Atomic spectrometry update. Environmental analysis

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This is the 27th annual review published in JAAS of the application of atomic spectrometry to the chemical analysis of environmental samples. This Update refers to papers published approximately between September 2010 and August 2011 and continues the series of Atomic Spectrometry Updates (ASUs) in Environmental Analysis[1] *that should be read in conjunction with other related ASU reviews in the series namely: clinical and biological materials, foods and beverages*[2]*; advances in atomic spectrometry and related techniques*[3]*; elemental speciation*[4]*; X-ray fluorescence spectrometry*[5]*and industrial analysis: metals, chemicals and advanced materials*[6]*. To celebrate the 25th anniversary of the Journal of Analytical Atomic Spectrometry, a 25-year retrospective of ASU reviews* has been published[7] *to highlight the development and evolution of atomic spectrometric techniques and their use in measurement applications.*

Specific to this review, in the field of air analysis there is ongoing interest in measuring atmospheric Hg species and evaluating procedures for the determination of the carbonaceous content of airborne particulate matter. In a measurement arena where RMs are relatively scarce, a number of useful interlaboratory comparison studies have been reported. In the field of water analysis, as in previous years, the main areas of activity are the development of preconcentration and extraction procedures and elemental speciation protocols for elements such as As, Cr and Hg. There is increasing interest in evaluating TXRF for trace analysis. In the field of soil and plant analysis, sample dissolution and extraction remain a major focus of interest – especially methods to assess bioavailability – and there is a hint that 'greener' *approaches, using less concentrated acid, are becoming important. Especially notable are the continued developments in LIBS, a shift towards more widespread use of techniques such as HPLC-ICP-MS and synchrotron-based XRF, and growth in studies where multiple techniques have been applied to the same sample for trace element mapping or speciation analysis. Less desirable are the publication of variants on well-established analytical methods with marginal novelty and several instances where substantially similar articles appeared almost simultaneously in more than one journal, thus generating 'two publications for the price of one'. It is evident that MC-ICP-MS and LA-MC-ICP-MS are now so widely available in geoanalytical laboratories that applications papers, that include little of novelty from an analytical perspective, dominate the literature. However, this trend should not mask the vital research required to underpin and improve the quality of the geochemical data on which any interpretation is based. Another observation is the high proportion of analytical and applications papers with Chinese authors, reflecting the rise of atomic spectrometry in China over the past number of years.*

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

1 Air analysis

This section highlights noteworthy areas of research and development in the analysis of aerosols, particulates and inorganic gases by atomic spectrometric and complementary analytical techniques published since the last Update[1]. Developments in air sampling and sample preparation are discussed first, followed by advances in analytical instrumentation and methodologies.

1.1 Sampling techniques

Monitoring workers' exposure to airborne particles through the use of *personal workplace air samplers* is an ongoing activity in many countries. Work is focused on developing new samplers and evaluating current designs and concepts because of reductions in exposure limit values, requirements to sample nanoparticles and re-evaluation of sampling conventions. French researchers[8] assessed the use of the CIP-10R sampler (Arelco, France) to collect sufficient sample mass so that concentrations of respirable crystalline silica in air could be measured. This sampler operated at a nominal flow rate of 10 L min^{-1}, a substantial improvement on historically used cyclonic samplers such as the Dorr Oliver design operating at 1.7 L min^{-1}. The higher flow rate was achievable using portable pumps because this sampler used foam of uniform porosity to trap airborne particles, thereby generating lower backpressures than the filters used in cyclonic samplers. There is increasing concern about the potential for worker exposure to engineered nanoparticles, i.e. particles with at least one dimension below 100 nm. To collect such particles, Thayer *et al.*[9] developed a personal thermal precipitator sampler, which used a thermophoretic force generated from an applied thermal gradient, orthogonal to the aerosol flow, to separate particles from a moving collection airstream. Collection efficiencies for test aerosols at a nominal 5 L min^{-1} were *ca.*100% over a particle size range of 15 – 240 nm. Increasing the flow rate by a factor of 4 to 20 L min^{-1} resulted in a halving of this collection efficiency. Using SEM and imaging software, it was shown that the particle deposition on the collection plate was generally homogeneous over a centre spot of 2 mm diameter. The authors suggested that this would allow a grid to be placed on the sampling plate for subsequent TEM analysis of the particles. Whilst the sampler showed promise, further work was required, most notably to test it under field conditions. Also a means of reconstructing, using correction factors, actual sampled aerosol concentrations from particle counts determined from electron microscopy analysis was needed. R'Mili *et al.*[10] used a thermal precipator sampler, based upon the collection of particles onto TEM grids, coupled with LIBS, to demonstrate the possibility of real time detection of carbon nanotubes in air. Sleeth and Vincent[11] proposed a modification to the ACGIH-EN-ISO inhalable aerosol convention, which was derived from historical laboratory wind tunnel studies conducted at windspeeds typically over the range 0.5 – 4 m s^{-1}. This modified algorithm made the convention more suitable for windspeeds below 0.2 m s^{-1} often encountered in many workplaces. In a tripartite endeavour, involving researchers from France, Germany and the UK[12], sampling methods for workplace pollutants such as HCl and HNO_3 mists and vapours, were evaluated and subsequently codified and published in an International Standard (ISO 21438-2:2009).

Sampling and measurement of trace levels of Hg species in ambient air remains a challenge. Researchers in the USA[13] tested the performance of KCl-coated denuders, used for sampling gaseous oxidised mercury (GOM) in the presence of co-sampled ozone. In laboratory studies they found that denuders loaded with Hg halides lost between 29 and 56% of these compounds when exposed to ozone in the concentration range 6 –100 ppb. Collection efficiencies decreased by 12 to 30% for denuders exposed to 50 ppb ozone when sampling mercuric chloride. The results suggested that the KCl-coated denuder system, widely used over the last ten years, might not be as robust as previously thought. The authors recommended further robustness testing, preferably under field conditions. They also recommended that field calibration methods be developed to allow *in situ* automated Hg measurement systems to be challenged with known GOM-spiked standards as a means of assessing such sampling artefacts. Whilst these measurement systems are widely used within Hg monitoring networks in the developed world, elsewhere manual sampling systems continue to be used because of the high capital investment required. True *et al.* [14] evaluated the use of hocalite™ sorbent tubes, widely used in workplace air monitoring exercises, to sample trace levels of total gaseous Hg in ambient air. In a paired field sampling exercise, lasting five months and involving weekly air samples, mean results obtained with such sorbent tubes were comparable (1.4 ± 0.4 ng m^{-3}) with those obtained using an *in situ* measurement approach (1.7 ± 1.9 ng m^{-3}). The authors concluded that this approach could be very cost effective, especially in developing nations, as it employed relatively inexpensive and widely available laboratory-based CVAAS instrumentation. There remains a lot to understand about atmospheric Hg and its biogeochemical cycle. Lai *et al.*[15] investigated several surrogate sampling surfaces designed to mimic the capture of airborne Hg species onto natural surfaces via dry deposition processes. These surrogates included both liquid and solid surfaces such as deionised water, acidified water, salt solutions, quartz fibre filters (QFFs), KCl–coated QFFs and gold-coated QFFs. The authors concluded that whilst surrogate surfaces could be used to measure dry deposition, extrapolating the results obtained to natural surfaces could be challenging!

Huang *et al*,[16] developed a diffusion denuder technique for the sampling of *molecular I species* in the atmosphere. Alpha-cyclodextrin, in conjunction with a ^{129}I spike applied prior to sampling, was an effective denuder coating for the efficient sampling of biogenic I_2. Following sampling, the coating was washed off and analysis carried out by GC-MS following derivatisation to a 4-iodo-N,N-dimethylaniline adduct. Parameters such as: the amount of coating and spike applied; denuder length; sampling flow rates and durations; effect of relative humidity and sample storage intervals were investigated. Laboratory procedures involving both desorption and derivatisation steps were evaluated and optimised. Under optimal conditions, collection efficiencies were over 98% and a LOD (3 σ) of 0.17 pptv was achievable for an air sample volume of 15 L (30 minutes at 500 mL min^{-1}). By replacing the ^{129}I spike with a ^{127}I spike and using multiple denuders, this sampling approach could also be used for the determination of ultratrace levels of radioactive I_2.

Evaluation of the *performance of ambient air sampling systems* continues to attract attention. Researchers in the USA [17] compared various commercially available air samplers designed to sample either the PM_{10}, $PM_{10-2.5}$ and $PM_{2.5}$ particle fractions. Samplers were co-located in the field on a mobile sampling platform. The study design consisted of 20, 45-hour sampling exercises carried out at a number of locations in the USA. This particular sampling period was used to ensure that sufficient mass was collected for gravimetric analysis. The intra–sampler precision was < 8.4 %. Brown and Keates[18] examined the spatial inhomogeneity of anions in ambient air particulate matter collected on air filters using a drift-corrected IC procedure. This is a useful publication as often, in air monitoring campaigns, air filter samples are subdivided to allow more than one chemical assay to be performed. Their study highlighted the need to use as much of the filter as possible for analysis. In practical terms this translated to the use of filter quarters and preferably filter halves. Sampling mixed–phase aerosols, as in the case of diesel fume, is a challenging process. Swanson and Kittelson[19] compared two approaches used to separate the solid and volatile components of an aerosol: the thermal denuder (TD) and the catalytic stripper . The catalytic stripper removed the semi-volatile species by passing the diesel fume over a heated oxidation catalyst, whereas the TD removed them by adsorption onto a charcoal bed following heating of the incoming airstreams. Comparative testing was carried out under laboratory conditions using either artificial test aerosols or real urban aerosol piped into the laboratory from a nearby busy road! With the TD approach, there were measurement artifacts which were attributed to formation of semi-volatile particles from nucleation process or condensation of vapours. No such artifacts were observed for the catalytic stripper system. The authors concluded that much more research was required in evaluating such systems in light of current and future regulatory methods that require measurements of solid particles.

Impactor samplers, where airborne particles are sampled by impaction upon a target, have been used for many years to separate airborne particles into discrete size ranges. However it is known that upon impaction particles can sometimes bounce and impact downwind on subsequent targets within the sampler. As a result a particle size distribution that is not representative of the sampled airstream can sometimes be profiled. Factors that influence this degree of bounce can include the relative humidity and whether the impaction target is coated or not with an oil or grease to minimise such bounce. Researchers in Taiwan [20] studied the influence of relative humidity on nanoparticle concentration and particle mass distribution measurements when using the micro-orifice uniform deposit impactor. Czech and Finnish researchers[21] comprehensively evaluated the sampling characteristics of the original 10-stage and 7-stage modified Berner type impactors which had lacked some published performance data. A Spanish research team[22] showed that it was possible to use a Berner–type impactor at low inlet pressures to assist in the study of aerosols emitted from high temperature processes such as biomass combustion.

1.2 Reference materials

New reference materials are available. In the field of elemental analysis, IRMM has released ERM-CZ120 – a PM_{10} type dust RM certified for As, Cd, Ni and Pb with informative values for a further 40 elements. This material was produced to underpin analytical measurement of air filter samples carried out using the standard method EN 14902 (microwave digestion procedure with an ETAAS/ICP-MS finish) in support of assessing compliance to European air quality directive limit values. This material complements two other similar CRMs, NIST SRM 1648a (Urban Particulate Matter) and NIES CRM 28 (Urban Aerosols), thus providing a useful range of materials with which to assess, in particular, the performance of the critical sample digestion step. Size-specific RMs, especially nanoparticle size materials, are increasingly required for the calibration of particle sizing instrumentation. Here, IRMM produced ERM FD100 (Colloidal Silica in Water) with a nominal 20 nm size. An overview of available RMs in this arena from various vendors can be found on a useful website hosted by BAM at www.nano-refmat.bam.de.

1.3 Sample preparation

The risk of *sample contamination* during air sampling, handling and preparation of filters and their subsequent analysis is a recurring theme. It is therefore instructive to hear about approaches to minimise such risks from trace analysts working in other measurement fields. Bowie *et al.* [23] presented an overview (54 references) of sampling and analytical methods for the determination of trace elements in marine particulate matter using SF-ICP-MS. They reported methods suitable for sampling, filtration, digestion and trace metal analysis of particles. Wagner and Mages[24] proposed the use of cold plasma ashing to prepare samples of particles collected onto polycarbonate filters for subsequent TXRF analysis. They suggested that this procedure was superior to conventional acid digestion with regard to ease of use and potential for contamination.

Sample preparation methods in the arena of nuclear safeguard measurements are highly topical. Spanish researchers[25] developed a microwave digestion method for the extraction of ^{127}I and ^{129}I from solid materials for measurement by ICP-MS and AMS, respectively. The proposed method was considered to be faster, less labour intensive and to consume less sample than previous procedures. It was validated through the measurement of ^{127}I by ICP-MS in a variety of CRMs encompassing biological, soil and sediment matrices. Average recovery against certified values was *ca*. 90% with some losses suggested as being volatile HI or I_2 species. Korean researchers[26] developed, what they claimed to be, an easy, fast and reliable measurement method for the quantitative determination of retained fission gases in an irradiated oxide fuel material. Initially a gas collection system was evaluated using Kr and Xe gas standard spikes resulting in optimal recoveries in the range 96–98%. An optimised fusion method involved fusing 0.1 g of irradiated oxide fuel with 1.0 g each of Ni and Sn in a graphite crucible in a helium atmosphere. To test the fusion step, spike recovery samples were prepared by wrapping 0.1 g of unirradiated oxide fuel in Al foil implanted with known quantities of Kr and Xe prior to the fusion step. Recoveries of these spikes were *ca*. 97%.

Cairns *et al.*[27] coupled a cation-exchange matrix separation system to ICP-MS to determine *PGEs* emitted from diesel-powered cars. Method LODs (3 σ) were 1.6 ng g^{-1} for Pd, 4.3 ng g^{-1} for Pt and 0.4 ng g^{-1} for Rh. The method was successfully validated using BCR CRM 723, a PGE-containing tunnel dust. Tailpipe emission factors for the PGEs ranged from 0.02 ng km^{-1} for Rh to 70.5 ng km^{-1} for Pt and it was found that particle emission dropped dramatically by up to 86 % for cars fitted with a diesel particulate filter. Mathur *et al.*[28] determined concentrations of PGEs in road dusts from the city of Hyderbad in India. A NiS-fire assay and a Te coprecipitation protocol were used to preconcentrate test samples prior to analysis by ICP-MS. Concentration ranges determined were 1.2 – 58 ng/g Pd; 1.5 – 43 ng/g Pt and 0.2 – 14.2 ng/g Rh. The authors concluded that whilst such concentrations are above crustal levels and are associated with road traffic sources, they are lower when compared to similar studies conducted in other worldwide cities, where presuamably there has been more widespread use of PGE car catalysts.

1.4 Instrumental analysis

1.4.1. Atomic absorption and atomic fluorescence spectrometry

Pandey *et al* [29] (109 references) critically evaluated measurement methodologies commonly employed for the analysis of *Hg species in ambient air*. Typically, AFS and, to a lesser extent, AAS techniques were employed as detectors. Gold-based trapping systems were used to preconcentrate gaseous Hg^0 from air samples and thermal desorption to liberate the analyte. In contrast, sampling and analysis of reactive gaseous mercury (RGM) species and particulate bound mercury (Hg_p) species could be hampered by reactivity of the former and extremely low concentrations, typically at low pg m^{-3} in air, of the latter. The authors suggested a number of future research directions: evaluation of instrument calibration protocols commonly used to reduce sources of bias; further development of methodologies for measurement of RGM and Hg_p; development of hyphenated GC-based systems for the speciation of organo-mercury and the development of fast response real-time sensors to measure transient Hg atmospheric concentrations. Researchers in the USA[30] compared manual Hg_p measurements with an automatic method at a number of marine/coastal sites. With the manual approach, aerosol samples were collected on open-faced filters. On return to a laboratory the Hg was desorbed in a BrCl/HCl leach solution and determined by CV-AFS. The automated approach, using the commercial Tekran system, involved sampling onto a quartz filter, a thermal desorption/reduction step and on-line analysis of the resultant Hg^0 by AFS. The manual filter Hg_p values were 21% higher than those obtained using the automated system and over 85% of the paired data was outside the ±25% region surrounding a nominal 1:1 regression line. Studies such as this supported the assertion by Pandey *et al.*[29] of a need to investigate further this very challenging field of ultratrace determination of Hg species in ambient air.

The use of *ETAAS for the determination of trace elemental species* in ambient air samples has largely been superseded by the use of ICP-MS. However, the recent development of a commercially available CS-AAS system may provide a renaissance in this measurement field. This technique was recently reviewed by Welz *et al.*[31] (93 references). A solid sampling introduction system is available for this CS-AAS system and, in the opinion of this reviewer, offers a potential means of directly measuring small quantities of airborne particles collected onto graphite impactor sampler targets for their elemental content.

1.4.2 Laser-induced breakdown spectroscopy

Gallou *et al* [32] evaluated the potential of *LIBS* for monitoring elemental species in emissions originating from exhaust stacks. They considered two approaches; using LIBS to determine the elemental composition of particles either *in situ* in an aerosol stream or collected on a filter for subsequent off-line analysis. A USN was used to produce $CuSO_4$ test aerosols. In this initial work, for similar sampling conditions, better LODs were achieved with the direct *in situ* approach (15 $\mu g\ m^{-3}$) compared to the off-line approach (60 $\mu g\ m^{-3}$). Russo and his research group[33] presented a useful overview of the current status of laser plasma spectrochemistry (46 references). Monkhouse[34] published a substantial review of on-line techniques, including LIBS and related techniques, for the determination of metal species, particularly alkali and heavy metals, in industrial processes (474 references).

1.4.3 Mass spectrometry

1.4.3.1 Inductively coupled plasma mass spectrometry. This technique remains at the forefront for the routine determination of trace levels of metals captured on air filter samples. Hence developments that have caught the eye of this reviewer tended to focus on method robustness testing or the development of more 'exotic' applications.

Brown *et al.*[35] suggested *method improvements in the use of ICP-MS,* as described in EN 14385, for the analysis of metals in emission test samples from stationary-sources such as incinerators. In particular they highlighted operational issues in using this standard method particularly if used potentially by less experienced analysts. The authors pointed out the inherent dangers of using internal standard elements to correct for instrumement drift, arising from test samples with a high TDS but which have an unknown elemental composition. To further alleviate effects of the sample matrix the authors presented the following pieces of common sense advice: matrix matching of samples and standards as far as possible; dilution of test samples as far as possible; randomised analysis and averaging of test sample digestion replicates to minimise effects of drift and the frequent reanalysis of a matrix matched QC solution run as a drift compensation sample. In some ways, this paper shed light on the difficulties in drafting and publishing standard methods where the target audience may have differing levels of analytical expertise! An improved method[36] for the determination of a wide range of trace elements in aerosol samples by quadrupole ICP-MS exploited the ion-molecule reactions in a DRC system using ammonia as the cell gas to minimise potential isobaric interferents.

The use of *hyphenated ICP-MS techniques* has been reported. A method[37] to determine Cr^{VI} in ambient air using IC-ICP-MS involved sampling onto $NaHCO_3$ precoated cellulose filters in an attempt to preserve the Cr speciation. Interconversion occurred, however, so filters prespiked (or spiked after sampling) with known quantities of species-specific Cr isotopes ($^{50}Cr^{III}$ and $^{53}Cr^{VI}$) were used to correct for such interconversions. Filters were subsequently extracted in HNO_3 in an ultrasonic bath for 40 minutes at 60 ºC. The method LOD was 0.08 ng m^{-3} (3 σ, based upon the repeat analysis of a 1 ng spiked filter and a nominal 24 m^3 air sample). The recovery of an enriched Cr^{VI} spike was *ca.* 60% throughout the entire sampling and measurement protocol. Levels of Cr^{VI} in air determined in a field study using this new method were *ca.* 0.4 ng m^{-3}. Further work was planned to evaluate the effects of environmental conditions (humidity and temperature) and other gaseous pollutants (NO_2, O_3 and SO_2) on Cr^{VI} recovery. Researchers in Taiwan[38], used LA-ICP-MS to investigate the elemental composition of size-segrated airborne particulate matter collected with an electric low-pressure impactor sampler. They prepared calibration standards by spiking filters with small quantities of standard solutions. Verification was achieved by reanalysis of test portions of samples spiked with metals of interest using a standard addition approach. The LODs (3 σ) ranged from 0.02 ng for Cd to 1.0 ng for Si. Repeat analysis of a calibrant filter gave a short-term instrumental precision of 3.5–17.8%. Results were compared with those from filter samples from a co-located sampler, which were subjected to a conventional acid digestion prior to ICP-MS analysis. The correlation coefficient (R^2) ranged from 0.68 for Zn in PM_{10} particles to 0.89 for Zn in $PM_{2.5}$ particles.

