuations from the light source to be corrected for. A one metre, long-path absorption cell is used to provide a detection limit of approximately 1 μg m^{-3}. The system was calibrated using a permeation tube assembly and its mercury emission rate was checked using a wet chemistry procedure based upon EPA Method 29. The prototype instrument was tested at the US EPA Rotary Kiln Incinerator Simulator in North Carolina alongside an alternative CEM design. Results were checked against those obtained using a regulatory reference method (Ontario Hydro (OH) impinger method). Results for total and elemental Hg from both systems were in good agreement with the OH method and were typically within ±25% of the values determined by the reference method. The online spectral correction procedure for the described system worked provided it had been precalibrated over the expected concentration ranges of the interfering species. Given the levels of HCl and Cl_2 found in the stack tests, the pyrolysis tube had to be operated at 1100 °C to ensure efficient conversation of oxidised Hg species to an elemental form. The authors claim that since no chemical solutions or traps are used in this system it should be easier to deploy it in the field. Planned modifications include investigating the use of a lower resolution spectrometer and modifying the system to allow the stack gas stream to be split into two for simultaneous, rather than sequential, measurement of elemental Hg and total Hg.

Measurement of the elemental composition of atmospheric particles using *shorter sampling intervals* is of interest to researchers undertaking source apportionment studies. Kidwell and Ondov[23] sampled ambient air at 170 l min^{-1} at 30-min intervals, collecting each sample as a concentrated slurry. The sampled particles are grown in a condensational process using steam injection. The resultant droplets are concentrated into a 10 l min^{-1} minor flow of a virtual impactor and subsequently separated from the airstream using a real impactor. The droplets accumulate at the bottom of this impactor as a liquid slurry at approximately 0.2 ml min^{-1}. No size selection sampling was attempted in this study but the inlet tube had a theoretical particle cut-off of around 20 μm. It was estimated that the typical preconcentration factor observed during this sampling exercise was around 20 μg particulate matter per ml of final solution. Using monodisperse fluorescent polystyrene latex particles, the overall collection efficiency of the system was estimated to be 40% for particles in the size range 0.1–0.5 μm, rising to 68% for particles in the size range 3–5.9 μm. Following each sampling interval, the slurry is pumped to a fraction collector and stored in preweighed glass vials for subsequent off-line analysis. Each vial contained 20 μl of concentrated HNO_3 to preserve the samples. Field blanks contained a 5 ml aliquot of high purity water and were left uncovered for a similar period of time to the samples in order to assess potential field contamination. Simultaneous ETAAS was used to analyse the resultant samples. Compromise furnace conditions were used to determine selected elements. These were separated into three groups based upon atomisation temperatures (Group one: As, Cr, Cu, Mn, Ni; and Group two: Cd, Pb, Sb, Se) and the anticipated concentration levels in solution (Group three: Al, Fe, Zn). The NIST SRM 1643d (Trace Elements in Water) was used to check the calibration functions; recoveries were typically within 10% of the certified values. As a further test of the measurement system, the authors analysed slurry samples prepared by diluting 1.5 mg of NIST SRM 1648 (Urban Particulate Matter) into 100 ml of acidified water. Recoveries for this material were within 20% of the certified values for elements such as As, Cd, Ni, Pb and Zn but, not unsurprisingly, incomplete recoveries were obtained for more refractory elements such as Al and Cr. The authors suggest that improved recoveries could be obtained by sonicating the samples prior to analysis. A suggestion from this reviewer would be to add some HF. Airborne concentrations were calculated by re-weighing the vials after sample collection, assuming a unit density, and dividing the mass collected by the measured air volume. Values determined for elemental concentrations in air were adjusted to take into account the sampling efficiencies of the system, using the predetermined sampler collection efficiency in combination with *a priori* knowledge of typical elemental size distribution profiles of airborne particles from this sampling location and the analytical elemental recoveries determined using NIST SRM 1648. Data collected with this prototype instrument suggests that thirty-minute sampling intervals permit far greater resolution of emission sources to be made than using samples taken over a longer interval, *e.g.*, 24 h. Further modifications to the system are planned including adding a rinsing function between the collection of samples and adding a 2.5 μm size selective inlet to the sampler. A fuller elemental picture could be obtained if an ICP-MS finish were to be used. It would also be useful in future sampling exercises to co-locate conventional filtration samplers and to obtain elemental data for comparative purposes.

An alternative instrumental approach has been suggested by Lithgow and co-workers,[24] who are investigating the use of a *field deployable LIBS system*. Their prototype consists of a Q-switched Nd:YAG laser operating at the fundamental 1064 nm wavelength that can be focused onto a 6 cm diameter cylindrical sample chamber into which air samples can be pumped. Emissions from the generated plasma are collected at right angles to the incident laser beam, collimated and transferred using fibre optics to the spectrometer. Light is dispersed with a 0.3 m spectrometer (1200 groove mm^{-1} grating) and detected using a CCD detector array having an effective dispersion of approximately 0.07 nm per pixel. Spectra are collected in four separate spectral windows, centred at 270, 340, 413 and 590 nm. The instrument is initially calibrated using an aerosol generated by the nebulisation of standard metal solutions. Here, a constant output atomiser (TSI Model 3075) is used with dry filtered air as the diluent. The aerosol is dried by passing it through a diffusion drier and analysed by a scanning mobility particle sizer (SMPS) prior to entry into the LIBS sample cell. Determination of the metal concentration in this calibration stream is somewhat convoluted. The SMPS calculates a total volume of particulate matter per unit volume of the carrier gas, based upon a measured electrical mobility diameter and the assumption of spherical particles. It is assumed that particles are composed of the most common chemical form of the metal, usually an oxide. The measured total particulate volume is then multiplied by the density of the particle and the mass fraction of the element of interest to yield the mass of the element per unit volume of carrier gas. A peak-to-base ratio measurement protocol is used, where peak intensities are normalised to the continuum emission of the plasma in the vicinity of the emission peak, in an attempt to reduce the effect of shot to shot variations in plasma energy. In field trials the LIBS system was connected to a sampling system consisting of a PM$_{2.5}$ cyclonic inlet and a virtual impactor. The system concentrates particles approximately five-fold at a total flow of 150 l min^{-1}. These were analysed for Al, Ca, Cr, Cu, Mg, Mn and Na. Particle hit rates, *i.e.*, the recorded elemental hit above detection threshold divided by total shot, were in the range 10^{-4}–10^{-5} with weekly average concentrations between 29 and 720 ng m^{-3}. With the current set-up, threshold detection limits for elements within individual particles were between 15 and 185 fg. The system illustrates the potential for rapid real-time measurements in deriving a greater understanding of chemical processes and for source apportionment studies. Further improvements for this instrument are planned including optimising laser pulse and optical components that should enable threshold detection limits to be lowered. The authors are awaiting some validation data from the analysis of impactor samples taken at the same time, succinctly illustrating the advantage of online (near) real-time measurements!

1.5 Isotopic analysis

Using *isotope ratios to trace sources of lead pollution* continues to interest many researchers. These include: Ettler *et al.*,[25] who traced sources contributing to the contamination of Czech soils; Zheng *et al.*,[26] who studied the air quality in Shanghai after leaded petrol was phased out; Haack *et al.*,[27] who assessed lead deposition in the European Arctic through the analysis of moss and soil sample; Bellis *et al.*[28] and Le Roux *et al.*,[29] who used tree bark pockets and peak bog samples as archival sources to assess historical atmospheric lead pollution levels. Of interest to potential researchers in this field is a paper published by Aung and co-workers.[30] In their own words the purpose of their work was to "provide Pb isotope data for widely available CRMs of Japanese origins which will facilitate future cross-checks of the accuracy of the analytical methods and the results in environmental lead isotope ratio analysis and which will serve as a basic data set of lead isotopic compositions in the Japanese environment". They analysed a range of CRMs from the Japanese Geological Survey (GSJ sediment, soil and ash materials) and from the National Institute of Environmental Sciences (NIES biological, sediment, soil and ash materials). Total lead concentrations in these materials ranged from 0.9 to 3300 mg kg^{-1}. CRM/SRMs from NIES and NIST, which have reported lead isotopic ratio values, were used as a cross check. NIST SRM 981 (certified common lead isotope standard) was used to perform mass bias correction on their QICP-MS measurements. As expected with this sort of instrument, typical within-run precisions were around 0.2% (1σ) for both ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb isotope ratio measurements but are adequate for certain environmental applications.

The increasing availability of HRICP-MS is now allowing researchers rapidly to *determine long-lived radionuclides in environmental samples*. The measurement of Pu in environmental matrices such as sediment and mosses is of interest to a number of research groups. Increased levels *via* atmospheric washout are historically due to nuclear weapon tests, but nowadays can result from releases, accidental or otherwise, from nuclear facilities and reactors or from debris from crashed nuclear powered satellites.[31–33] Agarande *et al.*,[31] for example, found that their ICP-MS measurements on moss samples and a certified IAEA soil sample agreed well with measurements of $^{240+239}$Pu by the much slower alpha spectrometry technique. Furthermore, the atom ratio ^{240}Pu : ^{239}Pu, which can be determined by mass spectrometry, can be useful for source apportionment studies.

Air quality regulations worldwide are tightening in response to increased concerns over smog episodes and health effects of air pollutants. As a result there is an increased need to measure chemical components in airborne particulate matter (APM) and to ascertain their origins. A significant proportion of APM consists of organic and elemental carbonaceous material. For certain processes, source-specific tracers (organic markers) have been identified, but these usually require considerable measurement resources to obtain useful datasets. *Measurement of the ^{14}C content in aerosols by accelerator mass spectrometry* is a growing tool for source apportionment studies. Notionally, such studies are based upon a two-source model: the carbon source may consist of a 'modern' form in equilibrium with current concentrations of atmospheric $^{14}CO_2$ that has formed from the interaction of cosmic radiation with atmospheric nitrogen, and a 'fossil' carbon source whose age greatly exceeds the half life of ^{14}C (*ca.* 5730 y) and therefore essentially contains no ^{14}C. For example, using this simple model, one could distinguish combustion sources that use fossil fuels from those burning contemporary wood. Complications that need to be considered include: the addition of extra ^{14}C into the atmosphere due to nuclear weapons testing and its resultant incorporation into plant materials; the firing of treated wood, *e.g.*, creosote coated timber; and dual burning systems which would give a both a 'modern' and 'fossil' signature. Nevertheless, use of the technique is growing. Tanner *et al.*[307] collected size-selected air samples on filters from a background site near the Great Smokey Mountains National Park in the USA over the period April 2000–November 2001. They estimated that the fossil-derived carbon contribution makes up around 20% of the $PM_{2.5}$ mass observed at this site. They suggested that contributions to the 'modern' organic carbon fraction comes from bioorganic sources such as natural emissions from trees and plants, resuspension of plant detritus and lightning-initiated forest fires. However, they believe that sizeable contributions also come from anthropogenic activities such as residential wood burning and burning of agricultural waste. It is these activities they suggest could be targeted in any future initiatives to improve air quality. A similar study by Bench[35] at the Yosemite National Park showed similar trends. It stressed that, although AMS has significant potential in fingerprinting carbon sources for receptor modelling, it does need to be used in conjunction with other measurement techniques, a viewpoint expressed at the beginning of this review.

2 Water analysis

This section *highlights new and novel analytical developments* in the use of atomic spectroscopy for the determination of trace metal(loid)s in environmental water samples that have been published since the last review.[308] No major instrumental developments have been reported, with most of the papers simply detailing improvements in methodology.

2.1 Sample preparation

2.1.1 Sample collection and preservation. The *analysis of environmental water samples* puts great demands on the protocols used for sample collection and preservation, particularly if the sample is not from a surface water source. This often overlooked part of the analytical procedure can be a major source of systematic bias in the analytical process. Improvements to sample collection and preservation, or investigations into possible bias, should be expected to significantly improve the data from expensive environmental monitoring campaigns. An alternative to the collection and preservation of samples for laboratory based analysis, is the use of *in situ* or on-site methods to determine the analytes of interest. Publications dealing with this are included under the relevant instrumental sections.

Collecting pore-water samples from sediments, without disturbing the distribution of the metal species, requires considerable attention to detail. Ouddane *et al.*[37] reported a method for determining the distribution of trace and major metals between their organic and inorganic forms, whilst maintaining the original oxidation state. They used solid phase extraction (SPE) with two different chelating resins (chelamine and C_{18}) connected in series and under inert conditions (nitrogen gas) to separate and preconcentrate the analytes, prior to measurement by ICP-AES. The authors discuss the relationship between the distribution of the metals and the pH and redox potential determined in the sediments.

An *environmental monitoring campaign to collect cloud water and precipitation* to be analysed for Hg and trace elements has been reported by Malcolm *et al.*[38] They designed and tested in the field a new collector for clean sequential sampling of cloud and fog water. Cloud water was collected during nine non-precipitating cloud events on Mt. Mansfield in north-eastern USA in 1998. The mean concentration of Hg in the clouds was 24.8 ng l^{-1}. The results were used to show pollutant transport routes for Hg and several trace elements, including As, Cu, Mg, Pb and Zn, which were determined by ICP-MS.

Ma *et al.*[39] have continued to investigate *the collection of size-classified fog droplets* by developing a new polymeric water absorbent film formed on a Nucleopore filter. They examined this using PIXE to determine the chemical composition of the size-aggregated fog droplets. They also used PIXE[40] for the quantitative determination of trace elements in individual raindrops. Reference standards with a uniform thickness were prepared by depositing CaF_2, Fe, KCl and Si on substrate films using an evaporation system. Calibration curves of mass thickness *versus* peak counts, obtained from a 2.6 MeV H^+ microbeam, were used for the quantification of samples obtained during field trials.

An investigation into *the preservation of arsenic speciation in water samples* with a high potential to form an iron/arsenic precipitate has been published by Gallagher *et al.*[41] They tested seven different storage conditions on water samples with different natural As^{III} and As^{V} distributions and used linear least squares to estimate the change in arsenic speciation over the 75 d study period. The samples without treatment showed a 40% drop in total arsenic concentration due to the formation of a precipitate in the iron rich sample, and on resolublization had a different As^{V} concentration compared with the natural sample. The primary storage treatments evaluated in the study included acetic acid on its own and EDTA combined with acetic acid. The acetic acid treatment eliminated the formation of a precipitate. However, with some of the samples, the As^{III} content was redistributed by 10%. The EDTA–acetic acid treatment did not cause a precipitate to form and the change in As^{III} concentration was negligible. At a storage temperature of 5 °C the rate of conversion of As was minimized compared with storage at 20 °C.

2.1.2 Pre-concentration and separation procedures. Numerous papers have been published recently on *the use of micro-columns packed with solid phase material to pre-concentrate elements from solution*, to improve detection limits or reduce interference from the matrix. Whilst a number of these report new phases, the majority do not make significant advances in the techniques used for water analysis and often complement already established methods.

Wang and Hansen[42] have published a comprehensive *review of on-line sample pre-treatment methods for the determination of metals* by coupling FI or sequential injection to ICP-MS. This covers 99 publications since 1984, many from the authors' own laboratory. It details in tabular form: the type of separation/pre-concentration scheme (solid phase extraction, on-wall adsorption, solvent extraction and hydride/vapour generation), the reaction medium or functional group used, the analytes studied and the sample type, *e.g.*, sea-water, river water and pore water. The review deals only with methods involving conventional ICP-MS, and although some of the case for applying this approach to the analysis of metals in different water matrices has been negated by the advent of collision and reaction cell ICP-MS instruments, there is still strong justification for using FI based sample introduction methods, particularly where small sample volumes are being analysed or the concomitant ions in the matrix are unknown and could form polyatomic interferences in the plasma.

Sharma *et al.*[43] have *critically reviewed the separation and pre-concentration of trace concentrations of metal ions* using silica-based chelating resins. Their review covers 60 papers published between 1964 and 2000. It describes methods for preparing such gels and includes a number of chemical structures for the different silica modifications. The review goes on to describe the use of different surface modified silicas, for a range of transition metals, REE and metalloids from different environmental water samples.

The *use of a micro-column* packed with quinolin-8-ol-immobilized fluorinated metal alkoxide glass for the pre-concentration of REE from sea-water has been reported.[44] The column was connected on-line to ICP-MS detection and used to determine Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y and Yb. A small volume of sea-water (6.4 ml) was passed through the column, which was then washed with deionised water and the analytes eluted into the plasma with nitric acid. The detection limits ranged from 0.11 ng l^{-1} for Y to 0.30 ng l^{-1} for Tb and the complete system was validated by analysis of two sea-water CRMs: CASS-4 and NASS-5. The method was ultimately used to analyse coastal sea-water from Hiroshima Bay, Japan. Sumida *et al.*[45] used a similar micro-column system, but packed with a chelating resin containing iminodiacetic acid groups, to preconcentrate trace metals and REE from deep ocean water. After adsorption of the metals, the column was washed with ammonium acetate buffer at pH 5.5 and then eluted with nitric acid, prior to the determination of 26 elements by ICP-MS and ICP-AES. Recoveries for the majority of elements were greater than 90% but, for some, particularly Al, Th and V, this dropped to 70%. The method was validated using the sea-water CRM NRC NASS-4.

