Atomic spectrometry update. Environmental analysis

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This is the 28th 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 2011 and August 2012 and continues the series of Atomic Spectrometry Updates (ASUs) in Environmental Analysis[1] *that should be read in conjunction with other related ASUs 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 spectrometry*[5] *and industrial analysis: metals, chemicals and advanced materials*[6].

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. Other noteworthy areas of interest include: development of LIBS and MS systems for in-situ measurement; and the use of synchrotron-based X-ray techniques for the solid-state speciation of airborne particles. In the field of water analysis, as in previous years, the main areas of activity are the development, some may say redevelopment, of preconcentration and extraction procedures and elemental speciation protocols for elements such as As, Cr and Sb. There is increasing interest in developing portable instrumentation for field use using AES or XRF techniques. In the field of soil and plant analysis, noteworthy developments this year include the emergence of nanoSIMS as a tool for trace element imaging, and greater use of techniques such as LIBS and PXRF with chemometric data processing to provide overall identification or classification of samples, rather than accurate quantification of specific analytes. Of concern however is the *publication of several articles 'reinventing the wheel'. For example, one study compared the analysis of dust by PIXE with results obtained by ICP-AES following* HNO_3 *digestion according to USEPA Method 3050B*[7]*, and another compared XRF data for soil samples with data from ICP-MS analysis of aqua regia soil digests*[8]*. Unsurprisingly, both concluded that the X-ray technique produced higher concentrations for some elements than pseudo-total digestion! This suggests that there is a need for greater engagement between analytical and environmental geochemists to ensure that users of atomic spectrometry – and perhaps also some journal editors – are aware of the established scope of different analytical techniques and methods. Developments in geochemical analysis include: production and certification of new geological RMs with well-constrained isotopic contents or the recertification of existing RMs to include such isotopic data; optimisation of LA-ICP-MS and TIMS techniques and the reported use of a new ICP-MS instrument equipped with a Mattauch-Herzog type array detector to deliver improved isotopic measurement capabilities.*

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

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1 Air analysis

1.1 Review papers

Reviews of *measurement methodologies for specific elements* addressed: arsenic speciation in air (46 references)[9]; PGEs in environmental and biological matrices (245 references)[10]; and, uniquely, analytical methods for the determination of osmium tetroxide (41 references)[11]. Of particular interest in a review on biological aerosol particles was the application of chemical tracers combined with the use of optical and MS techniques in studying the origins, pathways and fate of such particles (564 references)[12]. Review papers discussing specific instrument developments are discussed in the relevant sections below.

1.2 Sampling techniques

Whilst monitoring workers' exposure to airborne particles through the use of *personal air samplers* is a common and mature activity in many countries, some unknowns remain and ongoing work seeks to complete missing information gaps. Following previous work[13], Sleeth and Vincent[14] assessed, for the first time, the performance of commonly used inhalable aerosol samplers at windspeeds below 0.2 m s^{-1} in a controlled laboratory setting. Such windspeeds are often encountered in many workplaces. The inhalable aerosol samplers tested included the commonly used IOM, Button and GSP designs as well as the closed-faced cassette sampler. Although the samplers tested met the inhalability criterion relatively well, there was a significant effect of wind speed on sampling efficiency, with lower wind speeds clearly associated with an increase in sampling efficiency. The output from NIOSH has been notable this year. In a laboratory-based study[15], quartz in coal dust was sampled using high volume air samplers (4–10 L min^{-1}) to increase the sensitivity of the underlying FTIR and/or XRD measurement techniques. Sampling at higher volumes allowed more sample mass per unit time to be collected compared to lower flow rate samplers (*ca*. 2 L min^{-1}) currently used. It would be interesting to see how well such samplers work in the field given that, being bulkier and heavier, wearability of such samplers could be an issue. Conclusions, reported in previous ASU reviews[16], that losses of sampled particles to the walls of an air sampler, compared to masses collected on a filter, can be substantial, have been confirmed[17]. This ratio is clearly dependent, however, upon workplace activities and the size distributions of particles emitted from processes. An assessment was made of sampling efficiencies of three inhalable fraction samplers for solid and liquid particles (droplets) facing the wind[18]. Button and IOM samplers as well as a new prototype high volume sampler – the RASCAL – were evaluated. Large droplets had low penetration efficiencies through screened inlets and particle bounce, for solid particles, was an important determinant of aspiration and sampling efficiencies for samplers with screened inlets. In trials[19] of the Button, GSP and IOM samplers to collect welding fume under real world conditions, the range of fume concentrations was 2–5 mg m^{-3} and the sampled fume particle size distribution was characterised by a bimodal log-normal distribution, with MMADs of 0.7 µm and 8.2 µm. Based upon gravimetric analysis of fume-loaded filters, the Button and GSP samplers showed comparable performance but filters samples collected with the IOM sampler had fume masses typically 10% lower than those collected with the other two sampler designs.

Workers' potential exposure to *engineered nanoparticles*, which are often metallic in nature, is a field that is attracting increased attention. The sampling of nanoparticles can, however, be challenging. A low–pressure drop preselector was designed and validated for the elimination of co-sampled particles larger than 450 nm in diameter[20]. The latter can cause measurement artifacts in the determination of concentration and size of nanoparticles. A prototype portable thermophoretic precipitator sampler[21] for the collection of nanosize particles, in the range 1–300 nm, subsequently characterised by EM techniques, had a collection efficiency of 14–99% when challenged to polydisperse submicron NaCl test aerosols. Analysis of TEM images of samples collected confirmed that the size distributions of collected particles were in good agreement with those determined using FMPS. Discussions at the first international scientific workshop on the harmonisation of strategies to measure and analyse exposure to manufactured nano-objects in workplace air have been summarised[22]. This complemented an article on a strategy for assessing workplace exposures to nanomaterials published by US-based researchers[23].

Sampling and measurement of trace levels of gaseous Hg species in ambient air remains a challenge. Brown *et al.*[24] examined the short and long term memory effects associated with measurements of Hg^0 in air collected on gold-coated silica adsorption tubes. Studies were undertaken to quantify the extent of such effects and their dependence upon relevant measurement parameters, such as the number of heating cycles used for each analysis, age of adsorption tube, mass of Hg on adsorption tubes and tube storage times between sampling events. Long-term memory effects were due to adsorption of Hg within the bulk gold in the sorbent tube so sufficient time was needed for this Hg to diffuse to the gold surface and subsequently be liberated during a heating cycle. Recommendations made included: conditioning of new adsorption tubes prior to use in the field; deploying adsorption tubes to field locations where they are likely to sample similar masses of Hg during successive sampling periods; and logging of sorbent tube usage for audit purposes. A cost-effective passive sampling system for the collection of Hg^0 incorporated a polycarbonate external shield designed to reduce turbulence and exposure to precipitation and dust and a diffusive housing made from expanded PTFE tubing[25]. Of the two collection surfaces investigated, gold sputter-coated quartz plates and silver wires, the gold surface exhibited the better performance although gradual passivation could limit reuse. The system was considered to hold promise although further evaluations of collection surfaces were required.

The *performance of new ambient air sampling systems* continues to attract attention. A novel multi-filter sampler enabled the simultaneous collection of four PM_{10} and four $PM_{2.5}$ samples[26]. By using optimised critical orifices behind each filter assembly, a uniform airflow through each filter was achieved by using just one mass flow controller for each of the PM_{10} or $PM_{2.5}$ sampling lines. In contrast, existing multi-filter sampling systems typically require the use of multiple (and costly) mass flow controllers to ensure consistent flow through filters. An impressive portable modular multipollutant sampling system for measuring emissions from stationary and/or mobile sources could be broken down into modules for ease of transportation[27]. A sample of air was collected in the first module, diluted with filtered air, and transported to two measurement modules for both real time gas and particle analysis. For gases, various sensors could be employed and for particles, particle size distribution, particle number and mass concentration, and black carbon measurements could be performed. Futher samples could also be collected on various media for subsequent laboratory analysis. A Ford Transit van was customised as a mobile aerosol research laboratory for effective stationary and mobile field measurements[28]. It contained a range of sampling and measurement systems so both gaseous and particulate measurements could be undertaken. The attention to detail, as with the modular system described above, was impressive as exemplified by the system designed to vent exhaust emissions from the van's engine at least 25 m downwind, to minimise contamination.

Development of samplers to enable the collection of *elemental data at high temporal resolution* is a goal shared by a number of research groups. Watson and his group[29] developed an off-line method for the retrospective compositional analysis of filter tape samples retrieved from a β–attenuation monitor, a sampling device widely used in air monitoring networks to provide high resolution aerosol mass data. Sample filter punches could be analysed for elemental and morphological composition by XRF and SEM-EDS, respectively. Their study demonstrated the feasibility of analysing filter tape deposits for source attribution studies, especially for short duration fugitive dust events. Pancras and Landis[30], building on previous work[31], evaluated the performance of their semi-continuous elements-in-aerosol ($PM_{2.5}$) sampler (SEAS-III). The system was designed to sample particles continuously and to deposit them, at 30 minute time intervals, into vials containing water. Following acidification, the dilute–acid–extractable content of airborne particles was analysed using HR-ICP-MS. Over a period of four weeks of sampling, the up-time for two samplers was 90 and 84%. Agreement between the results for the two samplers, based upon subsequent elemental analysis, was typically better than 25%. Although measurements correlated well with elemental data derived from the analysis of filters samples obtained using a co-located $PM_{2.5}$ FRM sampler, the recoveries for Al, Fe, Pb, Sb and Sn were low because of their low solubilities in the collection medium.

Health-based assessments of exposure to particulate matter are leading researchers to investigate both the *physical-chemical and toxicological makeup of particles*. A comparison of the chemical and oxidative characteristics of particulate matter collected by different sampling systems – filters, impactors (nano-MOUDI) and biosamplers – showed good agreement overall for particulate matter collection efficiency and chemical composition[32]. Differences found in the results for the biosampler method, when compared with those for the filter and impactor approaches, could be explained by the different sample pretreatments used in the laboratory. A microwave digestion was used to dissolve the particulate residues for both filter and impactor samples but particles collected using the biosampler, as a slurry suspension, were simply acidified and analysed by SF-ICP-MS inferring incomplete extraction. Similarly, whilst the measured redox activities of water extract from filter and impactor derived samples were comparable, that derived from the analysis of the biosampler slurry was substantially higher. If such slurries were filtered however, all results became comparable suggesting that the contribution of insoluble particles to the redox activity of particulate matter should be considered in future evaluations of health impacts of exposure to particulate matter. A system consisting of a Dekati gravimetric impactor and a porous tube diluter was developed for the chemical and toxicological characterisation of particles[33]. Claimed advantages over previously used high volume sampling methods were compactness for field use, straightforward preparation of sample collection substrates and high extraction efficiencies.

1.3 Reference materials

A new *reference material*, NMIJ CRM 7308-a (Polycyclic Aromatic Hydrocarbons and Toxic Elements in Tunnel Dust), was certified for Cd, Cr, Mn, Ni and Pb concentrations[34]. A review article[35](92 references) on the current state of the availability and practicability of soot (carbon) particle SRMs resulted from a workshop held by a group of 50 internationally acclaimed experts in June 2011. Whilst no suitable SRMs met all criteria established by internationally recognised organisations that set protocols for the production of RMs, a number of potential candidates have been proposed and it is hoped that momentum from this workshop can drive developments forward. Although solution nebulisation is commonly used to produce test aerosols from liquid solutions, it can be difficult to produce physically and chemically pure nanoparticles from a particle solution in deionised water due to impurities in the water. An international collaboration between researchers in South Korea and the USA[36] demonstrated that it is possible to reduce the production of residual particles eleven-fold in deionised water by using a reverse osmosis membrane filtration procedure under high pressure (900 psi). The authors concluded that this commonly used and inexpensive approach, historically used to produce larger particles, could now be used to produce purer nanoparticles.

1.4 Sample preparation

Procedures and recommendations for the *handling and processing of nanoparticle samples* are highly topical. A Swiss group[37] reviewed (62 references) the critical aspects of sample handling for direct nanoparticle analysis and the analytical challenges faced when using A4F-ICP-MS techniques to provide size and compositional data. Sample dilution, changes in pH or ionic strength had significant impact on nanoparticle properties such as changes in size distribution or chemical transformation, e.g. dissolution. It was recommended that a fast sceening test such as dynamic light scattering should be initially employed to test the extent of such transformations prior to analysis for size-classified, chemical analysis using single particle ICP-MS or A4F-ICP-MS. The charge on nanoparticles could also influence the separation efficiency and recovery rate. Shifts in retention times in A4F resulting from the charge interactions between particles and the membrane materials could be more pronounced for particles <10 nm diameter. The authors concluded that such interactions should be studied in more detail. An ICP-AES method[38] was used to investigate the efficiency of coating metal nanoparticles with inert silica to reduce their biotoxicity. An HNO_3/HF acid digestion was used to derive a total elemental content whilst a less agrresive *aqua regia* leach procedure dissolved metallic particles not encapsulated in the silica coating. The coating of welding fume particles with silica derived from the tetramethylsilane precursor added to the shield weld gas had an efficiency of between 14 and 39%. It was suggested that this approach could be used for other coating efficiency studies.

Re-examination of established dissolution procedures has its merits. A hybrid method[39], involving both acid digestion and slurry nebulisation, has been developed for the determination of crustal (Al, Ca, Fe, Mg and Si) and trace (Ba, Cu, K, Mn, Na, Sr, Ti and Zn) elements in airborne particulate matter. Initially, a warm HNO_3/H_2O_2 mixture was used to dissolve the soluble fraction and the sampling filter substrate and the remaining insoluble fraction homogenised. The insoluble fraction was then analysed by slurry nebulisation ICP-AES. The analytical precisions for bulk crustal elements were 3.3-6.8 % and for trace elements 3.5–9.1%. The LODs (3 σ of the signal derived from the analysis of blank filters) ranged from 1 ng m^{-3} (Sr) to 71 ng m^{-3} (Ca). Results were comparable with those obtained using a high–performance closed–vessel microwave–assisted digestion procedure.

Valuable paleoclimatic information can be derived from the *analysis of ice cores*. Typically, ICP-MS analyses are performed on melted and acidified ice core samples, which contain particulate matter usually enriched in trace elements. Consequently, it is important to ascertain the effect of acidification on such particles and to assess, if any, the contribution of dust leaching to the trace element budget of ice cores. A systematic study[40] over several weeks of the leaching characteristics in dilute HNO_3 of powdered rock standards from various lithologies demonstrated that acidification of ice core samples that contain mineral dust results in time- and mineral-dependent leaching of trace elements. Ideally, core samples would require full digestion or filtering to eliminate error induced by partial leaching of trapped dust particles. The authors acknowledged that this would however be time-consuming and impractical for large numbers of samples, so recommended acidifying samples for as long as is practical in order to reach a maximum leachable concentration (equilibrium).

1.5 Instrumental analysis

1.5.1 Atomic absorption and atomic fluorescence spectrometry

Two papers advocated the use of *HR-CS–ETAAS* for the direct solid sample analysis of trace elements in airborne particulate matter collected on glass fiber filter media. The filter media and the collected particles could be ground ready for direct analysis. The reported[41] characteristic mass M_o for Hg was 22 pg when measured at the main absorption line of 253.652 nm. The LOD (3 σ of the signal derived from ten atomisations of a ground blank filter) was 40 ng g^{-1} equating to 0.12 ng m^{-3} in air for a sample air volume of 1440 m^3. The measurement repeatability was better than 17% (n=5). The LODs for all three elements (Cu, Mo and Sb) determined in particulate matter[42] were *ca.* 40 ng m^{-3} for a sample air volume of 1440 m^3. The measurement repeatabilities were 3-9% (n=5). The results obtained on air samples were comparable with those obtained using either a microwave-assisted leach or an ultrasonic-assisted extraction with *aqua regia*. The authors suggested that this direct measurement offered considerable time savings as sample preparation time was reduced.

Concerns about the health implications of As-containing species in airborne particles led researchers to undertake speciation analysis using *HPLC-HG-AFS*. Whereas As^V was the dominant species in particulate samples collected around a nearby copper smelter[43], the more toxic As^{III} species was nevertheless found at significant concentrations and represented 5–10% of the total As content. The As^{III} species tended to concentrate preferentially in the finer $PM_{2.5}$ fraction, thus posing a potentially enhanced inhalation risk to the local population. The dominant species in TSP samples of Beijing air[44] was As^V, accounting for 81–99% of the extractable As.

1.5.2 Emission spectroscopy

Hahn and co-workers[45], reviewed (31 references) the use of *LIBS* for analysis of micro and nanoparticles and concluded that although the technique offered immense potential for near–real-time multi-elemetal analysis of aerosol samples, several challenges remained, including poor measurement sensitivity. In contrast to the use of preconcentration techniques such as filter sampling or aerosol focusing systems used previously, they advocated a new approach combining an electrostatic charging and collection step for sampling and preconcentration of aerosol nanoparticles onto a micro-needle. These sample spots were then analysed using LIBS. A more detailed report[46] of this approach using test aerosols under laboratory conditions gave mass LODs (3 σ) of 0.018 – 5 ng for Cd, Cr, Cu, Mn, Na and Ti. These equated to LODs of 18–670 ng m^{-3} for a nominal 7.5 L air sample (1.5 L min^{-1} for 5 minutes). Instrumental precisions of better than 10% were achievable with >20 ng mass loadings of each element. These LODs were superior to those obtained in previous LIBS-based studies and the system is amenable to the miniaturisation essential for field-portable instrumentation. For readers who wish to learn more about LIBS, a comprehensive overview of the technique was published in two parts. The first[47] focused on the fundamental and diagnostics aspects (280 references) and the second[48] (719 references) discussed the vast panorama of practical applications of the technique.

Whilst using the same sample sampling and preconcentration system, these same authors[49] also experimented with a *spark-based excitation source* system in place of LIBS. The LODs (3 σ) were in the range 0.011 – 0.8 ng for the elements studied (Cr, Na, Pb and Ti). These figures equated to LODs of 0.44–70 ng m^{-3} for a nominal 25 L air sample (5 L min^{-1} for 5 minutes). Under the test conditions employed, the instrumental precisions were in the range 2–15%. The authors concluded that these figures of merit were superior to those reported with other micro-plasma based systems and that the simplicity and robustness of a spark-based system were appealing for implementation in any future portable system.

1.5.3 Mass spectrometry

*1.5.3.1 Inductively coupled plasma mass spectrometry***.** As ICP-MS is commonly employed for the routine determination of trace levels of metals captured on air filter samples, this section focuses on the use of ICP-MS as a single particle detector or as part of hyphenated systems for isotopic and speciation analysis.

Chinese researchers, in a continuation of work reviewed here last year, used[50] on-line ICP-MS *in the determination of particles in aerosol samples.* In particular they were interested in determining whether Pu-containing particles can penetrate HEPA filter systems employed in nuclear safety systems. Previously, in filter breakthrough studies they used ICP-MS in an off-line mode to determine whether ^{239}Pu–containing particles could penetrate such filters. The proposed new approach used an evacuated cylinder to collect air samples downstream from a challenged HEPA filter. The cylinder was subsequently coupled to a plasma torch for analysis. Calibration was achieved using a ^{242}Pu calibrant solution presented to the plasma as dried particles using a high efficiency desolvating nebuliser. Injection of air samples into the plasma however, be they from the sample collection cylinder or the calibration system, was limited to a 15 mL min^{-1} flow rate to minimise the reduction in instrument sensitivities and to maintain a stable plasma. Single collector– and MC–HR–ICP-MS systems gave ^{242}Pu LODs of 5.0 x 10^{-3} and 5.5 x 10^{-4} Bq m^{-3}, respectively. The ^{242}Pu concentrations in air downwind of HEPA filters were *ca.* 10^{-2} Bq m^{-3} indicating that some Pu–containing nanoparticles indeed penetrated the tested filters. These particles had not previously been detectable using the off-line approach. Future development work will focus on the optimisation of an ambient–aerosol–concentration enrichment device for coupling to ICP-MS to provide a more sensitive particle detection system. Injection of single particles into argon plasmas is a growing topic of both theoretical and practical interest. Readers therefore may be interested in a paper by Olesik and Gray[51] entitled "consideration for measurement of individual nanoparticles or microparticles by ICP-MS: determination of the number of particles and the analyte mass of each particle" and a paper by Gunther and co-workers[52] entitled " visualisation, velocimetry and mass spectrometric analysis of engineered and laser produced particles passing through inductively coupled plasma sources".