In the potential development of an *ICP-MS system for the real-time monitoring of airborne radioactive particles*[39], initial work focused on the optimisation of an Aridus™ desolvating sample introduction system used to deliver a calibrant source to the plasma and the determination of a relative sensitivity factor between ^{159}Tb (surrogate element of interest mimicking a radioactive element) and ^{174}Yb (calibrant element). A vibrating orifice aerosol generator was used to produce test ^{157}Tb particles from the liquid phase, which were then sampled, mixed with dried

^{174}Yb calibrant aerosol from the Aridus^{TM} system and analysed. Measurement precision was better than 17% but there was a discrepancy between the calculated Tb concentration, from the output of this aerosol generator, and the measured value determined by ICP-MS. The authors attributed such a difference to liquid sample losses within this vibrating orifice aerosol generator system.

A useful overview of the status of *ICP-MS for the determination of isotopic ratio*s for provenancing purposes was presented by researchers from the University of Ghent[40] (162 references). More specifically, Chinese researchers[41] reviewed (110 references) developments in the application of isotopic measurements to the study and fate of Hg species in the environment. French workers[42] investigated the Hg isotopic composition in urban topsoils and showed that it was possible to evaluate the anthropogenic contribution relative to background geochemical sources using relative isotope abundances. In an interesting application[43], the measurement of the foliar and soil uptake rates of Hg was successfully accomplished within a controlled atmospheric chamber using $Hg(0)_g$ enriched in the ^{198}Hg stable isotope.

1.4.3.2 Other mass spectrometry techniques. The status of nearly *real-time in–situ mass spectrometric techniques for measuring particles in the atmosphere* can be found in reviews by Lin *et al.*[44] (181 references) and Harris *et al.*[45] (219 references). A new Aircraft-based Laser ABlation Aerosol MAss spectrometer (ALABAMA)[46] was capable of measuring the chemical composition and size of aerosol particles in the 150–900 nm range. The instrument used a 532 nm laser to detect and size incoming particles, a pulsed 266 nm laser to ablate and ionise the particles and a bipolar, Z-shaped TOF mass spectrometer to detect both positive and negative ions. The 140 kg instrument fitted into a standard 19-inch rack making it one of the smallest and lightest in its class. A new aerosol chemical speciation monitor[47] could characterise and monitor the mass and chemical composition of non-refractory submicron particulate matter in near real time. It was based on the technology of Aerodyne aerosol mass spectrometers that are widely used for ambient air research programmes. This new instrument was tailored towards more routine regulatory air monitoring programmes and hence operated at a reduced sensitivity and provided a lower time resolution compared to the Aerodyne aerosol mass spectrometer. It also did not measure size distribution, helping to reduce the complexity of the system. Nevertheless the instrument LOD was *ca.* 0.2 $\mu g\ m^{-3}$ for a nominal 30 min sampling integration. It was deployed in three different field campaigns and in one campaign was operated continuously and unattended for eight weeks providing time integrated (30 minute resolution) chemical concentrations of particulate ammonium, chloride, nitrate, sulfate and organic species in air.

Mass spectrometry can be used for source apportionment studies. Heal *et al.*[48], in the first study of its kind in the UK, used AMS to determine ^{14}C abundance ratio in fractionated (total, organic and elemental) airborne carbonaceous particles as a means of distinguishing fossil and contemporary carbon sources. The study showed that ca. 50 % of the UK urban background $PM_{2.5}$ carbon is of contemporary origin and also noted the ubiquitous presence of biogenic soluble organic carbon, particularly for air masses passing over land. Cao *et al.*[49] used IRMS to determine the stable carbon isotopes (^{12}C, ^{13}C) in aerosols collected from 14 Chinese cities. The isotopic signatures indicated that coal combustion and vehicular emissions were the major sources of carbonaceous aerosols.

1.4.4 X-ray spectrometry

Characterisation of *airborne particulate matter* using X-ray techniques continues to be a fertile area for research. Van Grieken and Worobiec[50] summed up their work, conducted over the last decade or so, looking at the characterisation of indoor particulate pollutants in museums and other special heritage buildings, using a variety of X-ray based analytical techniques.

Hurst *et al.*[51] developed a procedure for the *XRF determination of metal-containing particles collected on filter*s, from welding processes, using a WDXRF system and employing UniQuant^{TM}, a fundamental parameter software package removing the need to prepare special calibrant filters. Average recoveries for Cr, Fe, Mn and Ni in 16 test welding fume filters samples from the UK Health and Safety Laboratory's WASP proficiency testing scheme were 97 –112% of the reference values obtained by ICP-AES. The RSDs were 3–10% for elemental filter loadings in the range 5 – 500 µg per filter. Results for real welding filter samples agreed favourably with those obtained with an external calibration approach using calibrant filters. In contrast, Turkish researchers[52] used real filter samples as calibrant filters. Filters were initially screened by EDXRF and raw elemental counts logged. The filters were then subjected to INAA or, in the case of Ni and Pb, AAS analysis. The calibration function was completed by entering the filter loading value for each element back into the XRF calibration software. As a check, further filters analysed with the now calibrated XRF instrument were reanalysed by INAA/AAS and paired data were found to agree to within 20%. An EDXRF procedure[53] for the analysis of size-segregated aerosol samples collected with impactors gave results comparable with those obtained by PIXE analysis.

The *interrogation of single particles* using X-ray based techniques allows elemental composition to be identified in order to understand their pollution sources and potential environmental fate. Two X-ray microbeam techniques[54], μ-PIXE and μ-SRXRF, gave very good agreement for measurement of Pu/U ratios in microscopic particles containing actinide elements. Instrumental resolution also allowed Pu/U distributions in particles down to a few μm to be studied. In two closely aligned papers, a Chinese research group[55-56] described the development of a μ–XRF system employing polycapillary X-ray optics for the quantitative analysis of single aerosol particles. There was a plateau at the focal point of the X-ray beam with a diameter of *ca.* 21 μm within which the X-ray beam intensity was homogeneous with a dispersion of <3%. This was deemed helpful for the interrogation of smaller particles and the quantification of elements within such particles. Geng *et al.*[57] characterised individual aerosols collected during an urban haze episode in Korea using a quantitative low-Z ED-EMPA technique and compared the results with those obtained on particles collected on non-haze days. It was noted that whereas on non-haze days the nitrate-containing sea salt and mineral dust particles in the < $PM_{2.5}$ significantly outnumbered the sulfate–containing particles, the reverse occurred on haze days. This finding suggested that different particle sources or formation mechanisms for fine particles exist during such haze episodes.

Solid-state speciation analysis of airborne particles using XAFS is a powerful tool and is increasingly being used to increase our knowledge of the origins, transformations and fate of particles in the atmosphere. Osan *et al.*[58] undertook the speciation of Cu and Zn in size-fractionated airborne particulate matter using SRXRF and XANES techniques. The SR techniques were sufficiently sensitive that species could be identified in particles collected in impactor samplers arising from airborne concentrations as low as 140 pg m^{-3}! The Cu and Zn in particles of <2 μm occurred typically as nitrate and sulfate. Tirez *et al.*[59] used XANES to evaluate the performance of the Zatka selective leaching procedure to differentiate between “soluble”, “sulfidic”, “metallic” and “oxidic” fractions of Ni in airborne particles. Whilst the use of XANES was able to confirm the potential of this Ni fractionation approach, it was less suitable for identifying Ni species within individual fractions. This limitation was due to the lack of availability of pure phase Ni compounds required to generate XANES reference spectra and the collinearity between the spectra of Ni species within a defined fractionation group e.g. soluble $NiSO_4.6H_20$ and $Ni(NO_3)_2.6H_20$. For airborne particulate matter collected in the vicinity of a steel mill, Ni included in a spinel structure, $NiFe_2O_4$, was identified as the principal Ni species. Airborne particulate matter collected at rural locations, away from anthropogenic sources, showed a 50:50 distribution between soluble and oxidic Ni species. Elzinga *et al.*[60] explored the use of μ-XAS in characterising the speciation of Fe in particles, originating from urban dust samples, as current thinking is that this dust source may contribute a substantial Fe load into the oceanic biogeochemical cycle where it is required for phytoplankton growth. Zelenay *et al.*[61] used a combination of STXM and XAS to investigate the *in-situ* water uptake and release in sub-μm sized ammonium sulfate particles.

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

1.4.5 Combustion and photometric based techniques

The *carbonaceous content of aerosols* remains difficult to quantify. The effects of co-sampled metals (salts) on the quantification of elemental (EC) and organic carbon (OC) in diesel exhaust particles were studied with the widely used thermal-optical approach[62]. Real ambient air filter samples and laboratory-generated test filter samples (diesel fume sampled initially onto filters, followed by sampling metal aerosols nebulised from pure metal salt solutions) were used. Co-sampled metals changed the CO_2 evolution profiles of carbon-containing particles, catalysed the oxidation of EC and the charring of OC and hence generally reduced the measured EC/OC ratios. Transition metals were more active than alkali and alkaline-earth metals but preliminary results suggested that the effects of metals were not simply additive. Therefore it was difficult to predict the activity of different metals and their resultant impact on EC/OC analysis for any particular filter sample. In similar work, Chinese researchers[63-64] measured EC/OC ratios from $PM_{2.5}$ air filters collected in Beijing using thermal-optical methods. Sampling artifacts were characterised and their influence on the measured OC concentrations presented, as were different artifact reduction approaches. Results from the intercomparison of thermal-optical methods, including the effects of charring correction protocols, were reported and interested readers should consult the paper.

Elemental carbon is sometimes reported as *black carbon*, a strongly light-absorbing component, although the two are not exactly the same, since they are operationally defined by different measurement systems. Quantification of black carbon is possible as there is a relationship between the amount of light absorbed and the extent of the blackness of a filter use to trap black carbon. Such relationships are exploited in commercial measurement systems such as the aethalometer^{TM}, multi-angle absorption and light transmission photometers. However such measurement systems can be expensive so Cheng *et al.*[65] proposed a low cost methodology involving the digitalisation of the blackness of filters, using a simple office scanner in conjunction with Adobe photoshop software^{TM}. When the digitalised colour scans were compared against EC values determined on the same filters using a thermal-optical approach, the resultant high degree of correlation could be exploited to generate a calibration model. Further “unknown” filter samples were analysed by both methodologies and the average differences were *ca.* 10%. Quick on the heels of this work, Ramanathan *et al.*[66] took this approach a step forward by demonstrating the use of camera technology and associated software embedded in modern mobile phones as a viable low-cost measurement system for potential use in the field. Quincey *et al.*[67] presented further datasets, from recent UK air monitoring programmes, to support the validity of the relationship he published in 2007[68] between OECD black smoke measurement index values and black carbon values via aethalometer measurements. This allows historical monitoring data, generated with a now defunct measurement technique, to be compared to current monitoring data generated with a newer measurement technique.

Whilst instrumental techniques dominate this air measurement arena, *photometric–based techniques* can still play a meaningful role in measuring chemical species in the atmosphere. Exposure to Pb found in old paint and subsequently released as particles into soils and house-dust remains a concern, particularly in the USA, given the high percentage of timber dwellings and the widespread historical use of leaded paints. A rapid, inexpensive, field method[69] for the determination of Pb in paint samples involved leaching the sample in 25% (v/v) HNO_3, filtering and forming a turbid solution of lead molybdate by mixing the filtrate with solid potassium molybdate in 1 M ammonium acetate. The Pb concentration was determined using an inexpensive and portable turbidity unit. Comparison between the proposed method and one involving a microwave-assisted digestion and ICP-AES analysis gave good agreement (R^2 =0.97). At the federally regulated level of 1 mg cm^{-2}, this proposed method met the performance requirements of the US EPA national lead laboratory accreditation programme. Gilfedder *et al.*[70] described a cheaper and widely available alternative method to NAA for the determination of total and non-water soluble I species in atmospheric aerosols. Filter sub-samples were combusted at 1000 ºC, and the liberated I_2 collected in water and quantified using UV/VIS spectrophotometry. The method LOD was 6 ng absolute (3 σ), equating to *ca.* 3 pmol m^{-3} and the precision was better than 5% RSD. The non-water-soluble I fraction was determined by difference between a total I value and a water-soluble I value determined by ICP-MS. The solubility of Fe in atmospheric particulate matter is important to assess its potential bioavailability to ocean phytoplankton. Using a colorimetric Fe(II)-ferrozine complex assay, Upadhyay *et al.*[71] assessed the performance of differing extractant solutions on Fe solubility measurements in atmospheric particulate matter. Results for the air samples they tested indicated that the soluble Fe fraction in $PM_{2.5}$ was ca 1 % and ca 0.2 % in larger particles. In this study the soluble Fe fraction in $PM_{2.5}$ was present almost exclusively as Fe^{II}. In contrast, for larger particles Fe^{III} was a substantial component (20 – 60 %) of this soluble Fe fraction, consistent with a soil particle origin.

1.4.6 Other instrumental techniques

A wide range of *other instrumental techniques*, some old, some mature, some forgotten, some rediscovered and some emerging are being used for the elemental, isotopic and morphological analysis of airborne particulate matter.

Lucarelli *et al.*[72] reminded readers, and particularly those brought up on ICP-MS, of the powerful attributes of *PIXE* for trace analysis, in particular the PIXE-PIGE combination for the unrivalled analysis of mineral dusts. Italian researchers[73] assessed the contribution to PM_{10}, $PM_{2.5}$ and $PM_{1.0}$ airborne levels in Rome arising from periodic Saharan dust episodes. The bulk composition of dust samples was examined using PIXE and individual particles were interrogated using SEM-EDS. This work is important for ascertaining the relative contribution from natural dusts episodes on urban air quality, which in Europe, as in many other parts of the world, is increasingly been regulated.

In K_0-*INAA* analysis of foundary air filters[74], Compton scattering effects elevated the spectra baseline and hindered the identification of some photopeaks. However, the application of a Compton suppression system improved the LODs for elements such as Fe and Zn.

Pointurier and Marie[75] evaluated *μ-Raman spectroscopy and SEM* to identify the chemical forms of U in μm-sized particles. Initial work demonstrated that characteristic Raman bands for several U compounds relevant to the nuclear industry, such as UO_2, U_3O_8 and UO_2F_2, could be identified in <1–30 μm particles. The method was tested in a nuclear facility where dusty surfaces were swabbed with adhesive carbon disks, which were analysed by SEM-EDS to locate and select particles containing U for further analysis. The sample holder was transferred to the μ-Raman instrument and the selected particles identified using landmarks. Particles as small as 5 μm could be surveyed and analysed efficiently but smaller particles could not be located. Wilkinson *et al.*[76] described the use of a new table-top SEM-EDS system for the interrogation of urban particles collected on filters and reported on the performance characteristics of the instrument for this particular application.

The chemical characterisation of airborne particles may require a *battery of instrumental techniques*. Jiang *et al.* [77] have characterised the chemical composition of nm-sized elemental carbon particles emitted from diesel vehicles using SEM-EDS, MALDI-TOF-MS, FTIR spectroscopy and ^{13}C NMR spectroscopy. The particles emitted from a diesel-powered bus, typically 50 nm spherical particles with smooth surfaces and with an OC/EC mass ratio of 0.07 ± 0.01 were deduced to be an aggregate of a new fullerene - $C_{36}(OH)_2$.

It is always welcome to learn about *new instrumentation*. Martin *et al.*[78] have demonstrated a new instrument for the *in-situ* measurement of atmospheric I species. The instrument titled ROFLEX (Resonance and Off-Resonace Fluorescence by Lamp Excitation) was optimised in laboratory experiments and achieved a LOD of 1.2 pptv for I atoms and a LOD of 13 pptv for I_2 (S/N =1, 10 minute integration). The system was subsequently deployed in a field campaign resulting in the first concurrent observation of ambient mixing ratios of I atoms and molecules in the 1–350 pptv range.

1.4.7 Intercomparison studies

Papers that compare the *performance of different methods and techniques or different laboratories* are always most welcome in the field of air analysis given the inherent challenges in developing robust QA/QC procedures. Ashley *et al.*[79] undertook a preliminary interlaboratory evaluation of a standardised ICP-MS method (ASTM D7439) for the determination of trace elements in workplace air filter samples. Performance evaluation filters were prepared by spiking filters with 21 elements of interest at nominal filter loadings of 0.5 or 5.0 µg/filter and were circulated to 20 laboratories. Resultant interlaboratory RSDs ranged from 0.073 to 0.273 with the majority of data below the design goal of 0.20 RSD. Recoveries from the spiked filters ranged from 88 to 120%. Further interlaboratory evaluations were proposed and this reviewer recommends, if possible, the use of real matrix samples to assess the performance of the key digestion step. Ashley *et al.*[80] also undertook an intercomparison exercise to ascertain the performance of a field-based fluorescence method for the determination of trace levels of Be in polyvinyl alcohol wipes used in surface swabbing monitoring exercises. Test wipes were spiked with a BeO CRM material to provide spiking levels in the range 0.03 to 5.6 µg Be/wipe. Eight laboratories took part and interlaboratory precisions ranged between 4.5 and 16%. Calculated spike recoveries were in the range 90–99% for dry wipes and 87–93 % for wetted wipes, after correction for water content.

Gerboles *et al.*[81] presented the results from an elegantly designed intercomparison exercise for the determination of As, Cd, Ni and Pb in PM_{10} using the *EN 14902 standard method*, which involves a microwave-assisted digestion and subsequent analysis using ETAAS or ICP-MS. Test samples distributed to 13 national reference laboratories were a spiked solution, an aliquot from a digested (blind) CRM, an aliquot of the same (blind) CRM undigested and two real PM_{10} air filter samples. Reference values were the spike values, values obtained from the CRM certificate or, in the case of the real air filter samples, values obtained *via* a robust statistical analysis of returned participant data. About 93% of all returned test results met data quality criteria of the EU air quality directive, although this dropped to 76% for the analysis of real air filter samples only probably as a result of digestion and contamination issues during sample workup.

Brown *et al.*[82] compared polarised EDXRF and LA-ICP-MS approaches for the determination of trace metals in PM_{10} air filter samples with the reference ICP-MS approach described in standard method EN 14902. The low systematic bias observed was not unexpected since these alternative approaches were calibrated using filter samples, previously ‘certified’ using the ICP-MS reference method, *i.e.* the calibrations were not independent! Given that the XRF and LA-ICP-MS approaches only interrogated a small area of a filter sample, it is not unsurprising to see random variability in such data sets arising from “nugget effects” (discrete particles trapped on filter samples that are enriched in one or more metals of interest compared to other collected particles) or “hotspot” effects (variability of particle deposition on filters which is a function of sampler design employed). In contrast, with the reference ICP-MS approach, the whole filter sample is generally analysed following an acid dissolution step. The authors rightly concluded that further instrumental and method improvements would be required before such alternative procedures could compete against the reference method approach.

2 Water Analysis

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

2.1 Sample preparation

The *preservation and stabilisation of As species* in water samples has been of great interest. Kumar and Riyazuddin[83] critically reviewed (65 references) current methods for the preservation of inorganic As species in environmental water samples. They concluded that filtration, refrigeration at 4 °C and storage in the dark were primary requisites, and noted that there is no universal preservation agent, so that each sample matrix has to be tested for stability before analysis. This conclusion was amply demonstrated by a study on the stabilisation of thioarsenates in iron-rich waters[84], which showed that the determination of these compounds could be problematic. Methods used for their preservation in sulfidic waters containing little Fe failed in the presence of elevated concentrations of Fe (from 1 up to 500 mg L^{-1}). It was recommended that these samples be flash frozen with dry ice at -79 °C with a minimal head space volume after the addition of a 0.01 M neutralised EDTA solution. Under this procedure the species were stable at -18 °C for up to 11 days. A different approach was followed by Watts *et al.*[85], who showed the utility of ion-exchange cartridges to selectively retain and preserve As species during field sampling prior to analysis in the laboratory.

A review (54 references) of state-of-the-art methods[23] for *the clean collection and processing of marine particulate matter* for trace metal determination covered sampling, size-fractionated filtration and digestions of samples for ICP-MS analysis

2.2 Preconcentration, extraction and separation procedures

Methods capable of selectively preconcentrating analytes above the LOD of instrumental techniques continue to be of great interest. These tend to be based on solid or liquid phase extraction or precipitation techniques.

2.2.1 Solid phase extraction

Solid phase extraction continues to be a very important methodology for preconcentrating analytes due to its flexibility and the ease of coupling to most atomic spectrometric instrumentation. The selectivity of the solid phase can be modified by adsorbing different chelating or complexing agents onto the surface. The choice of this modifier was often the only novelty in many of the articles published but sometimes interesting combinations of methods crop up. In one example, silica was modified with an ionic liquid[86] (1-methyl-3-butylimidazolium bromide) for the preconcentration of Pb^{II}. The modified silica retained Pb^{II} between pH 5-7, which was then eluted with 1.0 M HCl. The preconcentration factor was 185 for a 100 mL sample, the LOD with FAAS was 0.7 $\mu g\ L^{-1}$ (n=10) and the linear range was between 0.1 to 0.75 $\mu g\ mL^{-1}$ with an RSD of 4.2% at the bottom of the calibration curve.