Shaw *et al.*[46] reported a different approach to the *preconcentration and matrix reduction involved in the analysis of rare earth elements in sea-water and groundwater by ID-ICP-MS*. The method used the partitioning of REE with solid hydroxides to separate them from soluble matrix species, such as Ba^{2+} and major ions. Acidified samples were spiked and equilibrated with an enriched isotopic mix of ^{142}Ce, ^{145}Nd, ^{161}Dy and ^{171}Yb, prior to co-precipitation of the analytes with small amounts of Mg^{2+} and $Mg(OH)^{+}$ present in the sample, using aqueous ammonia. The precipitate was isolated by centrifugation and washed to remove Ba^{2+} (99.8% removal efficiency) and the majority of matrix ions. After dissolution in nitric acid the extract was analysed by ICP-MS. The four spiked elements were determined by IDMS, and the spikes were used as internal standards to determine the other REE. The method was validated using two different sea-water CRMs (NRC NASS-4 and NASS-5). The LODs for a 1.65 g sample were 0.02–0.1 pg g^{-1}.

Highly selective sample extraction and preconcentration procedures provide significant advantages in the development of highly specific analytical methods, or in overcoming difficult instrumental interferences encountered when analyzing some environmental matrices such as sea-water or waste water. A review on the use of ion-imprinted polymers for the preconcentration or separation of metals has been published. Ersoz *et al.*[47] have reported the synthesis, development and use of an ion-imprinted SPE material for the preconcentration of Ni from sea-water. A Ni^{II}–methacryloylhistidine dihydrate monomer was synthesized, then polymerized and cross-linked with ethylene glycol dimethacrylate to obtain the ion-imprinted polymer. After removal of the Ni^{II} ions it was tested in column form against the related non-imprinted polymer and found to give a higher adsorption capacity for Ni, determined by FAAS. The presence of Co^{II}, Cu^{II} and Zn^{II}, which have similar ionic radii to Ni, did not affect the uptake of Ni^{II} and this was also the case with a sea-water matrix. Calibration was linear between 0.3 and 25 μg l^{-1} and the LOD was 0.3 μg l^{-1}. This approach to the development of SPE materials appears to offer a number of advantages over more generic preconcentration methods. Puri *et al.*[48] have synthesized a new molecularly imprinted polymer for the specific preconcentration of tin and organotin compounds from sea-water samples. Only organotins were eluted from the absorbent using a HCl–methanol solution, whereas inorganic tin was removed with citric acid. The eluted species were determined using GFAAS, which provided a LOD of 20 ng l^{-1} for each analyte. Recovery from spiked sea-water samples was in the range 97–103% for all the tin species.

2.1.3 Hydride generation.

This section deals with techniques for analyzing metal(loid)s and their related chemical species following conversion to volatile analytes, most often hydrides, but also elemental mercury. Two useful *reviews of chemical vapour generation* have been published by Pawel Pohl.[49,50] The first covers 27 papers detailing developments between 1996 and 2002 in chemical vapour generation of transition and noble elements *via* reaction with sodium tetrahydroborate. It describes the instrumental operating conditions required for different elements and the figures of merit obtained. Whilst not dealing directly with environmental water samples, the review is of interest because it highlights the wide-ranging applicability of this technique to a number of elements not commonly associated with HG. The second review, involving 93 papers published since the first reported use of HG in 1969 up to 2003, focuses specifically on the coupling of HG with AES and covers a range of spectroscopic emission sources, including ICP, MIP, DCP and GD. It deals with the basic principles behind HG, the various emission sources that can and have been used, reaction conditions for different elements, sample pre-treatment, the use of pre-reduction, the elimination of interferences that limit the method, and future trends for the technique. It summarizes the range of real sample matrices that have been investigated with HG-AES, including river water, groundwater, drinking water, mineral water and tap water.

Zachariadis *et al.*[51] described the development of a *unified preconcentration column and gas–liquid separator for the determination of mercury* in river, tap and sea-water from Northern Greece by CV-AAS. The FI system involved the reaction of mercury with pyrrolidine dithiocarbamate to form a complex, which was preconcentrated on a column containing PTFE turnings. The complex was then reduced on-column using a tin chloride reagent solution and the elemental vapour expelled using nitrogen. The novel combination of preconcentration column and gas–liquid separator all in one gave an enrichment factor of 32 and a LOD of 6 ng l^{-1}, using a 60 s preconcentration period. The system was validated using spiked water samples.

Miravet *et al.*[52] compared different *reducing agents for antimony determination by HG-AFS*. They studied the main reagents used in the pre-reduction step, namely potassium iodide, L-cysteine and potassium iodide, in combination with ascorbic acid. Antimony can be present in environmental samples in two principal oxidation states, Sb^{III} and Sb^{V}. Because these react differently with the hydride-generating reagent it is necessary to convert the Sb present to the +3 oxidation state prior to analysis by AFS. All three agents gave similar limits of quantitation, repeatability and reproducibility, but the authors concluded that L-cysteine was the most appropriate reagent because it provided the best recovery at both of the spike concentrations tested. With the other two reagents, recovery was slightly less than 100% in most cases. The overall methodology was validated by analysis of five different spiked river, tap, mineral and well water samples and three CRMs

(NIST SRM 1640 and National Water Research Institute, Canada, TMDA-54.3 and TM-28.2).

Rupasinghe *et al.*[53] reported the use of a *novel hydride generation system for the determination of total arsenic* in industrial water samples. On-line arsine generation was carried out in a pervaporation FI system, followed by detection using decoloration of a dilute permanganate stream, which was monitored spectrophotometrically at 528 nm. Calibration was linear between 0.25 and 2000 μg l^{-1} and the system was able to tolerate common transition metal cations at concentrations of at least 10-fold excess by mass; the LOD was 0.18 μg l^{-1}. The methodology was applied to unfiltered wastewater samples having a range of pH, turbidity, conductivity and transition metal cation concentrations. The values for total arsenic compared well with those from a conventional HG-AAS method using filtered samples.

2.2 Speciation

One of the *advantages of using gas chromatography, rather than liquid based separations*, coupled to atomic spectroscopy for chemical speciation analysis, is the potential to develop multielemental methods. By converting the organometallic species of interest to a more volatile, yet stable, analogue, it is possible to obtain analyte species with similar boiling points, which can then be separated within a single chromatographic run. This is usually not possible with HPLC methods because of the range of different polarities each species will have, which means that generic separation methods are not applicable. Centineo *et al.*[54] developed a simple and rapid multielement chemical speciation method to determine inorganic Hg, methylmercury, trimethyllead, triethyllead, monobutyltin, dibutyltin and tributyltin in natural water samples. The protocol involved the ethylation of the analytes using sodium tetraethylborate with simultaneous headspace solid phase microextraction, followed by measurement by GC-MS. The system was optimized to give detection limits at the low ng l^{-1} concentration level, linear calibration curves over 3 orders of magnitude and repeatability between 3–20%. Low recoveries were observed from spiked sea-water samples and this necessitated the use of calibrations based on standard additions. The authors made no comment on the possible redistribution of the Hg chemical speciation during the ethylation step, which has been documented in solutions such as sea-water containing high concentrations of halide. The methodology was validated by analysing spiked river and sea-water samples and applied to the analysis of sea-water samples from a marina near Gijon in Spain. In a related paper[55] they reported studies on the speciation of Hg in sea-water samples using SPME-GC-ICP-MS. Strong matrix effects were again observed, which necessitated the use of calibration by standard additions. No redistribution of the mercury speciation was evaluated in this work either.

Vonderheide *et al.*[56] used GC-ICP-MS with an *octopole reaction cell to determine organophosphorus pesticides (OPs) in drinking water*. The relatively high first ionization potential of P (10.5 eV) and the presence of polyatomic interferences resulting from N_2 in the atmosphere, make this element particularly difficult to determine in environmental samples by ICP-MS. The authors investigated the effect of the addition of O_2, He and N_2 to the central channel of the plasma on the ^{31}P signal, and used He in the reaction cell to reduce the polyatomic interferences. No real difference in P signal was observed with He, although with O_2 there was a slight decrease in response due to formation of PO^+. However, the addition of N_2 resulted in an approximate 15-fold increase in the response for the OP used in the optimization experiment. The downside to this was an increase in the background observed during the chromatographic run, due to the formation of NO^+. To improve the S/N ratio they investigated the use of different collision cell gases and found that with He it was possible to reduce the background signal without attenuating the signals due to ^{31}P. The LODs for diazinon, disulfoton, terbufos and fonofos, calculated by a USEPA method, were 0.2 μg l^{-1}, which were lower than those for two current EPA methods.

Liu *et al.*[57] used *IC coupled to ICP-MS detection for the determination of haloacetic acids* in drinking water samples from Beijing. Some of these acids, formed during the disinfection of drinking water, are known animal carcinogens and, because of potential human health effects, the USEPA and WHO have established maximum contamination levels for these compounds in potable water. A hydrophilic anion-exchange column and a sodium hydroxide gradient were used to separate the halogenated species, prior to detection of the ions at *m*/*z* 35 (Cl), 51 (ClO^+) and 79 (Br) by quadrupole ICP-MS. An anion suppressor column between the separation column and the ICP-MS was used to remove interference from Na in the eluent. This greatly reduced the background and improved the limits of detection, which were between 16 and 24 μg l^{-1} for the chlorinated acids and 0.3 and 1.0 μg l^{-1} for the brominated compounds, detected at *m*/*z* 51 and *m*/*z* 79, respectively. Cai *et al.*[58] used a similar system to determine bromate and haloacetic acids in water, except that the water sample was pretreated with two resin-based SPE cartridges before analysis; the first was modified with Ag, the second with H^+. This pre-treatment effectively removed bromide from interfering with the closely eluting bromochloroacetic acid. Their anion exchange column was similar to that used by Liu *et al.*,[57] but the eluent was ammonium nitrate. The elution order was the same in both studies and the LODs ranged from 0.16 to 0.36 μg l^{-1} when monitoring Br at *m*/*z* 79. Spike recoveries from water samples were between 83 and 114%. The main differences in the reports relate to the presence or absence of Cl or Br ions in the chromatograms and this could result from the use of the suppressor column in the former paper and a different sample preparation method in the latter.

Determination of the *oxidation states of chromium in solution* presents a number of difficulties because the two redox forms are oppositely charged, which makes the chromatographic separation less straightforward. Motomizu *et al.*[59] used anion and cation exchange resin disks coupled in series to an ICP-OES to determine the Cr oxidation states in fresh water samples. The on-line FI system was sufficiently sensitive to allow small sample volumes (5 ml) to be used. Elution with nitric acid to determine Cr^{III} and Cr^{VI} gave LODs of 40 μg l^{-1} and 20 μg l^{-1}, respectively.

Minami *et al.*[60] have reported the use of *isotope dilution calibration for the determination of selenite and selenate in natural water samples* by MIP-MS. A solution containing both oxidation states, each enriched with a ^{78}Se spike, was added to the samples prior to adsorption on an anion exchange column (Bio-Rad AG1-X8). Selenite and then selenate were sequentially eluted from the column using different concentrations of nitric acid. Nitrogen MIP-MS has a significant advantage over ICP-MS for the measurement of Se because the most abundant isotope of selenium can be monitored without interferences from Ar in the mass spectrum. Instrumental and data acquisition parameters were optimized for measurement of the $^{78}Se/^{80}Se$ isotopic ratio by ID-MS to achieve a detection limit of 0.01 μg l^{-1}. The method was successfully applied to the determination of Se in groundwater, tap and mineral water samples from Japan.

Bednar *et al.*[61] compared *field and laboratory chemical speciation methods for the determination of arsenic* in natural water samples. They obtained quantitative results for arsenite, arsenate, monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and roxarsone when present in over a 100 different water samples, including groundwater, surface-water, and acid mine drainage waste. The laboratory method used strong anion exchange HPLC coupled to detection by ICP-MS. The field method used a SPE cartridge containing a strong anion exchange resin to separate the As species. The water sample was preserved with EDTA and filtered prior to being passed through the SPE cartridge using a syringe. The As^V, DMA and MMA were held on the column, whereas As^{III} passed through. The stability of the loaded column at room temperature in a sealed container was evaluated after 14 and 47 d and recovery of As^V was 100% over both time periods. Problems arose when the ion-exchange capacity of the column was exceeded, usually when high concentrations of other anions were present in the water sample. The data from the field and laboratory methods for As^V and As^{III} in the groundwater samples showed no significant difference at the 95% confidence level. For the acid mine drainage samples, the laboratory method for As^{III} gave slightly higher values than the field method, but for As^V there was no significant difference. Yu *et al.*[62] used ICP-MS to investigate the retention behaviour of As^{III}, As^V, MMA, DMA, arsenobetaine, arsenocholine, trimethylarsine oxide, and tetramethylarsonium ion on different SPE cartridges. They then developed a method based on isolation of the species on SCX or non-polar mixed SCX and SAX cartridges followed by selective elution with nitric acid. The method was used to analyse drinking and wastewater samples.

As part of an assessment of the factors that affect radioactive waste storage, Kuczewski *et al.*[63] used *capillary electrophoresis coupled to ICP-MS* detection to examine the different oxidation states of plutonium and neptunium in groundwater. They studied Pu in the (III)–(VI) oxidation states, Np^{IV} and Np^V, La^{III} and U^{VI} to determine the geochemical behaviour of these radionuclides during migration through the geosphere. The experimental system comprised a fused-silica capillary with a low flow rate nebuliser and a small volume cyclonic spray-chamber to give the necessary chromatographic resolution. Comparison of two concentric nebulisers indicated that the long-term stability of the microconcentric nebuliser was not satisfactory and that the MicroMist glass system showed a better signal stability and was not prone to blocking. By investigating the redox behaviour of Pu^{VI} under anaerobic conditions in groundwater samples, the authors showed that the methodology preserved the redox chemical speciation of the elements under investigation, which is a particular concern with this type of speciation analysis.

Coupling of CE to ICP-MS has been reported[64] for the determination of Nd–fulvic acid (Nd–FA) binding constants in solutions of differing pH and ionic strength. The authors used a strong ligand competition method to determine binding constants in the Nd–EDTA–FA–H_2O model system. Compared with traditional techniques for studying metal binding, such as those based on ion selective electrodes, the CE-ICP-MS system operates at low detection limits (pM–nM), tolerates a wide range of pH and ionic strength conditions and has a multi-elemental capability. The LOD for Nd speciation was 500 pM.

2.3 Instrumental analysis

2.3.1 Atomic absorption spectrometry. Felipe-Sotelo *et al.*[65] investigated *multivariate regression analysis* as a means of overcoming the spectral and chemical interference of concomitant iron on the determination of trace levels of Cr in water samples by ETAAS. Three multivariate regression methods (partial least squares (PLS), polynomial PLS and locally weighted regression) were applied to the determination of Cr in well and spring water and two CRMs (TM24 from CRN, Canada, and SPS-SW1 from Spectrapure, Oslo) and PLS was found to satisfactorily overcome the enhancement effect of iron. This approach offers new possibilities to deal with interferences in ETAAS and reduces the need for time-consuming sample clean-up procedures prior to analysis.

An *online sample preparation system for the chemical speciation of Cr* in natural water samples by ETAAS has been reported by Cordero *et al.*[66] The authors replaced the original autosampler probe tip with micro-columns (3 cm × 3 mm id, packed to a depth of 0.5 cm) containing either a silica gel chelating resin, functionalized with 1-(di-2-pyridyl)methylene thiocarbonohydrazide (DPTH–gel), or an anionic ion exchange resin, Amberlite IRA-910. The chelating gel retained both species, whereas only CrVI was retained by the anionic column. Using this system it was possible to preconcentrate the analytes of interest online, prior to elution into the graphite furnace. Total Cr and Cr^{VI} were determined directly and Cr^{III} calculated by difference. Calibration was linear between 0.3 and 8.0 $\mu g\ l^{-1}$ and the LODs were 0.14 and 0.08 $\mu g\ l^{-1}$ for Cr^{III} and Cr^{VI}, respectively.

A similar system has been developed to *determine the oxidation states of selenium in water samples*. Stripeikis *et al.*[67] used a strongly basic anionic exchange resin (Dowex 1 × 8, 100–200 mesh) packed into a micro-column (3.0 × 1.6 cm) placed in the autosampler probe, to determine Se^{IV} and Se^{VI} by ETAAS. The graphite tubes were pre-treated with 100 µl of a 1000 mg l^{-1} solution of iridium and then heated through a temperature progamme. This was repeated three times to permanently modify the tube in order to reduce the formation of the volatile species formed in the presence of high chloride levels in the samples. The LOD was 10 ng l^{-1} for both species, using a total sample volume of 9 ml. The precision for both species was less than 10% at the 200 ng l^{-1} concentration level in spiked tap water samples.