The use of *hyphenated ICP-MS for isotopic or speciation measurements* included the coupling of GC to MC-ICP-MS for the determination of methyl bromide, an important natural bromine contributor to stratospheric ozone depletion, in air samples[53]. The ^{81}Br/^{79}Br ratios were measured with a short-term precision of 0.1‰ (1 σ, n = 3) and a long-term precision of better than 0.4‰ (1 σ, n = 36, over 3 months) for sample masses in excess of 40 ng. This new system was three orders of magnitude more sensitive than previously reported IRMS approaches. It was intended to use this new method to undertake source apportionment studies to investigate the transport and fate of methyl bromide in the atmosphere. The impact of deliquescence and pH on Cr speciation in ambient air particulate matter samples collected on filters was studied using HPLC-ICP-MS[54]. At basic pH values, deliquescence influenced the loss of Cr^{VI} whereas precipation controlled the Cr^{III} solution chemistry. Under highly acidic atmospheric conditions, pH became very important for the interconversion of Cr^{VI} and Cr^{III} species but the effects of deliquescence were minimal. It was suggested that control of humidity to avoid deliquescence should be a design criterion for Cr^{VI} sampling systems of the future.

Iron is an element of interest due to its role in the oceanic sequestration and regulation of atmospheric CO_2. Its behaviour in the environment is strongly dependent upon its oxidation states given that Fe^{II} is more soluble than Fe^{III} and therefore more readily available for phytoplankton update and growth. To look to the future, environmental scientists, often look to the past. A novel analytical method for the speciation of Fe in ice core samples[55] used FIA-CRC-ICP-MS and a chelating resin, Ni-NTA Superflow, which retains Fe^{III} but not Fe^{II} at pH 2. The eluted Fe^{II} was oxidised to Fe^{III} using H_2O_2 and the Fe^{II} concentration calculated as the difference between the two measurements. Preliminary results indicated that concentrations of Fe^{II} were elevated during glacial periods compared to levels found in interglacial periods. This suggested that more Fe^{II} was available for phytoplankton growth during the last Glacial Maximum than would have been expected for measurements previously undertaken using proxies such as deposited total Fe or dust masses.

1.5.3.2 Other mass spectrometry techniques. Useful *reviews of mass spectrometric techniques applied to the analysis of gas and particle samples* covered: current instrumentation for aerosol MS[56] (53 references); the status of ambient MS[57-58] (185 and 31 references, respectively); developments since 2006 in ion mobility spectrometry[59] (343 references) and SIMS for the interrogation of nano-scaled objects and particles[60] (233 references).

A novel application for the measurement of atmospheric trace gases in real-time used a TOF *aerosol mass spectrometer*[61]. Such systems have historically been used for the measurement of particles rather than gases because the aerodynamic particle focus inlet typically used drastically reduces sensitivities for gaseous species. Artificially generated particles were injected into the sampled gas stream in order to trap gaseous molecules onto the particles for subsequent analysis. Trace levels of atmospheric molecular I_2 were measured by using α-cyclodextrin particles as selective sampling probes to transfer I_2 into the aTOF-MS instrument. Detection limits were in the sub-ppb range. Work on a new particle trap laser desorption mass spectrometer[62] for the on-line measurement of aerosol composition focused on the development and performance testing of the particle trap because particle bounce on collection targets employed in conventional mass spectrometers causes uncertainities in quantitative measurements. This new advanced particle trap consisted of a multi-layer mesh that allowed particles to lose their KE prior to being trapped in the mesh. Quantitative trapping of test KNO_3 particles was achievable in the laboratory but further system optimisation was required for the reliable measurement of ambient aerosols in the field. A new instrument[63], the soot particle aerosol mass spectrometer, for characterising and quantifying ambient refractory black carbon particles combined a commercially available HR-aTOF-MS instrument and the single particle soot photometer. The sensitivity was better than 140 carbon ions per pg of refractory black carbon, equating to a LOD (3 σ) of <100 ng m^{-3}.

The Earth's atmosphere is used as a standard reference gas for mass spectrometric determinations of *Ar isotopes* in geochronological studies. New high precision measurements of Ar isotope ratios in five different sources of air were made using a high sensitivity MC noble gas mass spectrometer[64]. The determined isotope ratios, corrected only for backgrounds, resided on an inverse square-root mass law fractionation line that passed through the air value proposed by another research group but different from other reported compositions. It was suggested that revised values should be employed in future. A new reference gas was developed for Ar isotopic measurements using a MC noble gas MS instrument[65]. Gases derived from neutron-irradiated sanidine were mixed with an enriched ^{38}Ar spike to produce a gas with known proportions of $^{38}Ar/^{39}Ar/^{40}Ar$. By combining atmospheric Ar with these synthetic gases in different proportions, isotopic ratio correction factors were measured over a wide span of ratios.

1.5.4 X-ray spectrometry

Characterisation of *airborne particulate matter* using X-ray techniques continues to be a fertile area for research. In an evaluation of EDXRF for the determination of trace elements on PM_{10} loaded filters[66], filter samples were collected from seven European locations with airborne concentrations ranging from low (background) to high (industrial sites). Samples were collected on commonly used filters such as pallflex^{TM} (teflon coated glass fibre), telfon and quartz filters to study any potential measurement artifacts due to the filter substrates. Two calibration approaches were compared: an external calibration approach using commonly employed Micromatter^{TM} standards and a standardless calibration strategy using a FP approach. Teflon filters were generally preferable for XRF analysis as impurity levels were lower and particles sat on the filter surface rather than in the filter thus minimising depth effects. The standardless calibration approach was better than the external calibration approach. Particular attention was paid to the four elements regulated by the European air quality directives. Standardless EDXRF analysis was suitable for measurement of Pb in PM_{10}. Whereas the LOD was sufficient to measure Ni, the measurement uncertainity did not meet the data quality objective set out in the air quality directive. The method was unsuitable for the determination of As and Cd because the LODs were higher than the quality directive's limit values if typical sampling volumes of 25-50 m^3 were used. Advantages of a new TXRF instrument[67] for the direct determination of airborne particulate matter included: the ability to determine the nature of the sample using X-ray standing wave in conjunction with TXRF; the selection of the total reflection angle; and the ability to switch the X-ray source in order that both light and heavy elements could be measured with increased accuracy.

Solid-state speciation analysis of airborne particles using XAS is a powerful tool and is increasingly being used to increase our knowledge of the origins, transformations and fate of particles in the atmosphere to meet growing concerns about the effect of inhalation of such particles and human health. In order to characterise Mn speciation[68] in airborne particulate matter for the first time, PM samples were collected from five locations across the USA. The fine fraction ($PM_{2.5}$) was analysed for total Mn concentration using ICP-MS and for oxidation state and species by XAS. Both Mn^{II} acetate and Mn^{II} oxide were present in all samples collected. Regional variations in Mn compositions indicated variation in sources and localised chemical atmospheric transformations. Because soluble Fe in atmospheric particles has been identified as a public health concern through its ability to participate in chemical reactions that can generate reactive oxygen species, XAS was used to characterise Fe in both urban and rural particles[69]. Both Fe^{II} and Fe^{III} were present in single particles, with the Fe^{II} content ranging between 5 and 35% (mean ca. 25%). The use of μ-XRF indicated that a majority (74%) of Fe–containing particles were best characterised as Al–substituted Fe-oxides with a Fe/Al molar ratio of 4.9. The next abundant group of particles (12%) were Fe-aluminosilicates with a Si/Al molar ratio of 1.4. The dominant V species[70] emitted in the exhaust from a diesel vehicle equipped with a prototype V-based selective catalytic reductor was V_2O_5.

The determination of *Cr^{VI} in ambient particulate matter* remains a challenge because of Cr species interconversion. An air quality guideline value of 0.2 ng Cr^{VI} m^{-3} in PM_{10} has been proposed in Europe thereby presenting a challenge to measurement scientists. Filters spiked with Cr^{VI} and Cr^{III} were analysed by XAS to study the potential for species interconversion [71]. Two 0.12 M $NaHCO_3$ impregnated ashless cellulose filters were spiked with a Cr^{III} solution and analysed directly after spiking. One filter was then mounted in a sampler and had ambient air drawn through it for 16 hours. The second filter was kept for the 16 hours under argon in a dessicator. Both filters were then reanalysed. No oxidation to Cr^{VI} was observed. When the experiment was repeated using Cr^{VI} instead of Cr^{III}, only minimal reduction to Cr^{III} occurred. However, prolonged exposure to X-rays in repeated analysis did result in reduction to Cr^{III}, a phenomenon also historically noted in this reviewer's laboratory when exposing Cr^{VI}–containing welding fume filter samples to prolonged X-rays in a WDXRF instrument. In contrast, an average Cr^{VI} spike reduction of 25% occurred in samples collected from around a steel plant and analysed using the well–established alkaline extraction procedure and spectrophotometric detection. The results demonstrated the inherent difficulties in replicating real-world conditions. Other matrix components in sampled air, such as Fe, contribute to Cr conversion processes during sampling or indeed the extraction step. In summary these studies demonstrated that solid-state techniques such as XAS are essential in elucidating species interconversion. Readers are directed to our companion Update for further information on developments and applications in X-ray spectrometry[5].

1.5.5 Combustion– and spectrometric–based techniques

It is recognized that the *carbonaceous content of anthropogenic aerosols* can impact greatly upon both climate and human health and there is much ongoing work in measuring the carbon content in airborne particles. Alas a single definition does not exist to describe this carbonaceous content. One approach is to define the black carbon component as an optical (measurement) property commonly used to denote the extent of light-absorption of an aerosol sample. It is however not a direct measure of the carbon content. In many urban environments, black carbon, produced by incomplete combustion of fuels, often dominates particulate light absorption. An alternative approach is to define the EC component, which also is an operationally (measurement) defined concept representing thermally refractory carbon with a graphitic structure. This is measured by combustion to CO_2, which can be subsequently quantified. Emissions from diesel–powered engines are a dominant source of elemental carbon in urban environments. In summary, black and elemental carbon are not measures of the same properties of carbonaceous particulate matter but are often well correlated especially in urban environments. Many measurement difficulties and knowledge gaps remain however as indicated by work reported in the following paragraph and in sections 1.3 (reference materials) and 1.6 (data analysis and quality).

Several studies have investigated differences in combustion conditions cited in various standardised operating protocols and differences in the two commonly used instrument designs (the Sunset analyser and the DRI analyser) to explain variations in elemental *carbon measurements by the thermal-optical approach*. In fact, despite differences in their designs, the two instruments produced similar results when following the same analysis (combustion) protocol[72]. Alas, as found previously, different analysis protocols produced different EC values on split filters samples. These differences were sample matrix dependent. An investigation of three different analytical protocols for measuring elemental carbon:organic carbon ratios in various aerosol samples concluded[73] that not one protocol can be considered applicable for all types of carbonaceous aerosols. It was recommended[74] that, in order to mimimise the influence of dust particles on the quantitative measurement of elemental carbon:organic carbon ratios in carbonaceous particles trapped in ice and snow samples, ultrasonication of melted samples should be performed to disaggregate dust-carbon particles. Dust particles should then be allowed to settle prior to filtering the supernatant through an analytical filter subsequently taken for combustion. Three combustion–based protocols (EUSAAR_2 and RT QUARTZ-700 and-840 protocols) were considered[75] for the determination of the naturally occurring CC content in aerosols in the presence of organic and elemental carbon through the careful optimisation of heating rates. All protocols could be used but it was suggested that CC values obtained using the RT-QUARTZ protocols should be checked using split samples using an alternative analytical approach. One such approach is to initially remove the CC from filters via acidification, measurement of the resultant liberated CO_2, prior to subsequent organic:elemental carbon analysis.

Worker exposure to silica can lead to silicosis, a potentially fatal lung disease. Two new *portable IR instruments* were evaluated[76] for the quantification of silica collected on filters through use of test filters loaded with either silica or silica-bearing coal dust (10 – 200 µg/filter). A correction for the presence of kaolin, an interferent within the IR spectrum and present in certain mine air dusts, was required. Measurements were also made on the same filters using an established laboratory based FTIR procedure. The correlations between results for one of the portable FTIR instruments and those for the laboratory FTIR instrument were linear with slopes of 0.90-0.97. The correlation between results obtained on the second portable instrument, a variable filter array spectrometer, and those obtained with the laboratory instrument were not so well correlated, due mainly to the poorer wavelength resolution of the portable system. These new instruments appear to hold promise for the analysis in the field of end–of–shift samples. This reviewer looks forward to seeing field trials in real workplace settings.

1.6 Data analysis and quality

Although *in-situ* analysis can provide air quality data at high temporal resolution in a timely fashion, a major challenge lies in dealing with the magnitude of data thus generated. It is encouraging that *data reduction* techiques being developed preserve the integrity of the orgininal data set. An advantage in making black carbon measurements is that they can be performed in near real-time with portable instrumentation such as the commercially available and widely used aethalometer™ instrument. However, negative values which can occur when measuring low airborne carbonaceous concentrations at high temporal resolution, need to be handled. An optimised noise–reduction averaging algorithm[77] reduced the occurance of such negative values to virtually zero while preserving the significant dynamic trends in the time series. Interpretation of the plethora of data derived from the measurement of single-particle ambient aerosols using aTOF-MS can be immensely labour intensive due to the high cyclic rate of such instruments. Several data analysis methods[78] were used to cluster and scale single particle data, which in turn were used to evaluate data derived from other monitoring instrumentation. Such procedures provided a valuable insight into the origins and fate of particles sampled in the atmosphere above the Great Lakes region of North America.

A research consortium[79] explored the *variations between black carbon and elemental carbon measurements* undertaken at a number of geographical locations. Good correlations were obtained if a fixed mass absorption coefficient of 9.7 m^2 g^{-1} was used in the optical measurement equation for black carbon determinations. The presence of black carbon derived from sources such as wood smoke particles, which have lower light absorptivity than traffic generated particles, resulted in poorer correlations. Continuity in environmental monitoring datasets is important. Heal and Quincey[80], in a continuation of previous work[81-82], developed a revised equation to describe the relationship between current black carbon data and black smoke data, the historical measure of ambient particle darkness.

Researchers at DRI[83], drawing upon many years of experience in this measurement field, documented *quality assurance and quality control protocols* that should be implemented to ensure consistency of organic and elemental carbon determinations by the thermal-optical technique. They recommended filter selection and handling procedures as well as methods to ensure that instruments operate satisfactorily. Participation in laboratory accreditation programmes and other external system audits and, if possible, in suitable interlaboratory comparisons was also recommended. Significant advances in the measurement of trace atmospheric Hg species have been made in the last 10 or so years yet limited QC protocols have been published in the literature. A comparison of the data ratification protocols[84] employed by two established atmospheric Hg monitoring networks, the Environment Canada monitoring network and the National Atmospheric Deposition Network, concluded that the two protocols produced comparable data and that either of the two protocols could be used as a QC template for other atmospheric Hg monitoring networks.

Deriving *measurement uncertainity budgets* is not for the faint–hearted chemist so it is most welcome to see worked examples published especially in the field of air analysis where such publications are relatively scarce compared to worked examples in other analytical measurement arenas. Coincidentally three papers described approaches used in calculating MU budgets associated with the sampling and measurement of water–soluble ionic species collected on filter samples and subsequently analysed by IC techniques. In one paper, a bottom–up approach examined variables associated with both sampling and analytical steps[85]. Using procedures advocated in ISO GUM, the relative expanded uncertainity was calculated to be *ca.* 20 % for both the cationic (K^+ and Li^+) and anionic species (NO_3^{2-} and SO_4^{2-}) studied. The biggest factor contributing to the MU was determined to be the IC instrumental repeatability. In another paper, an expanded uncertainity of 15–30% was obtained for the anionic species Cl^-, NO_3^{2-} and SO_4^{2-} when only the analytical steps were considered[86]. However in the third paper[87], the expanded uncertainity for the measurement step for the anionic species Cl^-, NO_3^{2-}, PO_4^{3-} and SO_4^{2-}) was only 3.7–6.4%. In summary, and to repeat, undertaking MU exercises is not facile and such papers are most informative, particularly so if the mode of MU calculation is fully described.

2 Water analysis

2.1 Sample preparation

The *preservation of mercury in solution* is a problem. For waters, the problem has largely been resolved by the collection of the sample in a glass or a fluorinated polymer container, with the addition of oxidising agents such as bromine chloride, potassium dichromate or gold nitrate. These solutions, however, are far from ideal for multi-elemental ICP-MS analysis of waters on a routine basis, when Hg is included in a suite of elements to be analysed. Louie *et al.*[88] demonstrated that the addition of 0.01% (v/v) HCl to a sample already stabilised with 1-2% (v/v) HNO_3 was enough to stabilise Hg in solution at sub µg L^{-1} concentrations for up to 50 days even in HDPE sample bottles. There was minimal addition to the chloride polyatomic related blank.

2.2 Sample preconcentration and extraction

The need for more *selective preconcentration of analytes and matrix elimination* to reach ever more stringent environmental control levels is still a great driving force in water analysis. This, coupled with the need for methods for use with less sensitive instrumentation, has resulted in a bewildering array of methods that are often more complicated than those reported previously. Methods where the analyst has to spend a day synthesising chelating agents and functionalising solid supports for them before carrying out an analysis are impractical in the routine laboratory. The most notable methods for the analysis of waters in this Update period are summarised in Tables 1-3.

In a *critical review* (63 references) of on-line SPE for ICP-based techniques, Das *et al.* [89] pointed out that its success was due to a number of factors: simplicity of operation, high preconcentration factors, rapid phase separation, reduced extraction time and ease of automation. They concluded that many reports focus on only one or a few elements and therefore do not make full use of the multi-elemental capabilities of modern ICP instrumentation. In addition, there was a lack of sorbents for the selective extraction of all the REEs.

2.3 Speciation

The occurrence of *antimony species* containing sulfur in geothermal waters has been proven using AEC-ICP-MS and XAS[90]. Two thioantimony species detected by AEC-ICP-MS in synthetic antimonite-sulfide oxic solutions were assigned as tri and tetrathioantimonate based on their S:Sb ratios and XAS spectra. As XAS confirmed, under anoxic conditions antimonite formed trithioantimonite in the presence of a 10-fold excess of sulfide but under oxic conditions this rapidly transformed into tetrathioantimonate. In an automated, low-pressure, dual-column FI-ICP-MS method[91] for the determination of Sb^{III} and Sb^{V} in aqueous samples (pH 8.4), first Sb^{III} was trapped on a controlled pore glass functionalised with the chelating resin [1,5-bis(2-pyridyl)-3-sulfophenyl methylene] thiocarbonohydrazide, and then Sb^{V} was collected on the anion-exchanger Amberlite™ IRA-910. The analytes were eluted sequentially with 0.04 % m/v thiourea in 5 % v/v HNO_3. The method LODs were 0.013 µg L^{-1} for Sb^{III} and 0.021 µg L^{-1} for Sb^{V}. Accuracy was checked against two CRMs NRCC CRM SLRS-5 (River Water) and NWRI TMDA-54.4 (Fortified Lake Water).

A review[92] (145 references) of *arsenic speciation* in environmental samples using HG-ETAAS as the detection technique noted that species pre-reduction with L-cysteine was more advantageous than the use of KI. The preferred chromatographic technique was ion pair RP chromatography, but a combination of anion and cation-exchange chromatography appeared to be promising.

The speciation of chromium was considered in a 197 reference review[93]. In a kinetic study using IC-ICP-MS [94] on the reduction of Cr^{VI} in natural water, spiking of CRM NRCC SLRS-2 (River Water) with 20 μL^{-1} Cr^{VI} showed that reduction of this species followed a pseudo first order reaction with a rate constant of 2.119×10^{-4} s^{-1} at pH 1.3 and 20 °C. The reduction rate increased with decreasing pH and increasing temperature, confirming why it is common practice to determine Cr^{VI} under more alkaline conditions. In a multiple-column FI-ICP-MS method[95] for the determination of Cr^{III} and Cr^{VI} in natural waters, adjusted to pH 5.5, Cr^{VI} was completely retained on the first two columns containing Amberlite™ IRA 910, and Cr^{III} was retained on a third column containing a silica gel chelating resin functionalised with 1-(di-2-pyridyl) methylene thiocarbonohydrazide. Both species were eluted with 2% v/v HNO_3. The LODs were 0.03 $\mu g\ L^{-1}$ for Cr^{III} and 0.009 $\mu g\ L^{-1}$ for Cr^{VI}.

A review (242 references)[96] on *iodine speciation* in environmental, biological and nutritional samples covered sample pretreatment and analytical techniques for the determination of total I, as well as the use of various detection techniques for speciation analysis. A multimode size-exclusion HPLC column (AsahiPak GS-220) was used with a mobile phase of 50 mM malonic acid, and 37 mM TMAH (pH 6.9) at a flow rate of 1.0 mL min^{-1} to separate iodate and iodide[97]. The SF-ICP-MS LODs were 20 ng L^{-1} for iodate and 30 ng L^{-1} for iodide measured in 1 + 9 diluted seawater. Vertical profiles of total iodine, iodate, iodide, total inorganic iodine ($I+IO_3^-$) and dissolved organic iodine (total iodine- total inorganic iodine) were reported for Pacific Ocean water.