In the *diffusion gradient in thin films* (DGT) *technique*, a time-integrated passive sampling technique, the dissolved analytes diffuse through a hydrogel of known thickness and bind to an analyte-specific binding phase underneath. These devices can be used *in situ* for aquatic monitoring and are reported to reduce analyte contamination or loss. A titanium-based adsorbent [87] accumulated As^{III}, As^{V} and Se^{IV} quantitatively, but <20% of Se^{VI} was absorbed. The analytes were eluted using 1M NaOH with an efficiency of 75.2 (As^{V}) to 88.7% (Se^{IV}) . The ICP-MS LODs after a 4-day deployment were 0.01 $\mu g\ L^{-1}$ for inorganic As and 0.05 $\mu g\ L^{-1}$ for Se^{IV}.

Total dissolved and labile concentrations of Cd, Cu, Ni and Pb[88] were determined in Black Sea waters. The total dissolved fraction was retained on silica spheres modified with 3-aminopropyltrimethoxysilane and the labile fraction was determined after sample collection using the DGT technique. The LODs ranged from 0.002 μg L^{-1} for Cd to 0.02 μg L^{-1} for Pb for the total dissolved fraction. The ratios between labile and total dissolved fractions were in the range of 0.2 (Cu) to 0.8 (Ni). Yebra-Biurrun and Carro-Marino *et al.* took a different approach[89] to the same problem. To obtain the total dissolved trace metal fraction, seawater was filtered (<0.45 μm), and immediately acidified in the field, the sample was then transported to the lab at 4°C. The total dissolved fractions of Cu, Mn and Zn were retained on a mini-column packed with Serdolit Chelite Che resin after on-line sonolysis of the samples. The analytes were then eluted with 110 μL of 3M HCl. The labile metallic fraction was obtained by pumping unacidified filtered (<0.45 μm) seawater through the column in the field, the analytes being eluted from the columns in the laboratory with the same eluent as used previously. The authors found that Mn and Zn were mainly in the labile fraction and that Cu was mostly present in the total dissolved fraction.

Methods for the determination of *total trace element concentrations in seawater* continue to be published. Lee *et al.*[90] determined total Cu, Cd, Fe and Pb in open ocean water by preconcentrating volumes as low as 1.5 mL off-line onto beads of nitriloacetate resin and analysing the resulting solution by ID-ICP-MS. The IDA was used to correct for the low recoveries of between 5% for Cd and 90% for Pb. The LODs were between 0.07 nM for Fe and 6 nM for Cd. The ICP-MS analysis of highly saline formation water from petroleum exploration[91], involved the preconcentration of Cd, Co, Ni, Pb, U, V and Zn on mini-columns packed with Toyopearl AF-Chelate 650M iminodiacetate resin. Iron was retained on Toyopearl 8 hydroxyquinoline resin and Mo on a silica column functionalized with 8-hydroxyquinoline. Any organometallic compounds were retained on a C_{18} sample pretreatment column. Sample volumes of 7.5 mL were used for quantification. Recoveries were affected by the sample salinity, which ranged from 16.6 to 166‰. Whereas multi-isotopic elements could be quantified by IDA, thereby negating any salinity effect, mono-isotopic elements had to be quantified by the method of standard additions. The LODs were between 0.0007 (Cd) and 0.041 (Mn) ng mL^{-1}.

Rare earth elements were isolated from seawater using 2,6-diacetylpyridine functionalised Amberlite XAD-4 [92] and from Lake Baikal samples [93] using syringe-driven chelating columns prior to ICP-MS analysis. However, Kim *et al.*[94] cautioned that the use of chelating columns could cause large fractionations of heavy REEs compared to light REEs. They suggested that this was due to unidentified complexation of heavy REEs with organic substances naturally present in the samples and recommended that either the extraction had to be quantitative (>95% recovery) or IDA be used when large matrix effects were expected.

Gadolinium-based MRI agents were extracted from surface and waste water samples using a bis-(2-ethylhexyl)-phosphate-coated RP C18 support[95]. Using this SPE material a 100-fold enrichment with >95% recovery for the contrast agents was possible. The results were in good agreement with direct ICP-MS measurements and the authors suggested that the method could be applied when less sensitive analytical techniques were available.

A review[96] (164 references) on the use of *nanoparticles in sample preparation* covered all fields of analytical chemistry, not just trace element analysis. The authors noted that the nanoparticles typically have four main uses: as sorbent agents, as an inert support for a sorbent such as a complexing agent, as magnetic particles and as an ionisation agent for SIMS. A more specific review by Pyrzynska[97] (94 references) considered the use of carbon nanostructures for separation, preconcentration and speciation of metal ions. Carbon nanotubes, the most common form of carbon nanostructure reported in the literature, were used for the preconcentration of Au^{III}[98] and Pd^{II}[99] from water samples. Karatapanis *et al.*[100] used silica-modified magnetic nanoparticles as a support for cetylpyridinium bromide for the preconcentration of Cd, Co, Cu, Mn and Pb complexed with 8-hydroxyquinoline. The nanoparticles with the adsorbed metal complexes attached were separated using a magnetic field and the complexes desorbed using acidic methanol and analysed by ETAAS. The LODs were between 2.3 ng L^{-1} (Cd) and 15.3 ng L^{-1} (Mn) spike recoveries 93-113% and RSD <3.6% (n=6).

Biological materials often have useful active sites that can be exploited for analytical chemistry purpose. For instance *penicillium digitatum* has been immobilised on pumice stone for the determination of Co, Fe and Ni in water[101]. In most applications the organisms are dead, but Tyburska *et al.*[102] showed that Se uptake by the bacterium *Lactobacillus plantarum* immobilised on silica was far superior if the bacteria were alive. Up to 66% of the Se was adsorbed on the external surface of the cell walls, whereas the remainder was actively accumulated inside the bacteria. To obtain a quantitative recovery, the stationary phase was dried and the Se quantified using a continuous powder introduction system coupled to an MIP-AES instrument. A LOD of 52 ng g^{-1} for Se in the stationary phase was achieved. This corresponded to 0.06 ng mL^{-1} in the sample solution with a preconcentration factor of 1000. The precision was 3% RSD (n=5).

An exciting development is the use of *lab-on-a-chip* technology to construct mini-SPE manifolds. A microdialysis probe has been coupled to ICP-MS using a chip-based system[103] with an interior channel functionalised with polymethylmethacrylate for the analysis of saline solutions. The LODs were 5.86 to 76.9 ng L^{-1} for Co, Cu, Mn, Ni and Pb with an enhancement factor of 5 for a 15 µL injection. A glass microfluidic device with 3 micro-channels packed with controlled pore glass functionalised with 8-hydroxyquinoline[104] was selective for Cd, Co and Ni, as might be expected for this functional group. When the system was operated at a flow rate of 20 µL min^{-1} and coupled to an ICP-MS, the LODs were between 0.006 ng mL^{-1} for Co and 0.009 ng mL^{-1} for Ni. Results for NRCC CRMs CASS-2 (Near Shore Seawater) and SLEW-1 (Estuarine Water) were in good agreement with the certified values.

2.2.2 Liquid Phase Extraction

C*loud point extraction* (CPE) methods for the isolation of trace elements from solution continue to be developed, although the number of new methods is diminishing as other approaches come into vogue. The growing number of methods that do not require a chelating agent is welcomed because the chelating agents are frequently synthesised and so are not commercially available. Methods without a chelating agent have been reported for Au^{III} [105] and Ni[106]. Interestingly, CPE was successfully coupled with CV-AFS[107] for the determination of Hg in waters and environmental RMs (GBW07310 (River Sediment) and GBW10020 (Citrus Leaf)). The use of surfactants during CPE of the analytes led to foaming. However, the use of $SnCl_2$ reduced formation of foam and a two-stage gas-liquid separator could be used to remove any foam produced. Using dithiazone as the complexing agent, an enhancement factor of 29 for a 45 mL sample was achieved, resulting in linearity between 0.05 to 5.0 ng mL^{-1} and a LOD of 5 pg mL^{-1}. At a concentration of 0.5 ng mL^{-1} the RSD was 5.2% (n=7).

A timely review on the use of *ionic liquids* for liquid phase extraction of trace elements and their species has been published[108] (73 references). In this case, ionic liquids refers to organic salts, composed of organic cations (such as imidazolium, phosphonium, pyrrolidinium, pyridinium or quaternary ammonium) and their anions (either hexafluorophosphate, tetrafluoroborate, alkylsulfates, alkylsulfonates, chloride or bromide). They are becoming more widely used as they are considered a 'greener' technique than the use of organic solvents. The chelating agents used to bind the metals before extraction are the same or very similar to those used for CPE so novel methods can be generated quite quickly. These liquids can be easily adapted to a number of modes of use, such as DLLME and single drop microextraction. The fact that these liquids have effectively no vapour pressure made them suitable as functional groups for SPE.

Dispersive liquid-liquid microextraction is a microextraction technique also well adapted for use with ETAAS. Its use was reported for the determination of Mo^{IV} in tap and waste waters[109] and Au in waters[110]. In the determination of Cr, Cu, Ni and Zn in waters with ICP-AES detection[111], the problem of injecting organic solvents into the plasma was overcome by evaporating the solvent phase after separation and redissolving the analytes in 1 M HNO_3. Jia *et al.* [112] adapted this technique for use with ICP-MS for the determination of Bi, Cd, and Pb in water samples. Flow injection with a methanol/water carrier was used to introduce the CCl_4 (17 µL) containing the metal NaDDTC complexes into the plasma. Despite the disadvantage of needing to add oxygen to the plasma, the high enrichment factors of 460 for Cd to 900 for Pb for a 5 mL water sample resulted in LODs of 0.5 (Cd) to 4.7 (Bi) ng L^{-1}. Spike recoveries were at least 83% at the 50 ng L^{-1} level with RSDs <6.7% (n=10).

2.2.3 Precipitation Methods

Bayon *et al.* [113] developed an improved *co-precipitation method* for the determination of REEs as well as Ba, Cu, Mn, Ni, Sc, Th, U, V, Y and Zr, using iron hydroxide as the precipitating agent and correction by Tm addition. Quantitative recoveries were obtained for all elements except Ba and Cu and good agreement was achieved with the certified and literature values for the elements investigated. Unfortunately LODs for the target elements with ICP-MS detection in either medium or high-resolution mode were not reported. In a novel method for the determination of Ag in water samples, reported[114] in Chinese with an English abstract, Ag was precipitated as its oxide after the addition of NaOH and collected on a microcolumn packed with silica beads. The precipitate was eluted using 10% *v/v* HNO_3 for FAAS detection. An enrichment factor of 25 from a sample volume of 5.4 mL was achieved. The LOD was

0.6 µg L^{-1}, the calibration was linear over a range of 2-150 µg L^{-1} and the precision was 2.0% RSD at the 40 µg L^{-1} level (n=11).

2.3 Speciation

Recent reports on *Sb speciation* in natural waters all involved non-chromatographic methods. Two were based on the use of DLLME for the determination of Sb^{III} and total Sb[115-116]. Both used N-benzoyl-N-phenylhydroxylamine as the chelating agent. The only other method of note[117] used a hollow-fiber-supported liquid membrane for the extraction of chelates of Sb^{III} with NaDDC onto 1-octanol immobilised into the pores of a polypropylene hollow fiber. Total Sb was determined after the reduction of Sb^{V} with L-cysteine. Under optimised conditions, the LOD was 0.8 ng mL^{-1} for a 160-fold enrichment. The RSD (n=5) for a 50 ng mL^{-1} Sb^{III} standard was 6.2%.

As noted in the ASU speciation Update[4], methods for *the speciation of As* are now well established and despite the fact that such analyses are carried out routinely in many laboratories, the development of new analytical protocols is still fertile ground. A review[118] (84 references) of methods for the speciation analysis of As in water samples by HPLC-ICP-MS over the last decade covered the important topics of interference mitigation and removal, either mathematically or using collision cells, and analytical validation. An interesting study [119] explained an apparent discrepancy between XAS and IC-ICP-MS results in the analysis of sulfidic waters by demonstrating that the (oxy)thioarsenites detected by XAS were extremely unstable and could rapidly be convert to (oxy)thioarsenates by oxygen present in the air or in the water used to dilute the samples. The problem was solved by carrying out the entire chromatographic process inside a glove box and by diluting the samples in an anoxic alkaline medium. The selective extraction and separation of inorganic As species using low pressure SPE columns is still of interest. In the period covered by this review, molecular recognition technology gels[120], magnetic nanoparticles[121], polyanaline[122] and single walled carbon nanotubes[123] were.used as packing materials for this purpose. In addition, the use of ionic liquids for LLME[124] and the combined use of an alumina microcolumn and CPE[125] have been reported. Tian *et al.*[126] preconcentrated As^{III}, As^{V}, DMA and MMA on a minicolumn packed with MnO_2 prior to HPLC separation. Because As^{III} is rapidly converted to As^{V} on this solid phase, they also selectively preconcentrated complexes of As^{III} with APDC on cellulose fibre. After HG-AAS detection, the LODs were 0.019 (As^{III}), 0.33 (As^{V}), 0.39 (MMA) and 0.62 (DMA) μg L^{-1} for a 20 μL injection after preconcentration from a 2.0 mL sample.

The *determination of Cr species in water* is entirely dominated by non-chromatographic methods. An anionic ionic liquid was immobilised onto a PVC microcolumn for the retention of Cr^{VI} [127] after elimination of Cr^{III} with a cation-exchange column. In a method that combined DLLME with LA-ICP-MS for the determination of Cr^{VI}[128], the chelate that Cr^{VI} formed with APDC was extracted and dried. Microdroplets (7 μL) of the extraction medium were laser ablated from a polystyrene substrate. The ICP-MS detection gave a LOD of 0.11 μg L^{-1} using the ^{52}Cr isotope and 0.31 μg L^{-1} using ^{53}Cr. Chen and co-workers reported two methods for the determination of Cr^{III} and Cr^{VI} based on the thermal separation and detection of the Cr species by combined ETV-ICP-MS. In one study[129], the thermally stable and volatile chelate of Cr^{III} with 1-phenyl-3-methyl-4-benzoyl-5-pyrazone was vapourised at 1000 °C whereas Cr^{VI} was retained in the graphite tube. In the second study[130], 8-hydroxyquinoline was used as a chemical modifier to form a complex with Cr^{III} that was volatile at 1100 °C. For a 10 μL sample injection, the LOD of the second method (0.013 ng mL^{-1}) was better than that of the first (0.031 ng mL^{-1}). The precision was 5% (RSD) at a concentration of 1.0 ng mL^{-1} (n=9). In a sequential CPE method involving selective extraction of Cr^{III} and Cr^{VI} followed by ICP-AES detection[131], the high extraction efficiency of the method resulted in LODs comparable to those of IC-ICP-MS methods using DRC–based instruments. The LODs for 30 mL samples were 0.02 and 0.05 ng mL^{-1} for Cr^{III} and Cr^{VI}, respectively. The precision was 2-4% (RSD) in the concentration range 10–40 ng mL^{-1} (n=6).

Methods for the *Hg speciation analysis of water samples* included an interesting non–chromatographic method which involved the functionalisation of cellulose fibers with L-cysteine to trap and preconcentrate the Hg species in a mini-column[132]. Discrimination between Hg^{2+} and $MeHg^{+}$ was achieved by changing the atomisation mode of the CV atomic fluorescence unit used. In cold atomisation mode only Hg^{2+} was seen, whereas the flame/ heat mode gave a total Hg signal. The $MeHg^{+}$ concentration was obtained by difference. The use of DLLME for the extraction of Hg^{2+} and $MeHg^{+}$ complexed with DDTC into CCl_4[133], gave enrichment factors of 138 and 350 for $MeHg^{+}$ and Hg^{2+}, respectively, for 5 mL sample and LODs of 0.0076 and 0.0014 ng mL^{-1}, respectively. The solvent was evaporated and the residue re-dissolved in the HPLC mobile phase before separation and ICP-MS detection.

The *chemical speciation of OTC* has been reviewed[134] (218 references) As with As speciation, these analyses are carried out on a routine basis and most of the novelty is in the preconcentration and sample preparation phase. A rapid method (7 minute GC separation) for the determination of OTC combined SPME with GC-ICP-MS[135]. A baker's yeast has been proposed as a suitable solid phase extractant[136].

Multi-element methods are always welcome as the effort required to carry out speciation analysis is still considerable. A method for the determination of Br and I species in drinking water by IC-ICP-MS [137] used an ICS-A23 column to separate the species present with a mobile phase of 0.03 M ammonium carbonate. The LODs of 0.032 (BrO_3^-) 0.063 (Br^-), 0.008 (IO_3^-) and 0.012 (I^-) µg L^{-1}were more than sufficient to determine that over 36 % of the samples had BrO_3^- above the Chinese drinking water limit of 10 µg L^{-1}.

2.4 Instrumental Methods

2.4.1 Atomic adsorption spectrometry

Inclusion of a *variable magnetic field for Zeeman background correction* in the ETAAS determination of a number of elements in water and sludge samples[138], improved the linearity from 1 order of magnitude to up to 3 orders of magnitude.

When gold nanoparticles were used as *a chemical modifier* for the determination of As and Sb in saline solutions[139], the analytes were stable in the graphite tube at temperatures of up to 1100 °C. The LODs of 2.3 and 3.0 µg L^{-1} for As and Sb, respectively,.were sufficient for measurement of the elements in seawater.

The F concentration in drinking waters was determined using ETAAS with a commercially available HR continuum–source AASinstrument[140]. The F was determined as GaF after the injection of 500 µg Ga into the graphite tube as a molecule forming agent. The use of sodium acetate and Ru^{III} nitrosyl nitrate as modifiers meant a maximum pyrolysis temperature of 550 °C could be used with an optimum molecule forming temperature of 1550 °C. The spike recovery was 97–106%. There was good agreement with results obtained using an ion selective electrode. The LOD as F was 5.2 pg.

2.4.2 Atomic emission spectroscopy

Most of the innovation reported in the period covered by this Update has been in the use and development of *tungsten coil atomic emission spectrometry*. A single coil instrument used to detect Co in a polluted water RM[141] may become a useful portable instrument for monitoring polluted samples in the field[142], especially as dual coil instruments[143] have been reported to boost sensitivity by a factor of between 2 (Cr and Yb) and 70 (Ag and Cu). At present the instrumentation appears unable to detect trace elements in unpolluted waters.

Another promising "portable" atomic emission source is the *electrolyte cathode atmospheric glow discharge*, in which a discharge is ignited between a metal anode and the surface of an electrolyte solution with the sample capillary acting as the cathode. The LODs reported in a Chinese language paper[144] were 1.95 and 0.008 mg $L^{-1}$for Mn and Na, respectively. Water samples have even been analysed for Cd and Na using an 18 W discharge driven by an ac power supply[145]. The LODs were 0.09 and 0.04 mg L^{-1} for Cd and Na, respectively.

2.4.3 Vapour generation techniques

Vapour generation remains an important method for augmenting the sensitivity of atomic spectrometric methods for a select group of elements. Although the technique is mature there is still some space for innovation, one being the development of a "*lab–on–a–valve*" manifold for Hg CV generation with a microscale reaction chamber and gas liquid separator[146].

Photochemical vapour generation, in which an organic acid and UV light are used to generate volatile species, was used for the determination of Co[147] with a vapour generation efficiency of 23-25%. Using AFS detection, the LOD was 0.08 ng mL^{-1} and the precision (RSD) for a 20 ng mL^{-1} standard was 2.2 % (n=11) . The same technique was reported for the vapour generation of Hg[148] but the touted advantage of it being more environmentally friendly compared to the use of borohydride of $Sn^{II}Cl_2$ seems dubious. Gil *et al.*[149] reported the more concrete advantage that this method can reduce Hg^{2+}, as well as $MeHg^+$, $EtHg^+$, $PhHg^+$ and thiomersal (the sodium salt of ethyl(2-mercaptobenzoato-(2-)-O,S) mercurate(1-)) to Hg^0 with equal efficiency.

2.4.4 X-ray fluorescence spectrometry

In the *determination of* Cr^{III} *and* Cr^{VI}, Whatman P81 and DE81 ion exchange celluloses were used for the selective separation and preconcentration of the Cr species prior to energy dispersive PIXE analysis[150]. Empore^{TM} cation and anion exchange disks were used[151] in series for the same purpose after pH adjustment to pH 3 of a 100 mL water sample. Each disk was dried then analysed using WDXRF spectrometry. Absolute LODs were 0.17 and 0.16 µg for Cr^{III} and Cr^{VI}, respectively, and the spike recovery at the 50 µg L^{-1} level was 94-114%.