2.3.2 Atomic emission and fluorescence spectrometry. Ma *et al.*[68] applied *a wavelet transform (WT) to improve the determination of elements with weak emission intensities*, such as As, Pb, Sb and Se, in samples exhibiting intense noise. They investigated the effect of the mother wavelet, the transform approach used and the decomposition number. This spectral smoothing method effectively removed the intense noise from the weak signals for these elements, allowing the baseline to be rapidly determined and the signal intensity calculated. The ICP-OES spectra were sufficiently improved so that the analysis of synthetic and lake water samples showed better precision compared to the unsmoothed data and the results were more in agreement with analysis by GF-AAS than when the transform was not used.

Fan *et al.*[69] have developed a *novel low temperature ETV-ICP-OES* method for the determination of Pt, Pd and Rh in artificial sea-water and tap water. The analytes were complexed with diethyldithiocarbamate in solution and then introduced into the ETV unit; LODs of 5.4, 1.4 and 0.8 $\mu g\ l^{-1}$ were achieved for Pt, Pd and Rh in natural water samples. Okamoto *et al.*[70] used electrothermal vaporization with a tungsten boat furnace to determine P and S by ICP-OES. In this type of furnace the loss of P, which can occur during the drying and ashing stages, was reduced due to the formation of a stable tungsten phosphate species. Detection limits of 1.5 ng and 0.12 ng were reported for P and S, respectively, and the methodology was applied to natural water samples.

Campillo *et al.*[71] used *purge-and-trap capillary gas chromatography coupled to MIP-AES* to determine 10 volatile halogenated organic compounds in tap and natural water samples. Analytes were stripped from the samples with helium, preconcentrated in a capillary trap and thermally desorbed into the GC-MIP-MS system. Emission lines for Cl (479 nm), Br (478 nm) and I (193 nm) were monitored and the detection limits for a 5 ml sample were between 0.05 and 0.5 $\mu g\ l^{-1}$.

2.3.3 X-ray fluorescence spectrometry. The development of methods to determine elemental concentrations in water samples on-site provides a number of advantages over laboratory-based methods. By eliminating the necessity to transport samples to the laboratory for analysis, a number of factors, such as sample preservation, analyte stability and contamination can be reduced or eliminated.

A *portable total reflection XRF spectrometer* was tested in the field for the determination of As, Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, Se, Sr and Zn in lake and river water samples.[72] The concentration of K and Ca in the same samples was found to be significantly different between the field and laboratory based methods and the Fe concentration was affected by contamination. The differences in Fe concentration were thought to result from airborne contamination, which was shown to increase over the 48 h that the control plate was left exposed. The accuracy of the method for the other elements was validated by analysing NIST SRM 1640.

Hou *et al.*[73] have published a review on *recent advances in portable XRF spectrometry*. Principles and instrumentation are briefly discussed, but the main part of the review focuses on the on-site analysis of natural and wastewater samples.

Daniel *et al.*[74] have used *solid-phase extraction disks for the determination of Cd, Ni, Cu and Pb in drinking water samples by XRF*. The analytes were extracted from solution (1000 ml) by filtration through the chelating disks, providing a 1600-fold preconcentration factor. The LODs were between 0.3–3.8 μg l^{-1} and no interference from Group I or II elements was observed. The extraction step could be completed in the field and the disks returned to the laboratory for analysis.

2.3.4 Mass spectrometry

2.3.4.1 Inductively coupled plasma mass spectrometry. A special issue of *J. Anal. At. Spectrom.* focuses on the use of *collision and reaction cell techniques in atomic mass spectrometry*. Scientists working with such instruments will find the majority of papers of interest. Those detailing the analysis of environmental water samples are summarized below. Fernandez *et al.*[75] reported a neat solution to *the elimination of the Ca polyatomic interferences* on the determination of Fe in natural water with high calcium content. Using hydrogen in the collision cell of the ICP-MS instrument, it was possible to remove the interference from Ar-based polyatomic species. However, some calcium species, most notably CaO^+ and $CaOH^+$, which interfere with ^{56}Fe and ^{57}Fe, respectively, were resistant to removal in the cell because of their high thermodynamic stability. The authors therefore used a conductivity suppressor column, commonly used in IC, between the sample injector and the ICP-MS, to remove the calcium ions from solution prior to its reaching the plasma. For Ca concentrations up to 1000 mg l^{-1} removal efficiency was almost 100% at a pH between 2.5 and 7. To avoid the removal of Fe by the column the samples were spiked with EDTA, which forms a negatively charged complex with Fe that is unaffected by the suppressor unit. Calcium was still observed in some of the samples but, because of the low yield of CaO^+ (0.0031%) in the plasma, it did not adversely affect the signal for Fe and it was possible to achieve an LOD of 0.16 μg l^{-1}. The authors observed that this simple approach could equally well be used to remove Group I and II metals prior to ICP-MS analysis. Segura *et al.*[76] reported another approach to the elimination of Ca and Ar interferences in the determination of Fe in mineral water and urban wastewater samples. They employed a conventional ICP-MS instrument without a reaction/collision cell, but used a shielded torch and "cool" plasma conditions (rf power 700 W) to reduce the interferences from Ar. However, interferences from Ca were increased, presumably because the torch position and gas flow rates enhanced the formation of oxide polyatomics in the plasma. A FI system was therefore developed using a microcolumn containing a specific iron-chelating agent, Desferal (mesylate salt of desferrioxamine B), which preconcentrated the iron present in solution by a factor of 92 and provided a LOD of 0.74 μg l^{-1}.

Benkhedda *et al.*[77] determined total lead and lead *isotope ratios in water using an ICP-MS instrument* with a TOF analyser. Sample introduction was *via* a FI pre-concentration system, which yielded a 20-fold enhancement over direct FI. They evaluated the need for detector dead-time correction and mass discrimination for this particular TOF instrument. The precisions of the isotope ratios for Pb at a concentration of 1 μg l^{-1} were 1.87, 0.70 and 0.28% for $^{204}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$, respectively. The methodology was validated using the certified lead isotope ratio values for NIST SRM 981 and the total lead value for the NIST fresh water SRM 1643d. Rouxel *et al.*[78] determined Sb isotopic variations in sea-water samples associated with hydrothermal vents, using a MC-ICP-MS instrument and hydride generation sample introduction. Samples were purified prior to analysis using a cation-exchange resin and cotton impregnated with thioglycollic acid. The $^{121}Sb/^{123}Sb$ isotopic ratio was determined with a precision of 0.4 epsilon units by bracketing samples with standards. Elliot *et al.*[79] used the same design of MC-ICP-MS to determine the concentration of ^{226}Ra in three water column samples from the Ross Sea, Antarctica, by ID-MS analysis. Using an interface decontaminated from Ba, it was possible to measure an accurate Ra/Ba ratio, which had a value consistent with that for open ocean samples and within the same error as measurements by TIMS. With these data the authors suggest that the Antarctic Ocean has not received significant groundwater or meltwater from the Antarctic continent.

Cairns *et al.*[80] used the sea-water CRM NASS-5 to *evaluate the performance of a low volume spray chamber with a microflow nebuliser* for use with ICP-MS. It comprised a low-volume (13 cm^3), single pass spraychamber and a PFA concentric nebuliser operated at a flow rate of 50 μl min^{-1} in total consumption mode. The wash out time was 4 s and memory effects from a 10 μg l^{-1} tune solution containing Co, Ce and Tl were low. The overall transport efficiency was approximately 82%. Matrix effects were evaluated by analysing 10-fold diluted sea-water, which suppressed the signal for most elements by only 10–20% compared with ultra-pure water. However, the detection limits were higher than those from a conventional sample introduction system. The main application area envisaged by the authors is the analysis of small sample volumes ($<$100 μl) by either FI or low flow HPLC.

2.3.4.2 Other mass spectrometric methods. The use of *AMS in marine environmental studies* for dating, tracing and source identification has been reviewed.[34] The traditional use of AMS for ^{14}C dating is no longer dominant, with greater use being made of ^{10}Be, ^{26}Al and ^{36}Cl measurements, particularly in relation to the understanding of global processes. Much research is now focused on understanding global climate change by studying oceanic circulation, atmospheric processes and past climates. Profiles of long-lived cosmogenic radionuclides in ice cores can provide important information on past climates. The review also addresses the measurement of heavy, long-lived isotopes, including ^{99}Tc, ^{129}I and ^{236}U, associated with radioactive releases from nuclear facilities. Determination of *the isotopic ratio of Ar in seawater by AMS* has been reported.[81] Interest in the determination of ^{39}Ar originates from its half-life which matches the timescales of the circulation of oceanic currents, so the $^{39}Ar/^{40}Ar$ ratio can be used to date water from different depths. However, this ratio is difficult to measure because of the low abundance of ^{39}Ar and the significant interference from ^{39}K. Research at the Argonne National Laboratory to develop a viable AMS method has investigated two approaches to reducing the magnitude of the interfering ion beam. One uses a quartz liner to provide a cleaner surface in the sample introduction system, the other uses a SiO_2 layer, formed by the introduction of oxygen and silane into the source, to bury the interference. Both methods reduced the ^{39}K background by a factor of 100 and allowed more precise isotope ratio measurements to be made.

2.4 Metrology and data quality

A special issue of *Trends in Analytical Chemistry* dealing with *traceability in environmental analysis* has been published.[82] It includes papers dealing with traceability, certified reference materials, quality control and quality assurance, relating to the analysis of environmental samples, including groundwater,[305] wastewater[306] and achieving traceability using isotope dilution in environmental analysis.

Roy and Fouillac[305] described a *methodology for estimating the uncertainties associated with the entire analytical chain used in groundwater analysis*, from the sampling stage to reporting of the overall findings. They studied groundwater samples from two industrial sites contaminated with metals or organochlorine compounds, but the crux of the publication details sampling strategies which allow for the estimation of the uncertainties associated with the pre-laboratory part of the analytical process. Each site was geochemically characterized, using borehole sampling and a multi-parameter probe (pH, temperature, conductivity, redox potential and dissolved oxygen) prior to samples being assayed in the laboratory by IC and ICP-MS for a number of anions and some major and trace metals. Repetitive sampling was then carried out to determine the internal variability in each borehole and the inter-borehole differences. Principal component analysis applied to the full multivariate dataset showed that four effects accounted for 91% of the variability in the chemical data. The two main effects were natural inter-borehole or spatial inconsistency and intra-borehole variability due to different groundwater flow patterns. The two minor effects were related to bacterial activity and analytical effects. The authors observed that, in view of the European Union's impending Groundwater Directive, there is currently a need to develop, within a regulatory context, specific sampling methodologies for groundwater.

Godon *et al.*[83] have conducted a *round-robin determination of chlorine isotope ratios of 24 sea-water samples* from worldwide locations. By using gas source isotope ratio mass spectrometry (IRMS) and TIMS, they were able to show that whatever the location of the sea-water samples, their distance from the coast, the sampling depth, the salinity, temperature, size of water reservoir or the potential of another geochemical reservoir, *e.g.*, geothermal vent, the standard deviation of the $\delta^{37}Cl$ data from all 24 samples was no larger than the reported measurement precision. They concluded that, within experimental error, oceanic waters seem to be a homogeneous reservoir and any sea-water sample could be representative of Standard Mean Ocean Chloride (SMOC) and used as a reference standard for chlorine stable isotopes.

3 Analysis of soils, plants and related materials

This section reports progress in the development of methods for the analysis of soils, plants and related materials such as settled sediments and dusts. Dominant themes during the past year include preconcentration and matrix separation techniques and, once again, speciation of particular elements of interest, especially arsenic. Also of note is the increased use of portable XRF spectrometers for *in situ* analysis.

3.1 Sample preparation

3.1.1 Preconcentration. Much attention has been paid to methods of preconcentrating elements of interest to reduce limits of detection, particularly for AAS analysis. In this context, the development of *solid phase extraction (SPE) techniques* has continued. SPE generally utilises adsorbent materials in micro-columns followed by elution of adsorbed elements with an appropriate reagent prior to analysis of the eluent. Ferreira *et al.*[84] developed an on-line preconcentration system for FAAS determination of Cu in food plants using a column of Amberlite XAD-2 loaded with 2-(2-thiazolylazo)-5-dimethylaminophenol as the functional group. A detection limit of 0.23 $\mu g\ l^{-1}$ and an enrichment factor (EF) of 62 were achieved with better that 4% precision and good agreement with CRM values. Preetha *et al.*[85] developed a method for analysing soils for Zn by using a C_{18} bonded silica gel micro-column and acidified methanol as the eluent. They claim EF and detection limit figures of 120 and 0.15 $\mu g\ l^{-1}$, respectively. A micro-column SPE technique was developed for the preconcentration of Pt in soils and plants using silica gel as the support matrix and 1,5-bis(di-2- pyridyl)methylene thiocarbohydrazide as the functional group.[86] An EF of 42 and a DL of 0.8 $\mu g\ l^{-1}$ were reported after elution by 2 M HNO_3 and analysis by ETAAS. Similarly successful developments have been reported for the determination of trace elements in river sediment porewaters by ICP-AES and ETAAS[37] and stream sediments by FAAS.[87]

Cellulose filters and various chelating sorbents have been used for *preconcentration and matrix separation* in the past year. Soylak *et al.*[88] reported a technique, verified by FAAS analysis of a stream sediment reference material (GBW07309), whereby Cd, Co, Cu and Fe are collected on a cellulose nitrate membrane filter which is subsequently dissolved in concentrated nitric acid: RSDs were <9% and recovery was 94%–102%. In a simple method that gave excellent recoveries, Lee *et al.*[89] packed chelating resin fibres in a syringe to preconcentrate 25 trace elements from aqueous samples, including acid-digested sediment and plant material, for ICP-AES determination after elution by molar nitric acid. Medved *et al.*[90] described a method for preconcentrating Au from environmental samples, including soils and sediments, for ETA-AAS analysis. A chelating sorbent (Spheron Thiol 1000) is added to acid-digested samples and the filtrate, with sorbed Au, is ashed before dissolution in *aqua regia*, giving a DL of 0.5 $ng\ g^{-1}$; however, RSDs of up to 16.4% were observed. Finally, polyvinylpyrrolidone (PVP), a water soluble polymer with chelating properties, has been used in a simple but novel method developed by Tokman *et al.*[91,92] for the preconcentration and separation of several trace elements in aqueous solutions prior to their determination by ETAAS. Low detection limits and good recoveries within 4% of certified values were reported.

3.1.2. Sample dissolution. A trend is again evident away from development of complete acid digestion procedures towards more selective extraction methods, driven by the need to understand parameters such as pollutant speciation and bioavailability. In spite of this, some *developments in total dissolution techniques* are worthy of mention. Chattopadhyay *et al.*[93] developed a magnesium nitrate assisted dry ashing procedure for the complete digestion of soil and sediment samples for direct ICP-AES and ICP-MS determination of Cd, Pb and Sb; good precision was obtained and an advantage of the procedure is its simplicity. Tighe *et al.*[94] assessed four common digestion techniques for extraction strength and analytical precision of the ICP-OES determination of a range of elements in soils with an emphasis on As and Sb. On both counts, microwave *aqua regia* digestion was found to give better results than open *aqua regia* and microwave/open nitric acid digestions for the widest range of analytes.

Developments have been reported in *total dissolution procedures for plant samples*. Huang *et al.*[95] noted the limitations—particularly high background and carry-over—of the common technique of using hot concentrated nitric acid in Pyrex test tubes. They report a rapid, microwave digestion system, utilising HNO_3 and H_2O_2 in capped but ventilated polypropylene tubes, followed by measurement of macro- and micronutrients by ICP-AES. Good precision and accuracy and several advantages were reported, including low background concentrations and time and cost savings. However, problems were encountered for Fe in terms of accuracy and percentage recovery. Oliva *et al.*[96] reported high accuracy for a range of nutrient elements in plant materials using a closed HNO_3–H_2O_2 microwave digestion system. Selenium in plants has been extensively studied this year. Smrkolj and Stibilj[97] described a plant digestion procedure for Se determination by HGAAS which utilises H_2SO_4, HNO_3, H_2O_2, HF and V_2O_5. A detection limit of 0.14 ng g^{-1} was achieved and the procedure is simple and low-cost.

Further developments have occurred in *fast thermal and slurry sampling techniques*. Lopez-Garcia *et al.*[98] determined Sn and Ti in soils and sediments by ETAAS by suspending samples in HF solution and using palladium and ammonium dihydrogen phosphate as matrix modifiers. Results were in agreement with those from a microwave total digestion procedure and good accuracy was achieved. The same authors described a similar technique for Ba, Mn and Sr.[99] Filgueiras *et al.*[100] developed a fast thermal programme to be used in conjunction with the BCR 3-stage sequential extraction scheme and successfully determined Cr, Cu, Ni and Pb by ETAAS.