The FI-ICP-MS determination of *iron species in Antarctic ice*[55] involved retention of Fe^{3+} on a Ni-NTA Superflow chelating resin at pH 2, and oxidation of the remaining Fe with H_2O_2 to give the Fe^{2+} concentration by difference. The LOD of 0.01 ng g^{-1} for both species was sufficient to determine the species in ice from glacial and interglacial periods. Preliminary results showed that more Fe^{2+} was available during glacial periods, more so than indicated from proxy measurements, such as of dust mass or total Fe.

In a fast method[98] *for the trace speciation analysis of mercury in seawater* by HPLC-ICP-MS, a short C-18 analytical column was used and the HPLC sample loop was replaced with an IonPac® CG5A cation-exchange guard column. The large capacity of the preconcentration column gave an enrichment factor of 1250 for a 30 mL sample, resulting in very low LODs of 0.042 ng L^{-1} for Hg^{2+}, 0.016 ng L^{-1} for $MeHg^+$ and 0.008 ng L^{-1} for $EtHg^+$.

Since the Update on elemental speciation[4] does not specifically deal with *operationally defined speciation*, such protocols for water analysis are included here. The total, labile and metal-humic acid complexes of Cd, Cu, Ni, Pb and Zn in freshwater were determined using a FI system coupled with ICP-MS[99]. The labile fraction was trapped on a microcolumn packed with unfunctionalised poly(methyl methacrylate). To break down the humic acid-metal complexes, a photocatalyst-assisted reactor, consisting of a pyrex glass tube coated with a TiO_2 film together with a UV-A lamp with a maximum emission at 365nm, was placed in-line before the microcolumn. The total metal content was determined by ICP-MS. In some lake samples over 80% of the elemental concentration was in the humic acid complexes. A commercially available DGT device was used to monitor the labile fractions of Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in both the river water and potable water produced in a water treatment plant[100]. The amount of most elements adsorbed on the device did not increase after 24 h of deployment. The metals were subsequently desorbed for 24 h in 1 M HNO_3 prior to detection by ICP-AES with a USN. The LOQs were 1.5 (Cd) to 28.3 μg L^{-1} (Zn).

Development of *elemental speciation* protocols continues to attract attention. Up to 13 selenium species in flue gas desulfurisation waters from a coal fired power plant were separated on an IonPac® AS 16 column fitted with an AG 16 guard column [101]. Using a suitable suppressor unit, a mobile phase of 100 mM NaOH allowed direct ICP-MS detection of the eluted species. The most frequently observed species were Se^{IV}, Se^{VI} and $SeSO_3^{2-}$; $SeCN^-$ was also identified for the first time in such samples. An additional nine unidentified species were detected. Thallium species in water samples were separated by ion-exchange SPE followed by DLLME using ILs[102]. The Tl^{3+} was retained on Dowex® anion-exchange resin as the tetrachlorothallate (III) anionic complex. The remaining Tl^+ was complexed with I^- and the IL CYPHOS® IL 101 was added as an ion pairing agent. Another IL, 1-hexyl-3-methylimidazolium hexafluorophosphate dispersed in ethanol, was used as the extracting solvent. After centrifugation the aqueous phase was removed by pipette and the sedimented phase was dissolved in methanol and analysed for Tl^+ by ETAAS. The Tl LOD was 3.3 ng L^{-1}.

Multi-elemental speciation remains difficult and limited to a few elements. An on-line anion exchange membrane separation system, coupled with ICP-MS, was used[103] to determine both the total and reduced species of Cr and V; the concentrations of the oxidised species were calculated by difference. The accuracy of the method was tested against the CRMs IERM GSBZ-50029-94 (Environmental Water) and NRCCRM GBW 08608 (Riverine Water). The LODs were 0.02 µg L^{-1} (V^{IV}) and 0.06 µg L^{-1} (Cr^{III}) and precision (n=10) <3.7 % RSD for a 10 µg L^{-1} standard. The derivatisation agents sodium tetrapropylborate ($NaBPr_4$) and sodium tetraphenylborate ($NaBPh_4$), were compared[104] for the determination of organolead and organomanganese compounds by GC-AES in seawater after SPME preconcentration. Propylation with sodium tetrapropylborate gave better results with LODs ranging from 0.04 ng L^{-1} for cyclopentadienyl manganese tricarbonyl to 0.10 ng L^{-1} for trimethyllead compared to 0.1 to 24.5 ng L^{-1} for the same compounds after phenylation.

2.4 Instrumental Analysis

2.4.1 Atomic Absorption Spectrometry.

The best results for the *ETAAS determination* of Mn in waters produced by petroleum exploitation were obtained[105] by pyrolysis with a permanent modifier of Ir-W at 1000 °C and atomisation at 2300 °C. The LODs were 0.24 µg L^{-1} in purified water and 0.34 µg L^{-1} in medium salinity (23%) waters. In an investigation[106] of suitable chemical modifiers for the ETAAS determination of V in natural waters matrix interferences were effectively eliminated using either ascorbic acid or ammonium nitrate. Accuracy was checked by analysing NIST SRM 1643e (Trace Elements in Water) and spike recoveries from tap, mineral, riverine and seawaters. The LOD was 1.56 µg L^{-1}. Spike recoveries varied between 98-105% and precision was always <5% RSD.

Factorial experimental design was used to optimise the *determination of Pb by HG-AAS with a quartz atom trap* using an instrument equipped with a high resolution continuum source[107]. The optimal reagent conditions were a carrier of 0.1 M HNO_3 with 1.0% (m/v) $NaBH_4$ and 1.0% (m/v) $K_3Fe(CN)_6$ for the production of plumbane gas. The method was validated by the analysis of the NIST SRM 1643d (Trace Elements in Water) and results for real samples compared with ICP-MS measurements. The LOD was 0.13 µg L^{-1} and the analytical precision was 6.36% RSD for a 10 µg L^{-1} standard.

2.4.2 Atomic emission and fluorescence spectrometry.

Progress is being made in the development of *field instruments capable of detecting trace elements in water*. One such instrument, a liquid electrode plasma atomic emission spectrometer[108], could achieve LODs of 0.52 µg L^{-1} for Cd and 19.0 µg L^{-1} for Pb. Liquid-liquid microextraction techniques were compatible with the plasma cell and gave an enrichment factor of 100 prior to sample introduction[109](in Japanese). Other low power instruments based on liquid film dielectric barrier discharge with AES[110] or AFS[111] detection were used for the determination of Cd, Cu, K, Na, and Zn (AES detection) or Hg (AFS). The LODs were 7 µg L^{-1} (Na) to 79 µg L^{-1} (Zn), and 0.02 µg L^{-1} for Hg. Trace levels of Hg were also detected using electrolyte cathode discharge with AES detection[112]. The addition of acetic acid to the sample enhanced sensitivity by 500 times, resulting in a LOD of 2 ng mL^{-1}.

Depoi *et al.*[113] have investigated *hydride generation and micronebulisation/ desolvation as potential ICP-AES sample introduction methods* for the alcohol-surfactant rich phase obtained at the end of the CPE process. Pneumatic nebulisation was used as the reference method and the analytes investigated were As, Bi, Cd and Pb. For As, HG was the best approach resulting in a LOD of 0.055 µg L^{-1}. For Bi, both HG and micronebulisation approaches generated similar LODs (0.057 and 0.063 µg L^{-1}) as the surfactant phase had to be diluted to prevent foaming thus reducing the potential HG enrichment factor from 18 to 7. For Cd and Pb, pneumatic nebulisation gave the best results with LODs of 0.047 and 0.28 µg L^{-1},respectively. Although the micronebulisation approach was potentially more sensitive, it had poorer measurement repeatability.

2.4.3 Vapour generation techniques.

A novel on-line *preconcentration chemical vapour generation method* involved trapping Sc at pH 7 on a microcolumn filled with activated carbon [114]. The analyte was eluted with 10% (v/v) HCl and merged with a 1.0 (m/v) $NaBH_4$ solution to generate volatile Sc. With detection by ICP-AES, an LOD of 4.0 µg L^{-1} was achieved for a sample volume of 25 mL. The precision (n=10) for a concentration of 100 µg L^{-1} was 4.0% RSD.

In a *multi-element method for the determination of As, Sb and Se* in water samples, the need for compromise flow conditions was avoided[115] by carrying out the vapour generation in reaction vessels connected to a fast sequential AAS instrument. The LODs for 10 mL samples were 0.05, 0.03 and 0.06 ng mL^{-1} for As, Sb and Se, respectively.

Total Hg in Antarctic surface snow was determined[116] in 147 samples taken along a transect, from sea level to nearly 4000 m altitude, during the International Trans Antarctic Scientific Expedition. Frozen snow samples were melted in the laboratory and stabilised with $AuCl_3$ or BrCl. The Hg levels varied from <LOD (0.4 pg g^{-1}) for coastal samples to 10 pg g^{-1} at the high altitude stations. The samples with higher results were often associated with higher uncertainties, which can be explained by the inhomogeneous distribution of particles in the snow. From this it is was assumed that a significant fraction of the Hg was particle bound, and would not have be oxidised by BrCl prior to cold vapour-AFS analysis and hence would have remained undetected. This could explain discrepancies between cold-vapour AFS and ICP-MS measurements given that particulate bound Hg could potentially be nebulised into a plasma.

2.4.4 X-ray fluorescence spectrometry.

A portable *TXRF* instrument was modified[117] with a diamond-like carbon-coated quartz glass sample holder for the determination of Cr in river water. Use of this target material, more hydrophobic than the traditional sample holder, resulted in less sample droplet dispersion, thereby allowing an absolute LOD of 28 pg of Cr to be achieved.

The *EDXRF* determination of phosphate in surface waters involved[118] suspended drop microextraction and measurement of the phosphomolybdenum blue complex using the Mo K-α line. An enrichment factor of 56.8 gave an LOD of 2.8 ng mL^{-1} for a 1.5 mL sample.

In a multielement method combining *DLLME and XRF*[119], the analytes (Co, Fe, Ga, Pb, Se and Zn) were extracted as complexes with APDC in a 20-30 µL drop. This drop was subsequently dried onto a solid substrate (a membrane filter or Mylar foil) for analysis. The LODs achieved ranged from 1.6 (Co) to 4.1 (Pb) ng mL^{-1} for a 5 mL sample with a preconcentration factor of 250.

An evaluation[120] of three *EDXRF* systems for the determination of Cd, Cu, Ni, Pb and Zn in aqueous samples, following preconcentration of 1 L samples on 47 mm diameter 3M Empore chelating filter disks concluded, rather unsurprisingly, that high energy polarised beam EDXRF instrument gave the best LODs. Hand held or bench tops instruments were only suitable when the concentrations were above 20 µg L^{-1}.

2.4.5 Inductively coupled plasma spectrometry.

One of the more interesting papers[121] described *the use of cryocell LA-ICP-MS* for detecting Al, Ca, Fe, Mg and Mn in sections from the North Greenland ice core project. Ice strips 50 mm long, 13 mm wide and 12 mm thick were cut from the ice core and the surface was subjected to limited mechanical cleaning. To complete decontamination, laser pre-cleaning of the surface was carried out three times using a spot size of 500 µm at a repetition rate of 30 Hz. The sample was then analysed using a spot size of 280 µm at a repetition rate of 20 Hz. The method offered a much higher temporal resolution than methods required cutting and melting of the core, and requires minimal manual sample decontamination. The method appeared promising but remains uncalibrated due to difficulties in producing homogeneous ice standards.

A SF-ICP-MS procedure[122] for the *determination of total I in seawater* involved dilution (1+99) with 0.5 % (v/v) TMAH prior to analysis. The LOD of 0.23 ng mL^{-1} allowed the determination of I concentrations in coastal seawaters from 14 estuaries.

A *modified ICP-MS sample introduction system* included[123] an in-line ETV unit used simultaneously with pneumatic nebulisation. Under wet plasma conditions LODs were up to 65 times better than those for conventional nebulisation. For elements without major polyatomic interferences, the LODs for the new hybrid unit were similar to those reported for ETV-ICP-MS under dry plasma conditions. The advantage of this system was that the analyst could switch between sample introduction modes without extinguishing the plasma.

Analysis of very small liquid samples (1 µL) was achieved[124] by use of dried drop LA-ICP-MS. Methylene blue was added to the sample to make it visible and then the sample was dried on a PTFE filter. Using a 213 nm laser with a 110 µm spot size, As, Cd, Co, Cu, Li, Mn, Mo, Ni, Pb, Sb, Tl, V and Zn were quantified with LODs of 0.05 µg L^{-1} (Li) to 0.81 µg L^{-1} (Ni and Cu).

Ultra-sensitive methods are required for the determination of Cd in natural waters if the maximum values allowed under European legislation (0.08 to 0.25 µg L^{-1}) are to be monitored. In an *ID-ICP-MS procedure*, an enrichment factor of 10 was achieved[125] by preconcentration of 50 g samples on a minicolumn pack with TiO_2 nanoparticles. Procedural blanks were 5.3 ± 2.8 ng kg^{-1} with a combined uncertainty of 3-4% (k=2 coverage factor) for a Cd content of 100 ng kg^{-1}. Results for CRMs IRMM ERM-CA615 (Groundwater) and IRMM BCR-713 (Effluent Wastewater) agreed with certified values within error.

High resolution measurements of sulfur isotopes in sediment porewaters involved[126] capture of of the dissolved sulfide as solid Ag_2S in DGT polyacrylamide gels and interrogation at a spatial resolution of 100 pm using LA-ICP-MS. The improved spatial resolution achieved could be essential for improving our understanding of S cycling in modern sediments. Analyses revealed microniches where the $\delta^{34}S$ shifted by up to 20‰ compared to local background measurements.

2.4.6 Laser Induced Breakdown Spectroscopy.

The *sensitivity of LIBS for the determination of B and Li in aqueous solutions* was improved by use of a dual-pulse instrument[127]. Sequential pulses from two Q-switched Nd:YAG lasers with a wavelength of 532 nm were employed. The first pulse generated a laser-induced water jet, and the second induced the plasma. The optimum time delay between the pulses was <3 µs for B and approximately 10 µs for Li. Under these conditions, the LODs were 0.8 mg L^{-1} for B and 0.8 µg L^{-1} for Li, two orders of magnitude better than currently reported literature values. The method was considered suitable for the analysis of boric acid and lithium hydroxide in coolant waters of pressurised water nuclear reactors where they are used as a neutron absorber and pH controller, respectively. Double-pulse LIBS has also been used to determine *Au, Fe and Pb in aqueous solutions* [128]. In this procedure, the first pulse (266 nm) was used to generate a plasma at the surface of the liquid and the second pulse (1064 nm) reheated the plasma to enhance excitation. A 10-fold improvement in sensitivity compared to use of single pulse LIBS gave LODs of 13.5 (Au), 8.0 (Fe) and 6.0 (Pb) mg L^{-1}.

2.5 Data Quality

An *interlaboratory comparison* of methods for the analysis of seawater was carried out under the GEOTRACES sampling program. For the determination of total Hg there was substantial disagreement between the results from 12 laboratories, which was attributed to bottle cleanliness and preservation procedures used[129]. The sampling system and filtration medium used had little affect on the results. A recommended workflow for the shipboard processing of samples for the determination of elemental, dimethy, monomethyl and total mercury was subsequently proposed. As part of the GEOTRACES project, a wider overview of method developments and laboratory intercalibrations for the determination of trace elements and their isotopes in seawater has been published[130].

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

Analytes	Matrix	Substrate coating or modifying agent	Column substrate	Detector	Notes	CRMs (or other validation)	Reference
REEs	Seawater		EDTA and iminodiacetic acid resin	ICP-MS	External (2σ) precision < 23%, LODs: Tb 1 pg L^{-1} to La 36 pg L^{-1}	Comparison with ID-ICP-MS results.	131
Ag^{I}, Cd^{II}, Co^{III}, Cr^{III}, Cu^{II}, Fe^{III}, Mn^{II}, Ni^{II}, Pb^{II} and Zn^{II}	Water		HyperSep™ SCX strong cation exchange resin	ICP-AES	LODs ranging from 0.05 – 0.2 µg L^{-1}, sampling frequency 24 samples h^{-1}		132
Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn	Seawater		Nobias-chelate PA1 resin	SF-ICP-MS	LODs: Mn 0.002 to Ni 0.085 nmol kg^{-1}, and Co 0.13 to Cd 0.86 pmol kg^{-1}	Laboratory intercomparison of a surface and deep-water sample.	133
Cd, Co, Cr, Mn, Ni, Pb, Zn	Seawater and water	1,5-bis (2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide resin	Controlled pore glass	ICP-MS	Preconcentration factors of between 2.2 and 6.8, LODs: Co 0.002 µg L^{-1} to Zn 0.260 µg L^{-1}	NRCC SLEW 3 (Estuarine Water), LGC 6016 (Estuarine Water) and NRCC CASS-5 (Near Shore Seawater), NRCC SLRS-5 (River Water) and NWRI TMDA-54.4	134

						(Fortified Lake Water)	
Cu^{II}, Fe^{III}, and Pb^{II}	Water	Phenyl-iminodiacetic acid	MWCNT	ICP-OES	Preconcentration factors of up to 100, LODs Cu 0.15 to Fe 0.26 ng mL^{-1}		135
Ag^{I}	Waste water	Complex with 2-mercaptobenzothiazole	MWCNT	FAAS	Preconcentration factor of 160, LOD of 0.21 µg L^{-1}		136
Pb	Water	Complex with dithizone	Graphene	FAAS	LOD of 0.61 µg L^{-1}, at 20 µg L^{-1} an RSD of 3.56 % (n=10)was found	Spike recovery 95 – 100%	137
Cr^{III}	Water	Complex with 8-hydroxyquinoline	Graphene	FAAS	Preconcentration factor of 125, LOD of 0.5 µg L^{-1}, 4.3% RSD n=10 at a concentration of 20.0 µg L-1		138
Cr^{III}, Cu^{II}, Pb^{II} and Zn^{II}	Water	Dithizone	Modified silica coated Fe_2O_3 nanoparticles	ICP-AES	LODs ranged from 8 ng L^{-1} for Zn^{II} to 62 ng L^{-1} for Pb^{II}	IERM GSBZ 50009-88 (environmental water)	139
Ge^{IV}	Water		TiO_2 nano colloid	ETAAS	LOD 43 ng L^{-1}, RSD 3.6 % (n=6) at a concentration of 0.4 µg L^{-1}	Comparison with ICP-MS results	140
Au^{III}, Pd^{II}, Pt^{II}	Water	L-cysteine	Silica Gel	ICP-AES	LODs Au 0.006 to		141

and Pt^{IV}					Pd 0.02 μg L^{-1}, RSD 5-9 % at 0.1 μg L^{-1}		
Bi^{III}, Cd^{II}, Cu^{II}, Ga^{III}, Ni^{II} and Pb^{II}	Seawater	Cetyltrimethylammonium chloride	Silica particles floated with sodium dodecyl sulfate	ICP-MS	LODs Ga 0.00007 μg L^{-1} to Ni 0.004 μg L^{-1}	NRCC CASS-4 (Nearshore seawater) and NRCC NASS-5 (Seawater)	142
As^{V}	Water		Ion imprinted 1-vinylimidazole, 4-vinylpyridine and styrene polymer	ICP-MS	LOD 0.025 μg L^{-1}, RSD 1.9 % at 0.5 μg L^{-1} (n=3).		143
Hg^{2+} and MeHg	Oxic water	3-Mercaptopropyl	Silica Gel	ICP-MS	LODs MeHg 0.1 ng L^{-1} and Hg^{2+} 0.7 ng L^{-1}		144
Cd and Pb	Water	2-(6-methyl-2-benzothiazolylazo)-orcinol	Polyurethane	FAAS	preconcentration factors Cd 38.6 and Pb 30.0, LODs Cd 0.08 μg L^{-1} and Pb 0.51 μg L^{-1}, RSDs of < 6.34% at nominal 5 μg L^{-1} (n=7).	NIST SRM 1643d (Trace Elements in Natural Water)	145

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

Analytes	Matrix	Method	Reagents	Detector	Notes	CRMs (or other validation approach)	Reference
Ni	Seawater and water	LLE	DDTC complex, MIBK	MIP-MS	LOD 1.3 ng L^{-1}, preconcentration factor 50, RSD < 4%	NRCC NASS-5 (seawater), NRCC SLRS-3 (river water) and NRCC	146

						SLRS-4 (river water)	
Pb	Water	CPE	Dithizone, Triton X-114®	FAAS	Preconcentration factor 39, LOD 4.3 µg L^{-1}.	NRCCRM GBW (E) 080393 (simulated water)	147
Bi	Water	CPE	Dithizone, Triton X-100®	FAAS	Preconcentration factor 43, LOD 4.0 µg L^{-1}	NRCCRM GBW(E) 080135 (water)	148
Sb^{III}, Sb^{total}	Water	LPME	Dithiocarbamate complex, xylene	ETAAS	Preconcentration factor 400, LOD of 2 µg L^{-1}.	NRCC SLRS-5 (River Water)	149
Bi^{3+}	Water	DLLME	2-(5-bromo-2-pyridylazo)-5-(diethyl amino) phenol, dichlorobenzene	FAAS	LOD 3.0 ng mL^{-1} RSD 1.5 % (n=7) at a concentration of 0.4 µg L^{-1}		150
U^{VI}	Seawater, ground water	DLLME	Complex with APDC in the presence of cetyltrimethyl ammonium bromide, chloroform	ICP-AES or FI-ICP-MS	Preconcentration factors of 11(ICP-AES) and 25 (FI-ICP-MS), LODs of 2.0 µg L^{-1} (ICP-AES) and 30 ng L^{-1} (ICP-MS)	Spike recovery and cross validation with laser fluorimetry.	151
Cr^{VI} (and Cr^{total})	Water	DLLME	APDC complexes, 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide	ETAAS	Preconcentration factor 300, LOD of 2 ng L^{-1}, RSD of 8 % (n=10) at a concentration of 0.05 µg L^{-1}.	Spike recoveries are between 95-104 %	152

Table 3. Alternate preconcentration methods for the analysis of water.

