Atomic Spectrometry Update – a review of advances in environmental analysis.

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SUMMARY OF CONTENTS

In the field of air analysis, highlights within this review period included: new isotopic data for reference dust materials; a new device for preparing and mounting delicate air filter samples for X-ray analysis and use of oxygen-mediated mass-shift ion chemistry for measuring sulfur in aerosol samples by ICP-MS.

The use of DGT and ionic liquids for preconcentrating trace elements and other analytes from waters has become more established. The resurgence of interest in As speciation has been noted with extensive reviews as well as methods for the challenging determination of thioarsenic species. Improvements in methodologies have achieved LODs with GC-MS that were once only possible with ICP-MS, thereby making it possible for a larger number of laboratories to undertake speciation analysis. Field preconcentration methods and hand-held XRF instruments have made it easier to screen contaminated waters, thereby allowing sampling sites to be selected more effectively.

There has been renewed interest in atomic emission sources such as the arc, GD and plasmatron for the analysis of plants and soils. The upward trend in publication of LIBS methods continued but many lacked validation through comparison with established methods or analysis of CRMs. There is a clear need for closer collaboration between the physicists driving fundamental developments in plasma spectroscopy and analytical geochemists, who understand the complexities of environmental samples and the requirement to implement robust QC procedures.

Interest in multivariate analysis of pXRFS spectra to predict soil properties related to fertility has increased.

Much research effort continues to be devoted to characterisation of matrix-matched geological RMs, both synthetic and natural samples, particularly for in situ analysis by microanalytical techniques, such as LA-MC-ICP-MS and SIMS. Such RMs are essential to compensate for matrix effects and need to be available in sufficient quantities to enable interlaboratory comparisons based on the same RM. The increased access to MC-ICP-MS instrumentation, especially in China, is reflected in the diverse range of isotopic systems now being studied. Most studies present incremental improvements to existing separation procedures or measurement protocols.

1. **Introduction**

This is the 36th annual review of the application of atomic spectrometry to the chemical analysis of environmental samples. This Update refers to papers published approximately between August 2019 and June 2020 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 metals, chemicals and functional materials[6]. This review is not intended to be a comprehensive overview but selective with the aim of providing a critical insight into developments in instrumentation, methodologies and data handling that represent a significant advance in the use of atomic spectrometry in the environmental sciences.

All the ASU reviews adhere to a number of conventions. An italicised phrase close to the beginning of each paragraph highlights the subject area of that individual paragraph. A list of abbreviations used in this review appears at the end. It is a convention of ASUs that information given in the paper being reported on is presented in the past tense whereas the views of the ASU reviewers are presented in the present tense.

General reviews applicable to all areas of environmental analysis included a tutorial review[7] (67 references) on the fundamentals and new approaches to calibration in atomic spectroscopy. In the context of direct solid sampling[8] (255 references), recent advances in different techniques such as FAAS, ETAAS, HR-CS-AAS, ETV, LA, LIBS, XRFS, GD AES and MS and arc/spark AES, were discussed.

2 Air analysis

2.1 Sampling techniques

A new disposable personal air sampler for *workplace aerosol sampling*, designed to match the ISO/CEN/ACGIH inhalability convention, incorporated[9] design features from two existing and widely-used samplers — the closed face cassette and IOM samplers. Initial wind tunnel evaluations were promising although further refinements are required to improve sampling efficiencies for particles >40 µm in size. The ultrasonic personal aerosol sampler, reviewed previously[1], was upgraded[10] to include interchangeable sampler inlet options for either respirable- or thoracic-particle sized sampling. Cyclonic samplers, commonly used to sample respirable-sized particles, can demonstrate sampling biases due to particle-size dependencies and can overload if high dust concentrations are sampled for extended time periods. A new virtual cyclonic design demonstrated[11]: a better fit with the ISO/CEN/ACGIH respirable convention curve; better ability to handle high dust loadings; and the ability to run at flow rates of up to 21.5 L min^{-1}. The ability to collect more sample mass per unit time and thereby improve method sensitivities will become more important as regulatory workplace exposure-limits for many chemical agents become lower. An apparatus for measuring aerosol deposition in lungs, fabricated[12] by 3D printers, simulated the human tracheobronchial airway to provide a better understanding of the potential for deposition of welding fume in welders' airways. In simulated exercises, 9-31% of welding fume particles in the size range 10-100 nm was deposited in this simulated airway.