3.1.3 Extraction techniques. An interesting study utilising *sequential extraction* to investigate the mobility of Pt in road tunnel dust is worthy of mention.[12] The authors developed a microwave digestion procedure for the extracts and measurement by ICP-MS indicated that up to 40% of the Pt was mobile—operationally defined, of course. In general, the development of selective extraction methods continues apace. Hydroxylamine hydrochloride and acidified H_2O_2 were used to selectively dissolve manganese oxides, *i.e.*, leaving Fe oxides intact, within Fe–Mn nodules from a lateritic soil in Brazil.[101] This facilitated investigations into trace element associations with manganese oxides and the technique may be useful in the development of sequential extraction schemes. Mosbaek *et al.*[102] developed a technique for solvent extraction of trace metals directly from acid digests of solid samples. Good accuracy and precision are reported and a particular advantage of the technique is the absence of matrix interference. A study of Al mobility in soils, sediments and rocks caused by environmental acidification found that four single extractants, H_2O, KCl, NH_4Cl and $BaCl_2$, and the first extractant of the BCR 3-stage extraction scheme (dilute CH_3COOH) were best for quantifying mobile Al concentrations by FAAS.[103] Huang *et al.*[104] developed a new extraction method for organotin, organolead and organomercury compounds from soils. 1 M $CaCl_2$, 0.1% tropolone and glacial acetic acid in combination extracted more of the organometallic compounds than microwave-assisted and ultrasound-assisted extraction or accelerated solvent extraction, allowing detection by GC-ICP-MS in the pg g^{-1} range.

Ultrasound-assisted extraction has again progressed as a technique for environmental samples. Krasnodebska-Ostrega and Kowalska[105] introduced sonication to the acetic acid step of the BCR 3-step extraction scheme to shorten the extraction time of 'available' Cd, Pb and Zn from soils. In an ETAAS study of Cd extractability from soils and sediments, Brasil *et al.*[106] found that 60 min sonication of the sample slurried in a 7% (1 : 1) HNO_3–HCl solution improved precision 2-fold and decreased the detection limit to 3 ng g^{-1}. In a Polish study,[107] surfactants (Triton X-100, didodecyldimethylammonium bromide and cetyltrimethylammonium bromide) were added to ultrasound-assisted acid extraction solutions of elements from plant materials determined by ICP-AES; their presence did not significantly affect various plasma parameters. Alvarez *et al.*[108] measured concentrations of Ca, Cu, Fe, K, Mn and Zn in onion plants by total reflection XRF after acid extraction of the elements from the plants in an ultrasonic bath. Good agreement was found with concentrations obtained by a standard FAAS procedure.

3.2 Speciation

Studies into the speciation of elements in soils, sediments and plants are now ubiquitous, driven mainly by the knowledge that the behaviour of elements, *e.g.*, their mobility in soils and their toxicity, are strongly influenced by their physico-chemical form. As in previous years, a preferred method has been HPLC coupled with ICP-MS, but *alternative speciation procedures* involving other chromatographic techniques and specific adsorbents have also been described. Various elements have been investigated but a particular focus has been the speciation of As in environmental samples, often using well-established methodology.

For the *speciation of As* in soils at an As-contaminated mining site in Cornwall, UK, Camm *et al.*[109] coupled HPLC with HG-AFS. This well established technique allowed the authors to differentiate between arsenate (As^{V}) species and the more toxic arsenite (As^{III}) species in water-soluble extracts; 0.3% and 1.7% of the total concentration of As (up to 4000 mg kg^{-1}) were present as the respective species. At another polluted site containing up to 1% As, Matera *et al.*[110] used HPLC-ICP-MS and found that more than 90% of soil As was present in the arsenate form. Pizarro *et al.*[111] employed HPLC-ICP-MS to determine As species in several different reagents used to extract As from soils and other media. They extracted and quantified As^{III}, As^{IV}, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). Chardin *et al.*[112] used HPLC-ICP-MS to study changes in the speciation of As and Cr after exposure to sulfate-reducing bacteria which are thought to have potential as bioremediation agents for these toxic elements. Reduction of Cr^{VI} to Cr^{III} and precipitation of As^{V} as sulfide were reported. Rattanachongkiat *et al.*[113] investigated the speciation of As in sediments and biota in a tin-mining area of Thailand. They extracted As from sediments with 1 M H_3PO_4 in an open focused microwave system. The main As species (arsenate, arsenite, MMA and DMA) were separated and measured by anion-exchange HPLC coupled to an ICP-MS. Arsenate was the dominant species. HPLC-ICP-MS has also been utilised extensively for As speciation in plant samples. In a noteworthy study, Zheng *et al.*[114] used the technique to investigate As speciation in submerged plants in a contaminated Canadian lake. Among the species reported were methylarsonic acid, dimethylarsinic acid, trimethylarsine oxide and tetramethylarsonium; arsenobetaine and arsenocholine were not detected. Our understanding of As metabolism in plants was further enhanced by another HPLC-ICP-MS study of As speciation in the As-tolerant plant *Holcus lanatus*; reduction of As^{V} to As^{III} in both roots and shoots was reported, although to a limited extent. On a similar theme, the discovery in recent years of the As hyperaccumulator *Pteris vittatta* L. (Chinese brake fern) has led to much research on this plant, including another HPLC-ICP-MS speciation study.[115] The results of this indicated for the first time that the plant can convert MMA to DMA by methylation. Detection limits for the species of interest, As^{III}, As^{V}, MMA and DMA, were, respectively, 0.5, 1.8, 0.3 and 0.4 ppb. Montes-Bayon *et al.*[116] investigated As speciation in plant samples (*Brassica juncea*), arguing that genetic engineering of natural As detoxification mechanisms will only be possible if a full understanding of As metabolism is achieved. Using size exclusion chromatography (SEC), again coupled to ICP-MS, the authors detected an As species associated with thiol groups. This was ascribed to As phytochelatins, which are now thought to be of utmost importance for As detoxification in plants. It is also worth mentioning a useful review article by Karthikeyan and Hirata.[117] This described recent progress in the field and revealed that over 20 As species have been reported in environmental samples. Detection limits of between 0.02 and 20 μg kg^{-1} were reported from the various analytical techniques applied.

Liquid chromatography coupled with various spectrometric techniques has been utilised to study a range of other elements of which only selected examples will be described here. Umemura *et al.*[118] used cation-exchange HPLC with ICP-AES to study Al speciation in the porewaters of acidified forest soils; concentrations of free Al (mainly Al^{3+} and $Al(OH)^{2+}$) and inert Al (complexed and/or colloidal forms) were reported. HPLC-ICP-MS was used by two independent studies into the speciation of Se in Se-enriched onion plants.[119,120] In both studies the chemopreventive species Se-methylselenocysteine was detected and in the latter study evidence was also found for the presence of Se-cystine, Se-methionine and inorganic Se. Lesniewska *et al.*[121] used SEC (coupled on-line to ICP-MS) to investigate Pt, Pd and Rh in low molecular mass fractions (< 10 kDa) of extracts from *Lolium multiflorum* grass leaves and roots. According to the authors, the association of the platinum group elements (PGEs) with C, Ca and S in these fractions may indicate the interaction of PGEs with phytochelatins and carbohydrates. SEC was used[122] along with ion chromatography, both coupled with on-line ICP-MS detection, to investigate thallium speciation in the Tl-hyperaccumulating plant *Iberis intermedia*: Tl^{I} was found to be the dominant chemical form in roots, stems and leaves. Wuilloud *et al.*[123,124] used SEC-ICP-MS to study trace element speciation in edible mushrooms. Separation into high and low molecular weight fractions was achieved with a Superdex 75 column. Most elements of interest were associated with the high MW fractions.

Several studies have used *gas chromatography coupled with various spectrometric techniques*. Leermakers *et al.*[125] developed a method for determining monomethylmercury (MMHg) in environmental samples that utilises static headspace GC with AFS detection. A detection limit of 0.002 ng g^{-1} was obtained for sediments and biological samples. GC coupled with microwave induced plasma-AES (MIP-AES) was utilised to detect methylmercury in sediments by Landaluze *et al.*[126] Extracts were ethylated and volatile products were preconcentrated in hexane. The authors state that 90 min magnetic stirring of the sample in 2 mol dm^{-3} HNO_3 is most effective for releasing methylmercury from the sediment whilst preserving its structure. Improvements to a GC technique for Hg speciation were described by Stoichev *et al.*[127] Chromatographic performance and DLs for Hg^{2+} and MMHg determined by AFS are improved significantly by incorporation of a soda lime moisture trap to remove water vapour. Multicapillary GC with MIP-AES was used by Dietz *et al.*[128] for Se speciation in plants grown hydroponically in inorganic-Se solutions. Solid phase microextraction (SPME) sampling was undertaken in fixed volume flow boxes in the headspace above the plants, including *Brassica juncea* and garlic. Speciation analysis indicated that the plants metabolise the Se taken up by roots into volatile organic species. Advantages are fast separation, low detection limits and low cost relative to GC-ICP-MS. Alternative approaches for Se speciation include a flow injection-hydride generation-atomic absorption spectrometry (FI-HG-AAS) technique developed by Korenovska[129] for the determination of Se in vegetables and fruits. A detection limit of 0.06 μg kg^{-1} was reported with 88–104% recovery.

In the context of *speciation*, two other studies merit inclusion. Chen *et al.*[130] developed a method for the speciation of Al from tea leaves. Tea infusions were exposed to a microcolumn packed with cationic exchange resin. Results suggested that all labile monomeric Al species were retained when the pH was between 5.5 and 8, while non-labile monomeric species passed through the column. After elution with molar HCl, Al species were detected by a fluorination-assisted electrothermal vaporization (FETV)-ICP-AES procedure. Puri *et al.*[48] synthesised a polymeric adsorbent for retention of organotin species from sediments. Tributyltin chloride (TBT), dibutyltin dichloride (DBT), monobutylytin trichloride (MBT) and triphenyltin chloride (TPhT) were quantitatively retained over a wide pH range and determined by ETAAS after elution with 0.1 M HCl in methanol solution. The detection limit for organotin is 30 ng l^{-1} and recovery is 82–90% for TBT, DBT and TPhT and 50–55% for MBT.

3.3 Instrumental analysis

3.3.1 Atomic absorption spectrometry. AAS is still very widely used in environmental analysis despite the increasing availability of ICP-MS. Medved *et al.*[131] compared and evaluated *electrothermal atomic absorption spectrometry* and FAAS, together with ICP-AES, for the determination of Cd, Cr, Ni, Pb and V in soils and plants. The authors found ETAAS to be most suitable for all sample types with good precision and detection limit values. Many authors have continued to describe studies with various modifiers for ETAAS analysis of environmental samples. Lima *et al.*[132] used Ir, Rh and Ru, both singly and mixed with W, as permanent modifiers, *i.e.*, thermally deposited on the integrated platform of a transversally heated graphite atomiser, in the analysis of soils, sediments and other materials for Sb by ETAAS. The W–Ir, W–Rh and W–Ru modifiers were more suitable than the single Ir, Rh and Ru modifiers, giving 95–105% recovery and a 40% longer tube lifetime. For the ETAAS determination of Cd and Pb in environmental samples, Acar[133] found that Zr–W and Zr–Ru were as efficient as the conventional modifier Pd + $Mg(NO_3)_2$ for obtaining thermal stabilisation and for avoiding most interferences. Baralkiewicz and Gramowska[134] found that a W–Rh modifier was most suitable for the determination of Cd in sediments by ETAAS. Lopez-Garcia *et al.*[135] described a procedure for the determination of Ag and Au in soils and sediments by ETAAS. Slurry suspensions of HNO_3–H_2O_2–HF for Ag and of HF for Au were allowed to cool to ambient temperature after a short, mild heating stage and then introduced to the atomiser; HF and H_2O_2 were used as modifiers and DLs of 0.02 and 0.01 mg kg^{-1} were recorded for Ag and Au, respectively. Amin *et al.*[136] used ultrasonic slurry sampling ETAAS (USS-ETAAS) to determine Cd in Bangladeshi vegetables and found levels in agreement with those from acid-digestion procedures. Matrix interference was eliminated by using thiourea as a modifier.

Asfaw and Wibetoe[137] developed an *ultrasonic slurry sampling-gas flame atomic absorbtion spectrometry* (USS-GFAAS) technique for determination of Ti in soils, plants and other solid materials. Ti is problematic as it forms stable carbides in the graphite tube, but in the method described this is prevented by applying trifluoromethane in the purge gas during or just before atomisation. At a relatively low gas flow rate (40 ml min^{-1}) accurate Ti measurement was achieved in a variety of sample types and over a wide range of Ti concentrations.

3.3.2 Atomic emission spectrometry. Several *novel applications of AES* have been reported in the past year. Chen[138] used a poly(tetrafluoroethylene) (PTFE) slurry as a chemical modifier in the determination of various trace elements in a number of environmental samples, including plant materials, by ETV-ICP-AES. The author described the optimisation parameters for the technique and achieved good precision and low detection limits, *e.g.*, 1.7 ng ml^{-1} for Cu. Zaskas *et al.*[309] used atomic emission spectrometry with spectral excitation in a two-jet arc plasmatron for simultaneous and direct determination of a suite of elements. Graphite powder treated with NaCl is used as a spectroscopic buffer and mixed with powdered samples of soils, sediments, plants and other solid materials.

Sample dissolution is thus not required and the authors report low detection limits and generally acceptable RSD values.

3.3.3 Atomic fluorescence spectrometry. Developments in AFS continue, although comments in previous ASU updates relating to the usefulness of the technique still appear to be valid. The elements determined by AFS in the last year have included As, Cd, Hg, Pb and Sb. Liang *et al.*[139] coupled *non-dispersive atomic fluorescence spectrometry* with vapour generation to determine As, Cd, Hg and Pb in soils and other environmental samples, such as sea-water and airborne particulates. Interferences during the vapour generation process were minimised by attention to pre-treatment and detection limits of 0.08, 0.03, 0.05 and 0.01 ng ml^{-1} were achieved for As, Cd, Hg and Pb, respectively. Respective RSD values (at 10 ng ml^{-1}) were 0.9%, 1.6%, 1.3% and 2.0%.

Hydride generation atomic fluorescence spectrometry (HG-AFS) was used on more than one occasion for the detection of trace elements in soil and plant samples. Chen *et al.*[140] developed HG-AFS for the determination of Sb in samples of peat and various plant materials. Samples were digested with HNO_3, H_2O_2 and HBF_4 in a closed, pressurised microwave system and Sb^V in the digests was pre-reduced using L-cysteine. The detection limit for Sb in peat was decreased significantly to 2 ng g^{-1} by the new procedure compared with previous work on the same instrument. As and Hg were determined in Chinese medicinal herbs by another procedural development for HG-AFS analysis which involved microwave digestion in closed Teflon vessels.[141] Detection limits of 0.1 ng l^{-1} and 0.03 ng l^{-1}, respectively, were reported for As and Hg, and the results were in good agreement with those obtained by ICP-MS on the same samples.

3.3.4 Mass spectrometry

3.3.4.1 Inductively coupled plasma-mass spectrometry. ICP-MS continues to be used extensively. As usual, a popular application of the technique in the past year has been in isotope studies, and some of these are considered separately at the end of this section. Chipley *et al.*[142] developed an online continuous leach procedure using *high resolution ICP-MS* to overcome some of the well-known limitations of sequential extraction procedures, particularly dissolution of non-target phases and incomplete dissolution and reprecipitation within target phases. A series of solvents (deionised water and HNO_3 at three different strengths) are sequentially passed through a column containing the soil sample: release patterns of trace and major elements in the solvents are then matched so that target elements can be assigned to specific minerals.

Laser ablation ICP-MS was used by Seltzer[143] to detect depleted uranium (DU) in soils. Pressed sample pellets were subjected to laser ablation and $^{235}U/^{238}U$ ratios measured to distinguish between DU and naturally occurring U. Measured ratios were in good agreement with those measured by gamma spectrometry and the author notes the significant reduction in sample preparation. However, problems were caused by the heterogeneity of the sample and sporadic introduction of analyte into the plasma. LA-ICP-MS was used to detect Pu in soil and sediment samples.[144] Matrix effects were compensated for by the isotope dilution technique and an extremely low detection limit of 3×10^{-13} g g^{-1} was achieved with the use of a modified laser ablation system coupled to a sector-field ICP-MS. However, sample heterogeneity was again identified as a limitation, for example if 'hot' particles are present. LA-ICP-MS was used to detect Ni and U on plant leaf surfaces near a radiological settling pond in South Carolina, USA.[145] Residual U was detected within surface irregularities after the leaves had been washed.