Analytes	Matrix	Method	Reagents	Detector	Notes	CRMs (or other validation)	Reference
Co, Cr Mn, Y	Seawater	*In situ* coprecipitation	$Mg(OH)_2$ precipitate after addition of 20-	SF-ICP-MS	LODs 1.03 (Cr) to 0.001 ng kg^{-1} (Lu), RSD < 11	NRCC NASS-5 (Seawater) and	153

and REE			22 % m/v NH_4OH		% (n=20)	CASS-4 (Nearshore seawater)	
Cr, Fe, Mn, Pb and Zn	Seawater	*In situ* coprecipitation	$Mg(OH)_2$ precipitate after addition NH_4OH	ICP-MS with DRC	LODs from Pb 0.002 to Zn 0.19 nM, RSD < 16 % (n=6) for all elements	NRCC NASS-5 (Seawater) and NRCC CASS-4 (Nearshore seawater)	154
MeHg	Seawater	Purge and trap	Ethylating agent	GC-cold vapour-AFS	LOD 2 fM for a 2 L sample		155

3 Analysis of soils, plants and related materials

3.1 Reference materials

In a review (121 references) of *the suitability of available CRMs for Hg speciation analysis*, researchers from Barcelona[156] concluded that there is still a paucity of materials covering an adequate range of certified values and matrix compositions.

New reference materials for the analysis of tea included: NMIJ CRM 7505-a (Tea Leaves Powder)[157], developed alongside a proficiency test[158] involving 41 laboratories; and NIST SRMs 3254 (Green Tea Leaves), 3255 (Green Tea Extract) and 3256 (Green Tea – Containing Solid Dosage Form)[159]. Zuliani *et al.*[160] characterised a laboratory QC material for TBT and DBT in sewage sludge. Huang *et al.*[161] assessed uncertainties when analysing different sized test portions (hundreds of mg down to tenths of ng) of a candidate stream sediment CRM, and dos Santos *et al.*[162] carried out homogeneity and stability tests on a candidate laboratory RM of soy leaves. Unfortunately it was not stated when the latter materials might be commercially available.

3.2 Sample preparation

3.2.1 Sample dissolution and extraction

Several research groups compared *sample digestion methods for particular applications*, though some with rather predictable outcomes. For example, when USEPA Method 3050B (HNO_3/H_2O_2 digestion) and ISO 14869-1:2001 ($HNO_3/HF/HClO_4$) were applied to sediments from Havana Bay[163], the mean average extraction efficiency for Co, Cu, Ni, Pb and Zn using Method 3050B was 86% of the value obtained with total digestion. Another study[164] showed that Method 3050B was less efficient than ashing followed by treatment with $HCl/HNO_3/HF/HClO_4$ in releasing elements such as Li and Ti from moss. More interesting was a comparison between Method 3050B and ISO 11466-3:1995 (*aqua regia* digestion) for the extraction of Cu, Ni and Pb from sediment samples[165]. Similar amounts of Cu were recovered with both methods, but the USEPA method generally extracted more Ni and the ISO method more Pb. Application of XRF and SEM-EDS after extraction suggested that residual Cu was bound to the silicate phase, hence unlikely to be released by either procedure. The Ni that was not released by the ISO method was associated with Fe(O)OH, which was not completely dissolved by *aqua regia*, whilst the presence of HCl favoured dissolution of PbS. In the comparison[166] of seven microwave-assisted and hotplate digestion methods, treatment of 0.1 g of plant, rock or soil with 2 mL 40% (v/v) HF + 0.5 mL HNO_3 on a hotplate gave the best performance overall for measurement of Pb, Sc, Th and Y by ICP-MS, as assessed by analysis of USGS BCR-1 (Basalt), USGS G-2 (Granite), NIST SRM 2711 (Montana Soil) and NIST SRM 1515 (Apple Leaves). Use of a graphite digestion block gave better recovery than microwave digestion for As species from plants using 0.3 M *o*-phosphoric acid[167]. An optimised sample digestion procedure[168] for the measurement of S in mine tailings by ICP-AES involved treatment of 0.1 g sample with 4 mL *aqua regia* in a hot block. Digesting plant leaves and grain[169] in closed, single-use polypropylene tubes was proposed as a cost-effective alternative to open-tube or microwave-assisted digestion, yielding recoveries of 94-113% for measurement of 18 elements in six RMs by ICP-AES.

The accurate measurement of Si in plants using a microwave-assisted *HF digestion* followed by ICP-AES such as sugarcane[170] is becoming more important because of potential risk to human health associated with exposure to crystalline silica formed during combustion of biofuels. Although certified values were unavailable, results were similar to previous literature values for NIST SRMs 1515 (Apple Leaves) and 1547 (Peach Leaves) and for NRCCRM CRM GBW07602 (Bush Branches and Leaves). Researchers in Oregon[171] found that concentrations of Al, Ba, Ca, Mg and Sr measured by ICP-AES in some HF sediment digests increased and stabilised over a period of 8-29 days, as poorly-soluble fluorides formed in the digestion process re-dissolved. The waiting time could be reduced to 6 days if the digests were heated to *ca.* 60 °C for 24 h.

Keen interest in *the determination of Hg*, perhaps prompted by the forthcoming UNEP Global Legal Binding Instrument on Mercury (http://www.unep.org/hazardoussubstances/MercuryNot/MercuryNegotiations/tabid/3320/language/en-US/Default.aspx), is reflected in the publication of a number of sample digestion procedures. These included a pyrolysis chamber method[172] for plant tissue, a microwave-induced combustion procedure[173] applicable to soil, and a 30% HNO_3 + 0.02% thiourea extraction[174] for sediments, performed in disposable vessels in a domestic microwave oven.

A two-level full factorial design[175] was used to optimise the *ultrasound-assisted extraction* of Co and Sb from inorganic environmental matrices, including soil, sludge and sediments, in closed Eppendorf vials prior to analysis by ETAAS. Using NIST SRM 2702 (Marine Sediment) as the test substrate, best results were obtained when 5 mg samples were sonicated for 20 min in 1 mL of 20% (v/v) HF + 20% (v/v) HNO_3. Method LODs were 0.06 µg g^{-1} for Co and 0.20 µg g^{-1} for Sb with RSDs <10% for both analytes (n=3).

New variants of *methods for the chromatographic separation of radionuclides* from environmental materials continue to be reported. One procedure [176] successfully separated Am, Np, Pu, Th and U with good recoveries (94–100%) using TEVA® and DGA resins. Another procedure[177] coupled a lab-on-valve, multisyringe FI system and UTEVA® column to an ICP-MS instrument to create a fully automated system for measurement of Th and U. An important feature of both systems was that the resins could be regenerated and re-used. Jeandel *et al.*[178] minimised the cost of their method in a different way, by selecting Dowex® AG1-X8 over TRU resin for the separation of Nd, Pa, Ra, Th and U. A novel method for the determination of ^{99}Tc by ICP-MS[179] also used TEVA® resin, in this case for removal of isobaric interferences from molybdenum and ruthenium that occurred during analysis of seaweed and soil digests.

The 'labile' or 'reactive' pool of a trace element in soil can be estimated by *stable isotope exchange methods*. Atkinson *et al.*[180] equilibrated contaminated soils with ^{204}Pb by shaking for three days in 5 x 10^{-4} M EDTA. Suspensions were filtered and isotopically-exchangeable Pb measured by ICP-MS. The non-labile Pb fraction determined by isotopic exchange did not correlate well with the residual Pb fraction determined by a 5-step extraction, confirming that the sum of the non-residual stages of a sequential extraction is not a good estimate of the available analyte pool. A French team[181] demonstrated that a multi-element spike solution containing ^{62}Ni, ^{65}Cu, ^{67}Zn, ^{106}Cd and ^{204}Pb could be used to determine isotopically exchangeable concentrations (E values) in fluvisols without inter-element competition. Laborda *et al.*[182] noted that extracts recovered in isotope exchange experiments may contain not only true solution species but also non-exchangeable metals bound to small colloid particles. This could lead to significant overestimation of the exchangeable fraction. Aqueous phases of compost suspensions previously spiked with ^{65}Cu and ^{206}Pb were analysed by coupling A4F with ICP-MS. No enhancement of E values were found, but the methodology developed is worthy of application elsewhere.

A simple phosphoric acid extraction[183] produced results similar to a two-stage physiologically-based *extraction procedure for bioaccessible concentrations* of Se, selenite and selenate in RTC soil CRMs 023-0505 and 025-0505 and in two Californian soils. Total Se was measured by HG-AFS and ICP-MS; Se species in PBET extracts by HPLC-ICP-MS and a HPLC-HG-AFS method in which the column eluate passed through a UV reactor prior to the hydride generation unit; and Se species in 1 M *o*-phosphoric acid also by HPLC-HG-AFS. An improved mode of column packing[184] for on-line leaching and determination of the bioaccessible As content in rice by ICP-MS, and for speciation of As in the bioaccessible fraction, has been reported. Tongesayi *et al.*[185] replaced glycine in the established SBET method with cysteine, which has a stronger affinity for some metals.

Rotating coiled columns are gaining in popularity as an alternative to sequential extraction for fractionation of trace elements in soils and sediment. Their utility has been reviewed (57 references) by Fedotov[186] who, together with Savonina and Wennrich, also compared microcolumns and RCCs for partitioning of Se in soil and sediment[187], and of As and Sb in soil and sludge[188] with detection by ICP-AES.

3.2.2 Sample preconcentration

Analyte preconcentration procedures remain a focus of interest. Methods for the analysis of soils, plants or related materials are summarised in Tables 4-6, together with procedures designed for other sample matrices that were applied to soil or plant CRMs during development.

3.3 Instrumental analysis

3.3.1 Atomic absorption spectrometry

Studies on *flame atomic absorption spectrometry* included the optimisation of a ultrasound-assisted slurry sampling procedure[189] for the determination of Fe in cassava leaves. Comparison of two background correction systems[190] showed that high-speed self-reversal was superior to use of a D_2 continuum source in compensating for spectral interferences in the determination of low concentrations of Zn in Fe-rich soils. A slotted quartz tube atom trap[191] provided a 400-fold increase in sensitivity for the determination of In compared to conventional FAAS analysis. Analyte was accumulated on the inner wall of the trap in the form of In_2O_3, and then re-atomised by introduction of 10 µL of MIBK. The LOD was 2.6 ng mL^{-1} and the result obtained for NIST SRM 2710 (Montana Soil) was 5.14 ± 0.06 mg kg^{-1} (*cf.* indicative value 5.10 mg kg^{-1}).

In investigations of Ir/Nd and Ir/W mixtures as permanent *modifiers in slurry sampling ETAAS*, 30 µg Ir + 40 µg Nb was optimal for the determination of Sb in soil and sediment with platform atomisation[192] whereas 2 µg Ir + 10 µg Nb was preferred for the determination of Cr in plants with wall atomisation[193]. An iridium permanent modifier did not stabilise Cd in its determination in fertilisers by HR-CS-ETAAS[194]. Better results were obtained when 10 µL of a 10 µg Pd + 6 µg Mg solution was added to the graphite tube. A similar mixture (10 µg Pb + 10 µg Mg) was successfully used to determine Zn in slurries of marine and lacustrine sediment CRMs[195].

The use of an *electrothermal atomiser crucible with separated zones for solid sample analysis* was revisited by Oreshhkin and Tsizin[196]. In their latest device, sample vapour was able to pass through the heated porous wall of a graphite tube into the analytical zone, whereas particles and aerosols were excluded, thereby reducing matrix interference effects. Spike recovery experiments for Ag, Cd and Pb added to sediments appeared to give promising results.

Use of *sedimentation FFF with cold vapour-ETAAS* confirmed the potential importance of soil colloids in the environmental transport of Hg[197]. The <1 µm size fractions of three highly contaminated soils were injected into the FFF apparatus and their particle size distribution determined. Aliquots of the eluate were collected every 3.5 min, acidified with HNO_3 and analysed. Both particle size distributions and Hg concentrations peaked in the 0.4-0.7 µm range for all three samples.

3.3.2 Atomic emission spectrometry

Electrolyte cathode discharge atomic emission spectrometry was proposed as a low-cost alternative to ICP-AES for the determination of Hg[112]. A stable plasma discharge was created between a tungsten pin anode and a liquid cathode (the sample solution in contact with a grounded Pt ring). Optimal conditions were 1 mm inter-electrode gap, 0.76 kV potential and 1 mL min^{-1} solution flow rate. The addition of 5% of 0.2 M acetic acid to the FI manifold gave a 5-fold signal enhancement, with a

LOD of 2 ng mL^{-1}. The result obtained for IRMM BCR 060 (Aquatic Plant) was within 6% of the certified value.

Interest in *use of tungsten coil atomisers* has continued. Hanna and Jones [198] described a unique ETV-FAES device in which analyte vapourised from a tungsten filament taken from projector light bulb was carried by a stream of 10% H_2 + 90% Ar into the flame of a standard metal-cutting torch. The LODs for 19 elements were below 0.2 ng mL^{-1}. Recoveries of Ag, Cu, Mn, Pb and Tl from NIST SRM 2711 (Montana Soil) were in the range 90-112%. Tungsten coil-AES was used for the determination of Sr in soil[199]. Buffering the analyte solution to pH 5.5 with ammonium carbonate, followed by filtration through a 0.45 μm pore size syringe filter removed interference due to Al.

A novel means for *removal of the reagent matrix*[200] prior to analysis of soil extracts by ICP-AES involved use of a cross flow FFF system, coupled between a CF sequential extraction unit and an ICP, and polyethyleneimine (molecular weight 25,000 Da) to complex the analyte elements. Matrix removal efficiency was 84% for a 0.1 M solution of $Mg(NO_3)_2$. The approach may prove useful in analysis of high-matrix samples, not only by ICP-AES but with other types of atomic spectrometry where matrix removal is desirable.

Some specific *errors and pitfalls in the application of ICP-AES* by unwary users have been highlighted in the past year. Falandysz[201] was strongly critical of authors who had reported data obtained at 196.0 nm for Se in mushrooms without allowing for previously reported matrix interference effects[202] due to Br, C, P and S that can cause significant signal enhancement. McBride[203] cautioned researchers who attempted to quantify low levels of Cd in soil at 226.5 nm and also highlighted a spectral interference at 228.8 nm that could affect the determination of Cd in As-rich soil.

3.3.3 Atomic fluorescence spectrometry

Gao and Liu[204] optimised *a method for the determination of MeHg and EtHg species by HPLC-cold vapour-AFS* in sewage sludge, following a 30 min, ultrasound-assisted extraction with TMAH and copper powder at 70 °C. No matrix-matched CRM was available but the result for MeHg in IAEA-405 (Estuarine Sediment) agreed with the certified value. A method for Hg speciation in sediments[205] involved extraction into

0.1% (v/v) 2-mercaptoethanol followed by injection into a HPLC-VG-AFS system. Inorganic mercury (Hg^{2+}), $MeHg^+$ and $EtHg^+$, baseline separated using a C-18 column, had LODs of 0.48, 0.58 and 1.1 ng g^{-1}, respectively.

Two articles described *non-chromatographic speciation of As by HG-AFS*. One[206] used different concentrations of HCl and $NaBH_4$ selectively to generate As^{III} or As^V hydrides from soil. The other method[207], for the analysis of garlic, was a minor modification of an earlier method[208] and based on the different efficiencies of HG with and without a pre-reduction step and use of proportional equations.

3.3.4 Inductively coupled plasma mass spectrometry

Mesko *et al.*[209] reviewed (157 references) in detail the different *sample preparation strategies* for the ICP-MS analysis of biological matrices. They highlighted trends in the past 15 years, including increased use of enzymes, ASE, ultrasound- and microwave-assisted extraction. They concluded that preserving analyte and, especially, species integrity during sample preparation remained challenging.

The application of *dynamic reaction cell technology* to overcome atomic and polyatomic interferences in the determination of As, Cr, Sr and V in polymers, biological and environmental samples was reviewed[210] (76 references) with particular emphasis on the selection of reagent gas. Several authors have used O_2 in DRCs, either reacting it with the interferent(s) to convert them to higher mass polyatomic species, or with the analyte, which was then quantified as an oxide. Guo *et al.*[211] recommended addition of 2.4 mL min^{-1} O_2 to minimise interferences from Mo, Nb, Y and Zr oxides and hydroxide in the determination of Ag in soil and sediment: $^{93}Nb^{16}O^+$, $^{92}Zr^{16}OH^+$ and $^{92}Mo^{16}OH^+$ were rapidly converted to oxides of higher mass, allowing quantification at ^{109}Ag, but interferences from $^{89}Y^{18}O^+$ and $^{91}Zr^{16}O^+$ on ^{107}Ag remained. Fujiwara *et al.*[212] found that 0.6 mL min^{-1} O_2 minimised interference from $^{129}Xe^+$ in the determination of ^{129}I in soil extracts. A further interference in this analysis, from $^{127}IH_2^+$, was removed by eliminating H_2 and H_2O from the reagent gas and carefully tuning the axial field of the cell. Addition of *ca.* 0.5 mL min^{-1} O_2 to a DRC allowed quantification of As in *aqua regia* digests of soil[213] as the $^{75}As^{16}O^+$ ion, whereas a flow rate of 0.35 mL min O_2 was preferred for quantification of V as VO^+ in lake sediment digests[214].

In the *measurement of Se in plants*[215], use of 0.8 mL min^{-1} ammonia and quantification based on $^{78}Se^+$ was preferred to the use of methane and $^{80}Se^+$ because this better suppressed interference from doubly charged lanthanide ions and thus gave better accuracy for the analysis of seven plant CRMs (recovery range 87-114% *cf.* 84-145%). Quantifying the analyte at *m/*z = 78 also avoided interference from $^1H^{79}Br^+$ that can occur when analysing Br-rich samples such as NIST SRM 1573a (Tomato Leaves).

Cizdziel *et al.*[216] used several *CRMs as calibrants in the LA-ICP-MS* analysis of binder-free pressed pellets of desert plants for Ba, Ca, Cd, Cu, Mg, Mn and Sr. The need for matrix matching was highlighted by a study[217] in which targets were prepared by treating mixtures of a CRM and zinc oxide with 2-methoxy-4-(2-propenyl)phenol. When NIST SRM 8704 (Buffalo River Sediment) was used as the calibrant in the determination of Co, Mn and Pb in CRMs IRMM BCR143R (Sewage Sludge Amended Soil) and IRMM BCR144R (Sewage Sludge From Domestic Origin), excellent agreement with certified values was found for the soil, which is chemically similar to sediment, but not for the sludge, which has a different matrix composition. Another approach[218] was first to use CRMs NIST SRM 1515 (Apple Leaves) and IRMM BCR 100 (Beech Leaves) to validate a method for the determination of Pb by solution ICP-MS, and then to use this as a reference method in the development of a LA-ICP-MS approach for the analysis of Antarctic lichen, as pressed pellets using ^{13}C as internal standard.

Use of palladium nanoparticles as a modifier for slurry sampling ETV-ICP-MS increased signal intensity for As, Cd, Hg, Pb, Sb and Zn up to 3-fold relative to that obtained when the same amount of Pd was supplied in solution[219]. No thermal treatment between injection of modifier and sample was needed. The particles were easy to produce in a one-step reduction. External calibration with aqueous standards was not possible, but results obtained by either standard additions or ID agreed with certified values for NIST SRMs 1568a (Rice Flour) and 1573a (Tomato Leaves).