Preconcentration methods typically used with FAAS or ICP-AES detection are now being combined with TXRF spectrometry for the detection of some trace elements in waters. For example, As^{III} and As^{V} in water samples were retained on alumina slurry and quantified by TXRF spectrometry[152]. The preconcentration factor was 100 and the LOD 0.7 µg L^{-1} for a 50 mL sample preconcentrated onto 10 mg of alumina. Mercury determination in waste water by TXRF spectrometry is a challenge due to the high vapour pressure and low boiling point of the element that could produce evaporative losses during drying onto the reflector. Margui *et al.*[153] overcame this problem by complexing Hg with thiourea before deposition of the sample on the reflector. The advantage of TXRF spectrometry over ICP or flame techniques that the analytes do not require eluting from the stationary phase, could be useful during the analysis of traditionally difficult–to–elute elements such as the PGEs.

2.4.5 Inductively coupled plasma mass spectrometry

There has been very little reported innovation in the development of ICP-MS instrumentation. All the innovation appears to be in the application of existing ICP-MS technology.

Total dissolved and particulate concentrations of trace elements were determined in Antarctic sea by ICP-MS using a high resolution instrument[154] after filtration of the sample through <0.2 µm and >0.5 µm filters. As would be expected, particulate metal concentrations in sea ice were higher than those in snow and seawater suggesting a signal from Antarctic shelf sediments.

The *ultratrace determination of Pu in marine samples*[155] was achieved using a MC–ICP-MS instrument combined with the use of a combination of an AG1-X8 and UTEVA®/TRU extraction columns. The instrumental LOD was 0.02 fg mL^{-1} with an absolute LOD of 0.11 fg. This method allowed the ^{239}Pu and ^{240}Pu concentrations and their atom ratios to be determined in just 15-20 L samples of NW Pacific ocean water.

With the proliferation of MC–ICP-MS instruments, *the isotopic analysis of environmental matrices* is a growth application area. The accuracy and precision of

^{238}Pu determination in water samples was improved by combining ICP-MS with α–spectrometry[156]. The activity of ^{238}Pu was calculated from the amount of ^{239}Pu and ^{240}Pu obtained from ID-ICP-MS analysis, together with the intensity ratio of ^{238}Pu: ^{239,} ^{240}Pu obtained by α–spectrometry. The bias (7%) and total uncertainty (5–12%) were better than values obtained previously (up to 44%). The use of MC–ICP–MS for the precise determination[157] of the open ocean ^{234}U: ^{238}U ratio gave a long term reproducibility of better than ±0.3‰ (2σ) for the measurement of δ^{234}U. The average δ^{234}U value of 146.8 ± 0.1‰ (2σ, n=19) constrained the vertical mixing times of the ocean to <1000 years. The challenge of obtaining accurate B isotope ratios was addressed in three papers. Louvat *et al.*[158] overcame the heavy memory effects associated with this element by using a DIHEN,. Sensitivity was improved by 2-5 times and the wash times were 10 times shorter than when using a double pass spray chamber. The reproducibility for δ^{11}B was ±0.25‰ (2σ) for seawater and coral samples. Guerrot *et al*[159] considered matrix separation to be necessary before B isotope ratio analysis, as the seawater matrix, even when diluted 100–fold could cause an offset in the results of up to –7‰. When B was separated from the matrix using an Amberlite IRA-743 column, the overall method reproducibility was ±0.4‰ (2σ). For a double pass spray chamber with a PFA microcentric spray chamber, wash out times were <20 minutes. Of interest for readers without a MC instrument is the paper by Vogl *et al.*[160] who managed to determine B isotope ratios in water and food samples with a single–detector instrument. By using a quartz cyclonic spray chamber, and a PFA micronebuliser working in free aspiration mode, the wash out time could be reduced to <6 minutes. The B was isolated from the matrix in a 3–step chromatographic separation using one column packed with AG50W-X8 and two columns in sequence packed with Amberlite IRA-743. The repeatability of the δ^{11}B measurements was 0.2 – 0.8‰ in low resolution mode and 0.3–0.5‰ in medium resolution mode. Another challenging element is Hg due to its low environmental concentrations and well–known memory effects. Chen *et al.*[161] developed a chromatographic preconcentration method for Hg from dilute solutions. The Hg was isolated from the sample on an AG1-X4 resin. The excess L-cysteine had to be digested with BrCl which in turn had to be neutralised with $NH_2OH.HCl$ before sample introduction. A variation of 2.4‰ in δ^{202}Hg was measured in the analysis of 16 natural water samples with Hg concentrations ranging from 0.9 to 15600 ng L^{-1}.

Both mass–dependant and mass –independent fractionation of Hg isotopes occurred in natural waters.

2.4.6 Laser-based Spectrometry

Laser–ignition–assisted spark–induced breakdown spectroscopy has been developed for the determination of Hg in water[162]. The Hg^{2+} ions were electrodeposited onto a copper plate and a laser pulse used as an ignition source prior to spark–induced breakdown spectroscopy. This allowed a reduced discharge voltage with an improved discharge stability to be used. The LOD was 2 μg L^{-1}.

Very few laser techniques at present are capable of detecting trace elements at natural unpolluted concentrations. However, *the combined ETA-LEAFS method* of Le Bihan *et al.*[163] for the determination of Hg at trace levels gave a LOD of 10 ng L^{-1} for a 10 µL sample. Measurements were made at 253.652 nm using 0.1 M oxalic acid as matrix modifier,.

Techniques typically associated with liquid phase atomic spectroscopy have been tested with the aim of improving *the sensitivity of LIBS.* Zhong *et al.*[164] coupled a USN with LIBS for the detection of Mg in pure water to achieve a LOD of 0.242 mg L^{-1}. Unal *et al.*[165] coupled continuous flow HG with LIBS to determine Sn in water with a LOD of 0.3 mg L^{-1}.

3 Analysis of soils, plants and related materials

This section highlights noteworthy areas of research and development in the analysis of soils, plants and related materials by atomic spectrometric and complementary analytical techniques published since the last Update[1]

3.1 Sample preparation

3.1.1 Sample dissolution and extraction

A new *automated method for the isolation of U* from environmental samples[166] coupled a multi-position $LiBO_2$/LiBr fusion system to extraction chromatography with commercial UTEVA® resin. Excess lithium arising from the flux was flushed from the resin with 20 mL of 3 M HNO_3 prior to elution of U in 10 mL of 0.1 M HCl for quantification by ICP-MS. Measurement of a ^{233}U yield tracer and results for analysis of CANMET RM CLV-2 (Spruce Needles), IAEA 384 (Lagoon Sediment) and NIST SRM 2709a (San Joaquin Soil) suggested that the method recovered >93% of U present.

A considerable number of articles dealing with the *pre-treatment of samples for quantification of Np and/or Pu by ICP-MS* have appeared. A flurry of papers by Qiao *et al.* described variants on the use of a FIAlab-3500b^{TM} system for the automated sequential–injection–based anion-exchange separation of Np[167], Pu[168] or both[169-170] from solid samples. The optimised methods offer huge savings in time relative to traditional radiochemical separations, but there still remains a need to dry the final eluate on a hot plate and reconstitute in 0.5 M HNO_3 to remove HCl prior to introduction to the instrument. Other new methods for isolation of Np[171] or Np and Pu[172] could be used with both ICP-MS and α-spectrometry.

Researchers continue to optimise *methods of acid digestion for particular analytes or types of sample.* A HNO_3-H_2O_2 mixture was recommended for measurement of Zn in Pakistani soils[173]; HCl-HNO_3-HF gave best performance for the digestion of mastic (plant resin from the Mediterranean evergreen shrub *Pistacia lentiscus*)[174]; and HF-$HClO_4$-HNO_3 was required to determine total K content in soils from Papua New Guinea[175] because *aqua regia* extracted only 66%, and $HClO_4$-HNO_3 only 25%, of the K obtained with the optimal acid mixture.

The application of *microwave-assisted methods* for extraction in Hg speciation analysis has been reviewed[176] (59 references). A central composite design of experiments[177] assisted researchers in optimising a microwave-based method suitable for *aqua regia* extraction of soil from a former industrial site. To reduce the amounts of concentrated acids used in the digestion of botanical samples, other workers[178] modified the atmosphere within closed microwave vessels. Digestion under air, argon, and various pressures (5, 10, 15 and 20 bar) of pure oxygen was compared, for 2, 3, 7 and 14 M HNO_3. Oregano served as a test material. Efficient digestion of a 500 mg sample could be achieved in 3 M HNO_3 under 5 bar of O_2. Concentrations of Al, Ca, Fe, K, Mg and Na obtained using the method, with quantification by ICP-AES, were in excellent agreement with certified values for BCR CRM 62 (Olive Leaves) and NIST SRMs 1515 (Apple Leaves), 1547 (Peach Leaves) and 1575a (Pine Needles). Microwave-induced combustion was recommended[179] for digesting humic acids extracted from forest soil in a method for the determination of Br, Cl and I by IC or ICP-MS.

Ultrasound-assisted extraction methods for Ag and Au[180] prior to determination by ETAAS have been developed using a suite of RMs. A mixture of 25% v/v HNO_3 + 25% HF v/v proved optimal for the extraction of Ag, whilst 25% v/v HNO_3 + 25% v/v HCl was preferred for the extraction of Au. An alternative extractant, 0.6% (m/v) thiourea in 2% v/v H_2SO_4, was also recommended for both analytes because extraction times could be reduced to 10 minutes for some matrices, rather than the 20 minutes required with the acid mixtures, and waste was less toxic. Methylmercury and inorganic Hg were extracted from BCR CRM 580 (Estuarine Sediment) into 1+1 methanol-HCl [181] and measured by IC with ICP-MS. The determination of As^{III} and As^{V} in harbour sediment[182] involved extraction into a 1+1 mixture of 0.5 M H_3PO_4 and 0.1 M $NH_2OH.Cl$ followed by HPLC-HG-AAS analysis. However, one group of researchers[183] was extremely sceptical about the effectiveness of ultrasound-assisted extraction, at least when applied to dried, powdered plant samples. Ultrasonic extraction using a variety of extractants, including water, HNO_3, EDTA, the surfactant CelLytic P™ and the enzyme lignin peroxidase, gave no better recovery of Cd or Cu from plant samples than simple magnetic stirring. It was suggested that previously reported improvements resulted from the rupture of cell walls by osmotic tension when dried samples were immersed in aqueous solutions.

Work has continued to refine *extraction methods for the determination of mobile or available elements in soil*. Matula[184] compared three extractants (water, ammonium acetate and the Mehlich 3 mixture) and two analytical techniques (colorimetry and ICP-AES) for the measurement of available P. Marked differences were found not only between the reagents, which is expected, but also between the techniques – for example the mean measured concentration of water-soluble P was 14 mg kg^{-1} by ICP-AES but 9.6 mg kg^{-1} by the colorimetric method – highlighting the need for standardised methodology in this area of analysis. Vasile and Tanase[185] used four different extraction procedures to determine mobile form of Cd, Ni and Zn in BCR CRM 483 (Sewage Sludge Amended Soil). They too concluded, unsurprisingly, that the nature of the extractant affected the amounts of analytes measured. Duzgoren-Aydin *et al.*[186] evaluated six extraction methods for use in routine environmental monitoring programmes and recommended cold extraction in 0.5 M HCl in tandem with microwave-assisted total digestion to determine the more labile metal fraction. In contrast, Huang *et al.*[187] investigated the possibility of eliminating chemical extractions altogether by measuring the metal pool available to plants by means of stable isotope dilution. Soil suspensions were spiked with ^{112}Cd and ^{206}Pb and shaken. Aliquots of the mixture removed at different times (from 1 minute to 25 days) were filtered, and their ^{111}Cd/^{112}Cd and ^{208}Pb/^{206}Pb ratios measured by ICP-MS. Amounts of isotopically exchangeable metals were compared with analyte concentrations in conventional single and sequential extracts.

Physiologically-based extraction tests are used to estimate metal solubility in the human gastro-intestinal tract following ingestion of plants or soils. Li *et al.*[188] applied a precursor of the unified bioaccessibility method[189] to assess the availability of Cu and Zn in the mouth, stomach and small intestine following ingestion of decoctions (boiling water extracts) of plants used in traditional Chinese herbal medicine. A novel aspect of the work was inclusion of a simulated biomembrane to represent the barrier between gastrointestinal tract and blood. Some traditional Indian medicines[190] composed of plant-derived material and inorganic compounds had extremely high concentrations of toxic elements (up to 304 μg g^{-1} As, 10 mg g^{-1} Hg and 36 mg g^{-1} Pb) extractable in a two-stage process simulating stomach and intestinal conditions . More than 80% of As and Pb species but <1% of the Hg species were bioaccessible. It was claimed that ingestion of some of these substances, at doses typically prescribed, represented a significant risk of metal poisoning. Beeston *et al.*[191] developed a mathematical particle diffusion model to describe the desorption of metals from soils undergoing leaching with simulated gastric fluid. The study showed that analytes that have very similar solid:extractant distribution coefficients in batch experiments may display very different leaching profiles due to diffusion-limited processes.

Le Bot *et al.*[192-193] developed a *two-step sequential extraction* for the determination of bioaccessible and pseudototal metal concentrations in dust wipes as a means to assess health risk arising from human exposure to metals in house dust. Step 1 involved addition of 1.4% HCl, 15 minutes sonication and then 1 hour extraction at 37 °C. Step 2 was a conventional acid digestion of the residue.

Parallel extraction of soil samples with different reagents has been proposed[194] as a time-saving alternative to sequential extraction and was used to study Se speciation in soil extracts by HPLC-ICP-MS. The Se extraction efficiencies of six reagents, and stabilities of Se species therein, were assessed and three – ultrapure water, 0.1 M phosphate buffer at pH 7 and 0.1 M NaOH – were selected. These reagents were applied to soils with total Se concentrations between 210 and 1560 μg kg^{-1} to estimate the water-soluble Se, exchangeable Se, and Se bound to organic matter, respectively.

The *fractionation of As in soil by sequential extraction* combined with measurement of arsenate and arsenite in extracts by HPLC-ICP-MS[195] has been proposed as a useful means of speciation analysis, especially where As concentrations are too low for application of X-ray absorption techniques. A novel seven-step procedure was designed with particular attention to maintaining the As^{III} and As^{V} states during extraction, for example by selective complexation of As^{III} or removal of redox-active matrix elements such as iron. Changes in As speciation and distribution[196] in individual sediment grains during sequential extraction were studied by μ–XRFS. A strong association between As and Fe in grain coatings survived treatment with 0.5 M NaH_2PO_4 (step 1) even though 66% of As was removed, but disappeared after step 2, which targeted the iron oxyhydroxide phase. The study found evidence of re-precipitation and of attack on non-target mineral phases, underlining the operational nature of sequential extraction procedures. A dynamic flow-through extraction system[197] was used to study the effects of soil additives on As fractionation. The extractograms obtained suggested that MnO_2 addition may decrease As leaching rates from contaminated soil.

The week or so needed to carry out the full *BCR sequential extraction procedure* can be considered a drawback so new approaches have been proposed in order to reduce the time requirement greatly. A microwave procedure[198] could be completed in only 22 minutes but involved a change of reagent in step 3 (5 M acetic acid replaced 1 M ammonium acetate) and omitted the advisory residual step. Results for Cd, Cr, Cu, Ni and Pb in BCR CRM 701 (Lake Sediment) agreed with certified values except for Ni in step 2, Cr in steps 2 and 3, and Cu and Pb in step 3. Amounts of analytes extracted from freshwater and marine sediment samples by conventional and microwave extraction were also comparable according to a paired t-test at 95% confidence interval Another approach[199] involved packing 0.5 g sediment and 1.0 g of sea sand (the dispersing agent) into a 10 mL syringe, through which 25 mL 0.11 M acetic acid in step 1; 25 mL 0.1 M hydroxylammonium chloride in step 2; and 10 mL hot 8.8 M H_2O_2 then 25 mL 1.0 M ammonium acetate in step 3 were drawn using a vacuum manifold. Results similar to target values were obtained for BCR CRMs 601 and 701 (Lake Sediments) in steps 1 and 3, but not in step 2. Additional data[200] have been published on amounts of Mo extractable from the Slovakian CRMs S-VM (Soil Eutric Cambisol), S-SP (Soil Rendzina) and S-MS (Soil Orthic Luvisol) by the revised BCR sequential extraction. A study of lagoon sediments from Lagos, Nigeria[201] re-iterated that the revised BCR procedure gives different results from the original protocol in step 2.

Systematic *errors arising from analyte absorption on filter papers*[202] used in pre-treatment procedures for environmental samples have been quantified. Losses ranging from 15% (Fe) to 27% (Cd) occurred when an *aqua regia* digest of soil was filtered. The authors recommended that filtration be replaced with other approaches such as centrifugation whenever possible.

3.1.2 Preconcentration procedures

Numerous *analyte preconcentration procedures* have appeared since our last Update[1]. Those intended for application to the analysis of soils, plants or related materials, or which used relevant CRMs in method validation are summarised in Tables 1-3. Table 1 covers various types of liquid and surfactant–assisted extraction, Table 2 precipitation methods and Table 3 SPE. These methods are undeniably useful in laboratories where instrumentation is limited to techniques with relatively poor LOD. However, concerns remain that not all studies are fully validated by analysis of CRM and that, where CRM are used, they are not matched to the sample in terms of matrix and element concentration levels.

3.2 Instrumental analysis

3.2.1 Atomic absorption spectrometry

Sardans *et al.*[203] have reviewed recent advances in, and future prospects for, *the application of ETAAS to the analysis of soils and sediments* (with 191 references).

Workers in Argentina[204] used *self-reversal background correction* to establish a method for the determination of Pb in airborne particles by ETAAS that was tolerant of up to 0.01 M of Si arising from the sample matrix. A related group[205] used self-reversal ETAAS to measure the Pb in sediment, sludge and soil with slurry sample introduction. The LOD were 0.025 μg g^{-1} at 217.0 nm and 0.1 μg g^{-1} at 283.3 nm, with RSD <8.2% for n = 5.

Slurry and solid sample introduction methods were used: in the measurement of Mn and Pb in sediment by FAAS with a slotted tube atom trap[206]; for the determination of Cd and Pb in soils and sediments by ETAAS using a permanent mixed Ir-Nb modifier[207]; and for the measurement of Cd and Pb[208] in soil with a flame furnace atomiser and $CaCO_3$ or KHF_2 as chemical modifiers. In the measurement of five elements in soils by solid sampling ETAAS[209], best results were obtained with mixed Pb-$Mg(NO_3)_2$ modifier for Cd, Pb, and Zn; NH_4F for Cu; and tungsten permanent modifier plus $Mg(NO_3)_2$ for Cr. A method[210] involving the electrodeposition of palladium from a single drop of modifier solution onto a graphite platform was successful for the determination of Hg in solid samples of soils, sediment and plants by ETAAS.

Articles described the performance of a *coupled HG-FAAS instrument with integrated atom trap* for the determination of Ge and Sn[211] and Ni[212]. The trap, which has been previously reported[213], consisted of a combination of a water-cooled single silica tube and a double-slotted quartz tube. *In-situ* preconcentration in the trap for 2 minutes yielded 10-, 200- and 14-fold enhancements in sensitivity for Ge, Ni and Sn, respectively. The procedures developed were tested by analysis of a suite of RMs, including coal fly ash, soils, sediments, and water, and then applied to real samples.

3.2.2 Atomic emission spectrometry

Compared to the use of an atmospheric pressure MIP, use of a *reduced pressure argon MIP emission source*[214] for elemental analysis gave better LODs ranging from 2.9 ng mL^{-1} for Cu to 33 ng mL^{-1} for Zn. Satisfactory results were obtained for the analysis of NIST SRM 2710 (Montana Soil) and IAEA 336 (Lichen).

Replacing the desolvation system of a USN with a pre-evaporation tube[215] improved the performance of ICP-AES for the analysis of complex matrices. At a sample uptake rate of 0.3 mL min^{-1} the sensitivity and LOD were enhanced roughly four-fold when a pre-evaporation tube heated to 400 °C was inserted between the USN and plasma torch in place of the conventional desolvation assembly (heated U tube, condenser and membrane desolvator). Loss of Hg in the heater/condenser was eliminated and plasma robustness was improved. In analysis of NIST SRMs 2710 and

2711 (Montana Soils), 83% of results agreed with certified values when the Ar emission line at 763.511 nm was used as an internal standard and calibrants were prepared in 2% HNO_3. This avoided the need to add an internal standard or to reagent-match the standard solutions.

There has been continued interest in *sample introduction procedures for ICP-AES*. An optimised method for slurry sample introduction[216] suitable for sewage sludge used a sample concentration of 0.2% w/v and 5% HNO_3 + 0.005% Triton X-100® as stabiliser. Calibration could be performed with aqueous standards. Results obtained were statistically similar to those from analysis of acid digests of the same samples and to certified values for RTC CRM 007-040 (Sewage Sludge). Masson[217] successfully determined P in plant RMs by ETV-ICP-MS. He used a computer-controlled ETV unit and introduced $CHClF_2$ into the furnace during the heating cycle. This allowed the analyte to be vaporised at 1200 °C thereby eliminating matrix interference effects. Replicate analysis of 2 mg test portions gave precision <10% RSD (n = 5) and a LOD of 30 $\mu g\ g^{-1}$.