Several studies have used ICP-MS for the detection of Pt and other *platinum group elements* (PGEs) in environmental samples.[15,16,146,147] These elements are of increasing interest to environmental scientists because of their use in autocatalysts and consequently their increased levels in the environment. Djngova *et al.*[146] investigated the problem of interferences from various elements on the determination of PGEs in environmental samples by ICP-MS. Corrections are possible for most sample types but direct determination of Pt in sediments may be difficult if high levels of Hf are present. The determination of Pd appears to be more problematic although correction in plant materials is possible. Detection limits of 0.015–0.03 ng g^{-1} were reported for all PGEs. Fritsche and Meisel[16] found elevated levels of PGEs in roadside soils by ICP-MS with online coupling of a chromatographic column to minimise matrix interference. A similar study of Australian roadside soils and dusts[17] detected elevated PGE levels by ICP-MS after microwave digestion and cation exchange.

Casartelli and Miekely[148] determined Ce, La, Nd and Th in soil water extracts in a mineralised area of Brazil using SEC coupled on-line to ICP-MS to investigate associations of these elements with dissolved organic carbon. They showed that the elements were mainly associated with high molecular weight (>2 kDa) organic compounds characteristic of humic and fulvic acids. Rare earth elements (REEs) were determined by ICP-MS in a study[149] to investigate soil loss and sediment movement. REE oxides in powder form were added to soils on a 10% slope which was then subjected to eight simulated falls of rain (60 mm h^{-1}). The REE concentrations of soil and run-off samples were subsequently used to estimate erosion rates and these estimates were found to be comparable to erosion estimates derived from laser scanning.

In recent years ICP-MS has become increasingly used for *isotope studies* and an excellent review by Becker[150] on the mass spectrometry of long-lived radionuclides illustrates this, noting that ICP-MS is increasingly replacing TIMS, which has been the dominant technique for many decades. The review reports progress on other MS techniques of importance in this field, including secondary ionisation MS, resonance ionisation MS, glow discharge MS and accelerator MS. Studies of note in the past year include an investigation of Pu isotopes in environmental samples[31,33,151–153] and the development of an ICP-MS method for the simultaneous detection of ^{239}Pu, ^{240}Pu and ^{237}Np in soils, sediments and biological samples.[151] In this last example, sector field ICP-MS was coupled to an automated sequential injection separation system for the detection of isotopes following purification with an actinide-specific chromatographic resin (TEVA-Spec). The advantages of the technique include $>90\%$ recovery, good accuracy and repeatability and low detection limits of 0.4–2.0 fg ml^{-1}. A similar procedure was developed by Zheng *et al.*[152] for the determination of ^{239}Pu and ^{240}Pu in marine sediments using quadrupole ICP-MS and an anion-exchange chromatography system for purification. Again, low detection limits and acceptable accuracy were achieved and, interestingly, by applying the method to sediments from Sagami Bay, Japan, the authors detected a 'close-in' Pu input in addition to the global fallout.

Lead isotopes have again been a focus of study by ICP-MS in the past year.[25,28,29,154] Krachler *et al.*[154] have developed an analytical protocol for determining Pb isotopes in peat by ICP-MS. Individual mass discrimination correction was applied to $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios, resulting in increased accuracy and precise determinations of the Pb isotopes. The value of accurate data for Pb isotopes in peat samples was demonstrated in a study by Le Roux *et al.*,[29] which utilised multiple ion collector ICP-MS and sector field ICP-MS and TIMS to measure Pb isotope ratios in peat cores from northern England. The results indicated that Pb contamination in this part of Britain dates from approximately 900 BC, significantly pre-dating the Roman occupation. Another interesting application was evident in the study of $^{206}Pb/^{201}Pb$ ratios in Beech bark pockets and tree rings, also in northern England, by

Bellis *et al.*[28] The results from this study indicated that use of indigenous Pb had decreased during the last century compared with an increase in imported sources.

A final isotope study worthy of mention is that by Izmer *et al.*,[155] which optimised the use of ICP-MS to determine *^{129}I/^{127}I ratios in soils*. Traditionally, during ICP-MS measurement, Xe impurities (^{129}Xe$^+$) in the argon plasma gas cause difficulties in the determination of ^{129}I, but the authors developed a technique to overcome this and other difficulties related to ICP-MS determination of these isotopes. The use of O and He as reaction gases in the hexapole collision cell of the ICP-MS system reduced the background intensity of ^{129}Xe$^+$ and the detection limit for ^{129}I$^+$ was improved by approximately 2 orders of magnitude compared with that from sector field ICP-MS.

3.3.4.2 Other mass spectrometric techniques. Following on from comments in the previous section, thermal ionisation mass spectrometry is clearly still utilised for the determination of isotope ratios as evidenced by two notable studies. Holmstrand *et al.*[156] improved the analytical sensitivity of stable Cl isotopes of organochlorines by the development of a procedure that coupled sealed tube combustion with TIMS. The accuracy of the method was confirmed by good agreement with stable isotope ratio mass spectrometry (SIR-MS) data for determination of chlorine isotopes in a sample of DDT. However, the excellent precision of their technique allows significantly smaller sample sizes in comparison with SIRMS analysis. TIMS was also used in a study of the isotopic composition of Pb in Arctic soils and mosses that indicated European and Russian urban centres as major sources.[27] Groenewold *et al.*[157] improved the detection of Cs$^+$ in soil by secondary ionisation mass spectrometry (SIMS) by the use of ultraviolet laser irradiation. The enhancement was dependent on the clay minerals present, with montmorillonite exhibiting marked enhancement compared with illite and kaolinite. This may have been due to thermal redistribution by irradiation of Cs$^+$ ions which had been adsorbed to the inter-layer sites characteristic of montmorillonite and which would not have been detectable at these sites by SIMS. Croft *et al.*[158] studied the potential of continuous-flow isotope-ratio mass spectrometry (CF-IRMS) in forensic studies of soil samples based on analysis of C and N isotopes. Results indicated that the combination of C and N isotope ratios determined by CF-IRMS may be a valuable tool in relating forensic soil samples, *e.g.*, on shoes, to source soils. Finally, Kamalakkannan[159] used gas chromatography mass spectrometry (GC-MS) with a solid phase extraction step to determine polycyclic aromatic hydrocarbons (PAHs) in sediments from a dry detention pond servicing the London Orbital M25 motorway. Most of the PAHs listed by the US Environmental Protection Agency were determined in the sediments with detection limits of 0.17–0.41 mg kg^{-1}. The author expressed concern about PAH concentrations in samples taken from beyond the dry detention pond and which could impact on the aquatic environment and/or the health of local farm animals.

3.3.5 X-ray fluorescence spectrometry. A notable trend in the development of XRF spectrometry in recent years has been the increased use of *portable spectrometers*. These are of considerable value to environmental scientists as long as their relatively low accuracy and precision are taken into account. Vanhoof *et al.*[160] evaluated the use of portable and laboratory energy dispersive XRF spectrometers for the analysis of contaminated soils and stated the advantages of portable and bench-top systems in terms of their portability—the latter by mobile van—for semi-quantitative analysis in the field. They noted also the value of homogenising the sample to be analysed to increase its 'representativeness'. The well-known limitations of the portable systems are their significantly higher detection limits by a factor of 10–20 and the loss of accuracy and precision. Hou *et al.*[73] reviewed the recent advances in portable XRF spectrometry and listed 80 references. A large number of environmental applications are described and the authors again emphasised that the benefits of portability must be balanced against relatively low accuracy and poor detection limits. Bachofer[161] described the use of a portable XRF spectrometer in a simple case study and highlighted the well-known advantages and disadvantages of its use—a particular recommendation is that samples are homogenised before analysis.

XRF spectrometry has been used extensively in the laboratory to analyse *soils and other environmental samples*. Schultz *et al.*[162] highlighted the potential limitations of the technique using benchtop machines if care is not exercised. They described the detection by XRF of an unexpected increase in the Cr content of wood which had been treated with chromated copper arsenate after it had been placed in contact with soil. It appears that Fe and Mn had migrated into the wood from the soil and that these elements interfered with the Cr measurement, giving erroneous results. Chuparina and Gunicheva[163] investigated possible matrix effects in the determination of a range of elements in powdered plant samples. They found that the main effects were absorption and scattering of both incident and fluorescence X-rays by the sample and additional fluorescence of the analyte caused by the fluorescence of heavier elements within the sample. Despite such uncertainties, the technique is clearly useful if used with care and has many benefits, including its non-destructive nature, which is important for certain sample types. Indeed, the technique was used successfully in the past year to determine a wide range of elements in various environmental samples, such as soils[164–166] peat cores,[6] road dusts,[167] house dusts,[165] plants[108] and foodstuffs.[168] In one of these studies,[166] energy-dispersive polarised XRF spectrometry, in conjunction with borate fusion, was evaluated for the simultaneous determination of common contaminant elements (As, Cd, Cr, Pb) and major elements in soils. The author concludes that the technique is suitable for the rapid and simultaneous determination of contaminant elements at low parts per million levels and major elements at percent levels.

4 Analysis of geological materials

4.1 Reference materials

Bulk reference materials for geoanalysis were first developed over 50 years ago. Nowadays there are more than 300 such materials, many of which were issued prior to the publication in 1989 of ISO guide 35, which outlines best practice for RM certification. Even fewer RMs have been issued with uncertainties developed in line with recent guides on measurement uncertainty and traceability of measurement. Against this background, the International Association of Geoanalysts (IAG) has developed a *protocol for the certification of geological and environmental reference materials*.[169] It outlines the basic principles and procedures by which IAG certifications will be made, balancing the requirements of the ISO guides with best practice in the field of geoanalysis. It applies equally to RMs for bulk and microprobe analysis. Other producers of geochemical RM are urged to use and contribute to the further development of this protocol.

The annual *bibliographic review* of literature concerned with geological and environmental RMs for 2002[170] confirmed the need for new RMs in the development of magnetic sector ICP-MS, laser ablation and in the analysis of environmental samples such as waters, soils and sediments. It would appear that as much effort goes into the characterisation of existing CRMs as new ones, by providing "recommended" values for elements that do not have certified values. Although this has the merit of extending the use of existing CRMs, it must be noted that these recommended values do not have the metrological status of certified values.

Few *geological RMs* have certified values for halogens, especially Br and I, so Michel and Villemant's[171] results for Br, Cl, F, I and S in seventeen RMs are a valuable addition. These were obtained by a combination of ICP-MS and ion chromatography after extraction by pyrohydrolysis, and included values for three new RMs: BHVO-2, BCR-2 and AGV-2. With the improvement in analytical techniques over recent decades, some certified values for old RMs may be called into question. The accepted values for basalt RM BHVO-1 were first published in 1976 but subsequent analyses of this RM have suggested that values for Pb, Rb, Th, Y and Zr may differ from the original consensus values by as much as 20%. Data from a variety of techniques, including ICP-MS, ICP-AES, LA-ICP-MS, SSMS and ID-TIMS, have been collated and new consensus values for these elements proposed by Chazey *et al.*[172]

Data for several batches of *new reference materials* has been reported. Seven soil RMs, GSS 10–16, representing some of the main agricultural soil types in China, have recently been certified for ten major and fifty-nine trace elements by the Institute of Geophysical and Geochemical Exploration (IGGE).[173] These RMs were designed to match the composition of samples collected for geochemical mapping across the plains of eastern China. The IGGE also prepared seven ores and concentrates of copper, lead and zinc with a wide range of compositions.[174] These samples were collected from several well-known mining areas in China and their certified values include major ore-forming elements, minor and associated trace elements and major gangue elements. The Geological Survey of Japan has reported data from a collaborative study on the chemical composition of two new geochemical RMs, copper ore JCu-1 and zinc ore JZn-1.[175] In a research project involving the preparation of three cobalt-rich seamount crust RMs, sixteen laboratories worldwide participated in the collaborative analysis programme that resulted in these materials being certified for forty-six elements.[176] The National Metrology Institute of Japan has certified two contrasting types of sediment RM for fourteen trace elements.[177] One material was a marine sediment from a bay influenced by industrial activity, whereas the other was a lake sediment.

Several new RMs with reliable values for *isotopic ratios* have been developed to meet specialised applications. A Palaeozoic zircon standard, TEMPORA 1, has been shown to have a constant Pb/U ratio from the sub-micron to the intergranular scale, and has been precisely and accurately dated by independent techniques. It is sufficiently abundant for use as a reference standard in microbeam geochronology.[178] Meisel *et al.*[179] looked at the suitability of UB-N, a well characterised RM typical of the earth's upper mantle, as a suitable RM for the study of Re–Os systematics. Although sample inhomogeneity was recognised, it was possible to give a well-defined average Os concentration of 3.85 ± 0.13 ng g^{-1}. Rhenium was very homogeneously distributed and the results highly reproducible; a value of 0.2095 ± 0.0040 ng g^{-1} Re was assigned. Their best estimate for the whole rock ^{187}Os/^{188}Os ratio was 0.1278 ± 0.0002. Measurements by multicollector ICP-MS were used to demonstrate heterogeneity in SRM980, the international isotopic standard for Mg supplied by NIST in the form of metal chips.[180] As an alternative, the authors prepared and characterised two large batches of pure Mg solutions. One of these, DSM3, had a Mg isotopic composition very similar to that of carbonaceous chondrites and its use as the primary isotopic RM to report Mg-isotope variations was advocated. Quadrupole ICP-MS was used to determine lead isotope ratios in eighteen commercially available CRMs[30] with the objective of validating a data set that could be used for quality assurance purposes in environmental analysis. Precisions of 0.19% and 0.14% RSD for ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratios, respectively, were achieved for triplicate analyses.

4.2 Sample treatment

4.2.1 Solid sample introduction

4.2.1.1 Laser ablation. The potential advantages of LA-ICP-MS to determine trace elements in *bulk geological samples prepared as lithium borate glasses* have long been recognised. Although the benefits include a simple and robust sample digestion procedure, its routine use has been hampered by the relatively poor precision (±10–15%) and detection limits reported in previous studies. Eggins[181] sought to improve these figures of merit by employing a laser rastering strategy that produced stable signal intensities without inter-element fractionation. Because he also had access to XRF to analyse his samples, he was able to use ^{43}Ca as the internal standard, rather than lithium. By judicious choice of isotopes and optimisation of the instrumental parameters for very low oxide species in a dry plasma, no corrections for interfering isobaric or molecular species were deemed necessary. The lack of suitable RMs for calibration was identified as the most significant problem, together with the need to control reagent impurities and sample contamination during preparation. Data from LA-ICP-MS and XRF analysis were integrated to provide a complete major and trace element characterisation on a single sample preparation.

It could be argued that digestion followed by analysis of solutions by ICP-MS is still superior to LA-ICP-MS for most bulk analysis, with limits of detection typically 2–3 orders of magnitude better. The real advantage of LA-ICP-MS lies in its microprobe capabilities. Sanborn and Telmer[182] investigated the acquisition of continuous *concentration profiles across heterogeneous materials* such as fish otoliths and zoned minerals as a way of increasing spatial resolution, and thus reduce the time and cost of analysis compared with spot analysis. One of the issues associated with line scans is measuring the spatial resolution that can be attained. Experiments were performed on a multi-layered sandwich consisting of three NIST glasses in order to quantify this parameter. To produce adequate counting statistics only Ca, Pb, Rb and Sr were determined. A Sr concentration profile from a fish otolith was generated and the resolutions from the glass sandwich applied, giving a minimum spatial resolution of 50 μm. Although variations in concentrations at smaller scales could be detected they could not be quantified. Wyndham *et al.*[183] have produced a high resolution record of Ba, Mn and REE in coastal corals from the Great Barrier Reef of Australia by LA-ICP-MS using an ArF excimer laser at 193 nm. The analysis was conducted in two consecutive traverses of the sample. The first one determined B, Ba, Ca, Mg, Mn, Sr and U, and was sampled with the laser beam masked to produce a spot 50 μm long and 500 μm wide. The second traverse determined a number of REE using a 100 × 500 μm laser spot to give the higher sensitivity required for this investigation and smooth the amount of material ablated from the heterogeneous coral surface. Calcium was used as an internal standard; an in-house pressed coral powder standard and NIST 614 silicate glass were used as calibration standards.

Laser sampling strategy is an area of continuing experimentation. Poitrasson *et al.*[184] compared the performance of fs and ns UV ablations in overcoming thermally induced chemical fractionation. Despite a less stable energy output, the fs laser produced Pb/U, Pb/Th and Pb isotope ratios that were more precise, repeatable and accurate than those with the ns laser. Measurements made on NIST glasses, monazites and zircon showed that the fs LA-ICP-MS calibration was less dependent on matrix matching and was therefore more versatile. The merits of ablating at a fixed position or rastering across the sample were assessed by Gonzalez *et al.*[185] using 213 nm LA-ICP-MS. Scanning at 50 μm s^{-1} produced a flat, steady signal compared with a signal that decayed with time with the single spot strategy. However, they found that single spot sampling provided better accuracy and precision when the first 15 s of sampling time was excluded from the data analysis. In addition, their single spot strategy showed less matrix dependence when ablating the four NIST 61X series of standard glasses.