Several *methods for evaluating the redox speciation of trace elements by HPLC-ICP-MS* have been reported. Thallium (I) and Tl^{III} were separated in plant extracts by anion-exchange HPLC[220] using a Hamilton PRP-X100 column and 100 mM ammonium acetate + 5 mM DTPA mobile phase, and by RP–HPLC[221] using a C-8 column and 1 mM tetrabutylammonium phosphate + 2 mM DTPA in 1% (v/v) methanol mobile phase. To assess potential risk to human health from inhalation of particulate matter associated with wildfires in California, a method previously used for the speciation of Cr has been adapted[222] for simultaneous measurement of As^{III}, As^{V}, Cr^{III}, Cr^{VI}, Se^{IV} and Se^{VI} in deionised water and simulated lung fluid extracts of soil and ash. A detailed investigation of potential interspecies conversion revealed that extracts should be stored at 10 °C, without the addition of preservatives, and analysed within 4 hours. The window of stability for Se species in 0.016 M KH_2PO_4 extracts of soils was even shorter (<1 h)[223]. A multi-national group of researchers[224] were so concerned about potential changes in Se speciation due to the difference in pH between their volcanic soil extracts in simulated acid rain (pH 2.2-4.4) and typical HPLC mobile phases (pH 4.8 or higher), that they developed a dedicated chromatographic method involving an anion-exchange column and low pH eluent (20 mM ammonium citrate at pH 3).

Methods for the determination of metal complexes included HPLC-ICP-MS procedures for quantification of Ni and V tetrapyrroles in oil-contaminated sediments[225], for the measurement of methylmercury in 5% (v/v) 2-mercaptoethanol extracts of sediments (also applicable to fish)[226], and for the determination of organotins[227-228] (in Chinese with English abstract). The complementary use of HPLC-ICP-MS with ESI-MS for identification and quantification of thiol peptides and their metal complexes in plants and fungi was discussed briefly in a broad review[229] of LC-MS techniques (87 references). Although strictly in the domain of molecular MS, a novel extractive ESI-MS method[230] was noteworthy because values obtained for $^{235}U/^{238}U$ isotope ratios in acid digests of five soils were within 5% of ICP-MS results.

3.3.5 Laser-induced breakdown spectroscopy

A 101– reference review[231] of the application of LIBS covered a myriad of sample types, including clinical materials, fruit, vegetables, medicinal plants and industrial waste.

Laser ablation fast pulse discharge plasma spectroscopy, an alternative to dual pulse LIBS for signal enhancement, was applied to the measurement of Mg, Pb and Sn in soil[232]. Calibrants, prepared by mixing CRMs NRCCRM GBW07406, 07419 and 07429 (Soils), gave a linear response over the concentration range studied for Mg, after normalisation of the analyte emission to that of Si at 288.16 nm. In contrast, Pb and Sn calibrations were non-linear at higher concentrations due to selfabsorption. The LODs based on the linear portions of the calibration graphs were 34, 1.5 and 0.16 μg g^{-1} for Mg, Pb and Sn, respectively. It was later reported [233] that even greater sensitivity enhancement could be obtained if the μs–pulse discharge was replaced with a ns discharge.

Calibration strategy in the application of LIBS to soil is still an active topic of research, with different research groups advocating different approaches. Jantzi and Almirall[234] simply used sand spiked with different concentrations of analytes. He *et al.*[235] recommended Fe as an internal standard for the measurement of Al, Ca, Cr, K, Mg, Mn, Si and Ti, although results obtained for Cr, Mn and Ti differed by 10-20% from reference data obtained by other techniques. Ferreira *et al.*[236] investigated the usefulness of multilayer perceptron (a type of ANN based on supervised learning) for determination of Ba, Co, Cu, Mn, Ni, V and Zn. A set of 19 soils was used to build the calibration model, which was then applied to determine the analyte concentrations in a validation set of nine soils. Data obtained with the ANN agreed more closely with those obtained by ICP-AES following total digestion than with conventional LIBS linear calibration.

Procedures for the comminution of plant leaves for LIBS analysis used sugarcane, orange tree and soy as test samples[237]. Both planetary ball milling and cryogenic grinding produced particles of <75 μm diameter, suitable for pressing into sample pellets without binder. Reproducible craters were formed on exposure to the 1064 nm laser and the site-to-site variation in emission intensity was 5-20% ($n = 30$). The time required for comminution depended on the fibre and cellulose content of the plant species.

Although challenges remain, there is evidence that *multivariate analysis of LIBS trace element profiles* is beginning to emerge as a useful tool for chemical fingerprinting. An assessment[234] of the capability of LIBS analysis at 266 nm followed by PCA to determine the provenance of soil samples in a forensic context showed that it was possible to discriminate between samples from different sites, and to associate samples from the same site, with few misclassifications. Use of LIBS with PCA or PLS regression[238] proved capable of differentiating between species of bacteria isolated from Jamaican bauxite soils.

3.3.6 X-ray spectrometry

A useful and informative *review* (159 references)[239] of trends in the application of μXRF to environmental samples, including soils and plants, covered the 2008-2012 period. Recent advances in synchrotron XRF[240] , such as the ability to carry out analysis *in vivo* in hydrated tissues, have contributed to the study of plant physiology (91 references). Revenko[241] discussed the important contributions to XRF made by Russian authors between 1991 and 2010 (281 references). The review[242] (195 references) of approaches for imaging elemental distribution and speciation in plants included X-ray techniques, nanoSIMS and LA-ICP-MS. Similarly the review[243] on ways of studying biogeochemical interfaces in soil (157 references) considered X-ray techniques, nanoSIMS and AFM.

A novel method[244] proposed for the determination of soil quality involved the *application of multivariate chemometric techniques to both fluorescence and scatter regions of the X-ray spectrum*, as opposed to analysis based on specific fluorescent peaks as is normally the case in EDXRF. The approach was tested using kaolin spiked with Cu, $H_2PO_4^-$, Fe, NO_3^-, SO_4^2 and Zn; CRMs IAEA Soil-1 and Soil-7; and two Kenyan soils. Soils could be readily distinguished based on the PCA of their EDXRF and scatter spectra. Both PLS and ANN could be used to predict analyte concentrations, although with variable accuracy. Further development and application of the approach to a wider series of Kenyan soils[245] showed that both PLS and ANN provided a reasonable estimate of C, N and Na content, whilst ANN performed better for the determination of Mg and P. Although semi-quantitative, the method could be a useful tool for rapid screening of large sample sets.

Shaltout *et al.*[246] studied a series of Nile sediments to assess *the effect of grain size on results of standardless quantitative WDXRF*. The fluorescence intensity increased with grain size for some elements, e.g. K, but decreased for others, e.g. Si. They developed a cubic spline interpolation algorithm relating intensity, grain size and atomic number, applicable to K lines with $Z<30$.

Progress in *the applications of a portable XRF unit* included the development of a genetic algorithm for rapid, automated, analysis of XRF spectra to guide adaptive sampling of seabed sediments on an autonomous underwater vehicle[247]. Differences in elemental concentrations, measured under field or laboratory conditions, enhanced visual differentiation between pedons within a soil profile[248]. An unusual but commendable article by Higueras *et al.*[249] described an attempt to simulate field analysis in a remote region affected by mining waste. The potential applicability, impact and benefit of portable XRF units in environmental monitoring and protection in developing countries were assessed. They commented critically on international aid strategies that donate complex analytical facilities to regions where insufficient infrastructure is available to sustain them, and suggested that simpler robust instruments such as portable XRF units are more fit-for-purpose.

A Canadian group[250] contributed to the discussion concerning the recent *detection of a hexa-coordinate* As^V*-glycerol species by XANES analysis.* This compound was unstable in the presence of a large excess of water, and could have been created as an artefact during drying. However, its detection in fresh samples of carnivorous sundew plant suggested that it may also be more prevalent in environmental samples than previously thought because it remains undetectable by speciation techniques used to analyse aqueous samples.

3.3.7 Secondary ion mass spectrometry

Secondary ion mass spectrometry shows promise as a complementary technique to synchrotron XRF for *element detection and imaging in both plants and soils*. The higher spatial resolution of SIMS allows features to be discriminated at <100 nm scales. The ability to measure stable isotopes presents opportunities for tracer studies. Challenges include differences in ion yield between analytes, matrix effects and maintaining the integrity of biological samples during preparation. The fundamental principles of nanoSIMS and its application to plants were reviewed[251] (85 references) and its capabilities compared with those of other techniques[242-243]. NanoSIMS was used to identify and show associations between major soil components[252]. A new internal calibration method[253] improved the accuracy of C/N and $^{15}N/^{14}N$ ratio measurement in soil organic matter.

3.4 Speciation

A detailed critique of the speciation literature can be found in our sister Update[4]. *Review articles* of note covered: As speciation in environmental samples involving voltammetry, chromatography (both HPLC and GC) and HG (86 references)[254]; As speciation with HG-AAS and ETAAS detection (145 references)[92]; chromatographic methods for organotins (70 references)[255]; trace element speciation in food with particular reference to As, Hg, and Sn (68 references)[256]; the speciation and spatial distribution of As and Se in rice (63 references)[257]; and quantification of phytochelatin species produced by plants as a means to detoxify metal(loid)s (55 references)[258].

Table 4. Preconcentration methods involving liquid-phase extraction used in the analysis of soils, plants and related materials

Analyte(s)	Matrix	Method	Reagent(s)	Detector	Notes	CRMs (or other validation)	Reference
As, Bi, Cd, Pb	Fertiliser, urine, river water, wine	CPE	Triton X-114®, *o,o*-diethyldithiophosphate chelator	ICP-AES	Preconcentration factor 10-18; LODs 0.05-0.06 µg L^{-1}, except Pb 0.28 µg L^{-1}	NIST SRM 1643e (Enriched Water), NIST SRM 1566b (Oyster Tissue), INCT CTA-OTL-1 (Oriental Tobacco Leaves), NRCCRM GBW 07602 (Bush Branches and Leaves)	113
Bi	Soil, seawater, tap water, waste water	LPME	S-methyl-3-salicylidene dithiocarbazate in chloroform	ETAAS	Preconcentration factor 100; LOD 19 pg mL^{-1}		259
Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Food, hair, water	IPE	2-(4-methoxybenzoyl)-N′-benzylidene-3-(4-methoxyphenyl)-3-oxo-N-phenyl-propono hydrazide	FAAS	LODs 0.33 – 0.90 µg L^{-1}	LGC CRM 6019 (River Water), RTC CRM 044 (Soil)	260
Cd, Hg, Pb	Sediment	SFE	*bis*-(2,4,4-trimethylpentyl)monothiophosphinic acid, CO_2	ICP-MS		NACIS NCS DC 73372 (Lake Sediment)	261
Cd, Pb	Soil	CPE	Octyl polyethylene glycol phenol ether, ammonium pyrrolidine dithiocarbamate	FAAS	Preconcentration factors Cd 49, Pb 62; LODs Cd 0.29 ng mL^{1}, Pb 2.1 ng mL^{-1}	Spike recovery	262
Cu, Fe	Food, water	CPE	Triton X-114®, Eriochrome Cyanine R	FAAS	Preconcentration factors Cu 99, Fe 141; LODs Cu 0.57 ng mL^{1}, Fe 0.33 ng mL^{-1}	NCS DC 73349 (Bush Branches and Leaves), NWRI TM 23.2 (Fortified Water)	263

Fe, Zn	Food, hair, water	SE	Methyl-2-(4-methoxybenzoyl)-3-(4-methoxyphenyl)-3-oxopropanoyl carbamate in MIBK	FAAS	Preconcentration factor 100; LODs Fe 0.26 μg L^{1}, Zn 0.32 μg L^{-1}	Spike recovery	264
Mn	Tea leaves, tea infusion, water	CPE	Triton X-100®, 8-hydroxyquinoline	FAAS	Preconcentration factor 10-20; LOD 1.9 μg L^{-1}	IRMM BCR 278R (Mussel Tissue)	265
Te	Soil, water	SFODME	1-undecanol solvent, ammonium pyrrolidinedithiocarbamate complexing agent	ETAAS	Preconcentration factor 342, LOD 0.003 ng mL^{-1}	NIST SRM 1643e (Trace Elements in Water)	266
Zn	Blood, plants	CPE	Triton X-114®, 2-methyl-8-hydroxyquinoline or 1-(2-pyridylazo)-2-naphthol	FAAS	Preconcentration factor 30 and 26, LODs 1.4 and 1.5 μg L^{-1}	IRMM BCR 101 (Spruce Needles)	267

Table 5 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, Ni, Pb, Zn	Cabbage, potato	La-2,2´-bipyridyl and rose Bengal	FAAS, ICP-AES	Preconcentration factor 40; LODs 0.71 – 5.8 μg L^{-1} (FAAS), 0.36 – 3.3 μg L^{-1} (ICP-AES)	NACIS NCS ZC 85006 (Tomato)	268
Cr	Soil, wastewater,	Ytterbium(III) hydroxide	FAAS	Preconcentration factor 30, LOD 1.1 μg L^{-1}	NWRI TMDA 54.4 (Fortified Lake Water), NIST SRM 2710 (Montana Soil)	269
Cu, Ni	Baby food, water	Mo(VI)/di-*tert*-butyl{methylene-*bis*-$^{270\text{-diyl}}$}*bis*-carbamate	FAAS	Preconcentration factor Cu 40, Ni 100; LODs Cu 0.43 μg L^{-1}, Ni 0.70 μg L^{-1}	NWRI TM-25.3 (Fortified Lake Water), HPS CRM-SA-C (Sandy Soil C)	270

Table 6. Preconcentration methods involving solid phase extraction used in the analysis of soils, plants and related materials

Analyte(s)	Matrix	Substrate coating or modifying agent	Column substrate	Detector	Notes	CRMs (or other validation)	Reference
Au	Ore, soil and water		Granular activated carbon	ETAAS	Preconcentration factor 50; LODs 0.9 ng g^{-1} in soil, 7 ng L^{-1} water	MINTEK SARM-7B (Platinum Ore), NIST SRM 330 (Copper Ore Mill Heads)	271
Au, Pd, Pt	Ore, soil, water	Cysteine	Silica gel	ETAAS (Au), ICP-AES (Pd, Pt)	LODs Au: 0.002 µg g^{-1} ore, 0.005 µg L^{-1} water; Pd: 0.006 µg g^{-1} ore, 003 µg L^{-1} water; Pt: 0.002 µg g^{-1} soil, 0.06 µg L^{-1} water	Copper Ore 327-98, spike recovery	141
Cd	Tobacco	Sodium diethyldithiocarbamate	Amberlite XAD-2	FAAS	Preconcentration factor 100; LOD 0.03 mg mL^{-1}	INCT CTA-OTL-1 (Oriental Tobacco Leaves)	272
Cd, Co, Cu	Tea leaves, water		ZrO_2/B_2O_3 nanohybrid material	FAAS	Preconcentration factor 10-15, LODs 3.1-3.8 µg L^{-1}	NRCCRM GBW07605 (Tea Leaves)	273
Cd, Co, Cu, Fe, Ni, Pb, Zn	Pharmaceutical samples, water	8-hydroxyquinoline	Multiwalled carbon nanotube disc		LODs 1.0 – 5.2 µg L^{-1}	NIST SRM 1577b (Bovine Liver), IAEA-336 (Lichen), IAEA HR-1 (Humber River Sediment)	274
Cd, Cu	Fish, sediment, water	Diphenylcarbazide	SBA-15 nanoporous silica	FAAS	Preconcentration factor 290; LODs Cd 0.15 ng mL^{-1}, Cu 0.45 ng mL^{-1}	NACIS NCS DC 73323 (Soil), OREAS BG 326 (Polymetallic Ore)	275
Cd, Cu, Pb	Sediment, urine, water		Mixed cellulose ester membrane	FAAS	LODs Cd 0.2 µg L^{-1}, Cu 2.0 µg L^{-1}, Pb 3.0 µg L^{-1}	NIST SRM 8704 (Buffalo River Sediment),	276

						Spike recovery	
Co, Cu, Pb	Soil, tea leaves, water		Nanoalumina - single walled carbon nanotube hybrid	FAAS	LODs Co 0.9 µg L^{-1}, Cu 1.1 µg L^{-1}, Pb 2.1 µg L^{-1}	IRMM BCR 150 (Skim milk powder, CMI 7003 (Silty Clay)	277
Cu	Tobacco leaves	Alizarin fluorine blue	Sisal fibre	FAAS	Preconcentration factor 75; LOD 0.018 µg L^{-1}	NIST SRM 1570a (Spinach Leaves)	278
Cu	Mussel, water		Functionalised multiwalled carbon nanotube	FAAS	Preconcentration factor 100; LOD 0.27 µg L^{-1}	IRMM BCR 320R (Channel Sediment)	279
Cu	Food, soil, water	1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone	Chloromethylated polystyrene	FAAS	Preconcentration factor 41; LOD 0.56 µg L^{-1}	Spike recovery	280
Cu, Ni, Pb, Zn	Soil	*Trans*-1,2-diaminocyclohexane -*N, N, N',N'*-tetraacetic acid	Nobias Chelate-PA1	ESI-MS	LODs 1.9-5.0 ng g^{-1}	JSAC-0401 (Brown Forest Soil)	281
Fe, Pb	Plant, water		Bucky tubes disc	FAAS	LODs Fe 1.6 µg L^{-1}, Pb 4.9 µg L^{-1}	NWRI TMDA 51.3 (Fortified Water)	282
Hg	Water	S-benzyldithiocarbazate	Modified activated carbon	ICP-AES	Preconcentration factor 80; LOD 0.09 ng mL^{-1}	NRCCRM GBW08301 (River Sediment)	283
Hg	Sediment		Triisobutylphosphine sulphide, CYANEX-471X®	Cold vapour AAS	Preconcentration factor 32; LOD 24 ng L^{-1}	NIST SRM 2709 (San Joaquin Soil), NRCCRM GSD-9 and GSD-11 (Sewage Sediment)	284
Ho, La, Tb			TiO_2 – grapheme composite	MPT-AES	Preconcentration factor 10-17; LODs 1.6 – 2.8 µg L^{-1}	NRCCRM GBW 07313 (Marine Sediment)	285
Ni, Pb	Sediment, sludge		CNT, oxidised CNT, L-alanine immobilised on CNT	ETAAS	LODs Ni 30 µg L^{-1}, Pb 10 µg L^{-1}	QC Municipal Sludge, TRAP-LRM Lake Sediment	286

Pb	Parenteral solutions, urine, water		Ion-imprinted polyvinylimidazol-silica hybrid copolymer	TS-FF-AAS	Preconcentration factor 128; LOD 0.75 μg L^{-1}	NRCC ORM-3 (Fish Protein), NRCC MESS-3 (Marine Sediment), NRCC PACS-2 (Marine Sediment)	287
Tl	Cement, soil, zinc		Chromosorb 105	ETAAS	LODs 0.05 μg L^{-1} (total Tl), 0.034 μg L^{-1} (Tl^{III})	NIST SRM 2710 (Montana Soil), NRCCRM GBW 07402 (Soil), NRCCRM GBW 07309 and NRCCRM GBW 07310 (Stream Sediments)	288

4 ANALYSIS OF GEOLOGICAL MATERIALS

4.1 Reference materials

Since the production of the first *geological reference materials* in 1951, USGS G1 (Granite) and W1 (Diabase), there has always been a demand for a wider range of better characterised RMs to keep pace with developments in analytical instrumentation and geological research. Meisel and Kane[289] discussed current challenges, including the production of RMs for isotope ratio and microanalytical measurements, and ways in which these issues may be addressed.

Some of the glass RMs most frequently used in the microanalysis of geological materials by techniques such as LA-ICP-MS and SIMS are the *NIST SRM 610-617 series (Trace Elements in Glass).* Because these glasses were not designed for microanalysis and were not originally certified for many elements, most practitioners rely on consensus values derived from compilations of published data, e.g. Pearce *et al.*[290]. Since then, many new high precision data have been published, inhomogeneities evaluated and protocols for the calculation of uncertainty budgets revised. For these reasons, the new reference values for SRMs 610-617 published by Jochum *et al.*[291] are a notable advance and will be widely welcomed by the geoanalytical community. The values were reported with a high degree of confidence as they were obtained by following ISO guidelines and the IAG protocol for certification of RMs, using a number of different analytical techniques. Test portions of 1.0, 0.1 and 0.02 µg were used to assess element inhomogeneities, and uncertainties at the 95% confidence level were reported for bulk and microanalytical applications. Although the new reference values agreed with the NIST certified values (with the exception of Mn in SRM 610), they differed typically by as much as 10% from the Pearce *et al.* compilation. The new dataset represents state-of-the-art values for interlaboratory comparisons and their use in microanalytical calibrations should lead to improvements in data quality.

Several *new geological RMs for elemental analysis* are available. Two new PGE RMs from IGGE, MCPt-1 and MCPt-2, cobalt-rich seamount crusts collected from the western and central Pacific Ocean, were characterised for 68 elements including all six PGEs[292]. These ultra-fine RMs have an average particle size of 1.8 and 1.5 µm respectively, and the minimum sampling mass for the determination of the PGEs was calculated to be 1 g. Donohue *et al.*[293] proposed the use of ilmenite ($FeTiO_3$) megacrystals collected from the Solomon Islands as secondary RMs in the microanalysis of similar materials by LA-ICP-MS. Although these megacrysts are not suitable for consideration as a CRM, accurate elemental abundances in ilmenite at high resolution were obtained using Ti as the internal standard and NIST SRM 610 glass as the external calibrant.