An article in Japanese with English abstract[218] described a type of *portable atomic emission spectrometry* in which a liquid electrode plasma was used to analyse 1 M HCl extracts of soil. In tungsten-coil AES[142], the poor LODs for elements with emission lines below 400 nm when using a 15 V, 150 W coil harvested from a slide projector bulb were improved substantially by use of a 24 V, 250 W coil from a commercial light bulb. Sensitivity enhancements of up to 2000-fold were reported, and elements such as Mg and Ni, which were previously undetectable, had LODs less than 1 mg L^{-1}. A portable instrument incorporating a hand-held CCD spectrometer gave results close to target values for NIST SRM 1643e (Trace Elements in Water), except for Rb, but performed less well for analysis of NIST SRM 2711 (Montana Soil). A more robust instrument with an aluminium, rather than glass, atomisation cell[219] was also described. Although tungsten-coil AES clearly has considerable potential for field analysis of aqueous samples, the methods needed to prepare soil samples for analysis – 2 hours in a block digestor at 100 °C with HNO_3 – may prove difficult to transfer out of the laboratory!

Determination of Cl in plants by an axially-viewed ICP-AES instrument[220] has been reported for the first time; an argon-filled spectrometer and VUV wavelengths were used. A relatively mild sample digestion regime (extraction in 4% HNO_3 at 95

°C for 90 minutes) was applied to minimise losses of Cl. However, because these conditions were insufficiently vigorous to oxidise carbohydrates in the matrix, spectral interference from residual C occurred. This was overcome by use of matrix-matched standards containing 4% v/v HNO_3 and 0.15% w/v sucrose. The instrumental LOD at the most sensitive wavelength, 134.7 nm, of 0.041 mg L^{-1} was similar to those previously-reported for ICP-AES methods for Cl determination in various matrices and corresponded to a method LOD of 16 mg kg^{-1} dry weight. Recoveries of Cl from three NIST and 14 ASPAC RMs were 100 ± 13%, except for 67% from NIST SRM 8433 (Corn Bran) and 78% from ASPAC 41 (Mung Bean Leaves).

3.2.3 Atomic fluorescence spectrometry

Two articles described methods for the *rapid simultaneous determination of As, Bi, Te and Se* in soil[221] and tea leaves[222] by multi-channel HG-AFS. Although the applications, and cited authors, differed in the two studies, there was an uncanny similarity in the text describing the development of the analytical methods. In both cases a four-channel AFS instrument was used and optimal performance was obtained with 0.3% m/v thiourea, 1.5 % m/v KBH_4, 10 % v/v HCl, 200 mL min^{-1} carrier gas flow rate, 900 mL min^{-1} shield gas flow rate and a viewing height of 4 mm.

The us*e of HPLC-HG-AFS in speciation analysis* continues. Improvement in the LOD for measurement of Sb^V in oxalic acid extracts of soil[223] from 0.3 to 0.07 μg L^{-1} was achieved by using post-column on-line reduction with L-cysteine. A method for the separation and determination of five As species[224] – arsenite, arsenate, MMA, DMA and roxarsone (a poultry feed additive) – in soil, plant, feed and chicken manure by RP-HPLC-HG-AFS with a NaH_2PO_4:CH_3OH solution containing tetrabutyl ammonium bromide as mobile phase and gradient elution has also been described (in Chinese with English abstract).

An interesting approach for *separation of volatile As species*[225] involved a combination of a short packed cotton column and cryotrapping. The column was placed in a specially-designed manifold, immersed in liquid nitrogen, and arsines (either synthetic standards generated on-line or arising from samples) were collected from a stream of He. The cold cotton column was then allowed to warm and the trapped species were released, in order of volatility, into the AFS instrument. Using this approach, AsH_3, CH_3AsH_2, $(CH_3)_2AsH$ and $(CH_3)_3As$ could be separated and measured in sediment samples with LODs ranging from 2.5 to 11 pg, and RSD < 5% (n = 5). The precise role of the sorbent in the separation process was unknown, although the authors speculated that the presence of amino groups on the cotton may be important. However, use of temperature ramping alone did not provide adequate separation of trapped volatile arsenicals.

3.2.4 Inductively coupled plasma mass spectrometry

Two *comprehensive and authoritative reviews* featured ICP-MS. Husted *et al.*[226] described approaches for multi-element and speciation analysis in plants by a range of atomic spectrometry techniques, with particular emphasis on the contribution of ICP-MS to plant metallomic research (310 references). Beauchemin[227] focussed exclusively on applications of ICP-MS to environmental samples including, but not limited to, plants and soils (243 references).

Ogawa *et al.*[228] recommended NH_3 as *the reagent gas for use in a DRC* when determining Cr and Fe by ICP-MS in rock, soil and water samples. An optimal flow-rate of 0.6 mL min^{-1} NH_3 suppressed or eliminated interferences due to polyatomic argon ions and there was no formation of clusters between NH_3 and Cl. A Chinese collaboration found that introduction of O_2 to a DRC at a flow rate of *ca.* 2 mL min^{-1} removed problems associated with the determination of Cd in samples rich in Mo and Zr[229] and of Hg in samples rich in W[230]. In both cases, interfering oxide or hydroxide species were converted to higher oxidation oxides. Excellent agreement with certified values was obtained for a range of GBW soil and sediment CRMs for which analyte concentrations had previously been overestimated.

Comparisons between ICP-QMS and SF-ICP-MS have illustrated that use of the latter, more expensive, approach is not always necessary. Tsai *et al.*[231] developed an ICP-QMS method to measure ^{226}Ra in water and sediment based on $BaSO_4$ coprecipitation and use of the γ-emitter ^{133}Ba as a yield tracer. The LODs (0.02 mBq L^{-1} for water and 0.10 Bq kg^{-1} for sediment) represented a substantial improvement over those obtained by the standard analytical method of radon emanation followed by liquid scintillation counting. Results agreed well with those from SF-ICP-MS (correlation coefficient = 0.982) and with the target value for SRM 4357 (Ocean Sediment). Clausen *et al.*[232] assessed the suitability of several instruments for measurement of W in soil and water from military small arms firing ranges in the

USA. They too concluded that ICP-QMS was fit-for-purpose. The major challenges in the analysis were memory effects and lack of suitable CRMs, although the former could be reduced using a desolvating fluoropolymer sample introduction system.

Stable isotope measurement by MC-ICP-MS continued to increase in popularity. Studies relevant to the global cycling of Hg[41] have been reviewed (110 references). A collaborative project based around new facilities at Imperial College London[233] developed an improved double-spike MC-ICP-MS method that involved the addition of ^{64}Zn and ^{67}Zn, acid digestion, then ion-exchange sample clean-up, to estimate the isotopic pool of plant-available Zn in soil. Takagi *et al.*[234] conducted a detailed evaluation of the influence of matrix elements Al, Ca, Fe and Na on the measurement of Pb isotope ratios. Concentrations >10 mg kg^{-1} (>1 mg kg^{-1} for Al) caused significant bias and it was necessary to separate Pb from the sample matrix by bromide complexation and anion-exchange chromatography before analysis of soil, dust, and blood. The method developed was used in a preliminary study, focusing on two children, which suggested that house-dust was an important source of Pb exposure for these individuals.

Duester *et al.*[235] described a *multi-element ETV-ICP-MS method* for measurement of Ag, Al, Sb, Sn, Ti and Zn in engineered nanoparticles that associated with leaves of the aquatic plant *Lemma minor* during an incubation experiment. A simple, two stage heating programme was used (400 °C then 2200 °C). The method could be calibrated with aqueous standards and gave recoveries in the range 85 to 116% for analysis of eight elements in GBW 07602 (Bush Twigs and Leaves). Both platform and wall atomisation[236] were deemed suitable for the measurement of Cr, La, Mo, Pb, Ti, V and Zr in GBW 07401 (Soil) by ETV-ICP-MS with the addition of PTFE as fluorination reagent. Similar results were obtained whether samples were introduced as slurries or in the form of acid digests.

Laser ablation ICP-MS is amongst the techniques discussed in an introductory review by Lombi *et al.*[237] of approaches to *in situ* analysis of metal(loids) in plants (167 references). The article was particularly aimed at non-specialist readers and provided valuable information on strengths and weaknesses of different types of analysis. The potential usefulness of LA-ICP-MS in environmental forensics[238] was highlighted in a study of soils and sediment; data obtained correlated well at the 95% confidence interval with results from ICP-AES and ICP-MS. The use of standards prepared in $CaCO_3$ and normalisation of the ^{208}Pb signal to ^{42}Ca allowed Pb pollution in coral to be measured[239]. A novel DGT gel[240] based on precipitated ferrihydrite had greater stability and higher P binding capacity than gels previously available. This has been used with LA-ICP-MS to obtain 2D maps of labile P species in soil. Important future applications are likely to include study of geochemical processes in the rhizosphere to aid understanding of nutrient uptake in plants.

Application of a *phenylation purge-and-trap GC-ICP-MS method*[241] has verified that monoethylmercury occurs in nature. The method, which has a LOD of 0.001 ng g^{-1}, found traces of $EtHg^+$ in soil from the Florida everglades. The authors speculated that the significance of this species in the global Hg cycle was not previously widely recognised due to a lack of suitable analytical methodology.

Use of enzymatic probe sonication[242] in the HPLC-ICP-MS *speciation of Se* in *Brassica* seeds and meal (the protein-rich residue from oil processing of the seeds used as animal feed) meant that Se could be extracted from samples in only 2 minutes compared to *ca.* 12 hours in an incubator. Other workers[243] used an optimised 16-hour enzymatic extraction and a CE-ICP-MS instrument to measure Se^{IV}, Se^{VI}, $SeCys_2$ and SeMet in rice. Spike recoveries were 90-103%, with RSD $< 7\%$ ($n = 6$) and instrumental LOD values of 0.1-0.9 ng mL^{-1}.

Studies involving *parallel elemental and molecular analyses* by ICP-based techniques and approaches such as ESI-MS have become more common. Interesting examples from the past year include the use of HPLC-ICP-MS[244] to study the degradation and transformation of roxarsone in soil, and the development of approaches involving IC-ICP-MS[245] to identify Fe-aminopolycarboxylic acid complexes in soil solution that provided insight into chelate-assisted phytoremediation.

3.2.5 Accelerator Mass Spectrometry

Improved methods for the extraction of I have been reported. One procedure[25] involved the addition of stable ^{127}I carrier followed by microwave-assisted digestion of solid samples in HNO_3. Iodine was extracted from the digests into $CHCl_3$, back-extracted into aqueous solution, and then precipitated as AgI for the measurement of ^{129}I by AMS or as KI for the measurement of I by ICP-MS. The ICP-MS results were evaluated by analysis of nine CRMs, including plants, soils and sediments, yielding an average ^{127}I recovery of 90%. The AMS data for IAEA 375 (Soil from Chernobyl) were also satisfactory. Other workers[246] combusted solid samples in a tube furnace and trapped the I released in alkaline solution before coprecipitation of AgI with AgCl, avoiding the need to add stable iodide carrier. The coprecipitate was dried, ground, mixed with niobium powder and pressed to form the target. Iodine in aqueous samples was isolated by anion-exchange chromatography and coprecipitation. Recoveries were >80% for solid samples and >65% for waters, determined by measurement of a ^{125}I yield tracer by γ–spectrometry. The method could measure ^{129}I/^{127}I ratios as low as 2×10^{-11}.

3.2.6 Laser-induced breakdown spectroscopy

Some *useful review articles* have been published focussing on LIBS. Gaudiuso *et al.*[247] provided an introduction to the technique before discussing analytical applications in environmental, cultural heritage and space science (154 references). Another review[248] dealt specifically with soil (60 references). Fortes and Laserna[249] discussed not only portable systems but also developments in remote analysis, where optical fibres are used between laser and sample, and stand-off analysis, where the laser beam travels through open space (89 references).

There has been considerable interest in developing *methods for enhancing the emitted spectral line intensity* in LIBS. Two papers[250-251] described how applying a carefully timed high-voltage discharge could effectively reheat the laser-induced plasma thereby improving sensitivity, precision and S/N in the measurement of a wide range of major and trace elements in soil. Confusingly, the approach was referred to by different names: LA fast pulse discharge plasma spectrometry[250] and LA spark-induced breakdown spectroscopy[251]. Workers in Japan and Korea recommended the use of a transversely excited atmospheric CO_2 laser at 10.6 μm, rather than the conventional Nd:YAG, in combination with a specially designed sample holder incorporating a metal sub-target to assist plasma formation. [252] The use of silicon grease as a sample binder allowed smaller samples of soil than previously possible (*ca.* 4 mg) to be analysed and LODs of 4 mg kg^{-1} for Cr and 13 mg kg^{-1} for Pb to be achieved. Placing a stainless steel mesh on top of the sample[253] further enhanced plasma formation, improving the Cr LOD to 0.6 mg kg^{-1}. Two further contributions, both in Chinese with English abstracts, showed that addition of 15% KCl increased the electron temperature and electron density of the plasma[254] and thus doubled signals for Mn and Ti in soil analysis and that decreasing soil moisture content from 20 to 0% increased plasma temperature[255] by *ca*. 4000 K.

Comparisons between data generated by LIBS and by ICP-AES have continued to fuel debate over whether LIBS has yet reached the point of being truly quantitative, or whether it remains best used for semi-quantitative screening. Workers in Italy[256] normalised emission intensities for Cr, Cu, Pb, V and Zn to the LIBS spectral background and plotted the results against data previously obtained for the same soil samples by ICP-AES. Relationships were linear with good correlations ($R^2 > 0.97$). The LODs of between 17 (Cr) and 60 (Cu) mg kg^{-1} were adequate for many applications. Other workers[257] found a poorer fit between LIBS data and ICP-AES results when measuring Cu, Fe and Pb in soils from Brittany. However, the agreement was still good enough for semi-quantitative 'LIBS maps' to be generated on site, which helped identify contaminated areas and hence inform the collection of samples for subsequent laboratory analysis. A PLS multivariate data analysis[258] based on the 300-350 nm region of the LIBS spectrum was found to give significant improvement in the measurement of Cu and Zn in a silty clay loam: correlations with ICP-AES (R^2 values) were 0.94 for both analytes (*cf.* 0.62 for Cu and 0.45 for Zn by univariate calibration). In contrast, univariate and multivariate calibration produced similar results to one another and to ICP-AES analysis for B, Ca, K, Mg, Mn, P and Zn – but not for Fe – when LIBS was applied to sugar cane leaves[259] provided calibrants were of similar matrix composition to samples.

The *measurement of soil organic C by LIBS* remains challenging, although a detailed study[260] of Fe interference on the 247.8 nm emission line led to the development of a method that can determine C at sub-percent levels and gave results that agreed well with those obtained by standard oxidation-combustion methods.

3.2.7 X-ray techniques

Several *review articles have featured X-ray techniques*. Our sister Update[5] covered the breadth of advances in the field (498 references). Mesjasz-Przybylowicz and Przybylowicz[261] focussed on the role of PIXE in understanding toxic metal hyperaccumulation in plants (54 references). Wu *et al.*[262] dealt exclusively with the measurement of REEs (85 references). Workers in the USA[263] reviewed the use of XANES and FTIR, NMR and Raman spectroscopies for P speciation in soils (213 references). Lombi *et al.*[237] included X-ray techniques in their tutorial review of approaches for visualising analyte distribution in plants (167 references) and provided the overview[264] introducing a special section of articles about *in situ* analysis in biogeochemistry, published in the May 2011 issue of the Journal of Environmental Quality.

In the area of *soil and sediment analysis,* EDXRF methods have been described for measuring Br and I[265] and Nd, Pr and Sm[266]. Multivariate calibration methods based on PLS[267] were evaluated for measurement of 14 elements in sediment by XRF spectrometry. The average prediction error was ±37% relative to reference data from ICP-MS. Application of both XRF and XRD spectrometries[268] to soil samples allowed researchers to carry out a rapid assessment of the migration of contamination from the Nisa uranium deposit in Portugal. The same techniques plus ICP-AES were used to study K reserves in Scottish soils[269], where it was noted that *aqua regia* digestion released K from phyllosilicates, excluding muscovite mica, but not from K-feldspars. Margui *et al.*[270-271] investigated the suitability of TXRF for measurement of trace Se in soils and soil extracts. With analyte preconcentration by DLLME, a LOD of 0.05 mg kg^{-1} was obtained. Good agreement was reported between SR-XRF and PIXE measurements of Pu:U mass ratios[54] in 'hot particles' of nuclear materials recovered from sediments in Greenland and Spain.

In the *analysis of plants*, optimised methods were reported for multi-element analysis[272] of cauliflower by EDXRF; for the measurement of Fe, Pb and Zn[273] in plants grown under hydroponic conditions by SR-XRF; and for the measurement of As[274] in onion by TXRF. Lombi *et al.*[275] used the new Maia detector system at the Australian Synchrotron facility successfully to obtain 2D tomograms of Ni and Zn across hydrated plant roots. The fast fluorescence detector meant that the experiment could be carried out rapidly, before the sample dehydrated or radiation damage became critical.

Portable XRF instruments for rapid field screening of soils remain popular. For example, Peinado *et al.*[276] described a method for measuring As, Cu, Pb and Zn that had LODs in the range 8-22 mg kg^{-1}, RSD 4-16% ($n = 9$) and gave good agreement with certified values for RTC CRM 052-050 (Loamy clay 1). In the study of soils affected by an abandoned mine, over 60 samples were collected, sieved and analysed on site in less than two days.

3.3 Speciation

Reviews focusing on speciation of Si[277] (203 references) and Sn[134] (211 references) both included information relevant to soil, plants and related materials. This topic is covered in depth in another Update[4].

3.4 Analytical quality control

There has been a notable increase in publications featuring the analysis of traditional herbal plants and medicines in recent years and so an *international proficiency test* [278] on the measurement of Cd and Pb in the herbal medicine *Herba Desmondii Styracifolii* was timely. More than 100 laboratories from 42 countries participated. Mean results were close to the assigned concentrations determined by ID-ICP-MS but it was noted that some laboratories had difficulty in providing a sensible estimation of the uncertainty associated with their analytical methods, reporting values from 0.6 to 71% for Cd and from 0.04 to 74% for Pb.