The debate over the most suitable wavelength for LA-ICP-MS has been tempered by a recent *comparison of 266, 213 and 193 nm wavelengths* under essentially identical laser ablation conditions while ablating silicate glasses.[186] Particle size distributions were measured and were found to increase in the order $193 < 213 < 266$ nm. None of the particles produced at 193 nm was greater than 150 nm in diameter, resulting in more efficient conversion of particles into ions within the ICP, more stable transient signals and reduced time dependent elemental fractionation. The behaviour of 213 nm ablations, although intermediate between 193 and 266 nm, was biased towards 193 nm for more opaque samples and towards 266 nm for the more transparent. Thus wavelengths shorter than 213 nm were recommended for laser ablation of silicates.

Barefoot[4] has reviewed the literature on the use of LA-ICP-MS in the *determination of PGEs and Au* in geological materials published between 1998 and 2002. Spectral interferences resulting from refractory oxides, doubly charged and polyatomic ions such as $ArCu^+$ and $ArZn^+$ are discussed, together with the preparation of calibration standards. Although it includes several references to the ablation of nickel sulfide fire assay buttons, only more recently has this approach been applied to lead fire assay buttons.[187] Quantitative recovery is obtained only for Pd, Pt and Rh by this method of preconcentration, but it has the advantage of removing many of the elements that could otherwise form interfering polyatomic ions. Matrix-matched standards were prepared by spiking conical lead ingots with an aqueous standard solution and re-melting the ingots to obtain homogeneous solid standards with known PGE concentrations. Ammonia was used as the reaction gas in a dynamic reaction cell to overcome the overlap of ^{103}Rh and $^{206}Pb^{2+}$ without interfering with the determination of Pd and Pt by ICP-MS. Limits of detection achievable using this approach were estimated to be <100 ng g^{-1} which, although not suitable for environmental monitoring, were fit for purpose when analysing platiniferous ores from South Africa. LA-ICP-MS was shown to be a useful tool for rapid, semi-quantitative determination of Os and Re in molybdenite prior to subsequent precise analysis by isotope dilution ICP-MS.[188] Although direct laser ablation of mineral separates was possible, pressed pellets prepared from powdered molybdenite were preferred as these provided an enhanced sensitivity by approximately a factor of five and reduced the possibility of sample inhomogeneity.

Recent advances in the quantitative multielement analysis of zoned crystals, *fluid and melt inclusions by LA-ICP-MS*, have been authoritively described by the group at ETH Zürich.[189] With 165 references, this paper should be compulsory reading for anyone working in LA-ICP-MS. The first part contains a substantial review of processes and instrumentation, including the principles of LA-ICP-MS, sample cells and aerosol transport, representative sampling and minimising elemental fractionation, and a discussion of ICP mass spectrometers and the problem of interferences. The second part addresses the complexities of calibration, the use of internal and external standards, verification of matrix-insensitive calibration for homogeneous solids and depth profiling without fractionation. Against this background, the third part discusses the practical approach to the analysis of inclusions in minerals, accurate quantification of signals and estimation of associated uncertainties for a range of typical applications. The concluding section on future developments compares the capabilities of LA-ICP-MS with those of alternative techniques such as SIMS, PIXE and the combination of LA with optical emission spectrometry. A complementary applications paper from the same group[190] described the analytical approach and data evaluation of silicate and sulfide melt inclusions in an andesitic complex.

Advances in the determination of *isotope ratios by LA-MC-ICP-MS* continue to attract much interest, particularly at conferences. The protocol described by Horstwood *et al.*[191] yielded reliable U–Pb geochronological data for accessory minerals with the minimum of preparation and analytical time. Key factors in their methodology were the control and correction of mass bias and inter-element fractionation, corrections for common-Pb and isobaric interference from ^{204}Hg, and error propagation. Reproducibilities of *ca.* 3% for $^{206}Pb/^{238}U$ and $<1\%$ (2σ) for $^{207}Pb/^{206}Pb$ were achieved, with the resulting age accurate to within 1%. Other recent applications include the *in situ* determination of boron isotopes in natural and synthetic glasses[192] and Pb isotope fingerprinting of Roman coins.[193]

The current capabilities of *quadrupole ICP-MS for isotopic measurements* have been demonstrated in several recent studies. Jeffries *et al.*[194] investigated the analytical potential of a 213 nm laser coupled to this technique for U–Pb geochronology and found that the use of helium carrier gas significantly improved the reproducibility and precision of elemental U/Pb ratios. They obtained data with a precision of $<1.5\%$ (2σ) for $^{206}Pb/^{238}U$ and $<2.5\%$ for $^{207}Pb/^{206}Pb$ at a sampling resolution of about 25×35 μm, which did not differ greatly from ID-TIMS dating of comparable amounts of zircon sample. In a similar study, Xia and co-workers[195] reported reduced elemental fractionation using a 213 nm Nd-YAG laser for depth profiling of zircons. Crowe *et al.*[196] used a 266 nm laser in their measurements of Pb isotope ratios in silicate and sulfide minerals with low Pb contents of about 2 ppm. They employed an external calibration scheme by bracketing unknown samples with CRMs, maximised the count rate by setting the laser focus above the sample surface and used an $Ar–N_2$ plasma, which increased the sensitivity and reduced the mass bias. They obtained a precision of 0.2% relative standard error for $^{206}Pb/^{207}Pb$ in NIST 614 glass and concluded that LA-ICP-MS was a cost effective alternative to TIMS, SHRIMP or MC-ICP-MS for making precise Pb isotope ratio measurements at low concentrations for some applications, particularly in tracer studies of ore deposits and a range of environmental problems.

Hu and colleagues[197] constructed a laser fluorination microprobe for the determination of *sulfur isotopes* with improved spatial resolution. The system used two lasers: a KrF excimer laser at $\lambda = 248$ nm for *in situ* spot analysis and a CO_2 laser at $\lambda = 1060$ nm for the analysis of powdered samples including RMs. The $\delta^{34}S$ and $\delta^{33}S$ compositions of the RMs analysed agreed with the recommended values given by the Sulfur Isotope Working Group of the IAEA. The *in situ* fluorination of sulfides with the KrF excimer laser was validated by comparison of measurements of laser craters and powders excavated from drill holes in close proximity to the craters.

For further examples of *developments in LA* for sample introduction, the Update on atomic mass spectrometry should be consulted.[198]

4.2.1.2 Slurry sampling.

Hydride generation, combined with *in situ* trapping of the analyte in a graphite tube, is a well established technique for the determination of trace elements by ETAAS. Published methods employing *hydride generation combined with slurry sampling* as a mode of analyte introduction into atomisation cells has been extensively reviewed by Matusiewicz.[199] Less common is the coupling of HG to an electrothermal vaporiser, followed by measurement by ICP-MS. Vieira *et al.*[200] evaluated the potential of this technique for determining As, Hg, Se and Sn in sediment slurries. Although concentrations obtained for Hg, Se and Sn in sediment CRMs were in agreement with the certified values, recoveries for As were systematically low even though they were in statistical agreement with the certified values. This was in accord with the findings of Ribeiro *et al.*[201] who determined As, Hg, Sb, Se and Sn in geological materials by reducing the analytes to their lower oxidation states during slurry preparation, before reacting them with sodium tetraborate in an on-line HG-ICP-MS system.

Various protocols for the *analysis of slurries of soils and sediments by ETAAS* have been proposed, depending on the element(s) sought. Felipe-Sotelo *et al.*[202] used 0.5% nitric acid to prepare slurries of soils and sediments for the determination of Co. They found that no additional chemical modifier was required for ETAAS and obtained a detection limit of 0.04 µg g^{-1}. For the determination of Cd in lake sediments, Baralkiewicz and Gramowska[134] suspended their samples in a solution containing 5% nitric acid and 0.1% Triton X-100. No ashing stage was used and platform atomisation was carried out at 2200 °C. A 0.5% w/v solution of ammonium dihydrogen phosphate was found to be a suitable chemical modifier, together with a tungsten–rhodium permanent modifier. They reported a detection limit of 0.56 ng ml^{-1} and a characteristic mass of 9.6 ± 0.7 pg Cd, with precisions in the range 5.2–7.6%. Lopez-Garcia and co-workers[98] determined Sn and Ti in soils and sediments by ETAAS by suspending the samples in HF and using a fast heating programme. Palladium and 7% w/v ammonium dihydrogen phosphate were used as matrix modifiers for Ti and Sn, respectively. The same group[135] used similar methods for the quantification of Ag and Au following slurry sampling. Detection limits of 0.02 and 0.01 mg kg^{-1} in the solid for Ag and Au, respectively, were achieved. Although good agreement with certified values for CRMs was reported for all these methodologies, relatively small amounts of sample were taken in most cases. For these protocols to be valid it is important that the samples are ground to a similar particle size to that of the CRMs.

A more novel approach was the *on-line monitoring of iron ore slurries* using laser-induced breakdown spectroscopy.[203] An examination of the characteristics of these slurries showed that the mean particle size and concentration of solids in the slurry influenced the measurement of silica, whereas the magnetite content gave rise to matrix effects. It was felt that it should be possible to control these variables within a few percent or implement a correction to make this a practicable method of quality control.

4.2.2 Sample dissolution. Now that it is possible to determine the *platinum group elements (PGE)* in rock samples at ppb concentrations and lower, it is important to assess all sources of contamination during their preparation prior to analysis. Although blanks taken through the sample dissolution process provide information on contamination from reagents and the laboratory environment, they do not provide any control on potential contamination from their physical preparation. Evans and co-workers[204] tested a range of equipment by processing high purity quartz in a tungsten carbide press, a manganese steel jaw crusher, a tungsten carbide mill, a ceramic mill and in manganese and chrome steel mills, to assess the likely contribution of Au and PGE to the samples at each stage. Agate was not used in this study because it was felt that there was an unacceptable risk of fracture or breakage of the relatively brittle agate when grinding hard materials such as the quartz. Guided by the results of their study, they adopted a procedure of crushing whole rocks in a manganese steel jaw crusher and milling in an α-alumina ceramic ring mill. The crucial part of the processing proved to be the milling, for which ceramic (or agate) mills are essential for the best detection limits.

The environmental impacts of mining and related industries are often studied using partial extractions to define different mineralogical phases. Thus a *sequential selective extraction procedure* was used in conjunction with mineralogical techniques to identify the controls on As mobility in a stream catchment affected by serious As contamination as a consequence of past mining activities.[205] In a study of Al mobility in rocks, soils and sediments affected by mining activity, results from the BCR three-step sequential extraction procedure were compared with a combination of single extractions with water, potassium chloride, ammonium chloride and barium chloride.[103] Both the single extractions and the first step of the BCR procedure, which uses acetic acid as the extractant, gave an estimate of the reactive Al content, the main species of concern. An alkaline extraction method has been developed for the determination of sulfate in mine tailings containing secondary sulfate minerals formed by the oxidation of primary sulfides.[206] The oxidized tailings were extracted with 0.3 M sodium hydroxide at a liquid : solid ratio of 30 at room temperature for 16 h. Ion chromatography was used to determine sulfate as ICP-AES only provided estimates of total S. However, novel methods of extraction followed by the direct measurement of S by ICP-AES have led to recommendations for a revised suite of tests for sulfur compounds in structural backfills, including appropriate methods of sampling and storage.[207]

Anyone conversant with the use of a *HF mixed acid attack* to effect the complete dissolution of geological samples will be aware of the potential for a Ca–Al–Mg fluoride precipitate to form. This leads to coprecipitation of elements such as Hf, Nb, Ta and Zr, known as the high field strength elements (HFSE), which are stabilised in solution as soluble fluoro-complexes in the presence of fluoride ions. Valuable research by Tanaka and co-workers[208] examined the co-precipitation mechanism in a synthetic Ca–Al–Mg–HF solution system using two different methods: one involving temperatures less than 70 °C in an ultrasonic bath, and the other using a Teflon bomb at 205 °C. Their results indicated that full recovery of the HFSE was not achieved where fluorite (CaF_2) forms in the precipitate. To suppress fluorite precipitation, they added a solution containing aluminium to the sample before decomposition to change the matrix solution to a composition in which no fluorite forms. Using the Al-addition method, the HFSE content of calcium-rich materials was determined by ICP-MS, employing an isotope dilution method for Hf and Zr and a calibration curve method for Nb and Ta. Extensive purification of the Al-solution was necessary to facilitate the determination of Ta at low concentrations.

4.2.3 Separation and preconcentration. The need to separate and preconcentrate the *rare earth elements (REE)* prior to their determination by ICP-AES is well established. If ICP-MS detection is employed, preconcentration is still often required to quantify trace or ultratrace concentrations of REE. Because there is a wealth of alternative approaches in the published literature, the recent review by Rao and Kala[209] provides a useful compendium. It covers both on-line and off-line preconcentration procedures developed for the lanthanides since 1980, and includes liquid–liquid extraction, ion-exchange, co-precipitation and solid phase or solid–liquid extraction. They also discuss future trends. Other methodologies published recently for use with ICP-AES utilise columns packed with nanometre-sized titanium dioxide[210] and cation exchange procedures specifically for refractory minerals.[211] Minowa and Ebihara[212] developed a procedure for the separation of the REE from scandium by extraction chromatography; this is a necessary prerequisite for the ultra-trace determination of the REE in geological samples by radiochemical neutron activation.

The quest for suitable methods for the *separation and preconcentration of Au and the PGE* continues unabated. Pu *et al.*[213] used a microcolumn packed with 2-mercaptothiazole immobilized silica gel to selectively adsorb Au and Pd prior to elution with thiourea and on-line measurement by FAAS. This group also published a closely allied method for the same elements based on mercaptopyrimidine chemically modified silica gel.[214] Tokalioglu *et al.*[215] developed a procedure based on the adsorption of a Pd–dimethylglyoxime complex on silica gel followed by elution with 1 mol l^{-1} HCl in acetone for the determination of Pd by FAAS. Medved and co-workers[90] employed the chelating agent Spherol Thiol 1000 for the extraction of Au from pulverised rock samples, after roasting them and performing a series of acid leaches. The Spherol Thiol 1000 containing the sorbed Au was filtered, washed, ignited at 550 °C and the residue dissolved prior to measurement by ETAAS. For a 10 g sample, the detection limit was 0.5 ng g^{-1}.

Although ICP-MS is much more sensitive than FAAS, significant isobaric and polyatomic interferences make *separation of the PGE from matrix elements* highly desirable for this technique as well. Most of the developments reported are variations of well-known approaches. Thus, Qi and co-workers[216] proposed a method for the determination of Ir, Pd, Pt and Ru in geological samples by ID-ICP-MS using sodium peroxide fusion and tellurium co-precipitation. Monoisotopic Au and Rh were quantified by external calibration using Lu as the internal standard. Nickel fire assay preconcentration together with ID-ICP-MS was employed in the determination of PGE abundances in standard rock JP-1 issued by the Geological Survey of Japan.[217] Djingova *et al.*[146] investigated potential matrix inferences on the PGEs during measurements by ICP-MS for a range of environmental samples, including sediments and ores, and developed a procedure for isolating Pd involving diethyldithiocarbamate.

Relatively simple chemical separations specifically designed for the *isotopic analysis of geological materials* by sector field ICP-MS are still evolving. Bizzarro *et al.*[218] modified an existing procedure previously developed for Hf isotopes only, to render it suitable for measuring Lu/Hf ratios as well. Samples were fused with lithium metaborate and dissolved in dilute acid. REE and HFSE were separated by co-precipitation with iron hydroxide, which was then dissolved in 2 mol l^{-1} HCl and loaded onto a cation exchange column to separate the heavy REE (Lu and Yb) from the middle and light REE and the HFSE (Hf). Further separation on a miniaturised column containing TEVA resin yielded a Hf fraction free of REE, Ti and Zr, as well as removing all the lithium and boron derived from the fusion flux. Total procedural blanks were <100 pg and <2 pg for Hf and Lu, respectively, even for digested samples as large as 0.5 g. This separation scheme could be adapted for the isotopic analysis of the Sm–Nd system or the other HFSE. Rouxel and co-workers[78] adapted a method previously used for Se isotopes to the measurement of Sb by on-line HG-MC-ICP-MS. Nygren *et al.*[219] demonstrated that a separation based on the TEVA resin followed by elution with 0.1% hydroxyethylidene diphosphonic acid was suitable for the determination of Pu in soils and sediments by sector field ICP-MS. Lithium borate fusion was preferred over an acid leach to obtain complete dissolution of the samples prior to separation.