As identified by Meisel and Kane[289], there is great demand for *RMs with well-constrained isotopic contents*. Fisher *et al.*[294] prepared synthetic zircon crystals doped with Hf and REEs for use as a potential RM for Lu-Hf isotopic measurements in zircon by LA-MC-ICP-MS. The crystals were doped to produce a large range of REEs/Hf ratios so that the ^{176}Yb and ^{176}Lu isobaric interferences on the low abundance ^{176}Hf in natural zircons, as well as potential REE oxide interferences, could be monitored and corrected. The synthetic zircon crystals were homogeneous both within and between grains for Hf isotope measurements. Conclusive evidence that zircon crystals doped with various amount of REEs and Hf were more reliable than Yb-doped Hf solutions for the accurate measurement of the Yb mass bias correction was obtained. Metal standards NIST SRM 976 (Cu) and Johnson Matthey JMC 3-0749 (Zn) used to be commonly used for Cu and Zn isotope measurements but are no longer available. To fill this gap, the IRMM produced new CRMs: ERM-AE633 and ERM-AE647 (Cu) and IRMM-3702 (Zn), which are elemental solutions in 1 M HNO_3, certified for isotope ratios. These new RMs have now been cross-calibrated against the old RMs to provide continuous comparability of published Cu and Zn isotope data with future measurements[295]. In addition, δ^{65}Cu and δ^{66}Zn data for five USGS RMs, BCR-2, BHVO-2, BIR-1 and G–2 (Basalts) and AGV-1 (Andesite) measured against the new CRMs, were presented as a reference dataset for future inter-laboratory comparisons. A set of two B isotope RMs and three offset δ^{11}B RMs were produced and certified[296]. The B isotope RMs ERM-AE102a and ERM-AE104a were designed for correcting mass bias in ICP-MS, whereas the three δ^{11}B RMs were intended to be used for QC and validation of procedures for the determination of δB^{11} in geological and environmental samples. The isotopic composition of all the materials was adjusted by mixing, under full gravimetric control, B parent solutions enriched in ^{10}B or ^{11}B. The materials were stable and homogeneous and covered about three quarters of the known natural variation in B isotopes. Using a protocol for the synthesis of halite crystals containing water inclusions with known values of δD and δ^{18}O, Rigaudier *et al.*[297] produced several hundreds of grams of halite RM within two days at low cost. The crystals were stable in a vacuum desiccator at ambient temperature for at least several months.

An alternative to creating new RMs is to supply *reference values for the isotope content of geological RMs currently available*. For example, reference values for the δ^7Li content of GSJ RM JP-1 (Peridotite) and USGS RM DTS-2 (Dunite) were measured [298] using a method developed to separate Li from ultramafic rocks, which normally have low Li contents. Prytulak *et al.*[299] presented some of the first measurements of V stable isotopes in six USGS RMs. The best attainable long-term reproducibility for $^{51}V/^{50}V$ isotope measurements in these complex matrices was 0.15‰ (2s), similar to that achievable with standard solutions. Although different analytical techniques and mass bias corrections were employed in an inter-laboratory comparison[300] to determine the Ge isotope composition of selected geological RMs, all methods provided relatively similar precisions of about 0.1‰ (2s) for δ^{74}Ge values. However, a double spike method was preferred as it corrected for potential Ge isotope fractionation during sample dissolution and purification. The Ge isotope composition of NIST SRM 312a (Ge reference solution) was calibrated relative to internal isotopic standard solutions used in previous studies and its use proposed to provide consistent measurements in the development of Ge isotopes as a geochemical tracer.

4.2 Solid sample introduction

4.2.1 Laser ablation

Although LA is a routine method of sampling geological materials prior to analysis by a range of ICP techniques, research continues to be directed at improving *performance characteristics of the ablation*. An ablation cell[301] capable of holding large objects (up to 230 mm long x 34 mm wide x 16 mm deep) was tested using NIST SRM 610 (Trace Elements in Glass) and JK CRM 2D (Carbon Steel). The washout of the new cell was 70% faster than that of a standard cylindrical ablation cell and provided washout times within 2.6 s for 99.9% of the signal. Its size allowed both analysis of a batch of samples without opening the cell between samples and fast switching between standards and samples. A study[302] of the performance of a commercial fs laser system, operating at its fundamental wavelength of 800 nm for the ablation of transparent minerals such as quartz, confirmed the reliability of IR fs LA of transparent materials and its potential for the analysis of fluid inclusions in quartz. Ablation craters up to 1300 μm in depth were created without the ablation rate being influenced by the sample's crystalline orientation.

Other studies have considered the *characteristics of the plasma and mass spectrometer in LA-ICP-MS*. Addition of carbon to the central channel of the ICP, either as methane or a methane-water mixture, enhanced the ion signals during ablation of NIST SRM 610 (Trace Elements in Glass)[303]. Up to 20-fold enhancements for elements such as As, I, Se and Te were explained by a combination of carbon charge transfer, increase in plasma temperature and change of the plasma shape in the central channel. Because *in situ* determination of PGEs by LA-ICP-MS is hampered by argide interferences, Guillong *et al.*[304] sought to develop a better understanding of the controls on the formation of argides in quadrupole ICP mass spectrometers. Argide levels could vary by as much as 30 times between common makes of instruments, whereas other polyatomic ions, like oxides, varied by <3 times. The key parameter was the pressure between the skimmer and extraction lenses; instrument designs resulting in a relatively high pressure produced more collisions in this region, resulting in disruption of weak argide bonds. A prototype miniature LA mass spectrometer, based on Mattauch Herzog geometry, was designed to undertake elemental and isotopic measurements of the surface of extraterrestrial bodies[305]. For measurements in minerals such as microcline, lepidolite and anorthoclase, an LOD of 0.4% and precisions of 0.077±0.004 for $^{41}K/^{39}K$ and 0.052±0.006 for $^{29}Si/^{28}Si$ were obtained.

Laser ablation ICP-MS is capable of providing *spatial distributions of trace element and isotopic information* but its widespread application has been hindered by the lack of appropriate processing software. In a novel approach, a module called CellSpace was developed to create spatially registered LA images for use with the freely distributed software package Iolite[306]. This module created images by synchronising the state of the laser, i.e. whether it was firing or not, and its position on the sample and these were recorded concurrently with data from the mass spectrometer. It was possible to overlay LA data onto other images, such as those produced by SEM, allowing the analyst to view the LA data in context. The code had the advantages of averaging the data spatially rather than just with time and presenting the data as a laser spot rather than a simple rectangular pixel. An alternative software package (*LAICPMS*) for 2D mapping of LA-ICP-MS trace element distributions[307], based on the R language for statistical computing, determined many input parameters automatically and used empirical cumulative density function for optimised colour coding of the maps rather than linear or logarithmic scale. Major and trace element distribution maps of natural calcite samples demonstrated the utility of the package.

The characteristics of LA-ICP-MS make it a particularly attractive method for the *analysis of silicate minerals*. Pearce *et al.*[308] provided an excellent overview of many aspects of this technique in their description of the analysis of individual glass shards from tephra deposits using a 193 nm excimer laser coupled to SF-ICP-MS. They illustrated how improvements in laser and spectrometer hardware have enabled analysis using crater diameters of 20 µm and 10 µm to become essentially routine. Problems with the characterisation of single, sub-10 µm glass shards were highlighted. A major study[309,310] of ocean floor basaltic glasses reported data for over 60 elements in 616 samples obtained by

LA-ICP-MS and complemented by EPMA data. Interferences and choice of isotopes were discussed together with the optimised analytical routine based on a 193 mn wavelength excimer laser coupled to quadrupole ICP-MS. Yuan *et al.*[311] used a 213 nm Nd:YAG laser coupled to SF-ICP-MS to evaluate matrix effects for 49 elements in 17 glass RMs plus 10 elements in 10 silicate mineral RMs developed for EPMA use. They confirmed that the differences in behaviour between glass RMs and natural silicate minerals were insignificant and that calcium was a suitable internal standard for the analysis of silicate minerals. An analytical protocol for screening chert microbands in a banded iron formation was based on LA-ICP-MS [312]. Although solution ICP-MS was required to obtain high quality data for Cr, Ni and REEs because of the very low trace element contents of cherts, the selection of suitable areas for sub-sampling ensured that the chemistry of the individual microbands was truly representative and not influenced by inclusions of carbonate or iron oxide minerals.

Laser ablation ICP-MS has been used in many contexts for *elemental fingerprinting*. Recent examples included the geographical classification of gem corundum samples of different colours[313] and of coltan, the African trade name for columbite-tantalite, a tantalum ore[314]. Coltan is one of several raw materials that finance the civil wars in the eastern provinces of the Democratic Republic of the Congo, so in 2008 a procedure was developed to verify the origin of coltan based on mineralogical and geochemical parameters. An improved, more rapid, procedure, based on mineral liberation analysis and LA–SF–ICP–MS, provided quantification of all major and many trace elements in the same analytical step without the need for the measurement of an internal standard element by an independent analytical method. The U-Pb age estimates had sufficient precision to discriminate age provinces of Nb-Ta in Africa.

The production of *XRF glass bead and pressed powder pellets* is well-tested for preparing geological samples for bulk LA analysis. The main prerequisite is that the elements of interest are distributed uniformly in the sub-sample presented for analysis. Matrix effects[315] observed during the measurement of ^{232}Th by LA-ICP-MS in rock pressed powders, even when the sample grain size was relatively small (<10 μm), were attributed to incomplete vaporisation of the particles in the plasma. Kon *et al.*[316] devised a protocol for ablating XRF glass beads, made from 0.1 g sample and 1.0 g of lithium tetraborate, using a fs laser for minimal elemental fractionation. A novel design of ablation cell to enhance the transport efficiency of the sample aerosol, plus new software to control the laser, sample stage movement and firing of the laser, reduced the analysis time to 100 s per sample and gave precisions of better than 10% for many elements. A similar strategy[317] of preparing standards and samples as borate glasses for the multielemental analysis of silicate rocks by LA-ICP-MS confirmed that if the fusion was carried out at moderate temperatures in the presence of meta-tetra borate, loss of volatile elements was minimised and conferred flexibility to include an internal standard of choice.

Ways of improving the quality of *data obtained from the ablation of fire assay beads* have been investigated by a number of research groups. A combination of ID (for Ag, Pd and Pt) and single standard addition and internal standardisation (for Au and Rh) was evaluated as a calibration method for the determination of such metals in lead buttons[318]. As no significant difference was observed between the concentrations obtained *via* these approaches and external calibration with matrix-matched lead standards, it was concluded that ID LA-ICP-MS offered no advantages for the routine analysis of lead buttons, although it could be deployed for obtaining reference values. An alternative approach[319] for the determination of Pd, Pt and Rh in lead buttons used a LA system with a large beam size (780 µm diameter) to compensate for the lower sensitivity of ICP-AES. Spectral interferences were avoided by careful selection of the emission wavelengths monitored. The method precision was typically better than 5% RSD. The LODs of 2.5–12 $\mu g\ g^{-1}$ in the Pb button were considered sufficient for the analysis of automotive exhaust catalysts but not ore materials. The potential of a new type of commercially-available Mattauch-Herzog type ICP-MS instrument equipped with an array detector with 4800 independent channels was evaluated for the determination of Au and the PGEs in NiS buttons produced from platiniferous ores[320]. Because of its geometry, this instrument is capable of truly simultaneous monitoring of the entire elemental mass spectrum between *m/z* 5 and 240, including $^{40}Ar^+$, which is particularly advantageous when handling transient signals from sample introduction techniques such as LA. Buttons prepared from 40-75 g of sample were ground to a powder and pelletised using polyethylene wax as a binder. Using in-house matrix-matched standards for calibration, excellent precisions of 2-3% RSD for the most abundant analytes, Pd, Pt, Rh and Ru, and 6-11% RSD for Au and Ir, were obtained. These figures of merit were attributed to the simultaneous acquisitions plus the extended linear range, giving an improved performance of the ^{61}Ni internal standard. In addition, low LODs, in the region of 10 $ng\ g^{-1}$, were made possible by the low level of argide-based interferences compared to some quadrupole-based ICP-MS instruments, and the ability to monitor elements affected by $ArNi^+$ and $ArCu^+$ overlaps.

Finding *suitable matrix-matched calibration standards for the analysis of sulfide minerals* by LA-ICP-MS presents its own challenges. The homogeneity[321] of a sulfur–based chalcogenide glass standard (designated IMER-1), synthesised by incorporating four minor and 34 trace elements into a chalcogenide glass matrix containing Ge, S and Sb, was confirmed by analysis using a range of techniques. This standard is complementary to other available standards because it contains a wider range of elements and is suitable for determining sub–ppm levels of elements in sulfides. Ke *et al.*[322] demonstrated the varying behaviour of five different sulfide minerals when ablated with a 193 nm excimer LA system and concluded that the most suitable laser parameters for accurate analysis were a large spot size, low repetition rate and low laser energy. A novel strategy for the analysis of sulfide minerals by LA-ICP-MS, using glass RMs with matrix normalisation and sulfur internal standardisation, overcame the lack of matrix-matched standards[323].

An excellent article[324] (195 references) reviewed *recent developments in the analysis of individual fluid inclusions* by LA-ICP-MS and LA-MC-ICP-MS. It contained a comprehensive account of the factors involved in producing reliable data for the elemental and isotopic composition of fluid inclusions and is obligatory reading for anyone new to this field of analysis. All the data cited were produced using a GeoLas pulsed 193 nm ArF excimer laser. The optical setup of this, and most other, laser systems limits the depth of accessible inclusions to within about 100 µm of the sample surface, depending on the size of the inclusion. Guillong and Pettke[325] assessed the capabilities of a new, commercially available, laser system (Resonetics M50) for the analysis of fluid inclusions between depths of 20 and 500 µm. There was a marked change in element ratios in shallow inclusions compared with those in deep inclusions (by up to a factor of 2.5) with Cl/Na and Pb/Na ratios being affected the most. Such marked fractionation of Cl was thought to be due to condensation-deposition and remobilisation effects within the LA crater, and is significant because this element is sometimes used as an internal standard for quantification of solute in fluid inclusions. The specific difficulties of determining S in fluid inclusions by LA-ICP-MS was addressed in a substantial review (112 references) of analytical methods for the determination of S in glasses, rocks and minerals[326].

As noted in last year's Environmental Update[1], the *widespread availability of LA-MC-ICP-MS* has opened the door to a wide range of new applications in the Earth sciences based on the interpretation of isotopic ratios. Issues pertinent to the measurement of Pb isotopes in olivine-hosted melt inclusions[327] included the need to remove surface contamination by ultrasonicating the sample in dilute HNO_3, as cleaning with ethanol was not effective. The figures of merit for a protocol[328] adopted for the determination of Pb isotope ratios in volcanic glass shards compared well with results obtained by other workers using various techniques. A novel combination[126] of LA-MC-ICP-MS with DGT, for studying 2D S isotope variations in sediment pore waters at a spatial resolution of *ca.* 100 µm, provided information relevant to microbiological processes and the formation of individual iron sulfide grains in surface sediments.

An improved understanding of LA fundamentals has allowed *application of U-Pb dating by LA-ICP-MS to many different accessory phases* including apatite[329], rutile[330], xenotime[331] and allanite[332]. However, every laboratory set-up tends to be different so that LA and MS parameters need to be evaluated carefully for each application. Methods of data reduction also vary. Kooijman *et al.*[333] developed a robust method for U-Pb dating of zircon and provided a systematic approach for optimising instrumental parameters. This method should be applicable to any LA-ICP-MS system. Using a 193 nm excimer laser coupled to SF-ICP-MS, laser cell design, signal intensity, ablation parameters, data reduction software, isobaric interferences from Hg and elemental fractionation were investigated. Their method was shown to be robust for zircons with a range of ages and U content; optimal results were usually obtained with a spot size of 25 µm. Of the different data reduction methods[334] assessed for the calculation of zircon U-Pb ages – ratio of the means, mean of the ratios and intercept methods – a procedure based on the ratio of the mean intensities, combined with low sampling rates, was the most mathematically accurate for treating data produced by LA–SF-ICP-MS.

Historically, protocols devised to determine *U-Pb ages and Hf isotope compositions from the same growth zone of complicated zircons*, have had varying degrees of success. Recently, a quasi-simultaneous method[335] was developed using a 193 nm excimer laser coupled to a MC–ICP–MS instrument equipped with a unique fixed–collector–array and a series of variable–zoom lenses to change the dispersion of the analyte and bring ion beams into the collectors coincidentally. This feature allowed rapid switching between U-Pb and Hf collector configurations. A spot size of 40 µm and a laser repetition rate of 5 Hz were chosen. Results for three zircon RMs demonstrated that this relatively simple instrument configuration was capable of measuring zircon U-Pb age and Hf isotope composition accurately on one single spot. In contrast, Tollstrup *et al.*[336] opted for a much more complicated instrumental setup to acquire truly simultaneous measurements. This involved coupling an excimer LA system, equipped with a dual–volume sample cell, to both a single collector SF ICP mass spectrometer and a MC ICP mass spectrometer and splitting the sample aerosol as it left the sample cell. The relative proportion of sample aerosol reaching each mass spectrometer needed to be carefully controlled to ensure sufficient signal for precise measurements. Measurements of a suite of zircon standards provided U-Pb ages within 0.3-2.5% (2s) of the nominal value, with internal errors of better than 0.4-0.7%. The Hf isotope ratios were within one epsilon unit of those from solution analyses and internal errors were typically <0.008%.

4.2.2 Laser-induced breakdown spectroscopy

Laser-induced breakdown spectroscopy is used in a wide variety of applications including the provenancing of archaeological artifacts[337], quality control in the mining industry[338] and identification of geological samples in the field[339]. However, there is still much debate over the selection of the most appropriate *chemometric method for processing LIBS data*, depending on the application. For the determination of Fe in iron ore[340], particular emphasis was placed on how spectral data from two separate spectrometers covering UV and visible wavelengths were combined. Standard PLS regression and PCR produced similar accuracies, whereas those for multi-block PLS and serial partial PLS were inferior. Optimisation of an ANN algorithm, advocated[341] for the accurate identification of geological samples by LIBS, included the selection of input information and the adoption of various training techniques. The trained network was tested using a variety of natural rocks (silicates, carbonates, sulfide and oxides). Despite differences in the surface texture and minor variations in chemical composition, the technique was able to identify 88% of the samples correctly using 10-shot averaged spectra. In contrast, PLS without spectral averaging performed best for the LIBS instrument on the Mars Science Laboratory (see below)[342]. In general, the ANN-based methods did not provide any improvement over the PLS methods, suggesting that the LIBS spectra had no significant non-linearities.

Because LIBS is able to probe remote targets without any sample preparation, it has become a *technique of choice in space exploration*. On board the Mars Science Laboratory *Curiosity* rover that landed on Mars in August 2012 is the ChemCam instrument suite consisting of a LIBS instrument and a remote micro-imager to supply contextual images of the LIBS analysis spots. The primary objective is to investigate Martian geochemistry, using a 1067 nm laser with a spot size of ~490 μm to ablate targets within 7 m of the rover. As ChemCam will be the first LIBS experiment on another planet, a wealth of information has been published on the operation of this equipment, including papers on: the choice of onboard calibration standards[343]; a reference database of LIBS lines taking account of the effects of the Martian atmosphere[344]; assessment of the most appropriate multivariate technique for quantitative analysis[342, 345]; and calibrations to derive the elemental composition and degrees of hydration of various hydrous sulfates[346]. Plans to probe Jupiter’s icy moon

Europa in a mission to be launched in 2020 are focussed on confirming its potential to sustain life. To this end, a miniaturised LIBS system was developed and preliminary tests on analogue materials under simulated Europan conditions carried out[347]. Mezzacappa *et al.*[348] reviewed the capability and advantage of LIBS to analyse the Moon's surface at 1.5 m distance from a lunar rover and its potential for detecting the water content of lunar soils.

4.3 Solid sample introduction

4.3.1 Sample dissolution

Complete dissolution of geological materials requires the use of HF acid to breakdown the bonds in silicate matrices. Apart from the hazards associated with handling this acid, there is the potential for the *formation of relatively insoluble fluoride complexes*. Muratli *et al.*[171] observed that insoluble fluorides formed during microwave-assisted digestion of marine sediments dissolved slowly over time at room temperature in 12.5% (v/v) HNO_3, with the least soluble fluorides of Al and Mg taking up to four weeks to dissolve. However, this time was reduced to 6 days if the samples were heated at 60° C for 24 h; no reprecipitation of the fluorides after heating was evident. The formation of insoluble AlF_3, a major obstacle in a new dissolution procedure[349] in which rock powders were reacted in a high pressure asher with a mixture of HF and HNO_3, was overcome by using an appropriate digestion temperature and adding magnesium to the samples before digestion. The high pressure ashing procedure was particularly well suited for the determination of trace elements in samples containing resistant minerals; 41 trace elements were determined by ICP-MS equipped with a collision cell. The measurement bias for eight RMs was generally better than ±5% RSD.