Table 1. Preconcentration methods involving liquid-phase extraction used in the analysis of soils, plants and related materials

Analyte(s)	Matrix	Method	Digestion	Reagent(s)	Detector	Notes	CRMs	Reference
As	Maize, soil	CPE	HNO_3/H_2O_2 Microwave	Triton X-114® surfactant; ammonium pyrrolidine dithiocarbamate chelator	ETAAS	Preconcentration factor 50; LOD 0.025 μg g^{-1}	BCR CRM 189 Wholemeal Flour	[279]
Au	Sediment, soil, water	DLLME	HNO_3/HCl Ultrasound	Tetra-*n*-butylammonium ion pairing agent; acetone dispersant, chlorobenzene solvent	ETAAS	Preconcentration factor 220; LOD 42 ng L^{-1} (water), 1.5 ng g^{-1} (solids)	NIST SRMs 2782 Industrial Sludge, 2710 and 2711 Montana Soil	[110]
Cd	Soil, water	LPME		S-methyl-3-salicylidine dithiocarbazate chelator; chloroform solvent	ETAAS	Preconcentration factor 100; LOD 6 pg mL^{-1}		[280]
Cr	Hair, sediment, soil, water	LPME	HNO_3/H_2O_2 Hot plate	2-(4-methoxybenzoyl)-N'-benzylidine-3-(4-methoxyphenyl)-3-oxo-N-phenyl-propono hydrazide chelator; MIBK solvent	FAAS	LOD 0.32 μg L^{-1}; Cr^{III} measured then total Cr after reduction of Cr^{VI}	LGC 6019 River Water, RTC-CRM044 Soil	[281]
Cu	Soil, water	CPE		Triton X-100® surfactant; N, N'-bis(salicylaldehyde) ethylenediamine chelator	FAAS	LOD 0.82 μg L^{-1}		[282]
Mn, Ni	Soil, vegetable, water	DLLME		Ionic liquid solvent	FAAS	Preconcentration factor 80; LOD 0.93 μg L^{-1} for Ni and 0.52 μg L^{-1} for Mn	NWRI TMDW-500 Drinking Water	[283]
Se, Te	Soil, water	LPME	Cold acid digestion	Ammonium pyrrolidine carbodithioate chelator; toluene solvent	ETAAS	Preconcentration factor 500; LOD 5 ng L^{-1} for Se and 4 ng L^{-1} for Te	NIST SRM 1643e Trace Elements in Water	[284]

CPE = cloud-point extraction, DLLME = dispersive liquid-liquid microextraction, LPME = liquid phase microextraction

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

Analyte(s)	Matrix	Carrier	Detector	Notes	CRMs	Reference
Cd, Co, Cu, Fe, Mn, Ni, Pb	Environmental samples, food	Thulium hydroxide	FAAS	LOD 0.1-1.6 μg L^{-1}	NWRI TMDA 54.4 Fortified Lake Water, HR-1 Humber River Sediment	[285]
Cd, Co, Cu, Fe, Mn, Ni, Pb	Food, plants, water	Neodymium hydroxide	FAAS	LOD 0.2-3.3 μg L^{-1}	NIST SRM 1570a Spinach Leaves, NWRI TMDA 54.4 Fortified Lake Water	[286]
Cd, Cu	Hazelnut, tea, tobacco, water	2-{[4-(4-fluorophenyl)-5-sulfanyl-4H-1,2,4-triazol-3-yl]methyl}-4-{[(4-fluorophenyl)methylene]amino}-5-(4-methylphenyl)-2,4-dihydro-3H-1,2,4-triazol-3-one	FAAS	LOD 1.5 μg L^{-1} for Cu and 0.45 μg L^{-1} for Cd	NWRI TMDW-5000 Drinking Water, HPS SA-C Sandy Soil C	[287]
Co, Cr, Fe, Pb, Zn	Hair, peritoneal fluid, sediment, soil, urine, water	Cu-N-benzoyl-N-phenyl-hydroxylamine	FAAS	LOD 0.3-2.3 μg L^{-1}	NIST SRM 1547 Peach leaves, LGC 6019 River water	[288]
Fe, Ni	Food, water	Cu-4-(2-pyridylazo)-resorcinol	FAAS	LOD 0.68 μg L^{-1} for Fe, 0.43 μg L^{-1} for Ni	NWRI TMDA 54.4 Fortified Lake Water, NIST SRM 1568a Rice Flour, GBW 07605 Tea	[289]

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

Analyte(s)	Matrix	Substrate coating	Column substrate	Detector	Notes	CRMs (or other validation)	Reference
Bi	Sediment, water	Gallic acid	Silica gel	FAAS	Preconcentration factor 250; LOD 0.26 ng mL^{-1}	GBW 07350 Sediment	[290]
Bi	Blood	None	Bamboo carbon	HG-AFS, ICP-MS	LOD 13 ng L^{-1} HG-AFS, 10 ng L^{-1}ICP-MS	BCR CRM 320 River Sediment	[291]
Cd, Cu	Plant, water	N'-{4-methylidene}-5-(4-H)oxazolone]phenyl}acetamide	Alumina	FAAS	Preconcentration factor 160 for Cd, 400 for Cu; LOD 0.05 ng mL^{-1} for Cd, 0.06 ng mL^{-1} for Cu	NIES No.2 Pond Sediment, No.3 Chlorella	[292]
Cd, Ni, Zn	Leaves, fish liver, water	Aminophenol and azo derivative	Polyurethane foam	FAAS	Preconcentration factors 125 (aminophenol foam) and 430-500 (azo derivative foam); LOD 0.06-0.22 μg L^{-1}	NIST SRM 1577b Bovine Liver	[293]
Cd, Pb	water	Nitroso R salt resin	Amberlite XAD-2	FAAS		IAEA 336 Lichen, NIST SRM 1515 Apple Leaves	[294]
Co, Fe, Ni	Carrot, parsley, water	*Penicillium digitatum*	Pumice stone	FAAS	LOD 1.4-1.9 ng mL^{-1}	GBW 07605 Tea Leaves	[101]
Cr	Eggplant, tobacco, water	None	Tea industry waste activated carbon	FAAS	Preconcentration factor 50; LOD 0.27 μg L^{-1}; Cr^{III} measured then total Cr after reduction of Cr^{VI}	NRWI TMDW-500 Drinking Water, HPS SA-C Sandy Soil C	[295]
Cr, Cu, Ni, Zn	Plant, soil, water	4-[(*E*)-3-phenylallylidene)amino]benzenethiol	Sepabeads SP70	FAAS	Preconcentration factor 157; LOD 1.6-2.6 μg L^{-1}	Spike recovery	[296]

Cu, Fe, Mn, Pb	Plants, rice flour	None	Multi-walled carbon nanotubes	FAAS	Preconcentration factor 20; LOD 3.5-8.0 μg L^{-1}	NWRI TMDA 54.4 Fortified Lake Water, HR-1 Humber River Sediment	297
Cu, Fe, Ni	Spices	None	Diaion HP-20	FAAS	Analytes sorbed as com plexes with 2-[2-[α(2-hydroxy-5-sulfophenylazo)benzylidine]hydrazino]benzoic acid; LOD 0.72-1.4 μg L^{-1}	NIST SRM 1515 Apple Leaves	298
Cu, Mn, Zn	Fruit, soil, water	3-((1H-indol-3-yl)(3-nitrophenol)methyl)-1H-indole	Triton X-100® coated PVC	FAAS	Preconcentration factor 270; LOD 1.8-2.1 ng mL^{-1}	Spike recovery	299
Hg	Water	None	Multi-walled carbon nanotubes	CV-AAS	LOD 0.012 μg L^{-1}	INCT-PVTL-6 Polish Virginia Tobacco Leaves	300
Mn	Leaves, water	2-aminothiophenol	Amberlite XAD-4	FAAS	Preconcentration factor 14; LOD 2.0 μg L^{-1}	NIST SRMs 1515 Apple Leaves, 1570 Spinach Leaves	301
Mo	Liver, milk, vegetables	None	Activated carbon	FAAS	Analytes sorbed as complexes with cupferron; Preconcentration factor 100; LOD 1.0 ng mL^{-1}	GBW 07602 (NCS DC73348) Bush Branches and Leaves	302
Pb	Sediment, water	none	Ion-imprinted mesoporous sorbent	FAAS	LOD 15 μg L^{-1}	GBW 08619 Water	303
Pb	Water	4-(8-hydroxyquinoline-azo)benzamidine	Activated carbon	ICP-AES	Preconcentration factor 100; LOD 0.43 ng mL^{-1}	GBW 08301 River Sediment, 08302 Tibet Soil	304
Pb	Water	Ionic liquid	Silica	FAAS	Preconcentration factor 185; LOD 0.7 μg L^{-1}	NIST SRM 2709 San Joaquin Soil	86

4 Analysis of geological materials

This section highlights noteworthy areas of research and development in the analysis of geological materials by atomic spectrometric and complementary analytical techniques published since the last Update[1]. In this review period there were insufficient developments in sample dissolution, preconcentration and separation techniques to warrant a separate section as in previous reviews; instead they have been included with the relevant instrumental technique.

Several trends were apparent in recent publications related to the analysis of geological materials. While techniques such as FAAS, ICP-AES and ICP-MS reached a state of maturity some time ago, it is evident that MC-ICP-MS and LA-MC-ICP-MS are now so widely available in geoanalytical laboratories that the literature is dominated by applications papers that include little of novelty from an analytical perspective. However, this trend should not mask the vital research required to underpin and improve the quality of the geochemical data on which any interpretation is based[305]. One of the main purposes of this Update is to highlight such developments. Another observation is the high proportion of analytical and applications papers with Chinese authors, reflecting the rise of atomic spectrometry in China over the past 25 years[306].

4.1 Quality control and reference materials

The role of ISO's Committee on Reference Materials in formalising *procedures for the certification of RMs* was described by Botha[307]. She provided an instructive background to ISO Guide 34, which specified a list of metrologically valid procedures for the characterisation of a RM, together with a case study to demonstrate its application. This paper should be read in conjunction with Kane's account of the experience of the International Association of Geoanalysts (IAG) as a certifying body[308]. She described some of the practical problems that arise in the application of the recommendations of the ISO Guides to specific certification exercises. Some of the most challenging issues in this respect were deriving uncertainties compliant with the Guide to Uncertainty in Measurement (GUM) and establishing the traceability of certified values.

Problems can arise if a *common analytical terminology* is not adopted across scientific fields. Potts[309] noted the general low awareness of the correct use of metrological terms across the geoanalytical community and the influence that editors of scientific journals can exercise by promoting good practice in the use of international terminology. The difficulties faced in the geoanalytical community by some of the revised definitions in the International Vocabulary of Metrology were eloquently expressed by Ramsey[310]. Ideally, definitions should make the meaning of a term clear to specialists and generalists alike but this is not always the case in practice. He suggested reasons for this lack of clarity and proposed improvements in terminology to address the real concerns of producers and users of the geoanalytical measurements alike.

A review of *RMs*[311] *in geoanalytical and environmental research* (322 refs) identified that in spite of the number of RMs available, additional homogenous microanalytical RMs and certified materials for stable isotope work were still required. In an annual review of papers containing data on RMs of geological interest, Jochum *et al.*[312] included a selection of Chinese journals for the first time. They noted that the Chinese journal *Rock and Mineral Analysis* contained many relevant articles, demonstrating the importance of RMs for calibration and quality assurance in Chinese laboratories. Many laboratories in China have been developing increasing numbers of geochemical RMs, which are certified and issued by GBW. As many of the data on these RMs are inaccessible to western scientists because of the linguistic barrier, an overview of Chinese RMs in current use has been made available[311].

Several groups of workers have reported *extensive data sets for the isotopic contents of some commonly used geological RMs*. Jochum *et al.*[313] undertook an extensive study of USGS GSD-1G (Synthetic Glass) and the MPI-DING reference glasses, involving a range of bulk and microanalytical techniques in 13 laboratories. Reference and information values were determined for B, Ca, H, Hf, Li, Nd, Pb, Si, Sr, Th and U isotopes using the recommendations of the IAG for certification of RMs. The glasses were homogeneous for nearly all isotope systems from ng to mg levels of test mass. Matthews *et al.*[314] reported bulk Th and U concentrations and isotope ratios of five microanalytical RMs from the USGS and MPI-DING series of glass RMs. A comparison of results for the powdered and glass versions of BHVO-2 (Basalt, Hawaiian Volcano Observatory) and BCR-2 (Basalt, Colombia River) showed small but significant differences, particularly for U concentrations and ^{230}Th/^{238}U in BHVO-2. Chauvel *et al.*[315] presented major and trace element data as well as Hf, Nd, Pb and Sr isotopic compositions for eight basalt and five sediment RMs. In contrast to the volcanic rocks, the sediments were characterised by much larger uncertainties on all measurements, even though the concentrations were not particularly low. It was concluded that the sediment powders were inhomogeneous so very fine grinding of the sediments, dissolution of relatively large test masses and the systematic use of Parr bombs were recommended.

The *$n(^{238}U)/n(^{235}U)$ of NIST SRM 960* (Uranium Metal Standard), for which the commonly accepted consensus value is 137.88, has been re-measured in a collaborative effort between several geochemistry laboratories and the IRMM[316]. The new value is about 0.031% lower than the old one, is SI traceable and has an uncertainty calculated according to GUM. However, this value should not be considered as the officially certified value as certification is currently underway at the US Department of Energy laboratories in New Brunswick.

Although there are several well-characterised *natural zircon RMs*, many are limited in quantity or originate from relatively inaccessible locations. A potential new secondary RM is from the Penglai zircon megacrysts, hosted in Early Pliocene alkaline basalts from Hainan Island, China and available in large quantities[317]. New U-Pb ages were determined by SIMS and ID-TIMS, O isotopes by SIMS and IRMS, and Hf isotopes by LA- and solution-MC-ICP-MS. Results suggested that this material was fairly homogeneous in Hf and O isotopic compositions. These zircons may be too young and contain variable high amounts of common Pb to be a suitable RM for the calibration of unknown samples, but could act as a QC material for microbeam U-Pb measurements of young zircons (<10 Ma). Li *et al.*[318] made some reconnaissance measurements of Li concentrations and isotope ratios by SIMS in five commonly used zircon standards. Only one of the five RMs, the University of Mainz M257 zircon standard, was sufficiently homogeneous to be employed as a working RM for this purpose.

Other *potential RMs for microanalysis* have been characterised recently. Kennedy *et al.*[319] assessed the potential of Grenville Skarn Titanite from the Canadian Shield as a RM for microanalytical Pb-Th-U dating. Careful selection of chips for TIMS and of analysis areas during SIMS allowed high quality isotopic data to be obtained from these large crystals of titanite. Garnet P1, a megacryst garnet from the Premier kimberlite, had a suitable composition to act as a QC monitor for the routine analysis of garnets by EPMA in the exploration for kimberlite deposits[320]. Four new silicate glasses, prepared by fusion of about 1 kg each of powdered material to provide basalt, syenite, soil and andesite RMs of natural composition for microanalytical work were characterised using a variety of techniques[321]. In general these glasses, referred to, as 'Chinese Geological Standard Glasses' are well homogenised with respect to major and trace elements. Preliminary reference and information values for 55 elements, together with the analytical uncertainties were reported.

Crowley[322] provided some baseline data on the mineralogical and chemical composition of some RMs prepared from naturally occurring marble and carbonatite for the *measurement of C and O isotopes*. The NIST NBS 19 (TS-Limestone) and IAEA-CO-1 (Marble) RMs were essentially pure samples of calcite containing minimal (<1%) amounts of quartz whereas both NIST NBS 18 (Calcite) and IAEA-CO-8 (Calcite) contained a range of phases, in addition to the calcite. It was recommended that IAEA-CO-8, which was estimated to contain at least 4% non-carbonate material, should be refined to remove the non-carbonate material or be replaced by a material of more suitable composition.

4.2 Solid sample introduction

4.2.1 Laser ablation

Several *recent reviews of advances in LA-ICP-MS* have been written from a geoanalytical perspective. In their distillation of papers published in 2008 and 2009, Arevalo *et al.*[323] (55 refs) highlighted developments in fs laser ablation, ablation cell design and the influence of different carrier gases. Continued efforts to improve the precision and accuracy of LA-ICP-MS measurements were also noted. In a complementary paper, Woodhead[324] (111 refs) summarised the diversity of geological problems that are now being addressed through the application of LA-ICP-MS data.

Laser ablation has been adopted in many geoanalytical laboratories for the *quantitative determination of trace elements in bulk rocks* in preference to lengthy sample preparation procedures. For the determination of 54 major and trace elements in carbonate materials by LA-ICP-MS, Chen *et al.*[325] assumed that the sum of the major matrix components expressed as carbonates was equal to 100%, and corrected the minor element concentrations on this basis, as an alternative to applying an internal standard obtained by stoichiometry considerations or another technique. Calibration against multiple silicate glass RMs gave results that agreed with data from solution ICP-MS to within 10% for Mg, Mn, Sc, Sr and REEs. When calibrating against MPI-DING reference glasses rather than NIST SRM 610, improved accuracy was achieved for small laser spot sizes (≤32 μm), whereas no difference was observed for spot sizes of 44 and 60 μm.

The ablation of fire assay buttons to determine PGEs after fusion of the original material with a lead or nickel sulphide collector is not a new concept. However, Vanhaecke *et al.*[326] have now evaluated the merits of a 795 nm fs LA system, combined with a quadrupole-based ICP-MS instrument equipped with DRC, for analysing Pb fire assay buttons. The use of matrix-matched standards permitted accurate results to be obtained despite the severe signal suppression observed on introduction of the heavy matrix into the ICP. Spectral interferences on some of the target nuclides due to the presence of Pb^{2+} ions were overcome by pressurising the reaction cell with ammonia. The performance of the fs LA system was superior to that of a 193 nm excimer-based ns system giving a 3–10 fold improvement in detection capabilities, as well as better accuracy. The LODs for Au, Pd, Pt and Rh were <0.010 $\mu g\ g^{-1}$.

Matrix effects observed during LA are well documented if not totally understood. Hu *et al.*[327] confirmed the difference in laser-induced fractionation when ablating the NIST SRMs 610-614 (Trace Elements in Glass) compared to ablating natural silicate materials. They advocated the use of USGS RMs GSD-1G and GSE-1G (synthetic glasses) in the analysis of geological samples by LA-ICP-MS. Janney *et al.*[328] studied matrix effects during *in situ* measurement of Mg and Si isotope ratios in natural and silicate glasses using two different 193 nm LA-MC-ICP-MS systems. Isotopic fractionation at the ablation site was the main source of matrix effects when employing a double-focusing mass spectrometer. In contrast, the large non-mass-dependent matrix effects observed when measuring Mg isotope ratios using a single-focussing instrument were attributed to non-linear scattering processes occurring in the hexapole collision cell as Mg became increasingly diluted by matrix elements.

A procedure[329] for *measurement of the abundances of Ga, Ge and first-row transition metals* used a 213 nm laser coupled to a SF-ICP-MS instrument at medium resolution ($M/\Delta M = 4000$). The analytical protocol hinged on maximising the ablation rate of the laser system and the sensitivity of the ICP-MS instrument, while minimising the production of isobaric oxide and argide polyatomic ions. Using ^{43}Ca as an internal standard and multiple reference glasses for calibration, the uncertainties were *ca.* ±3% (2s) and measured concentrations were statistically indistinguishable from reference values (except for Ti) when analysing MPI-DING reference glasses.

Laser-induced fractionation may necessitate the development of *matrix-matched calibration standards*. In order to prepare a calibration standard for multi-elemental analysis of sulfide minerals, Danyushevsky *et al.*[330] doped a mixture of CANMET RMs RTS-4 (Sulphide Ore Mill Tailings) and CZN-1 (Zinc Concentrate) with a range of trace elements before fusing with lithium borate flux in a conventional XRF bead preparation technique. The standard was shown to be homogenous to <5% for all 55 elements determined except for Au, Pt, Se and Tl. Its use significantly improved the accuracy of sulfide analysis compared to the use of other RMs, such as the NIST 600 series.

Hou *et al.*[331] assessed the feasibility of determining *B isotope ratios in geological materials by LA-MC-ICP-MS*. Instrumental mass bias and isotope fractionation were calibrated using the standard-sample-standard bracketing method. The δ^{11}B values obtained were consistent, within analytical error, with literature values or those obtained by positive ionisation TIMS. Long-term analytical precisions were ±0.58‰ (2σ, n=50) for IAEA B4 (Tourmaline) and ±0.97‰ (2σ, n=57) for an in-house tourmaline standard IMR RB1, both of which had relatively high B contents (31,400 ppm for B4). No matrix effects were encountered when different calibration standards were used. In a similar approach, Fietzke *et al.*[332] developed a LA-MC-ICP-MS method based on a 193 nm excimer laser for measuring B isotope ratios in carbonates with a reproducibility of 0.5‰ (SD) within single periods of sample ablation for samples containing 35 ppm B. The instrumental fractionation behaviour was similar for three types of standard: NIST SRMs 610-612 (Trace Elements in Glass), carbonate pressed powder pellets and seawater evaporates. This finding provided confidence to employ NIST glasses as internal standards, thus overcoming the problem of finding a suitable matrix-matched carbonate standard.

A novel method[333] for the *determination of Th and U isotope ratios in silicate glasses and carbonates* by LA-ICP-MS, applicable to samples with U concentrations as low as 0.4 $\mu g\ g^{-1}$, used a 213 nm Nd:YAG laser connected to a single collector SF–ICP-MS instrument. Measurements were made on zircon, travertine and silicate glass RMs of basaltic to intermediate composition. Corrections for U-Th elemental fractionation made using USGS BCR-2G (Basalt Glass) as the reference standard appeared to be equally applicable to zircon and calcium carbonate within the errors of the technique. This was not the case when NIST SRM 612 (Trace Elements in Glass) was employed for this purpose. Precision and accuracy were largely independent of

Th and U concentrations and of the Th/U ratio. The use of SF-ICP-MS provided the potential to combine Th-U isotope ratio determinations with additional multi-element and isotope analyses during a single line scan.

Although protocols for U-Pb dating of zircons are well established, there are still significant challenges in the *dating of apatite by LA-ICP-MS*. Chew *et al.*[334] assessed methods for correcting for both the presence of "common Pb" and the occurrence of laser-induced fractionation when determining U-Pb and Th-Pb ages of apatites. Mathematical corrections based on either ^{207}Pb or ^{208}Pb were the most suitable for dating single grain detrital apatites. Laser-induced Pb/U fractionation was relatively minor and easily corrected for by using the back-calculated intercept of the time-resolved signal. Of the seven well-known apatites analysed using a 193 nm excimer laser coupled to single collector ICP-MS, the Kovdor carbonatite apatite exhibited the most promise as an apatite standard for dating by LA-ICP-MS.

An ICP-QMS instrument[335] equipped with an *extended range pulse counting detector* was capable of making isotope ratio measurements that require a substantial dynamic range, such as U-Pb dating of zircons, without having to switch between pulse counting and analogue modes. The linear response of the detector over the range 2,000 to 110 million cps indicated that the next generation of quadrupole instruments could be viable alternatives to MC-ICP-MS instruments.