4.2.4 Speciation studies. Two reviews of the *determination of arsenic species*[117,220] describe recent progress in the extraction and identification of arsenic species in a variety of environmental samples, including sediments and soils. Coupling HPLC to ICP-MS was the approach adopted in studies of arsenic contamination arising from the mining of gold[114] and tin.[113] In the latter study, arsenic species were determined in sediments following extraction with 1 M phosphoric acid in an open focused microwave system, using 45 W power and a 20 min heating period for 0.5 g of sediment. The major species found in all the sediment samples was As^{V}, with smaller quantities of As^{III}.

As noted in last year's Environmental Update in this series,[308] the development of methods to determine *butyltin compounds in marine sediments* continues to attract much interest. Both GC and HPLC have been successfully coupled to ICP-MS for this purpose. More recently, species-specific isotope dilution (SS-ID) has been applied to the determination of butyltins to obtain more accurate and precise results. Wahlen and Wolff-Briche[221] compared the use of GC- and HPLC-ICP-MS for the measurement of tributyltin (TBT) in sediments by SS-ID after accelerated solvent extraction. They concluded that, although both techniques provided good accuracy, the GC approach was more precise and provided superior detection limits by about an order of magnitude. These observations were very much in accord with those of Yang *et al.*,[222] who reported method detection limits of 0.006, 0.001 and 0.002 μg g^{-1} for MBT, DBT and TBT, respectively, by GC-ICP-MS, based on a 0.5 g sample, compared with detection limits of 0.08, 0.05 and 0.03 μg g^{-1} obtained using HPLC-ICP-MS. Yang and co-workers[223] also reported the first use of GC separation with sector field ICP-MS for the accurate and precise determination of organotin in sediments by ID. Not surprisingly, they obtained better detection limits than those achieved by GC-quadrupole ICP-MS using SS-ID because of the three-fold enhancement in signal-to-background ratio for the sector field instrument. A new marine sediment reference material, NMIJ CRM 7301-a, certified for MBT, DBT and TBT, has recently been prepared by the National Metrological Institute of Japan.[224] Two different types of species-specific ID mass spectrometry were used to characterise this CRM, which contains lower levels of organotins than other CRMs currently available. Comparable precision and accuracy were demonstrated by Centineo and co-workers[225] for the simultaneous determination of butyltin species by ID-GC-MS and ID-GC-ICP-MS. They concluded that reliable quantitative organotin speciation could be achieved using the more widespread and inexpensive GC-MS instrumentation.

Kumar *et al.*[226] developed a rapid method for *synthesizing a mixed standard of phenyltin species* enriched with ^{124}Sn based on the phenylation of tin iodide and ^{124}Sn enriched metal. Using GC-ICP-MS with SS-ID calibration, the isotope-enriched standard was employed to evaluate different extraction procedures currently in use for the determination of phenyltin species in sediments.

Other studies have focused on the *extraction of butyltin compounds* from sediments. The performance of single-drop microextraction was assessed against conventional solid phase microextraction and liquid–liquid extraction.[227] Another strategy reported was complexation with sodium diethyldithiocarbarmate and retention on a C_{60} sorbent.[228] Neutral chelates of butytin compounds were eluted with ethyl acetate containing $NaBPr_4$ as a derivatising reagent, prior to measurement by GC-MS. A new polymeric absorbent for the preconcentration of organotin compounds prior to determination by ETAAS was described by Puri *et al.*,[48] while Bowles and co-workers[229] studied the interferences affecting the determination of butyltin species following sodium tetraethylborate derivatisation and purge–trap preconcentration.

4.3 Instrumental analysis

4.3.1 Atomic absorption spectrometry. The use of *permanent modifiers* in ETAAS can confer several benefits over conventional modifiers. Acar[133] evaluated the difference in performance of Ru, W, Zr, Zr–Ru and Zr–W as permanent modifiers in the determination of Cd and Pb in sediments, soils and coal fly ash. These modifiers were thermally deposited on platforms inserted in pyrolytic graphite tubes. He confirmed that improved analytical characteristics are obtained with Zr–Ru and Zr–W compared with a single permanent or Pd + $Mg(NO_3)_2$ conventional modifier. In a similar study, Lima *et al.*[132] employed single noble metal permanent modifiers as well as mixed tungsten plus metal, *i.e.*, W–Rh, W–Ru and W–Ir, for the determination of Sb in sediment, coal and ash. For these matrices, the combined tungsten-metal modifiers provided better recoveries, improved long-term stability and longer tube life.

An alternative approach with complex matrices is to *separate the analyte* from the matrix prior to measurement. Mosbaek and co-workers[102] developed an automated on-line solvent extraction system for the quantification of Cd, Cu and Pb in acid digests of soils and sediments. The system was designed to deliver solvent extracted samples to the autosampler of a graphite furnace using IBMK as the organic phase; improved analytical performance as well as savings in time were reported. Monteiro *et al.*[230] reassessed the methodology for extracting gold in IBMK from *aqua regia* digests of ore material before measurement by ETAAS. They studied the stability of Au in the IBMK extract and concluded that it was stable in closed polypropylene containers for up to 22 h. Using a forked pyrolytic graphite platform, they reported a detection limit of 4 $\mu g\ kg^{-1}$ in ore samples. Ampan *et al.*[231] exploited the use of Sephadex G-25 beads impregnated with dithizone to scavenge Pb from solutions of geological materials. The beads, which were part of a lab-on-valve system, were propelled directly into a graphite tube where they were pyrolyzed and the Pb ions atomised.

Various methods for improving the productivity of *flame atomic absorption spectrometry* have been reported. An automated flow injection system with microwave-assisted sample digestion was used to dissolve silicate rock in an acid medium for the determination of Fe by FAAS.[232] A slurry of rock sample in a $HF–HClO_4–HNO_3$ acid mixture was pumped into a PTFE reactor coil and irradiated for 210 s at 90 W power, before being pumped into the 500 µl sampling loop. Under these conditions, a detection limit of 0.46% Fe_2O_3 in the solid was achieved with a throughput of 10 samples per hour. Flores and co-workers[233] proposed a procedure involving direct analysis of solids by FAAS for the determination of Mn in coals. Ground coal samples were carried as a dry aerosol to a slotted quartz vaporisation cell placed between the flame burner and spectrometer. The figures of merit were considered fit for purpose with a precision of better than 6% RSD. Integration of the short transient signals allowed the analysis of up to 80 test samples per hour. Projahn *et al.*[234] demonstrated the application of fast sequential FAAS to the analysis of coals to perform multielement analysis. Analytes were determined in sequence at their respective wavelengths during one scan of the monochromator and the reference-element technique was used to correct for long-term drift and changes in transport properties.

4.3.2 Atomic fluorescence spectrometry. There are few developments to report in the *application of atomic fluorescence spectrometry to geochemical analysis*. As Liang *et al.*[235] emphasized, sample dissolution is the key to the quantitative determination of Hg in rocks. Traditional acid digestion methods usually involve vigorous reactions in which the Hg may be lost, yet Hg is often present at concentrations near to or lower than the blanks of these methods. They adopted a combustion/trap technique previously designed for the analysis of Hg in crude oil and related products, using tantalum boats to introduce the samples directly into the combustion system. The Hg vapour generated was collected on a gold trap prior to measurement by AFS; a detection limit of around 0.1 $ng\ g^{-1}$ was achieved. Li and co-workers[236] found that L-cysteine enhanced the analytical signal in the determination of Ge in geological samples by HG-AFS. In addition, it reduced or eliminated interferences from elements such as Cu, Cr, Ni, Pb, Se and Te. They obtained a detection limit equivalent to 0.01 $\mu g\ g^{-1}$, based on a sample mass of 0.5 g.

4.3.3 Atomic emission spectrometry. Many of the developments in ICP-AES have been concerned with *extending the elemental coverage and range of matrices*. These have tended to focus on the most appropriate method for sample dissolution, depending on the overall purpose of the analyses, plus separation and preconcentration of the analytes of interest (see Sections 4.2.2 and 4.2.3). A flow injection liquid–liquid extraction system was coupled to ICP-AES for the determination of REE in geological samples.[237] The robustness of the plasma to the introduction of tributyl phosphate organic phase was diagnosed using the intensity ratio of the Mg II 279.55 nm and Mg I 285.21 nm lines. For the chemical characterisation of columbite–tantalite minerals, Premadas and co-workers[238] used three different dissolution procedures to prepare appropriate solutions in an oxalic acid medium for the determination of 32 geochemically important elements by ICP-AES and FAAS. Assessments were made of the most suitable spectral lines and associated interferences. Srivastava *et al.*[239] proposed a method for determining Hf, Nb, Sn, Ta, Ti, W and Zr in columbite–tantalite and tin slag samples based on sample decomposition with a mixture of NaF and KHF_2, followed by co-precipitation in the presence of $(NH_4)_2HPO_4$. The precipitate was filtered, washed with dilute HCl and dissolved in a mixture of oxalic acid and hydrogen peroxide. Because Ta interferes with the determination of W in tantalite samples with low W contents, W was separated from the precipitate by washing with dilute ammonia and the W recovered from the washings.

There is still much interest in the simultaneous determination of *hydride forming elements* by atomic emission techniques. Bolea *et al.*[240] devised an electrochemical hydride generator based on a concentric arrangement with a porous cathode for the measurement of As, Ge, Sb, Se and Sn by HG-ICP-AES. Operating in a continuous flow mode, the generation efficiencies were estimated to be greater than 80%, with precisions of better than 5% and detection limits in the range 0.1–3.6 $ng\ ml^{-1}$. Matusiewicz and Kopras[241] combined HG with *in situ* trapping in a graphite furnace prior to the measurement of As, Bi, Ge, Hg, Sb and Se by MIP-AES. Silicate samples, such as sediments, were first digested in a mixture of HF, HNO_3 and H_2O_2 using a microwave-assisted technique. Once generated, either continuously or in batch mode, the hydrides of As, Bi, Ge, Sb and Se were preconcentrated on palladium (or gold for Hg) coated on the interior walls of a pretreated graphite furnace tube at 300 °C for 60 s. Finally, the analytes were vaporised for 3 s at a temperature of 2100 °C and swept into the MIP-AES system, in a flow of argon or helium gas, for detection. Although the transport losses in the system were substantial, amounting to approximately 55% of the analyte vaporised from the graphite tube, the authors claimed that this does not limit the applicability of the technique to quantitative analysis.

Methods for the *separation and preconcentration of Au and the PGE* are covered in Section 4.2.3. Wu and colleagues[242] devised a method for determining trace concentrations of Au, Pd and Pt in geological samples by ETV-ICP-AES using a chelating resin called YPA(4) as both the solid phase extractant and chemical modifier. Once the analytes had been loaded onto the resin, it was made into a slurry and introduced into the graphite furnace without any pre-treatment. In the presence of YPA(4), Au and Pd could be vaporised quantitatively at 1900 °C, 700 °C lower than the temperature required without the modifier, giving a three-fold improvement in detection limits. However, YPA(4) had little effect on the determination of Pt by ETV-ICP-AES. Detection limits of 75, 60 and 217 pg were obtained for Au, Pd and Pt, respectively.

A simplified generalised standard additions method, based on *slurry nebulisation ICP-AES*, was investigated as an alternative approach for the analysis of cement, gypsum and basic slags.[243] The preparation of slurried samples dispersed in glycerol and HCl avoided the use of more hazardous chemicals, incomplete dissolution and loss of some volatile elements. Both the sample mass and the amount of standard solution added were varied and a linear relationship between sample mass, the amount of standard solution added and signal intensity assumed.

4.3.4 Inductively coupled plasma mass spectrometry. *Recent advances in ICP-MS*, including fundamental studies and analytical methodology, were reviewed in the latest Atomic Spectrometry Update on atomic mass spectrometry.[198] It confirmed that ICP-MS continues to play a major role in the development of new applications for the geochemical community, with significant activity in laser ablation and the determination of isotope ratios by MC-ICP-MS.

4.3.4.1 Quadrupole-based instrumentation. Although much of the cutting edge research tends to be dominated by the advances afforded by the magnetic sector instrumentation, quadrupole ICP-MS provides large amounts of trace element geochemical data on a routine basis. Pearce *et al.*[244] have reviewed the contribution made by both solution and laser ablation ICP-MS to the characterisation of tephra deposits for stratigraphic correlation. Recently published applications have included the analysis of iron meteorites[245] and the reconstruction of paleodiets from the elemental composition of archaeological bones.[246] In the former study, two aliquots of each meteorite sample were prepared, one in nitric acid and the other in *aqua regia*, to accommodate the different chemistries of the elements sought. Isobaric interferences from iron and nickel oxides and hydroxides significantly impaired the data quality for As and Ge at low concentrations.

Improved methods for *determining gold and the PGE* continue to be sought in order to meet the varied and demanding requirements of earth scientists, exploration programmes and environmental studies. Because of their low abundances and the potential for interferences from matrix elements, strategies to separate and preconcentrate the PGE are required; some of these are covered in Section 4.2.3. Meisel *et al.*[36] developed a procedure for the determination of all the PGE and Re by ID-ICP-MS that satisfied the need for complete digestion, spike–sample equilibration, low procedural blanks and simple separation of analytes from the matrix elements. Samples were spiked with ^{99}Ru, ^{108}Pd, ^{185}Re, ^{190}Os, ^{191}Ir and ^{198}Pt and digested in a high pressure asher with concentrated HNO_3 and HCl. After the Os concentration had been determined, the solutions were dried and redissolved before the PGE were separated on-line on a cation-exchange column (Dowex AG50Wx8) coupled to a quadrupole ICP-MS instrument. By this technique, it was possible to monitor isotopes of the analytes and those elements known to cause isobaric or polyatomic interferences. The method was designed to be simple and inexpensive, although the off-line concentration calculations were acknowledged to be complex. It was shown to be effective for ultramafic rocks and road dust CRMs and was applied to the analysis of soils along Austrian motorways.[16] As a separate exercise, this group of workers also calculated an uncertainty budget for this ID measurement protocol,[247] which was surprisingly small considering the low concentrations, transient signals and the sophisticated correction model involved. Qi *et al.*[216] also used ID-ICP-MS to determine Ir, Pd, Pt and Ru in geological materials following a sodium peroxide fusion and tellurium coprecipitation. Monoisotopic Au and Rh were quantified by external calibration using Lu as the internal standard. Using model solutions, real samples and comparisons with ICP-AES data, Djingova and co-workers[146] evaluated potential interferences from matrix elements in geological and environmental samples on isotopes of Ir, Pd, Pt, Rh and Ru when measured by ICP-MS. Barefoot[4] has reviewed the ability of magnetic sector ICP-MS instruments to resolve some of the spectral interferences encountered in complex matrices if separation techniques are not employed.

Another approach to minimising interferences in ICP-MS that has been attracting attention is the use of *collision and reaction cells*. A summary of their application to geological and other sample types between 2000 and 2003 was included in an informative review of the development and utilisation of collision and reaction cells in atomic mass spectrometry.[248] In the measurement of radioisotopes by ICP-MS, Epov and co-workers[249] demonstrated an improvement in detection limits by a factor of 33, 22, 500, 50 and 100 for ^{135}Cs, ^{137}Cs, ^{210}Pb, ^{226}Ra and ^{90}Sr, respectively, after optimisation of the collision cell parameters. However, Cs and Sr required different cell conditions, depending on whether Ba and Zr, respectively, were present or absent.

Although magnetic sector instruments dominate the *measurement of isotope ratios* by ICP-MS, there are applications where the precision afforded by quadrupole instruments is fit for purpose. Zheng *et al.*[152] developed a method for determining ^{239}Pu and ^{240}Pu in marine sediments following separation and purification on a simple anion-exchange chromatography system. Sufficient uranium was removed during this process to obtain accurate ^{239}Pu data free from tailing from the ^{238}U peak and overlap with $^{238}UH^+$. The low detection limit of 8 fg ml^{-1} obtained in solution using the shield torch technique enabled the authors to deduce that the Pu in the sediments studied contained additional Pu derived from a local source, in addition to the average global fallout. Willbold *et al.*[250] validated a multielement ID-ICP-MS method for the simultaneous measurement of up to 12 trace elements in geological samples. In addition, they used the ID-determined trace elements as internal standards to improve indirectly the determination of 14 other, mainly monoisotopic, trace elements. The overall analytical uncertainty of the method was 1–2% for the ID spiked elements and around 2–3% for the others.

The *coupling of separation technology to ICP-MS* continues to attract much interest: relevant applications are discussed in Section 4.2.4.

4.3.4.2 Magnetic sector instrumentation. The new generation of multiple collector ICP mass spectrometers continue to dominate developments in the measurement of isotope ratios and their application to geochemical studies. Their popularity stems from their relatively rapid sample throughput and the ability of ICP sources to ionise most elements in the periodic table. However, the acquisition of precise and accurate isotopic data still requires a good understanding of *instrumental fractionation processes*. Albarède *et al.*[251] discussed the advantages and limitations of alternative strategies to correct for both mass-dependent and mass-independent biases. They proposed a strategy involving the repetitive calibration of cup efficiencies and rigorous assessment of mass bias, combined with sample–standard bracketing. Wombacher and Rehkamper[252] concluded that the generalised power law was a valuable tool for correcting for instrumental mass bias, based on their study of Nd isotope ratio data. Thirlwall and Anczkiewicz[253] discussed the causes of secular drift in multidynamic measurements of Hf, Nd and Pb isotope ratios by MC-ICP-MS.