An alternative[350] to the Carius tube method of digesting geological samples for the *measurement of the PGEs* involved addition of an enriched isotope spike solution to 2-5 g of powdered sample and digestion in HF in a custom-made 120 ml PTFE beaker on a hot plate. The dried residue was further digested with HF and HNO_3 at 190 °C for 48 h after sealing the beaker in a stainless steel pressure bomb. Although only HF and HNO_3 were used at a relatively low temperature, ultramafic rocks containing refractory minerals were effectively decomposed, as confirmed by results for the CANMET RMs measured. The method gave LODs and precision nearly the same as those obtained by the Carius tube technique but had the advantages of being relatively simple, low cost and applicable to mafic and ultramafic rocks and Ni-Cu sulfides. Osmium was not retained in solution by this method.

Measurement of Sm/Nd isotopes can be used to date ores such as *scheelite*, $CaWO_4$, a common accessory mineral in hydrothermal gold or tungsten ore deposits and one of the few minerals characterised by high Sm/Nd ratios. However, it is difficult to dissolve scheelite completely in mineral acids because of the protective coating of tungstic acid that forms on its surface. In both low temperature and Teflon bomb acid dissolution[351] for the determination of Sm-Nd isotopes by MC-ICP-MS, a large amount of tungstic acid remained after the addition of 2.5 M HCl prior to cation-exchange separation, although less than 10% of the Nd and Sm resided in the precipitate. On the addition of a ^{149}Sm-^{150}Nd spike for quantification by ID, spike-sample isotopic equilibration was only completely achieved in the Teflon bomb method, making it the procedure of choice for this application.

4.3.2 Sample separation and preconcentration

Automation of the processes involved in complex chemical separations has always appeared attractive but robots capable of tolerating corrosive acid vapours can be elusive. A fully automated column–separation system[352], called COLUMNSPIDER, for the determination of Nd, Pb and Sr isotope ratios consisted of a micropipetting robot that dispensed reagents and sample solutions into an open–column resin bed for elemental separation. Up to ten samples could be handled in parallel in a single automated run. When multiple column separations with different resins were required, e.g. for the separation of Nd-Pb-Sr isotopes, COLUMNSPIDER completed these separations using multiple runs. Total procedural blanks and isotopic compositions determined for basalt RMs JB-2 and JB-3 (JSP) and BCR-2 (USGS) were comparable to those obtained by careful manual operation by skilled operators. This system could be customised for a range of potential applications and is commercially available.

Many of the separation and preconcentration techniques reported recently are concerned with the *determination of precious metals by ICP techniques*. Chicken eggshell membrane packed into a microcolumn was used for solid phase extraction of trace amounts of Ag and Au from geological samples prior to FAAS[353] or ICP-MS detection[354], respectively. The membrane was prepared from eggshells provided by the university catering facilities and represented a low cost and environmentally friendly approach that might be ripe for commercial exploitation. A new sorbent based on cysteine–modified silica gel was highly selective for column solid–phase extraction and determination of low levels of Au, Pd and Pt in geological samples[141]. Recoveries of 93-97% from acidic media containing 0.1 to 2 M HCl were achieved. The analytes retained on the sorbent were eluted with 0.1 M thiourea in 0.1 M

HCl and measured by ETAAS or ICP-AES. The LODs for Au in copper ore and copper concentrate were 0.002 and 0.006 µg g^{-1} using ETAAS and ICP-AES detection, respectively. The LOD for Pd by ICP-AES was also 0.006 µg g^{-1}. Silica modified with ethylenediamine, prepared using the sol-gel technique, was also employed to preconcentrate Au and Pd from a platinum ore RM[355]. A procedure for the separation of Pt from ferrous matrices was based on the sorption of Pt as chloride complexes on polyurethane foam, prior to determination by ICP-AES[356]. Measurement LODs in solution were 66 µm L^{-1} and the precision 1.2% RSD (n=10). A simple method[271], based on the sorption of Au on granular activated carbon in acidic medium and then placing the dried activated carbon directly into a graphite tube atomiser for measurement by ETAAS, was applied successfully to the determination of Au in copper and platinum ores. Activated carbon modified with 2,6-diaminopyridine selectively extracted Au, Pd and Pt from several ore and rock RMs prior to measurement by ICP-AES[357].

*Separation and preconcentration of REE*s are often required when the natural levels in the samples are very low, the detection technique is not particularly sensitive or potential interferents need to be removed. A method[358] to determine REEs at sub-ng g^{-1} levels in rocks used ion-exchange chromatographic separation on AG50W-X8 cation resin and analysis by quadrupole ICP-MS. Samples were dissolved in a mixture of HF and $HClO_4$ acids maintained at 140 °C for 5 days in Parr bombs to achieve complete dissolution. When concentrated HNO_3 and H_2O_2 were added to the samples after chemical separation to destroy organic molecules from the resin and Tm was added as internal spike, the reproducibility of the data improved from 5% to about 1% RSD (n=5). Cation exchange chromatography is commonly used to separate lanthanide elements from geological materials prior to measurement by ICP-AES. Alternative procedures based on co-precipitation of REEs and Th with oxalate in the presence of calcium[359] and the use of copper DDTC to co-precipitate REEs and Y[360] have been evaluated.

4.4 Instrumental analysis

4.4.1 Atomic absorption spectrometry and atomic emission spectrometry

Developments pertinent to the application of AAS and ICP-AES to the analysis of geological materials are covered in sections 4.3.1 and 4.3.2 of this Update. Advances in fundamental aspects of these techniques are described in the recent Update on atomic spectrometry[3].

4.4.2 Inductively coupled plasma mass spectrometry

This year the distinction has been made between elemental determinations (bulk analysis) and the measurement of isotope ratios irrespective of the mass spectrometer in use.

4.4.2.1 Bulk analysis *The use of collision/reaction cells to reduce polyatomic interferences in quadrupole ICP-MS* continues to be highlighted. D'Ilio *et al.*[210] reviewed (76 references) the analytical challenges when determining As, Cr, Se and V by DRC-ICP-MS. They illustrated the approaches and mechanisms involved in the analysis of a range of complex matrices, including rocks and soils. A method for determining Au concentrations[361] directly in *aqua regia* solutions of rocks containing high levels of hafnium and tantalum without separation used an ICP-MS instrument fitted with a hexapole collision cell. Interferences from isobaric $^{181}Ta^{16}O^+$ and $^{180}Hf^{16}O^1H^+$ were eliminated by adding oxygen as a reaction gas thereby converting them to TaO_2^+ and HfO_2H^+ respectively, without significant loss of Au^+. The method employed hot plasma conditions, a metal screen between the torch and the load coil to enhance the Au signal intensity by 50%, and helium as collision gas. The method LOD was 3.06 pg g^{-1} but recoveries of Au from spiked samples were relatively high (131-141%). Other developments in bulk analysis by ICP-MS were mainly concerned with *methods to preconcentrate the elements of interest.* A fully automated system, consisting of a miniaturised LOV connected to a multisyringe flow injection outlet for sample introduction to ICP-MS, was designed for the determination of Th and U in environmental samples, including a phophogypsum and channel sediment[177]. On-line separation and preconcentration of the analytes was achieved by means of UTEVA® resin in a microcolumn located on one of the LOV channels and the resin was regenerated automatically on-line. Other advantages of the system included LODs of 2.8 ng L^{-1} for Th and 0.4 ng L^{-1} for U, a precision of 1.7% RSD (n=5), a wide working range and an injection frequency of up to 9 per hour. The paucity of reliable data for Se and Te in rocks prompted König *et al.*[362] to develop a method to measure these elements, often present at the low ppb and sub-ppb level, simultaneously in the same sample split. They employed ID with ^{77}Se and ^{125}Te, separation on thiol cotton fibre and HG-ICP-MS, using a home-made hydride generator. Analysis of a range of rock RMs containing 30-350 ppb Se and 0.7-12 ppb Te gave precisions of 3-8% for Se and 0.4-11% for Te (2 RSD, n=3).

There have been several studies of *the measurement of elemental concentrations by MC-ICP-MS.* A novel procedure[363] for the analysis of the REEs, Sc and Y involved lithium metaborate fusion of the rock samples followed by extraction chromatography with TODGA resin as the preferred medium. This resin was also used to purify the lithium metaborate flux before use to provide low procedural blanks. Nine Faraday cups and a dynamic collector on a MC-ICP-MS instrument were employed in five configurations to measure the concentrations of 14 REEs, Sc and Y by the standard-sample bracketing technique. The use of zoom optics was essential to minimise peak overlaps for 14 lanthanide isotopes. With matrix removal and judicious isotope selection, polyatomic interferences from oxide species were negligible and no corrections were required. The accuracy of the proposed procedure was verified using a range of USGS rock RMs and the average reproducibility was ca. 2% RSD (n=5). A new sequential extraction procedure[178] produced five distinct fractions of Nd, Pa, Ra, Th and U from the same initial sample using a single 4 mm internal diameter chromatographic column packed with Dowex AG1X-8, following dissolution and the addition of Pa, Ra, Th and U spikes for ID calculations. No further purification of the Th and U fractions was required for MC-ICP-MS analysis, whereas the Nd, Pa and Ra fractions required additional steps. Recoveries were generally greater than 95% for all elements, with negligible blanks. The fractions obtained were used to obtain Nd and U isotope ratios as well as Pa, Ra, Th and U concentration data.

4.4.2.2 Isotope ratio measurements It is evident that the application of new isotope data to the geosciences continues to be a major growth area of research, covering a wide range of stable and radioactive isotopic systems. For simplicity, analytical developments in this section will be covered in order of mass number as far as possible.

Schemes for separating and measuring *Mg isotope ratios* often incorporate a step to determine Al isotopes as well. Methods for determining ^{27}Al/^{24}Mg ratios have seen little improvement over the last decade so a novel method[364] for measuring this ratio in unpurified sample solution by MC-ICP-MS is welcome. A mixed spike solution, containing isotopically enriched ^{25}Mg and natural ^{27}Al in a known ratio, was added to the samples which were analysed without the separation required in conventional ID schemes. To determine the spike to sample ratio for monoisotopic Al, measurements of spiked aliquots were bracketed by unspiked aliquots to minimise the impact of elemental bias. Repeat measurements of USGS rock standards, as well as a gravimetrically prepared Al-Mg reference solution, indicated that the method was accurate and reproducible to 0.2%. This represented a 4- to 10-fold improvement in precision over that of previously used methods. A new estimate of the ^{27}Al/^{24}Mg ratio for the Ivuna CI chondrite of 0.09781 ± 0.00029 was proposed. A modified procedure[365] for separating Al and Mg from meteorites and terrestrial silicate rocks on a single ion-exchange column filled with AG50W-X12 resin involved elution of Mg and Al with 1 M and 4 M HNO_3, respectively. This procedure removed all matrix elements with the exception of Co, Cu and Ni. The >99% recovery for Mg was important for limiting mass-dependent fractionation to <0.05‰. No matrix effects were detected and the total procedural blank was <2 ng Mg. Figures of merit obtained on *ca.* 50 mg of sample indicated the method was suitable for the chronological study of the early solar system. The Mg isotopic composition of some terrestrial rocks was identical within experimental error to that of three chrondrites analysed. A procedure[366] for measuring Mg stable isotope compositions in marine biogenic aragonite and calcite involved sampling with a microdrill after removing surface layers, dissolution in mineral acids and analysis by MC-ICP-MS using the standard-sample bracketing technique for mass bias correction. Based on measurements of GSJ RM JCp-1 (Coral), the δ^{26}Mg precision (2SD, n=37) was ±0.22‰. The data were used to evaluate mechanisms for cation isotope fractionation during carbonate precipitation. Pogge von Strandmann *et al.*[367] reported Li and Mg isotope compositions of 33 ultramafic zenoliths from the mantle and compared these with data for 30 meteorites, most of which were chondritic. They too noted that recently published Mg isotopic data for mantle-derived samples were not always consistent, and so made strenuous efforts to assess the accuracy of their data by several different approaches, including standard addition experiments, two different separation chemistries and three different sample introduction systems for MC-ICP-MS. Their estimate of the Mg isotope composition of the primitive mantle was within the error of the average values for the relevant chondrites and compatible with the data of Wang *et al.*[365].

There have been significant advances in the measurement of stable isotope ratios for so-called ‘non-traditional isotope’ systems. A novel approach to the *determination of Ca isotopes in geological materials*[368], including the low abundance ^{46}Ca (0.003%) isotope, involved a four-step purification scheme to ensure 99.9% recovery of Ca and excellent separation of Ca from elements that may create isobaric interferences or affect the instrumental mass fractionation during analysis. Samples were analysed by HR–MC-ICP-MS but because intense beams were used to detect the low abundance isotopes, no data were collected for ^{40}Ca. The samples were reanalysed by TIMS to obtain the ^{40}Ca data. In this way all isotopes from ^{40}Ca to ^{48}Ca could be measured with precisions considerably better than previously reported, e.g. the external reproducibilities of the non-mass-dependent abundances of μ^{43}Ca, μ^{46}Ca and μ^{48}Ca (normalised to ^{42}Ca/^{44}Ca) were 1.8, 45 and 12.5 ppm respectively by HR-MC-ICP-MS.

The *determination of $^{51}V/^{50}V$ ratios* requires a separation procedure that provides virtually complete recovery of V and separation from matrix elements, and a measurement strategy that copes with the large isotope ratio of *ca.* 415. Data for $^{51}V/^{50}V$ ratios in geological RMs[299] were obtained using a protocol[369] that involved quantitative chemical separation of V from matrix elements using five separate ion-exchange columns before analysis by HR–MC-ICP-MS on an instrument equipped with a non-standard array of collectors to facilitate simultaneous collection of masses 49 to 54. The ^{51}V Faraday cup was equipped with a 10^9 Ω resistor to accommodate the intense beam of this isotope. The measurement precision of $\delta^{51}V$ in an in-house secondary standard solution was ±0.12‰ (2s, n=600), an improvement on previous techniques of almost two orders of magnitude.

The key step in a new analytical method[370] for studying *Ti isotope anomalies in meteorites* was the separation of Ti using TODGA and AG1-X8 resins before analysis by MC-ICP-MS. The isobaric interferences from Ca, Cr and V could be adequately corrected as long as these elements were present at atomic ratios of Ca/Ti <20, Cr/Ti <0.1 and V/Ti <2. The separation procedure produced ratios several orders of magnitude lower than these, demonstrating the effectiveness of the chemistry employed.

In order to identify *stable Fe isotope variations in rocks* formed in high temperature environments, highly precise measurements are required. In the method developed by Millet *et al.*[371], chemical separation of Fe was based on its affinity for chloride complexes and their high partition coefficients on anion-exchange resins, such as AG1-X4. The MC-ICP-MS instrument was configured in a pseudo-high resolution mode, by narrowing the source slit to 0.03 mm and closing the alpha slits to correct for beam aberrations. The instrumental mass bias was corrected by adding a ^{57}Fe-^{58}Fe double spike to IRMM-014 Fe isotope standard solution and using the sample-standard bracketing method. The precision (2 SD, n=51) for $\delta^{56}Fe$ was ±0.02‰ for an acquisition time of 15 min. Replicate digestions and measurements of USGS RM BHVO-2 (Basalt) demonstrated that this precision was obtainable on natural samples. Theoretical calculations suggested that a greater dynamic range for the Faraday collectors and the addition of the double spike before the chemistry could improve the method precision.

A new approach[372] to correcting for short-term drift and mass bias effects during *Sr isotope measurements by MC-ICP-MS* was to measure the $^{92}Zr/^{90}Zr$ ratio from a high purity Zr spike solution added after column separation on Eichrom Sr Spec resin. A modified empirical external normalisation protocol was used to correct for mass bias, allowing the simultaneous measurement of $^{87}Sr/^{86}Sr$, $\delta^{87}Sr$ and $\delta^{88}Sr$. Omission of standard-sample bracketing resulted in increased sample throughput. Use of the $^{92}Zr/^{90}Zr$ ratio gave a 2-fold better precision of $\delta^{88}Sr$ measurements than correction with $^{91}Zr/^{90}Zr$. The long-term reproducibility (2SD, n=34) for $\delta^{87}Sr$ and $\delta^{88}Sr$ was better than ±0.040‰ and ±0.018‰, respectively, using NIST SRM 987 (Strontium Carbonate Powder). Data determined for three USGS igneous rock standards were consistent with literature values.

A single collector SF–ICP-MS instrument was preferred[373] over MC-ICP-MS for the *measurement of Pb isotopes in samples containing ≤0.2 ng amounts of Pb* because of its fast electrostatic scanning data acquisition. The long-term precision (2SD) for a 0.1 ng mL^{-1} solution of NIST SRM 981 (Natural Lead Isotopes) was 0.11% for $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$, and 0.21-0.23% for the ^{204}Pb ratios. These figures were comparable, for equivalent amounts of total Pb, with precisions reported elsewhere when using a high efficiency sample cone together with ion counter arrays or conventional Faraday collectors. Chemical purification was not required for digests of basaltic and andesitic rocks, as the final solution in 2% HNO_3 contained <10 µg mL^{-1} total cations and <1.5 µg mL^{-1} of easily ionisable elements. However, the significant matrix effects observed for natural waters required removal of major cations prior to analysis.

A simple and rapid method for the determination of *Os and Re concentrations and isotope compositions by ID MC-ICP-MS* was developed for the analysis of sedimentary rocks[374]. The Os isotopes were measured simultaneously using four Channeltron ion counters. Direct introduction of volatile OsO_4 molecules into the ICP torch by the sparging method reduced the measurement time significantly. The measured Os isotope ratios were corrected by the sample-standard bracketing method to allow for temporal changes in amplification efficiencies of the ion counters. The measurement of Re isotopes, after separation by anion-exchange chromatography, involved solution nebulisation, an ultrasonic membrane desolvator and eight Faraday cup detectors. Either inverse *aqua regia* (3+1 HNO_3:HCl) or Carius tube (CrO_3-H_2SO_4) digestions could be used as both gave the same Os and Re compositions for two sedimentary rock RMs. Although the data were not as precise as methods employed for the determination of Os and Re isotopes in volcanic rocks, it was felt that they were suitable for the reconstruction of the marine Os isotope record.

With the advances in MS, analysts are faced with *ever larger datasets to manipulate*. Iolite[375], a non-commercial freeware package developed to aid the processing of MS data, was different from other data reduction packages in that its focus was the interpolation of data that vary with time by using a variety of user-selectable methods and the reduction of data on the basis of time-slices. It was well suited for generating images from LA rasters, and combining information for up to four separate elemental concentrations. Large datasets such as multi-day ICP-MS measurements were handled rapidly. Iolite is clearly being widely adopted and was used in other work described in this section.

Improvements in the *precision and accuracy of U-Pb geochronology by ID TIMS* have revealed some significant discrepancies among data from different laboratories. One way of resolving these differences would be adoption of a common software platform to standardise the protocols used for data processing. Progress in an on-going collaboration to develop cyber infrastructure for high precision U-Pb geochronology based on analysing accessory minerals by TIMS was reported by Bowring *et al.*[376]. This activity is part of the EARTHTIME (http://earth-time.org) initiative and is probably one of the first collaborations of its kind between computer scientists and Earth scientists. The backbone of the cyber infrastructure consisted of two open source software programmes: Tripoli and U-Pb_Redux. The first programme allowed the user to review measured isotopic data interactively before exporting them to U-Pb_Redux, which managed the workflows, reduced data, propagated uncertainties and visualised the results. The new set of algorithms embedded in U-Pb_Redux for data reduction and estimating uncertainty of U-Pb ID data was discussed in more detail in a separate paper[377].

4.4.3 Other mass spectrometric techniques

The fact that dolomite reacts more slowly than calcite with acids was exploited in a semi-automatic on-line method[378] for determination of *carbon and oxygen stable isotopes in natural mixtures of calcite and dolomite by IRMS*. The isotopic composition of the calcite component and the bulk sample were determined using the CO_2 liberated by reaction with phosphoric acid, and an isotopic mass balance was used to calculate $\delta^{13}C$ and $\delta^{18}O$ for the dolomite component. The best results were obtained with a 20 minute digestion at 40 °C for calcite and a 45 minute digestion at 90 °C for complete dissolution, i.e. calcite plus dolomite. This procedure allowed accurate determination of isotope ratios from smaller samples (300 μg of $CaCO_3$) in a shorter time than by published off-line methods, but was heavily dependent on the accurate quantification of the relative amounts of calcite and dolomite in the samples by XRD.