Fisher *et al.*[336] identified three main factors that needed to be addressed in order to improve the accuracy and precision of *measurements of Sm-Nd isotopic ratios by LA-MC-ICP-MS*. Correction for the isobaric interference of ^{144}Sm on ^{147}Nd was calculated using the measured ^{149}Sm concentration and recently published Sm isotopic abundances. Samarium mass bias was determined using an exponential law and the ^{147}Sm/^{149}Sm measured in the sample. Accurate measurement of ^{147}Sm/^{144}Nd, which is vital for providing robust initial Nd isotope compositions, was achieved by calibration to an external glass RM synthesised specifically for this purpose. The accuracy of the proposed LA-MC-ICP-MS protocol was demonstrated by comparing values obtained by ID-TIMS in the analysis of several well-characterised mineral RMs (apatite, titanite, allanite and monazite). The instrumental configuration in this study also allowed the determination of Eu and Gd concentrations, thereby permitting simultaneous determination of Eu anomalies along with Sm-Nd isotopic composition. A similar approach was adopted by Iizuka *et al.*[337], who demonstrated that the substantial (>5%) fractionation of ^{147}Sm/^{144}Nd observed during the ablation of monazite could be corrected using a suitable matrix-matched standard. An Archean monazite standard 16-F-6 provided correction of ^{147}Sm/^{144}Nd fractionation with an uncertainty of *ca.* 1%. Other improvements to the analytical precision and accuracy were achieved by calibration of the Faraday amplifier responses and normalisation of Nd isotope ratios using a synthetic monazite standard containing a negligible amount of Sm.

A rigorous assessment of *the accuracy and precision of the measurement of* ^{176}*Hf/*^{177}*Hf in rutile by LA-MC-ICP-MS* was undertaken by Ewing *et al.*[338]. Key features of the protocol adopted were interpolation between long baseline measurements every ten analyses, correction for all potential isobaric interferences and application of an external correction for Hf mass bias, when appropriate, based on regular measurements of a synthetic rutile containing *ca.* 5000 ppm Hf. Because rutile contains negligible Yb, the Yb mass bias coefficient was calculated from several measurements on zircon using a 233 μm diameter crater. The precision obtained was typically of the order of ±10-12 ε_{Hf} units for individual analyses of rutile with 40-50 ppm Hf.

Laser ablation ICP-MS is now established as a routine technique for *multi-element analysis of fluid inclusions* and has proved to be a powerful tool in understanding processes of ore formation[339]. Quantitative measurement of anions in an individual fluid inclusion by LA-ICP-MS is more challenging than that of cations because of their high first IPs, resulting in relatively low sensitivities, and polyatomic interferences on S from ambient air, e.g. $^{16}O^{16}O^+$. In the determination of Br, Cl and S in fluid inclusions, Seo *et al.*[340] used a scapolite mineral sample as a RM for Br and Cl and NIST SRM 610 (Trace Elements in Glass) as a RM for S. For reliable S measurements, repeated cleaning of the ablation chamber and careful background corrections for the host material were critical in order to minimise S background signals caused by remobilisation of S from the inner surfaces of the ablation chamber. For a 25-35 μm diameter fluid inclusion, the LODs were 17±10 μg g^{-1}, 340±220 μg g^{-1} and 160±110 μg g^{-1} for Br, Cl and S respectively.

One of the first attempts to determine accurate *Pb isotope ratios of individual fluid inclusions* by LA-MC-ICP-MS has been reported by Pettke *et al.*[341]. They prepared fluid inclusion standards with known Pb and Tl isotopic compositions and explored different schemes for correcting for mass bias. Isotope ratios were derived from bulk integration of the transient signal. Instrumental mass bias correction was based on Tl admixed *via* desolvated nebulisation. Isotopic fractionation at the ablation site posed no limitation on accuracy provided the ablation was well controlled. The external precision of ablation of NIST SRM 610 (Trace Elements in Glass) with a 60 µm beam was ±0.011% (2SD, relative) for $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$, whereas inclusion-to-inclusion reproducibilities for the same ratios were ±0.05% (2SD, n=11); each inclusion contained *ca.* 1 ng Pb. The accuracy of the technique was demonstrated by analysis of synthetic fluid inclusions containing NIST SRM 981 (Natural Lead (Isotopic)).

Construction of an *improved cryogenic sample cell for LA-ICP-MS* enabled Aerts *et al.*[342] to measure quartz solubility by diamond-trap experiments. The ablation chamber, cooled by Peltier elements and insulated to prevent condensation, was capable of cooling samples to -35 °C.

A novel technique that has great potential for geochemical analysis is *Laser Ablation of a Sample in Liquid (LASIL)*, in which the ablation occurs at a solid sample surface submerged in a liquid[343]. The ablation could be performed in a 25 µL freestanding droplet, which acted as a micro-laser cavity, to produce a stable suspension of particles. Post-ablation chemistry provided true solutions for direct calibration against aqueous standards. As LASIL was an off-line sampling technique, the resulting solution was not confined to analysis by ICP-MS. Initial experiments using NIST SRM 611 (Trace Elements in Glass) were very promising.

4.2.2 Laser-induced breakdown spectroscopy

Laser-induced breakdown spectroscopy is used on a regular basis for making geochemical measurements, often in remote locations or for QC purposes. *Recent applications of LIBS* included elemental mapping of speleothems[344], quantitative measurements of loss on ignition in iron ore[345], the identification of REEs and associated elements in monazite sands[346] and characterisation of historical building materials according to the quarries from which they were mined[347].

Methods for analysis by LIBS without the use of calibration samples continue to be reported even though matrix-matched calibration standards are normally required and *calibration-free LIBS* is often only semi-quantitative. Praher *et al.*[348] developed a new algorithm for more accurate calibration-free LIBS of samples containing CaO, Fe_2O_3 and MgO as major constituents. In the algorithm the width and intensity of selected lines were corrected for self-absorption by a fast iteration procedure. The calculated oxide concentrations were within 10%, 20% and 5% of the nominal contents for Fe_2O_3, MgO and CaO respectively, with RSDs of <20%.

Interest in the application of LIBS to geochemical analysis has been stimulated in part by *space missions to Mars and other planets*. Ongoing studies to develop miniaturised LIBS systems to perform *in situ* analysis under Martian atmospheric conditions demonstrated that the LODs and accuracy of such instruments for multielemental measurements were very promising[349]. Agreement with certified or independently measured compositions was typically within 10-20%. Tucker *et al.*[350] acquired LIBS spectra for 100 igneous rocks at 9 m standoff distance under Mars atmospheric conditions to determine the most effective protocols for calibrating and modelling the data to predict major element compositions. Their prescription for a successful calibration was also applicable to terrestrial studies. Another study focussed on the measurement of sulfur in a simulated Mars atmosphere[351]. Partial least squares analysis was successful at modelling S concentrations for a subset of samples with similar matrices. Optimal results were obtained by restricting the wavelength range to channels close to the most intense S lines ~ 540-570 nm. The lowest S content in this study was 0.76 wt% S. A decision tree for the identification and quantification of S in remote LIBS analysis was constructed on the basis of these experiments.

Another laser-based technique, *off-axis integrated cavity output spectroscopy*, is capable of measuring stable isotope ratios in gases. A novel prototype portable instrument[352] based on this technology had potential for rapid measurements of the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ composition of carbonate minerals in the field. Carbon and oxygen ratios were recorded from absorption spectra (in the near-IR region) of carbon dioxide evolved from acidification of carbonates. Analyses were accurate to better than 0.5‰ for both $\delta^{13}C$ and $\delta^{18}O$ and could be improved by applying standard-sample bracketing corrections.

4.3 Instrumental analysis

4.3.1 Atomic absorption spectrometry

Because of the technique's relatively low sensitivity, FAAS usually requires preconcentration of the elements to be determined. For the *measurement of Pd in gold ores*, Bulut *et al.*[353] employed a N_4O_2 mixed-donor-ligand derivative (TNACIN) as chelating agent on Amberlite XAD-2010 resin. After a mixed acid digestion in

$HCl/HNO_3/HF$, the samples were added to the column and Pd eluted with 1.0 M HCl in acetone. The eluate was evaporated to near dryness and taken up in 2 mL of 1.0 M HNO_3 before analysis by FAAS. The analytical LOD of 0.82 µg L^{-1} was calculated from the instrumental LOD and the overall preconcentration factor of 250. Precision was <1% (n=10) at a concentration of 1.25 µg mL^{-1} Pd.

Kaya and Volkan[354] designed a new chloride-generation system for the *determination of Ge in geochemical samples* by nitrous oxide–acetylene AAS. A glass cylindrical reaction chamber with four valves was positioned in a home-made oven and the temperature maintained at 80±3 °C: this increased the vapour pressure of the $GeCl_4$ generated by 10-fold. Hydrochloric acid and the digested rock sample were introduced into the system and the reaction chamber closed for 1 min before the $GeCl_4$ produced was swept to the AAS nebuliser by argon carrier gas. After the measurement period, the carrier gas was used to purge the system and dehumidify the reactor. The LOD was 0.01 ng mL^{-1} (3s) and the precision (RSD) 2.4% (n=9) for a Ge solution of 1 ng mL^{-1}.

4.3.2 Atomic emission spectrometry

A review of publications for 2008-2009 involving the use of AAS, ICP-AES, INAA and XRF spectrometry for geochemical analysis noted that *novel developments in ICP-AES* are relatively scarce and tend to involve new methods of sample preparation[355]. This trend has continued. Padmasubashini and Murty[356] investigated the use of activated carbon and chitin for batch preconcentration of Nb and Ta prior to determination by ICP-AES. After fumation with HF/H_2SO_4 on a sand bath and fusing of the dried residue with $KHSO_4$, the samples were dissolved in a mixture of H_2SO_4 and H_2O_2. Ascorbic acid was added to an aliquot of the sample digest and the pH adjusted to 3 before adding the carbon or chitin. After an hour, the carbon/chitin was processed to recover the analytes in a final solution of 0.2% citric acid. The accuracy of the method for Nb was demonstrated by the analysis of a range of NIST SRMs; similar results were obtained using either activiated carbon or chitin for the solid phase extraction. However, the method lacked adequate sensitivity to measure Ta in these materials.

Sulfate in francolite, the major mineral phase of phosphorites, can act as a potential indicator of seawater sulfate concentrations in palaeoenvironmental reconstructions. Goldberg *et al.*[357] evaluated *methods for extracting trace sulfate from* *francolite and measuring its concentration and sulfur isotopic composition.* They advocated the use of 10% v/v acetic acid to remove calcite, dolomite and ankerite without affecting francolite, and rinsing several times with 10% v/v NaCl to remove calcium sulfates and absorbed sulfates. For S isotope determination, sample combustion at 600 °C was found to be an efficient way of removing non-francolite S-bearing phases. Techniques evaluated for the quantification of trace amounts of sulfate included XRF spectrometry (fused bead and pressed powder pellet), elemental analysis with a CNS analyser, gravimetry and ICP-AES. The most accurate S data were obtained by dissolution of the sample in 10% HCl and measurement by ICP-AES, except when sulfate concentrations were very low, in which case the gravimetric method was the only option.

4.3.3 Inductively coupled plasma mass spectrometry

4.3.3.1 Quadrupole ICP-MS. Inductively coupled plasma MS has revolutionised elemental and isotopic analysis in many fields since its commercial introduction in 1983. For a historical perspective on the development of ICP-MS in relation to environmental analysis, a *review* by Beauchemin[227] (243 references) should be consulted. A summary of trends in the coupling of IC with ICP-MS for the determination of halide and metal species in various sample types, including geological materials, is available[358] (131 references).

Although alkali fusion is an efficient method for the decomposition of silicate rocks, it can be prone to high blanks arising from impurities in the flux. Shimizu *et al.*[359] developed a *flux-free fusion* that did not require the resulting fused glasses to be homogenous as long as any refractory minerals were completely dissolved. A pressed pellet of powdered sample was fused in a platinum crucible inside a Siliconit® tube furnace at 1600 °C for 2-3 mins. After quenching, the glass was dissolved using a (2 + 1) mixture of HF and $HClO_4$ before final uptake in 2% HNO_3 with a trace of HF and analysis by ICP-QMS. Complete digestion of felsic samples containing refractory minerals such as zircon and tourmaline was demonstrated. For most of the elements measured the data obtained were well within the range of those previously published for the geological RMs analysed. However, the method was not considered to be valid for highly volatile elements such as Pb and Tl.

The advantages of ICP-MS over ICP-AES for the *measurement of REEs in geological samples* have long been recognised as simpler spectra and better LODs. In a comparison of ICP spectrometric techniques, Ardini *et al.*[360] confirmed that both ICP-QMS and SF-ICP-MS operating in high resolution mode could provide accurate data for REEs in sediment digests with a precision of 3-8% (RSD). The LODs were 18-52 ng g^{-1} for SF-ICP-MS and 10-780 ng g^{-1} for ICP-QMS. Although attempts were made to measure the REEs concentrations in these solutions directly by ICP-AES, rather than after separation, through careful selection of emission wavelengths and the application of on-line internal standardisation, Ho, Lu, Pr, Tb, and Tm could not be measured because of strong spectral interferences and insufficient sensitivity. The same authors[361] also investigated the measurement of REEs in geological samples with an ICP-QMS instrument equipped with a DRC pressurised with oxygen. Only some of the REEs were amenable to measurement at *m/z* M+16 and Eu, Gd, Lu and Yb had to be determined in standard mode. Although it was possible to switch from the vented to the pressurised mode relatively rapidly, no direct comparison was carried out of the accuracy achievable by the DRC method with that of the normal mode using mathematical corrections to compensate for polyatomic interferences.

Despite the fact that the NiS fire assay is a mature technique for *accurate determination of Au and PGEs*, questions have been raised about its reliability. Savard *et al.*[362] compared the performance of NiS fire assay followed by Te coprecipitation to that of high-pressure asher (HPA) digestion combined with ID for the determination of PGEs in ten geological RMs by ICP-MS. No systematic differences in the recoveries of Ir, Os, Pd, Pt and Ru were discerned. The advantages of NiS fire assay were that it was possible to include Au and Rh in the analytical scheme, the relatively large test mass (15 g) reduced the nugget effect and it was faster and less expensive than HPA. In contrast, it was possible to determine Re in addition to the PGEs when using ID-HPA. This technique, which had lower blank levels and consequently lower LODs, provided better precision for the analysis of homogeneous samples with low PGE content but was more susceptible to the nugget effect as ID techniques can only treat small test masses, e.g. 2 g. This valuable study showed that these techniques should be regarded as complementary rather than competing approaches and should lay to rest any further argument on this subject.

Information on long-term instrumental performance in other laboratories can be extremely valuable for comparative purposes. Ulrich *et al.*[363] reported long-term observations on Ba and Nd oxide formation in relation to the determination of REEs by ICP-QMS, as well as the interferences of DyO^+ and ZrO^+ on Hf and Ag, respectively. The efficacy of corrections for these interferences was demonstrated by data from 51 individual analysis of the USGS RM BHVO-2 (Basalt, Hawaiian Volcanic Observatory) at high and low rates of oxide formation. Because the use of enriched isotopes ^{6}Li, ^{147}Sm and ^{235}U as internal standards required the measurement of Li, Sm and U isotope ratios, data for these ratios in rock RMs USGS AGV-2 (Andesite) and GSJ JA-3 (Andesite) were acquired over a three-year period. Long-term RSDs were 7% for $^{6}Li/^{7}Li$, 0.67% for $^{147}Sm/^{149}Sm$ and 1.01% for $^{235}U/^{238}U$. The authors argued that the accurate and moderately precise Pb isotope data obtainable by ICP-QMS make the technique particularly suitable for the analysis of samples with very low Pb content, which otherwise would need to be analysed with ion counters on SF instruments.

4.3.3.2 Sector field ICP-MS. Rapid advances in MC-ICP-MS technology and its widespread availability in recent years have stimulated an unprecedented growth in the measurement of *isotope ratios for geochemical applications*. In contrast, significant analytical developments have not been as evident as in previous years.

There is much interest in the *determination of B isotopes in environmental samples by MC-ICP-MS*. Ni *et al.*[364] investigated inter-laboratory biases in $\delta^{11}B$ values for foraminiferal shells, which have the potential to provide records of palaeo-oceanic pH. There was no fundamental bias between TE NTIMS and MC-ICP-MS in the measurement of the $\delta^{11}B$ values of pure boric acid solutions. However, $\delta^{11}B$ values for non-foraminiferal carbonates were about 2‰ lighter when measured by NTIMS, whereas $\delta^{11}B$ values for foraminifera measured by the same NTIMS procedure were 2 to 6‰ heavier than those measured by MC-ICP-MS. It was inferred that organic material released on dissolution of the forminifera gave rise to biases in the NTIMS measurements. No residual organic material was present in the MC-ICP-MS determinations as the matrix was separated from the sample before analysis. Use of a standard addition approach allowed accurate (±0.35‰, 2σ) $\delta^{11}B$ measurements of foraminifera by MC-ICP-MS to be obtained. Treatment of the samples with concentrated H_2O_2 did not completely resolve the discrepancy in the TIMS values and it was concluded that very careful protocols are required to ensure that the inaccuracies in the NTIMS approach are kept to a minimum. Although the procedures developed by Vogl *et al.*[160] concerned the measurement of B isotopes in water and food samples, many of the principles discussed are applicable to a much wider range of environmental samples. The protocols were based on a three-step matrix separation using IC followed by single collector SF-ICP-MS in either low or medium resolution mode. Expanded uncertainties were 1.4-1.6‰ at low resolution and 2.9-3.2‰ at medium resolution. Their author's assessment of matrix tolerance to 2 mg kg^{-1} of alkaline and alkaline earth elements in the final measurement solution was particularly relevant, as this is not always appreciated in the determination of non-traditional isotopes where variations of only a few ‰ can be very significant. The reader may also wish to note the approach of Guerrot *et al.*[159] to the separation of B isotopes from seawater using Amberlite IRA-743 B-specific resin prior to determination by MC-ICP-MS.

In principle, sample introduction into MC-ICP-MS *via* a *demountable direct injection high efficiency nebuliser (d-DIHEN)* offers several advantages for isotopic measurements of B and other elements that suffer from memory effects. Sensitivity should be improved because 100% of the sample is introduced into the plasma and considerably shorter washout times should result. In practice, however, these potential benefits are often not realised because of difficulties in the operation and optimisation of this type of nebuliser. In the procedure adopted by Louvat *et al.*[158], the spray from a d-DIHEN was first optimised outside of the torch. The major parameter affecting the quality of the spray was the distance between the capillary and the needle tip, which was adjusted under a 4x magnification binocular microscope. Once the device was inserted into the plasma torch, another important consideration was the distance between the needle tip and the end of the auxiliary gas tube in the torch. This determined the proximity of the plasma to the nebuliser. Compared to the use of a dual Scott – cyclonic spray chamber, sensitivity for B was improved 2-5 times and the washout time was up to 10 times shorter. A stabilisation time of approximately two hours after lighting the plasma was required before the MC-ICP-MS instrument was ready for B isotope measurements. The long-term stability of the $^{11}B/^{10}B$ ratio using sample-standard bracketing was 0.25‰ (2s). A comparison between $\delta^{11}B$ values of four modern corals determined by d-DIHEN MC-ICP-MS and positive TIMS showed excellent agreement with a bias of <0.4‰.

Most *Mg isotope studies* focus on the evolution of the early solar system, for which high precision measurements are necessary. Adoption of new chemical purification techniques[365] resulted in superior figures of merit for the MC-ICP-MS determination of Mg ratios in silicate rocks than was previously possible. Although time-consuming, the six-step Mg purification scheme ensured 99.9% recovery and excellent separation of Mg from elements that can pose direct isobaric interferences or influence instrumental mass bias compared to standards. A double-spike method employing an approximately equal mixture of highly purified ^{24}Mg and ^{26}Mg was used to determine the absolute isotopic ratios. Total procedural blanks were <15 ng, a negligible level compared to the typical 200 µg amount of Mg processed through the purification protocol. External reproducibilities of 2.5, 20, 195 and 235 ppm were reported for the measurement of ^{26}Mg* (excess ^{26}Mg resulting from the *in situ* decay of ^{26}Al), relative ^{25}Mg/^{24}Mg (without ^{24}Mg-^{26}Mg spike), absolute ^{25}Mg/^{24}Mg and absolute ^{26}Mg/^{24}Mg, respectively. The chemical purification steps in this procedure were a modification of the technique reported by Schiller *et al.*[366] in a study of ^{26}Al-^{26}Mg dating of basaltic meteorites.