Various improvements in the determination of *uranium isotope ratios* in geological materials by MC-ICP-MS have been reported. Deschamps *et al.*[254] measured $^{234}U/^{238}U$ using

Faraday collectors in the static mode only, as this technique removed the difficulty of proper calibration of the Daly/Faraday gain ratio. Because the instrument in question had poor abundance sensitivity, the main problem was tail correction. For this they employed a modified version of a method originally developed by Thirlwall *et al.*[255] The correction of the tail contribution under each peak was based on the tail shape measurements on monisotopic ion beams, rather than the usual half-mass zeros baseline estimation. A ^{236}U–^{233}U double spike was used to correct for mass bias. Sample introduction was *via* a microconcentric, desolvating nebuliser, which allowed precise ^{234}U/^{238}U ratios to be determined on a minimum of 200 ng U, with a ^{234}U signal of approximately 4–5 mV being monitored for 50 measurement cycles of 5 s each. The total reproducibility, including chemical separation and analysis, was assessed using a coral and a carbonate rock, and was found to be about 1.3% (2σ). Seth and co-workers[256] presented an advanced protocol for the measurement of Th and U isotope data on very small samples of speleothem, marine calcite and coral for carbonate geochronology. No separation of Th and U was necessary because of the excellent recoveries obtained. Th and U isotopic determinations were carried out in two separate runs, with either mass ^{230}Th or ^{234}U on the Daly detector, depending on the ratio sought. Data obtained by MC-ICP-MS and TIMS compared well, but less material was required to obtain comparable precision for Th by MC-ICP-MS. Zoriy *et al.*[257] used D_2O (heavy water) as a solvent in the dissolution and dilution of geological samples to reduce the isobaric interference $^{235}UH^+$ in the measurement of ^{236}U.

Weiss and co-workers[258] presented analytical protocols for the *measurement of Pb isotopes* in a range of environmental materials including ore-bearing granites. After acid dissolution, the Pb was separated using EiChrom® Sr-resin, using only HCl and one column pass. Thallium was used to correct for mass discrimination effects and the accuracy achieved was less than 80 ppm for all ratios. This involved an optimisation procedure for ^{205}Tl/^{203}Tl using least square fits relative to Pb values for NIST SRM 981. After studying the most appropriate way to correct for time dependent mass bias, Reuer *et al.*[259] also employed external normalisation to the same CRM following the thallium correction in their determination of Pb in marine carbonates.

The reference values for *Hf and Lu isotopic ratios* of the zircon standard 91500 have been redefined by Gollaerts *et al.*,[260] following an extensive characterisation of relevant standard solutions. High pressure and temperature dissolution of the zircon followed by two-step ion exchange chromatography resulted in better than 94% recovery of the analytes. Lapen and co-workers[261] presented a new approach to the correction of instrumental mass fractionation of spiked and unspiked samples. Correction of ^{176}Hf/^{177}Hf ratios for unspiked samples followed a traditional approach of internal normalisation using an exponential law followed by normalisation to a standard of known composition. For spiked samples, standards were used to determine a linear instrumental mass bias coefficient defined by the slope of a line between the measured and true values. This approximation resulted in identical precision and accuracy for measurements of spiked and unspiked samples, with a 2σ external reproducibility of ±0.005%. The measured ^{176}Lu/^{175}Lu ratios were corrected by doping the sample with Er and using ^{167}Er/^{166}Er to externally normalise the ^{176}Lu/^{175}Lu using an exponential law. Equilibration of the spike with the sample was confirmed through the analysis of varying physical mixtures of garnet and hornblende; a precision of ±0.2% (2σ) for ^{176}Lu/^{177}Hf was obtained. Barfod *et al.*[262] reported a new method for the separation of Lu and Hf from apatite. Spikes of ^{180}Hf and ^{176}Lu were allowed to equilibrate with the sample digest prior to separation of Hf and Lu in separate fractions using a single column containing EiChrom® Ln-Spec as the stationary phase, followed by a second anion-exchange column to separate Lu from iron and uranium. The ^{176}Lu/^{177}Hf ratios obtained were used to demonstrate the potential of the Lu–Hf system for directly dating sedimentary formations.

Cold plasma MC-ICP-MS was used to eliminate argon based polyatomic ions in the measurement of Fe isotopes in meteorites.[263] The rf generator was operated at 600 W, about half the normal operating power. A conventional concentric Meinhard-style nebuliser was employed because argide reduction could not be achieved using a commercial desolvating sample introduction system under cold plasma conditions. Instrumental mass bias corrections were performed by sample-standard bracketing and copper was used to monitor changes in mass bias. Repeated measurements of a basalt RM gave an external reproducibility of ±0.06% for ^{56}Fe and ±0.25% for ^{58}Fe (1σ). The cold plasma technique was used by Fietzke *et al.*[264] in the determination of ^{44}Ca/^{40}Ca ratios in aragonite samples. By reducing the plasma power to about 400 W, the isobaric interference from ^{40}Ar was significantly reduced, enabling simultaneous and precise measurement of ^{44}Ca and ^{40}Ca beam intensities in different Faraday cups. By measuring the Ca isotopes near the low-mass edge of their peaks, any interference from the overlap of $^{24}Mg^{16}O^+$ and $^{23}Na^{16}OH^+$ with ^{40}Ca and $^{26}Mg^{16}OH_2{}^+$ with ^{44}Ca could be neglected. However, Arnold *et al.*[265] were dismissive of the cold plasma technique for the determination of Fe isotopes because there was little to no attenuation of hydroxides, so that $ArOH^+$ ions still persisted at mass 57. Cold plasma conditions also resulted in a reduced Fe ionisation efficiency. Instead they relied on high mass resolution MC-ICP-MS to resolve polyatomic interferences, especially $^{40}Ar^{14}N^+$, $^{40}Ar^{16}O^+$ and $^{40}Ar^{16}OH^+$. Copper was used as an internal standard to correct for variations in mass bias and the Fe was extracted and purified by a single step anion exchange chromatography procedure.

Different methods of correcting for mass discrimination effects associated with *Cu and Zn isotopic measurements* were assessed by Mason and co-workers.[266] They compared the sample–standard bracketing (SSB) and the empirical external normalisation (EEN) methods. The EEN correction appeared to be more robust and yielded ^{65}Cu/^{63}Cu and ^{66}Zn/^{64}Zn data of high precision. However, it was unable to account for a systematic drift in the ^{67}Zn and ^{68}Zn signals with time. Both SSB and EEN corrections gave long-term reproducibilities of less than ±0.07% (2σ) for ^{65}Cu/^{63}Cu and ^{66}Zn/^{64}Zn ratios, which was deemed to be sufficient to resolve mass-dependent isotopic variability in a range of materials. Archer and Vance[267] used the Cu–Zn system to demonstrate two improvements to mass discrimination corrections in MC-ICP-MS. By adding strontium to mixed Cu–Zn standard solutions, they generated extreme variations in mass bias, thus allowing the empirical mass bias relationship between analyte and spike to be much better constrained. They also showed that it was important to remove Fe and Ti from the matrix completely in order to ensure that the mass discrimination relationships between the Cu and Zn isotopes were applicable to the samples as well as the standards. Values of $\delta^{66}\text{Zn} = 0.20 \pm 0.09\%$ and $\delta^{65}\text{Cu} = 0.07 \pm 0.08\%$ were obtained for BCR-1 basalt RM at the 95% confidence level. Larson *et al.*[268] used MC-ICP-MS to obtain data on the natural variations in Cu isotope ratios in minerals from magmatic and hydrothermal ore deposits. Copper minerals prepared by direct dissolution with and without chromatographic purification yielded identical Cu isotope ratios within an analytical precision of $\sim$0.04% (1σ).

The first assessment of the *variation in the Sb isotopic composition* of geological samples was made by Rouxel and co-workers.[78] This was something of a challenge given that the mass fractionation of Sb isotopes in nature is not large and Sb is a trace element present below 100 ng g^{-1} in most geological samples. Following dissolution, matrix elements were removed by cation exchange, Sb^V was reduced to Sb^{III} with KI in ascorbic acid and then passed though a column containing thiol cotton impregnated with thioglycollic acid to remove other hydride forming elements, particularly isobaric Te. Isotopes were measured by continuous flow HG coupled to MC-ICP-MS. Instrumental mass fractionation was corrected using the SSB approach. The minimum Sb required was 10 ng for an estimated external precision of 0.4 ε units (1σ) for $^{123}Sb/^{121}Sb$.

Because Te has a very high first ionisation potential, MC-ICP-MS is much more suitable than TIMS for the determination of *Te isotope compositions*. Fehr *et al.*[269] developed a suitable method for analysing stony and iron meteorites, as well as sulfide mineral separates. Tellurium was first separated using a two-stage liquid chromatography procedure; for iron meteorites, solvent extraction was required to isolate Te from iron prior to the column separation. Approximately 100 ng of Te was required for a single high precision measurement.

Studies of *isotope systematics* for a wide range of elements are now routinely performed by MC-ICP-MS. Wombacher *et al.*[270] devised an improved procedure to determine Cd isotope ratios in geological materials and meteorites by MC-ICP-MS. A two-stage column chemistry procedure was used to separate Cd from potential interfering ions and mass bias correction was accomplished using external normalisation to silver. As little as 5–20 ng of Cd were sufficient for the acquisition of precise and accurate data. Schonbachler and co-workers[271] developed a new method of measuring Zr isotopic compositions at high precision, with the ultimate aim of producing internal meteorite isochrons. Selective dissolution was used in conjunction with conventional physical methods to obtain the required mineral separates, and the chemical separation protocol was optimised for Zr.

4.3.5 Other mass spectrometric techniques. Although MC-ICP-MS has become the technique of choice for many isotope determinations, there are still applications where it is advantageous to employ *thermal ionisation mass spectrometry*. One such application was the precise measurement of $^{228}Ra/^{226}Ra$ ratios required for geochemical interpretation of U–Th–Ra disequilibria. Using a new tandem column technique, Yokoyama and Nakamura[272] improved the chromatographic separation of Ra to achieve the high yield and purity necessary for more precise and accurate determinations of ^{226}Ra content and isotope ratios than previously recorded by conventional TIMS on a few fg of Ra. Kuritani and Nakamura[273] demonstrated the use of the double spike technique with TIMS for the very precise and accurate isotopic analysis of small amounts of Pb. The double spike method requires two runs for each unknown sample. In this study, the samples in each run were doped with different double spikes, ^{207}Pb–^{204}Pb and ^{205}Pb–^{204}Pb, which enabled correction of instrumental mass fractionation and reduction of the measurement uncertainty on ^{204}Pb. The use of ID-TIMS in zircon U–Th–Pb geochronology was reviewed by Parrish and Noble[274] and the ID-TIMS documentation for two new Palaeozoic zircon standards has been published.[275] Paquette *et al.*[276] combined textural analysis by EPMA with ID TIMS U–Pb dating of single monazite crystals to unravel the complex metamorphic history of single monazites.

In recent years *accelerator mass spectrometry* has expanded into many areas of science. In their review of AMS applications in the marine environment, Skipperud and Oughton[34] noted that traditional ^{14}C dating was no longer the dominant application of AMS measurements. Much of the research is now directed towards understanding global climate change, for which profiles of long-lived cosmogenic radionuclides in sediment and ice cores, including ^{99}Tc, ^{129}I, ^{236}U and other actinide isotopes, provide key information. Bard *et al.*[277] presented a new set of ^{14}C ages obtained by AMS on planktonic foraminifera from a deep sea core and demonstrated how to obtain reliable ^{14}C ages beyond 20 000 year BP. Depth profiles of ^{129}I and $^{129}I/^{127}I$ ratios in a sediment core determined by AMS provided information on the transfer of these isotopes from nuclear fuel reprocessing plants to marine sediments.[278]

The versatility of *secondary ion mass spectrometry* in providing spatial information on the distribution of elements on mineral surfaces has been exploited in a variety of geochemical applications. The influence of terrestrial weathering on the mobility of REE in meteorites found in Antarctica and hot deserts was evaluated from the analysis of individual minerals by SIMS;[279] REE abundances in two primitive carbonaceous chondrites have also been mapped using this technique.[280] Measurements of B in silicate minerals by SIMS were impeded by surface contamination.[281] Cleaning the samples with ultrapure water in an ultrasonic bath, and setting the imaged field of the ion probe smaller than the primary beam spot, reduced the B background to <2 ng g^{-1}. Herasil 102, a synthetic silica glass standard, was recommended for testing B contamination levels. Microscale variations of $\delta^{13}C$ and N content in natural diamonds,[282] *in situ* Ir concentrations in sedimentary layers around the KT boundary[283] and Au distribution in silicates[284] have all been studied using SIMS.

The characterisation of particles by ToF-SIMS has helped to refine *mineral processing* operations. Iron rich coatings detected on Au-rich particles were found to decrease recoveries in mini-scale floatation tests;[285] acid leaching removed these surface layers and dramatically improved the ore recovery. Similarly, surface analysis of sphalerite and pyrite particles in flotation and tailing samples revealed that iron hydroxide coatings were responsible for reducing the efficiency of the recovery processes from both the concentrate and the tailings.[286]

It would appear that the nanoSIMS, a secondary ion mass spectrometer characterised by very high transmission and spatial resolution, is starting to make a significant contribution to studies of *pre-solar grains and other rare minerals in meteorites*. Oxygen isotope distributions in oxide grains less than 1 μm in size from two carbonaceous chondrites have been determined by this technique.[287] Other applications of nanoSIMS include the measurement of ^{26}Al, ^{53}Mn, ^{60}Fe and Ba isotopes in meteoritic minerals, and ^{44}Ti and ^{49}V in pre-solar silicon carbide.[288,289] Complementary information on these types of materials can be provided by RIMS.[290,291] For a wider overview *of recent developments in atomic mass spectrometry*, the Update by Bacon *et al.*[198] should be consulted.

4.3.6 X-ray techniques. While *X-ray fluorescence spectrometry* continues to be widely used in geological applications, there are relatively few developments to report. There have been several studies of potential sources of error arising from the preparation of fused glass beads for XRF analysis.[292–294] Incomplete dissolution of chromite in lithium tetraborate flux was improved by increasing the fusion time and flux : sample ratio.[294] Loubster and colleagues[293] demonstrated that lithium borate fluxes volatilise at temperatures over 1050 °C, which could lead to inaccurate results. Hettipathirana *et al.*[292] prepared synthetic standards for Cl and S in Al_2O_3 matrices because of the poor reproducibility they obtained for these elements using a SiO_2 matrix when fusing with a mixture of lithium borate and metaborate. However, it was not possible to determine Cl and S accurately in samples containing high amounts of silica because of the variable retention of these elements during fusion. For the analysis of contaminated soils by EDXRF, Hettipathirana[166] again fused the samples and calibrated for trace elements with synthetic standards based on an Al_2O_3 matrix and a SiO_2 matrix for major elements. A more usual approach to rapid multielement analysis of geological materials by EDXRF, based on pressed powder pellets, was described by Zhan and Luo;[295] fundamental parameter and

Compton scattering methods were used for matrix correction. Thirty-four elements were quantified in 600 s with detection limits between 0.5 and 30 ppm. An EDXRF spectrometer has been specifically developed for the non-destructive determination of Au, Pd and Pt in South African ores.[296] About 100 g of pulverised sample in a 20 mm diameter tube were presented for analysis and the X-rays detected by an array of up to 12 high-purity germanium detectors. This instrument was capable of measuring Au concentrations down to less than 1 ppm.

Recent advances in *portable X-ray fluorescence spectrometry* have been reviewed by Hou *et al.*,[73] citing 80 references. Bachofer[161] recorded his experiences when using this type of equipment to quantify Pb in soil samples near to a major road. The ultimate application of portable X-ray instrumentation is in space research. A miniaturised XRF/XRD analyser that will be incorporated into a future Japanese lunar lander and rover mission was described by Shirai and co-workers.[297]

Particle induced X-ray emission permits the non-destructive *in situ* imaging of buried structures such as mineral, melt and fluid inclusions within geological materials. Several recent studies have employed this technique to provide an improved understanding of the formation of gold deposits.[298–300] The elemental composition of individual inclusions in hydrothermal quartz,[301] partitioning of Ba and Pb between silicate melts and aqueous fluids at high pressures and temperatures,[302] and the relationship between chemical composition and the colour of minerals[303] have all benefited from data provided by PIXE. For a comprehensive review of the *current status of X-ray techniques*, the reader is directed to the latest Atomic Spectrometry Update on this subject.[304]

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