Barry *et al.*[379] favoured *noble gas mass spectrometry* rather than IRMS for high precision measurements of N isotope ratios in ocean basalts because these samples had a low N abundance. A newly designed extraction and purification system was interfaced to a noble gas mass spectrometer configured with two Faraday collectors for masses 28 and 29 and a single axial Daly collector positioned in front of a Faraday cage for mass 30. Mass resolution of *ca.* 620 on the axial detector was adequate to resolve the N_2 and CO species from C_2H_6. The $^{15}N^{15}N$ contribution (typically <2% of the signal), calculated from the measured $^{14}N^{14}N$ ratio assuming similar proportions to that in air, was subtracted from the signal at mass 30. The residual value at this mass equated to CO ($^{12}C^{18}O$ + $^{13}C^{17}O$), which was then used to apply corrections from the corresponding CO contributions at masses 28 and 29, again assuming air-like proportions of the species. These corrections resulted in substantial improvements in reproducibility and the overall accuracy when the contribution of CO was significant. A novel procedure[380] for high precision measurements of the halogen content of geological materials by the noble gas method was ideally suited to mg-size aliquots of minerals and glasses containing ppm levels of Cl and ppb levels of Br and I. Samples were irradiated by neutrons to produce the radioactive isotopes ^{38}Cl, ^{82}Br and ^{128}I, which then decayed to the noble gas isotopes ^{38}Ar, ^{80}Kr and ^{128}Xe, respectively. Measurements were made two to twelve months after radiation. Techniques used to extract the noble gases from their fluid inclusion or mineral hosts included LA, *in vacuo* crushing of fluid inclusions and fusion in a resistance furnace at 1600 °C. The analytical precision for analysis of four scapolite gems was about 2% (2σ). These materials had sufficiently reproducible compositions (Br/Cl 11.2 x 10^{-3} ±4.5% and I/Cl of 9.3 x 10^{-6} ±10%) to be useful as Br, Cl and I standards. A new reference gas for detector calibration in the MC–MS measurement of $^{40}Ar/^{39}Ar$ was prepared[65] by mixing gasses derived from neutron-irradiated sanidine with an enriched ^{38}Ar spike. By combining atmospheric Ar and reference gas in different ways, correction factors for Ar ratios measured with different detector combinations could be obtained over a wide range of signal size. These correction factors were reproducible to better than ±0.5‰ (2σ standard error). A straightforward way of characterising the non-linearity of individual electron multipliers over a wide dynamic range using $^{38}Ar/^{39}Ar$ measurements of the reference gas was proposed.

4.4.3.1 TIMS The high ionisation energy of Zn makes it difficult to ionise Zn thermally with the good precision necessary for the *measurement of Zn isotope fractionation (δZn) by TIMS.* , An ID TIMS procedure[381] using a mixed ^{67}Zn-^{70}Zn spike required <1 µg of Zn for measurements. The δZn reproducibility (0.039‰ amu^{-1}) achieved was sufficient to determine sub-‰ δZn variations in a range of geological RMs. The finding that the δZn values in two metamorphic samples were similar to those in igneous rocks but different to those in sedimentary rocks was consistent with the understanding that processes involving high temperature and pressures do not affect the isotopic composition of chalcophile elements such as Zn. Chondrite samples could be put[382] into two groups based on Zn isotope fractionation, thereby supporting a previous proposal that chondrites are a mixture of materials from two different temperature sources.

Although MC-ICP-MS provides a greater sample throughput than TIMS, the latter has better sensitivity and accuracy for the *measurement of Nd isotopic ratios* in geological samples. Traditionally, two-step column chromatography has been employed, in which REEs are first separated from the matrix elements, and then Nd is purified further to minimise the isobaric interferences from other REEs. To reduce the work involved, Li *et al.*[383] developed a method to measure ^{143}Nd/^{144}Nd directly in the REE fraction. Columns containing cation-exchange resin AG50W x 12 were used to remove the majority of matrix elements and some of the heavy REEs from the elements of interest, with yields of >90% for Nd and Sm. The key to the success of this method was the accurate correction of the isobaric inference of ^{144}Sm on ^{144}Nd. Data for 13 USGS and GSJ geological RMs spanning a wide range of Sm/Nd ratios (0.13 to 0.46) and bulk compositions agreed within 0.004% with previously published TIMS and MC-ICP-MS data after Nd-Sm separation. The same group of researchers[384] also developed a single-step separation method based on Eichrom LN Spec resin for the high–purity separation of Nd or Sm. Very small samples (1-3 mg) could be processed in 3-4 h with low procedural blanks of <10 pg. Results for 11 silicate RMs agreed at the 95% confidence limit to within ±0.004% for ^{143}Nd/^{144}Nd and ±2% for Nd-Sm with the recommended values. The proposed protocol was preferred for the analysis of very small samples even though the uncertainty was about three times larger than that achievable with the full two-stage separation, for which much larger amounts of Nd are required.

A new method[385] for measuring the *isotopic abundance of tungsten in silicate samples* by TIMS involved a four-step separation of W by ion-exchange chromatography and the NTIMS measurement of WO_3^-. Data were initially corrected for oxide interferences and mass fractionation by normalisation to ^{186}W/^{184}W or ^{186}W/^{183}W, using an exponential law, and then for a mass–dependent change of oxygen isotope composition in the measured W oxides by normalisation to ^{183}W/^{184}W using a linear law. The long-term reproducibility of ±4.5 ppm (2σ, n=39) for ^{182}W/^{184}W measured on about 1.5 µg of W purified from natural samples was a five–fold improvement on the precision of conventional W isotope measurements by MC-ICP-MS.

4.4.3.2 SIMS Graphite is the most common form of elemental carbon in crustal rocks and preserves the *carbon isotopic composition* achieved at the time of its formation. A SIMS method[386] with an improved spatial resolution of 2-3 μm was used to unravel C isotope heterogeneities on a micrometer scale in single graphite crystals precipitated from a partially melted metamorphic rock. Remarkable core–to–rim variations were observed. The $^{13}C/^{12}C$ measurements, calibrated against a new in-house C isotope standard graphite from Madagascar previously analysed by conventional IRMS, had a precision of 0.3‰ (1σ)

The recently developed *titanium-in-quartz geothermobarometer*, which is based on the pressure and temperature dependence of Ti substitution for tetrahedral silicon in quartz, has the potential to be applied to a wide range of igneous and metamorphic rocks. Behr *et al.*[387] analysed synthetic quartz crystals with Ti concentrations of 18 to 813 ppm (as determined by EPMA) by SIMS using HR and CEF techniques. In HR mode, the mass spectrometer was operated at a mass resolving power of about 2000 to separate molecular ions from elemental Ti peaks. For analysis by CEF, the instrument detected secondary ions sputtered from the sample with excess KEs of 75±20 eV. Although the Ti ion yield was higher for NIST SRMs 610, 612 and 614 (Trace Elements in Glass) than for the synthetic quartz, the NIST glasses were used to quantify Ti concentrations in quartz with errors of ±3.8% by HR and ±8.2% by CEF, by applying a simple correction factor. Regardless of the technique chosen, it was important to monitor other elements, such as Al and Ca, to ensure that only quartz was being analysed.

A high precision SIMS procedure[388] for *in situ measurements of Fe isotope compositions* of different sulfides and oxides with a spatial resolution of 15-20 μm had a mass resolution of about 7000. Secondary $^{54}Fe^+$ and $^{56}Fe^+$ ions were measured in multicollection mode using two off-axis Faraday cups, and the $^{52}Cr^+$ intensity was measured on an electron multiplier. The long-term precision for $\delta^{56}Fe$ was typically ±0.2-0.3‰ (2SD, n=41) for a suite of well-characterised Fe minerals. In comparison, a reproducibility of 0.1‰ (2σ) is typically obtained by LA-MC-ICP-MS with a spatial resolution of 35 μm. The $\delta^{56}Fe$ values obtained by SIMS and MC-ICP-MS for three magnetite RMs agreed within experimental error.

In situ microanalysis by SIMS is well suited for the determination of *oxygen and silicon isotope ratios* in sub-mm quartz bands within BIFs. Accurate (±0.3‰) data for $\delta^{18}O$ and $\delta^{30}Si$ were obtained[389] with a spatial resolution of *ca.* 10 μm for quartz from several well characterised BIFs. The $\delta^{18}O$ and $\delta^{30}Si$ values of +7.9‰ to +27.5‰ and -3.7‰ to +1.2‰, respectively, provided information on the different sources of Si during the formation of the

BIF quartz. The ion microprobe was the technique of choice for providing high precision measurements of oxygen isotope ratios in tiny extraterrestrial particles <100 µm in diameter[390]. To address the difficulties of handling these samples, a novel sample holder with multiple holes was designed, into which epoxy disks containing a single unknown sample and a standard grain were cast and polished. Measured oxygen isotope ratios were used to assess the possible origin of a range of chondrules.

There are increasing requirements for *U-Pb and Pb-Pb geochronology in a variety of minerals at high spatial resolution*. The NanoSIMS technique[391] was capable of accurate Pb-Pb dating of zircon and baddeleyite with a spatial resolution of <2 µm, and U-Pb dating of zircons at a scale of <5 µm. The *ca.* 500 pA O^- primary beam with a diameter of 1.7 mm was substantially brighter and smaller than those previously reported and improved the lateral resolution and precision for Pb-Pb dating. Samples were measured in scanning mode by rastering 3 x 3 μm^2 areas in order to eliminate U-Pb fractionation related to pit depth. Results for four zircon standards were consistent within error with the reported ages determined by ID TIMS and demonstrated that the technique could have important applications for the dating of minerals at high lateral resolution.

It has generally been considered that analysis of geological materials by SIMS was not affected by *crystal orientation* because the high energy beam destroyed the crystal structure at depths of up to 10 µm in the sputtered area. However, high precision U-Pb analysis of rutile by SIMS[392] revealed that instrumental bias for isotope ratios and count rates varied with crystal orientation. To overcome this effect, it was recommended that a large number of randomly-orientated standard grains of rutile be analysed to provide an appropriate standard dataset for calibration.

Precise *U-Pb dating of apatite*, particularly in young samples, can be challenging because of the low U abundance and the difficulties in making accurate corrections for the presence of common Pb. Analytical and data reduction protocols for SIMS data[393] gave accurate ages (within 2-4%) for apatites containing <3 ppm U and >50% common Pb. Two key considerations were the careful determination of the common Pb composition and choice of a suitable apatite calibration standard.

4.4.4 X-ray techniques

For a *comprehensive overview of recent developments in XRF techniques* and their application to the analysis of geological materials, the Update[5] on XRF should be consulted (452 references).

Samples are normally presented to XRF spectrometers either as *pressed powder pellets or fused glass beads* depending on the application. A study of the effect of differences in mineralogy on XRF measurements of major elements in ferromanganese alloy slag[394] highlighted the importance of proper assessment of sample particle size and the binder employed in the preparation of pressed powder pellets. A simple method[395] for making in-house matrix-matched pressed pellet standards for determining Cu, Mn, Ni, U and V in carbonate lithologies used pure calcium carbonate power (99.999%) spiked with single element standard solutions to give multi-element concentrations in the pellets of between 1 and 100 ppm. The compositions of the in-house carbonate standards were verified by ICP-MS following acid digestion and by XRF using PANalytical's PROTrace XRF trace element standards and calibration routine. The in-house standards, whose homogeneity was confirmed by LA-ICP-MS, were used to refine pre-existing XRF calibrations originally constructed with silicate rock standards. Fused glass beads prepared from only 11 mg of material for the analysis of ancient pottery and igneous rocks[396] had a sample to lithium tetraborate flux ratio of 1:300. Their performance was comparable with that for beads prepared with the more usual sample–to–flux ratio of 1:10 for WDXRF analysis. Major elements were determined using calibration curves constructed by measuring synthetic calibration standards prepared from solid chemical reagents.

The increased use of *portable XRF* included applications to mineral exploration. Data from a hand-held XRF instrument were used[397], together with Au assay data, to reveal stratigraphic control on Au mineralisation in a gold deposit in Australia that was not apparent at the macroscopic level. Individual lava flows were identified on the basis of their elemental concentrations (Cr, K, Ti and Zr). In the evaluation of a copper deposit in Chile[398], portable XRF equipment was used to determine Ca, Cu, Fe, K, Mn, Pb, Rb, Sr, Ti and Zn in samples collected during a drill-hole survey. When subjected to different statistical pattern–recognition techniques, the data confirmed the rock classes, based on visual inspection, for >70% of the samples. The practicalities of using a portable XRF instrument to undertake low cost geochemical surveys was demonstrated by analysing samples from some abandoned mine sites in a highly polluted Pb-Zn mining district in central Spain for As, Cd, Cu, Pb and Zn under field and laboratory conditions[249]. The study concluded that such portable instruments should become equipment of choice for environmental monitoring in developing countries where little or no other supporting facilities were available.

Analytical techniques such as *synchrotron XRF and PIXE* are well suited for non-destructive elemental imaging. Ryan[399] reviewed (117 references) developments that have underpinned the growth in geological applications using PIXE and the exciting outlook for PIXE imaging. Use of a system with an external beam rather than the more commonly used in-vacuum nuclear microprobes, which require the sample to be analysed under vacuum, illustrated[400] the advances being made in the chemical imaging of rocks by PIXE at the µm scale or less. Synchrotron µ-XRF was used, together with LA-ICP-MS, for studying the migration of Cs in Opalinus clay, which has been proposed as a host rock for high-level radioactive waste[401]. Combining the outputs of these two techniques provided a significant enhancement of the imaging capabilities and robustness of the quantification when investigating heterogeneous media.

5 Glossary of terms

2D	two-dimensional
A4F	asymmetrical flow field flow fractionation
AAS	atomic absorption spectrometry
AEC	anion exchange chromatography
AES	atomic emission spectrometry
AFM	atomic force microscopy
AFS	atomic fluorescence spectrometry
ANN	artifical neural network
amu	atomic mass unit
APDC	ammonium pyrrolidine dithiocarbamate
ASE	accelerated solvent extraction
ASU	Atomic Spectrometry Update
aTOF-MS	aerosol time of flight mass spectrometry
BIF	banded iron formation
BCR	Community Bureau of Reference (*of the European Community*) now IRMM
CC	carbonate carbon
CANMET	Canada Centre for Mineral and Energy Technology
CEF	conventional energy filtering
CF	continuous flow
CNT	carbon nanotubes
CPE	cloud point extraction
CRC	collision reaction cell
CRM	certified reference material
CS	continuum source
DBT	dibutyltin
DDTC	diethyldithiocarbamate
DGA	N,N.N'N' tetraoctyl-1,5-diglycolamide or N,N,N',N'-tetrakis-2-ethylhexyldiglycolamide based resins
DGT	diffusion gradient in thin films
DLLME	dispersive liquid liquid microextraction

DRC	dynamic reaction cell
DRI	Desert Reseach Institute (USA)
DTPA	diethylenetriaminepentaacetic acid
EC	elemental carbon
EDS	energy dispersive spectrometry
EDTA	ethyldiaminetetraacetic acid
EDXRF	energy dispersive X-ray fluorescence
EM	electron microscopy
EPMA	electron probe microanalyser
ERM	European Reference Material
ESI-MS	electrospray ionisation mass spectrometry
ETAAS	electrothermal atomic absorption spectrometry
ETV	electrothermal vaporisation
ETV-FAES	electrothermal vaporisation flame atomic emission spectrometry
ETV-ICP-MS	electrothermal vaporisation inductively couple plasma mass spectrometry
FAAS	flame atomic absorption spectrometry
FFF	field flow fractionation
FI	flow injection
FIA	flow injection analysis
FMPS	fast mobility particle sizer
FP	fundamental parameter
FRM	federal reference method (USA)
FTIR	Fourier transform infrared
GC	gas chromatography
GC-AES	gas chromatography atomic emission spectrometry
GSJ	Geological Survey of Japan
GSP	inhalable personal sampler design produced by GSA Messgerätebau (Germany)
GUM	Guide to Uncertainity in Measurement
HDPE	high density polyethylene
HEPA	high efficiency particulate air
HG	hydride generation
HG-AAS	hydride generation atomic absorption spectrometry

HG-AFS	hydride generation atomic fluorescence spectrometry
HG–ETAAS	hydride generation electrothermal atomic absorption spectrometry
HPLC	high performance liquid chromatography
HPLC-HG-AFS	high performance hydride generation atomic fluorescence spectrometry
HPLC-ICP-MS	high performance inductively coupled plasma mass spectrometry
HPLC-VG-AFS	high performance vapour generation atomic fluorescence spectrometry
HPS	High Purity Standards (USA)
HR	high resolution
HR–ICP-MS	high resolution inductively coupled plasma mass spectrometry
HR-CS-ETAAS	high resolution continuum source electrothermal atomic absorption spectrometry
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
ID	isotope dilution
IERM	Institute for Environmental Reference Materials (of Ministry of Environmental Protection, China)
IGGE	Institute of Geophysical and Geochemical Exploration (China)
IL	ionic liquid
INCT	Institute of Nuclear Chemistry and Technology (Poland)
IOM	Institute of Occupational Medicine (UK)
IPE	ion pair extraction
IR	infrared
IRMM	Institute for Reference Materials and Measurements
IRMS	isotope ratio mass spectrometry
ISO	International Organisation for Standardization
JK	Jernkontoret/Corrosion and Metals Research Institute (Sweden)
JSAC	Japan Society for Analyical Chemistry
KE	kinetic energy
LA	laser ablation
LA-ICP-MS	laser ablation inductively coupled plasma mass spectrometry

LA-MC-ICP-MS	laser ablation multicollector inductively coupled plasma mass spectrometry
LC-MS	liquid chromatography mass spectrometry
LDPE	liquid drop microextraction
LGC	Laboratory of the Government Chemist (UK)
LIBS	laser induced breakdown spectroscopy
LLE	liquid liquid extraction
LOD	limit of detection
LOQ	limit of quantification
LOV	lab-on-valve
MC	multicollector
MC-ICP-MS	multicollector inductively coupled plasma mass spectrometry
MeHg	methyl mercury
Me_2Hg	diethyl mercury
MIBK	methyl isobutyl ketone
MIP-MS	microwave induced plasma mass spectrometry
MMAD	mass median aerodynamic diameter
MOUDI	micro orifice uniform deposition impactor
MPT	microwave plasma torch
MS	mass spectrometry
MPT-AES	microwave plasma torch atomic emission spectrometry
MWCNT	multiwalled carbon nanotube
MU	measurement uncertainity
m/z	mass to charge ratio
NACIS	National Analysis Centre for Iron and Steel (China)
NCS	China National Analysis Centre for Iron and Steel
Nd:YAG	neodymium doped:yttrium aluminum garnet
NIOSH	National Institute of Occupational Safety and Health (USA)
NIST	National Institute of Standards and Technology (USA)
NMIJ	National Metrology Institute of Japan
NRCC	National Research Council of Canada
NRCCRM	National Research Centre for Certified Reference Materials (China)
NTIMS	negative thermal ionisation mass spectrometry
NWRI	National Water Research Institute (Canada)

OREAS	Ore Research and Exploration Pty Ltd Assay Standards (Australia)
PBET	physiologically based extraction test
PCA	principal component analysis
PCR	principal component regression
PGE	platinum group element
PIXE	particle induced X-ray emission
PLS	partial least square
PM	particulate matter
$PM_{2.5}$	particulate matter (with an aerodynamic diameter of up to 2.5 µm)
PM_{10}	particulate matter (with an aerodynamic diameter of up to 10 µm)
ppm	part per million
PTFE	poly(tetrafluoroethylene)
QC	quality control
RCC	rotating coiled column
REE	rare earth element
RM	reference material
RP	reverse phase
RP–HPLC	reversed phase high performance liquid chromatography
RSD	relative standard deviation
RTC	Resource Techology Corporation (USA)
s	standard deviation of sample
SARM	South African producers of Metallurgical and Geological Certified Reference Materials
SBET	simplified bioaccessibility extraction test
SD	standard deviation
SE	solvent extraction
SEM	scanning electron microscopy
SEM-EDS	scanning electron microscopy energy dispersive spectrometry
SF	sector field
SFE	supercritical fluid extraction
SF-ICP-MS	sector field inductively coupled plasma mass spectrometry
SFODME	solidification of floating organic drop microextraction
SIMS	secondary ion mass spectrometry
SPE	solid phase extraction

SPME	solid phase microextraction
SRM	standard reference material
TBT	tributyltin
TEM	transmission electron microscopy
TIMS	thermal ionisation mass spectrometry
TMAH	tetramethylammonium hydroxide
TODGA	N,N.N'N' tetraoctyl-1,5-diglycolamide based resin
TOF	time of flight
TRAP-LRM	Training in production and use of laboratory reference materials for use in routine quality control (EC-Growth Programme Contract G6MA-CT-2000-02006)
TS-FF-AAS	thermospray flame furnace atomic absorption spectrometry
TSP	total suspended particles
TXRF	total reflection X-ray fluorescence
UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
USN	ultrasonic nebuliser
UV	ultra violet
VG	vapour generation
WDXRF	wavelength dispersive X-ray fluorescence
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectrometry
XRD	X-ray diffraction
XRF	X-ray fluorescence
YAG	yttrium aluminium garnet
σ	population standard deviation

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