A method developed by Zambardi and Poitrasson[367] sets a new benchmark for the precision achievable in the *measurement of Si isotopes in silicate rocks by MC-ICP-MS*. Samples were decomposed by fusion with NaOH in silver crucibles and the Si was purified by ion-exchange chromatography using Bio-Rad AG50-X12 cation-specific resin. A 1 µg g^{-1} Mg spike was added to correct for mass bias. Total procedural blanks for ^{28}Si were 30 ng, corresponding to 0.1-0.2% of the ^{28}Si signal. Over a year, the reproducibilities for a natural silicate rock were ±0.05 and ±0.08‰ for δ^{29}Si and δ^{30}Si, respectively (2s, n=42). These values were significantly better than those reported by other workers, especially for δ^{30}Si. Measurement of δ^{29}Si and δ^{30}Si in 12 geological RMs led to the conclusion that spiking the solutions with Mg for on-line mass bias correction provided much more reliable results than the simple sample-calibrator bracketing approach.

It is difficult to discern much of novelty in some recent analytical papers concerned with *radiogenic isotope systems*[368-369]. While investigating the calibration of in-house Th isotope standards, Mason and Henderson[370] documented all of the relevant issues involved in the correction of instrumental biases when undertaking high precision measurements for U-Th chronology. Linear law mass bias provided a reasonable approximation for Th-U and Th mass fractionation and its use was likely to lead to inaccuracies of <0.5‰. A MC-ICP-MS method[369] for determining Nd and Sm concentrations and Nd isotope ratios in geological samples used a ^{149}Sm–^{150}Nd spike. The values obtained for a selection of silicate RMs agreed with previously published values to within 1% for Nd and Sm concentrations and to within 22 ppm (2σ) for ^{143}Nd/^{144}Nd ratios. The internal run precision was better than 15 ppm (2σ) for ^{143}Nd/^{144}Nd. However, these results did not justify the claim that MC-ICP-MS was superior to TIMS given that modern TIMS instruments are capable of precisions of <5 ppm for the same ratio.

Chemical abrasion is used on a regular basis in U–Pb zircon geochronology for minimising or removing the effects of Pb loss. This involves high temperature annealing to repair radiation damage in zircon and prevents preferential leaching of Pb relative to U during multi-step digestions. Data obtained using such techniques[371] indicated that multi-step chemical abrasion in its current form could not be routinely applied to baddeleyite geochronology. However, a newly developed HCl–HF discrete digestion method was successful at isolating the zircon and baddeleyite components of composite grains. Initial HCl digestion steps completely dissolved the baddeleyite grains with minimal impact to the zircons rims and intergrowths. The zircon was then dissolved in a single or two-step HF digestion to determine the date of the igneous or metamorphic over-growths.

Because of the very small quantities of Pa and Ra in volcanic rocks and the extreme ratios between the daughter and parent isotopes, *mass spectrometric analyses of U-Th-Pa-Ra disequilibria* in such samples are analytically challenging. Although numerous studies have reported U-series disequilibria measurements in silicate samples, Koornneef *et al.*[372] were the first to publish a study in which all the elements were separated from a single spike sample aliquot and the same solution used to determine elemental concentrations and isotopic compositions by MC-ICP-MS. In this way, any errors due to sample heterogeneity were removed. The method was also less time-consuming than previously used methods because it involved fewer columns in the chemical separation and the concentrations and isotope ratios were determined on the same sample aliquot. The reproducibility of ^{234}U/^{238}U, ^{230}Th/^{238}U, ^{231}Pa/^{235}U and ^{226}Ra/^{230}Th activity ratios from ten separate dissolutions of USGS BCR-2 (Basalt, Columbia River) were 0.4%, 1.4%, 1.1% and 2.4% (2SD) respectively. The method was suitable for samples with Pa and Ra contents as low as *ca.* 25 fg.

Yang *et al.*[373] described a straightforward one-step chemical separation using anion-exchange chromatography on AG1-X8 resin which gave 90% *recovery of Hf for isotopic analysis* by MC-ICP-MS. Rock powders were subjected to a HNO_3-HF mixed acid attack and boric acid used to complex any residual fluorides. The total procedural blank of <20 pg was considered to be negligible. From multiple measurements of several USGS RMs and standard zircons and baddeleyite used in U-Pb geochronology, the authors concluded that the procedure provided a significant improvement in Hf isotope determinations by MC-ICP-MS because of the greatly reduced time in sample preparation without compromising the precision and accuracy of the measurements.

Yin *et al.*[41] reviewed the current status of research on *Hg isotope variations in the environment*. For high precision measurements by MC-ICP-MS, a cold Hg vapour was usually introduced into the plasma. This allowed Tl to be introduced, *via* a desolvating nebuliser, to correct for instrumental mass bias. Measurement precision was good enough (<0.2‰) for natural fractionation processes to be evaluated. The results were used to elucidate the sources and the fate of Hg in the environment.

4.3.4 Other mass spectrometric techniques

4.3.4.1 TIMS. *High precision measurements of K isotopes*, previously dependent on SIMS analysis, have applications in cosmochemistry and ^{41}Ca–^{41}K chronometry studies. Precise measurements of K isotope ratios are challenging because of the large ratios involved and their accuracy can be compromised by issues related to isobaric interferences and abundance sensitivity. A novel TIMS method[374] for the measurement of ^{39}K, ^{40}K and ^{41}K utilised the expanded dynamic range and improved S/N of a Triton^{TM} instrument that had an amplifier array adapted to analyse samples of terrestrial basalts. Samples were prepared by IC using AG50W-X8 200-400 mesh cation-exchange resin in Teflon micro-columns. For samples containing 150 ng K, reproducibilities of 100 ppm (2 SD) for ^{41}K/^{39}K were achieved; for smaller samples with 10 ng K, the precision was 200 ppm or better. The method was thus suitable for high-precision K isotope measurements of material from refractory inclusions in chondritic meteorites. A simple procedure[375], based on spiking with ^{40}K and use of the power law to correct for mass fractionation in the determination of K isotopes in natural samples, gave a precision of <0.1% for ^{41}K/^{41}Ca in the dating of micas and other K-rich minerals.

The excellent external precisions achievable make TIMS the favoured technique for the *measurement of Nd isotope ratios in geological materials*. As an example of the reproducibilities that can be achieved[376], external precisions of ±15 ppm for $^{143}Nd/^{144}Nd$ (2σ) and ±8 ppm for $^{142}Nd/^{144}Nd$ (2σ) were reported for USGS RM BCR-2 (Basalt, Colombia River). Complete acid dissolution of rock samples was achieved in a two-step procedure involving both Savillex and Parr bombs. Chemical separation *via* a three column protocol ensured efficient removal of Ce and Sm from Nd, a necessary prerequisite for high precision measurements of Nd isotope ratios by TIMS. Copard *et al.*[377] described the rigorous cleaning techniques needed to measure Nd isotopic compositions of living and fossil deep sea coral species. These data were required to investigate whether it was possible to reconstruct seawater Nd isotope signatures and past changes in ocean circulation. After mechanical and chemical cleaning of samples to avoid Nd contamination from manganese oxide and iron hydroxide coatings, Nd was purified using a combination of Eichrom TRU and Ln resin columns. The Nd isotopic compositions of modern coral were similar to those of adjacent water masses.

As noted in section 4.3.3.2, chemical abrasion in conjunction with MC-ICP-MS or TIMS is now used regularly in *U–Pb zircon geochronology* for minimising or removing the effects of Pb loss. While its successful application on low to moderately damaged zircons is not disputed, Das and Davis[378] investigated its application to Precambrian zircons with a wide range of radiation damage. Annealing at 1450 °C followed by HF leaching worked well for restoring primary U-Pb ages of weakly to moderately damaged uncracked zircons. Cracked grains were more effectively treated by annealing at 1000 °C so that disturbed Pb remained more accessible to leach solutions. However, once a zircon had been severely damaged, CA was unlikely to yield primary U-Pb ages from the grain. In a detailed multi-step CA-TIMS analysis of a suite of natural zircons, Mattinson[379] confirmed that the accepted value for the ^{235}U decay constant was too low by *ca.* 0.087%. As other research had suggested the need for revision of the natural $^{235}U/^{238}U$ ratio as well, Mattinson strongly recommended that both values be revised and adopted for use in U-Pb geochronology. Schoene *et al.*[380] used the same sample solution to perform both highly precise ID-TIMS measurements for U-Pb geochronology and trace element analysis by SF-ICP-MS. Following zircon dissolution and ion-exchange separation to obtain a fraction for U-Pb dating by TIMS, the "zircon wash" fraction was collected, dried and redissolved in a solution of HNO_3 and HF doped with 1 ppb Ir as internal standard. This approach yielded a large amount of additional geochemical information for very little additional effort. Future work will involve applying the method to a wider range of minerals and elements in a plethora of geological environments.

Richter *et al.*[381] reported significant improvements in routine U isotope ratio measurements using a *modified TE method for TIMS*. It was developed for use in the nuclear industry but can be applied to geochemical analysis. In the modified protocol, the TE process was interrupted on a regular basis to permit correction for peak tailing, internal calibration of a secondary electron multiplier versus the Faraday cups, peak-centering and refocusing of the ion source. The measurement uncertainty (k=2) for $n(^{234}U)/\ n(^{238}U)$ of better than 0.12%, which represented an improvement of 5-10 fold compared to the normal TE protocol. The modified TE method presented a significant improvement in terms of uncertainty and accuracy and has been applied to other studies, e.g. Ca isotope measurements. To encourage its adoption, it has been incorporated into the operating software of the Triton™ TIMS instrument.

4.3.4.2 SIMS. As noted in a review by Widenbeck[382], *applications of SIMS in Earth sciences* increased over the past decade as more SIMS facilities became available and matrix effects were understood better. The impact of the SHRIMP on research into lunar geochronology has been described from an Australian perspective [383].

Although SIMS is routinely used for *U-Pb age determinations* in zircons at a lateral resolution of 10-30 μm, dating at a scale of *ca.* 5 μm remains challenging. Lui *et al.*[384] demonstrated that a CAMECA 1280 SIMS instrument was capable of *in situ* U-Pb dating of zircons at a scale of <5 μm using a Gaussian illumination O_2^- or O^- primary beam. Three zircon standards with a range of ages were dated with 1-2% precision and accuracy by pooling 15-20 repeat measurements; these figures of merit were comparable to those obtained by routine measurements at the 10-30 μm scale with an alternative primary beam. The Gaussian illumination primary beam produced shallow craters *ca.* 500 nm, resulting in negligible U/Pb fractionation. Chamberlain *et al.*[385] reported U-Pb dating of micro-baddeleyite crystals as small as 3 μm in mafic rocks with a CAMECA 1270 SIMS instrument, using the field aperture in the transfer column to screen out ions from host phases. The method relied on locating target grains in thin section by X-ray mapping and back-scattered electron imaging prior to SIMS.

Researchers at Wisconsin[386] developed a SIMS method for the *determination of Fe, O and S isotope ratios in geological materials* at a resolution of 10 μm.

Accuracy and precision of 0.3‰ was achieved routinely for $^{18}O/^{16}O$ measurements using Faraday cup detectors and a 10 µm primary Cs^+ beam. Smaller beams of 3 µm to <1 µm yielded precisions of 0.7–2‰ using electron multipliers in pulse-counting mode for measuring ^{18}O. Analytical artefacts related to sample topography and crystal orientation effects were overcome by careful sample preparation to ensure that variations in surface relief were of the order of a few µm or less for individual samples. Anomalies resulting from crystal orientation were reduced by decreasing the sputtering energy of the primary ions from 20 to 10 keV. Further experiments at the same SIMS facility[387] showed that *in situ* S isotope measurements could be performed with a grain-to-grain precision of ±0.3‰ in chalcopyrite, galena and pyrrhotite, and ±0.2‰ in pyrite (2 SD). The precision for sphalerite under comparable conditions was ±1.7‰. This degraded performance was related to preferred directions of beam transmission within the sphalerite crystal structure and was improved by reducing the depth of the analysis pits or lowering the total impact energy of the primary ions. Rollion-Bard and Marin-Carbonne[388] demonstrated that instrumental mass fractionation in the SIMS determination of O isotopes in carbonates was related to the MgO content for carbonates containing small amounts of iron and manganese (FeO + MnO <1 wt%). For Fe- and Mn-rich carbonates, the Fe and Mn contents needed to be taken into account when correcting for IMF. Because of the large variation in the Mg content of natural carbonates, calibration using carbonate RMs with different Mg contents was advocated to obtain accurate $\delta^{18}O$ data by SIMS.

Quantification of the ^{40}Ca–^{40}K decay system by SIMS is not usually undertaken as it requires a mass resolution of 25,000 for full separation of the two ions. Harrison *et al.*[389] overcame this difficulty by measuring the doubly-charged species Ca^{2+} and K^{2+} instead. Their method exploited the fact that although the first IPs of K and Ca are similar, the second IP of K is nearly three times that of Ca. The K^{2+} species were suppressed by a factor of *ca.* 10^3 relative to the singly-charged species, permitting direct $^{40}Ca^{2+}/^{39}K^{2+}$ dating in K-rich minerals at moderate mass resolution (*ca.* 4000).

4.3.5 X-ray techniques

For a comprehensive *review of recent applications of XRF spectrometry to the analysis of geological materials*, our sister Update[5] on XRF should be consulted. A short summary[355] of trends in XRF analysis in relation to the Earth Sciences identified significant developments in 3D µ-XRF and advances in enabling XRF and XRD analysis to be performed on the same spot.

The ability to determine *iodine in situ by XRF techniques* has been exploited. A combination of EPMA and sychrontron-based µ-XRF[390] was used to map the micro-scale distribution of I in biocarbonates in a marine clayey formation in order to understand natural I behaviour in clay rock systems. Bioaccumulation of I in carbonate shells of *ca*. 160 Ma in age was demonstrated. However, the difference in results obtained by these two techniques highlighted the experimental challenges in measuring I in calcium carbonates. In a study of Pd-Pt aggregates from an alluvial deposit[391], SFXRF confirmed the biogenic origin of the precious metal compounds, which were found to contain surprisingly high levels of I, in the range 10–120 µg g^{-1}. Of the three techniques used, only SFXRF was sufficiently sensitive; PIXE and a mobile µ-XRF spectrometer failed to detect I in these samples.

XRF techniques have been used to characterise *As speciation in geothermal systems*. *In situ* measurements of the redox state and molecular structure of As in rhyolitic peraluminous glass by XAFS[392] provided information on species controlling the partitioning of As between hydrous melts and aqueous fluids. Hydrous silicate melts were shown to be important in transporting As, and similar elements like B and Sb, in shallow magmatic hydrothermal settings because of their high affinity for water and hydroxide ligands. James-Smith *et al.*[393] employed SRXRF to determine As speciation in fluid inclusions in samples from gold ore deposits. Arsenic *K* edge XAS spectra were obtained from fluid inclusions at temperatures ranging from 25 to 200 °C and compared with spectra of aqueous As^{III} and As^{V} solutions and minerals. However, the XAS information was limited by the rapid photooxidation that occurred in all inclusions, despite the relatively low photon flux density used, as a result of a complex interaction between redox-sensitive complexes in solution and the products of water radiolysis generated by the beam.

5 Glossary of terms

2D	two-dimensional
3D	three-dimensional
AAS	atomic absorption spectrometry
ACGIH	American Conference of Governmental Industrial Hygienists
AES	atomic emission spectrometry
AFS	atomic fluorescence spectrometry
AMS	accelerator mass spectrometry
APDC	ammonium pyrrolidine dithiocarbamate
ASPAC	The Australasian Soil and Plant Analysis Council
ASTM	American Society for Testing and Materials
ASU	Atomic Spectrometry Updates
BAM	Federal Institute for Materials Research and Testing (Germany)
BCR	Community Bureau of Reference (*of the European Community*)
CCD	charge coupled detector
CANMET	Canada Centre for Mineral and Energy Technology
CE	capillary electrophoresis
CNS	carbon,nitrogen,sulfur
CPE	cloud point extraction
CRM	certified reference material
CS	continuum source
CV	cold vapour
DDTC	diethyldithiocarbamate
DGT	diffusion gradient in thin films
d-DIHEN	demountable direct injection high efficiency nebuliser
DIHEN	direct injection high efficiency nebuliser
DLLME	dispersive liquid liquid microextraction
DMA	dimethyl arsenic acid
DRC	dynamic reaction cell
ED	energy dispersive
EDS	energy dispersive spectrometry
EDTA	ethyldiaminetetraacetic acid

EDXRF	energy dispersive X-ray fluorescence
EN	European Standard
EPA	Environmental Protection Agency
EPMA	electron probe microanalyser
ERM	European Reference Material
ESI-MS	electrospray ionisation mass spectrometry
ETA	electrothermal atomisation
ETAAS	electrothermal atomic absorption spectrometry
ETV	electrothermal vaporisation
EU	European Union
FAAS	flame atomic absorption spectrometry
FTIR	Fourier transform infrared
GBW	National Research Center for Certified Reference Materials (China)
GC	gas chromatography
GSJ	Geological Survey of Japan
GUM	Guide to Uncertainity in Measurement
HG	hydride generation
Hg_p	particulate bound mercury
HPA	high pressure asher
HPLC	high performance liquid chromatography
HPS	High Purity Standards (USA)
HR	high resolution
IAEA	International Atomic Energy Agency
IAG	International Association of Geoanalysts
IC	ion chromatography
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma atomic emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
ICP-QMS	inductively coupled plasma quadrupole mass spectrometry
ID	isotope dilution
IDA	isotope dilution analysis
IMF	instrumental mass fractionation
IMR	Insitute of Mineral Resources (China)

INAA	instrumental neutron activation analysis
INCT	Institute of Nuclear Chemistry and Technology (Poland)
IP	ionisation potential
IR	infrared
IRMM	Institute for Reference Materials and Measurements
IRMS	isotope ratio mass spectrometry
ISO	International Organisation for Standardization
LA	laser ablation
LASIL	laser ablation of a sample in liquid
LEAFS	laser excited atomic fluorescence spectrometry
LGC	Laboratory of the Government Chemist
LIBS	laser induced breakdown spectroscopy
LLME	liquid liquid microextraction
LOD	limit of detection
LPME	liquid drop microextraction
Ma	million years
MALDI	matrix-assisted laser desorption/ionisation
MC	multicollector
MeHg	methyl mercury
MIBK	methyl isobutyl ketone
MIP	microwave induced plasma
MMA	monomethylarsonic acid
MPI	Max Planck Institute (Germany)
MRI	magnetic resonance imaging
MS	mass spectrometry
m/z	mass to charge ratio
NAA	neutron activation analysis
NaDDTC	sodium diethyldithiocarbamate
NCS	China National Analysis Centre for Iron and Steel
Nd:YAG	neodymium doped:yttrium aluminum garnet
NIES	National Institute for Environmental Sciences (Japan)
NIST	National Institute of Standards and Technology (USA)
NMR	nuclear magnetic resonance
NRCC	National Research Council of Canada

NTIMS	negative thermal ionisation mass spectrometry
NWRI	National Water Research Institute (Canada)
OECD	Organisation for Economic Co-operation and Development
OTC	organotin compound
PFA	perfluoroalkyl
PGE	platinum group element
PIGE	particle induced gamma-ray emission
PIXE	particle induced X-ray emission
PLS	partial least square
$PM_{1.0}$	particulate matter (with an aerodynamic diameter of up to 1.0 µm)
$PM_{2.5}$	particulate matter (with an aerodynamic diameter of up to 2.5 µm)
$PM_{10-2.5}$	particulate matter (with an aerodynamic diameter of between 2.5 and 10 µm)
PM_{10}	particulate matter (with an aerodynamic diameter of up to 10 µm)
ppm	part per million
pptv	part per trillion volume
PTFE	poly(tetrafluoroethylene)
PVC	poly(vinyl chloride)
QA	quality assurance
QC	quality control
REE	rare earth element
REMCO	Committee on Reference Materials (ISO technical committee)
RGM	reactive gas phase mercury
RM	reference material
RP	reversed phase
RSD	relative standard deviation
RTC	Resource Techology Corporation (USA)
s	standard deviation of sample
SD	standard deviation
$SeCys_2$	selenocycstine
SEM	scanning electron microscopy
SeMet	selenomethionine
SF	sector field
SHRIMP	sensitive high resolution ion microprobe
SI	système international d'unités

σ	population standard deviation
SIMS	secondary ion mass spectrometry
S/N	signal to noise ratio
SPE	solid phase extraction
SR	synchrotron radiation
SRM	standard reference material
SRXRF	synchrotron radiation X-ray fluorescence
STXM	scanning transmission X-ray microscopy
TD	thermal desorption
TDS	total dissolved solids
TE	total evaporation
TEM	transmission electron microscopy
TIMS	thermal ionisation mass spectrometry
TOF	time of flight
TXRF	total reflection X-ray fluorescence
USGS	United States Geological Survey
USN	ultrasonic nebuliser
UV	ultra violet
UV/VIS	ultra violet / visible
VUV	vacuum ultraviolet
WDXRF	wavelength dispersive X-ray fluorescence
XAFS	X-ray absorption fine structure spectrometry
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectrometry
XRD	X-ray diffraction
XRF	X-ray fluorescence
YAG	yttrium aluminium garnet

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