Sampling the regulatory $PM_{2.5}$ and PM_{10} *particle size fractions in ambient air* requires air sampler devices to meet performance specifications embodied in particle-size-collection efficiency curves that are characterised by their cutpoint (d_{50}) and the steepness of the curve (σ_g). Whereas performance specifications for PM_{10} samplers are well established, those for $PM_{2.5}$ samplers are less so. A Chinese-US research collaboration concluded[13] that for an ideal $PM_{2.5}$ size separator, the cutpoint tolerance should be 2.5±0.2 µm and σ_g should be ≤ 1.3, whereas for a PM_1 size separator, an emerging measurand of interest, values of 1.0±0.02 µm and ≤ 1.2, respectively, were suggested. A cascade air sampler device, designed to sample PM_{10}, $PM_{2.5}$, PM_1 and $PM_{0.5}$ particles simultaneously, was modified[14] to collect the residual $PM_{0.1}$ particle size fraction uniformly on a filter. The aim was to facilitate either direct-on-filter analysis using beam techniques such as XRFS or to enable a representative portion of filter to be removed for chemical analysis.

The development of *new air-sampling devices* included an electrostatic precipitator (ESP) sampler[15] for dust collection at a high flow rate and an ambient air sampler[16] for dust collection at a low flow rate. Deployment of the ESP sampler over monthly intervals enabled sufficient mg quantities of indoor dusts to be collected for analysis. Similarly, the ambient air sampler collected sufficient sample mass for analysis when deployed over 1-2 month sampling intervals.

The authors concluded that as only low flow rates (0.5 L min^{-1}) were required, such samplers could be produced at relatively low cost allowing widespread deployment for sampling.

Deposition sampling can be an alternative approach to pumped sampling for collecting airborne particles and is attractive because it requires no power. Concerns about sampling performance still persist, however. A comparison of dry deposition samplers, based on[17] single-particle SEM characterisation of collected dust, concluded that differences in deposition rates between sampler types did indeed exist. A side-by-side comparison exercise, in which passive UNC samplers were worn by mine workers alongside pumped respirable air samplers as reference, demonstrated[18] that there was a *ca.* 30-fold over-estimation of sampled particle mass. It was concluded that performance might be improved by adjusting the positioning of the UNC sampler on the worker and grounding the device so as to minimise static charging.

2.2 Reference materials and calibrants

Small variations in the stable isotopic compositions of certain metals can identify the provenance of certain airborne dusts. Studies that provided new isotopic data for reference materials included one[19] on the isotopic composition of Hg in NIES CRM 28 (urban aerosols) and one[20] on new isotopic data for Cu, Fe, Nd, Pb, Sr and Zn in IRMM CRM BCR-723 (road dust) and in Powder Technologies RM ATD (Arizona test dust). Complementary to this work, the Cu, Pb and Zn isotopic compositions in representative windblown mineral samples collected from both African and Asian dust events were determined and tabulated[21].

In a continuation of work reported in last year's ASU[1], two approaches for the assignment of elemental values to new candidate filter-based (thin-layer) *XRFS calibrants* were evaluated[22].

Consensus values, derived from an interlaboratory comparison exercise, agreed with *a priori* values determined during batch homogeneity testing of filter samples.

The reliability of monitoring *mercury* in stacks is constrained by the availability of accurate and metrologically traceable calibrants. Researchers at NIST[23], in collaboration with colleagues from the US EPA, devised a new calibration chain with traceability to the SI. This work involved certifying the Hg^0 output of a calibration-gas generator (termed NIST prime) as the primary calibrant that then could be used to cross-calibrate vendor calibrant systems (secondary calibrant) by side-by-side testing conducted at NIST. This gave vendors a means of conferring traceability to their customer units (tertiary calibrant) installed alongside Hg^0 analysers at stacks. Certification of this NIST prime unit involved sampling defined volumes of Hg^0 on sorbent tubes and analysis using an accurate and precise ID-cold vapour-ICP-MS method (see section 2.4.2.1). Traceable calibrants are also required for Hg^{2+} species, which can be emitted from combustion processes together with Hg^0. Within the MercOX project, funded under the European EMPIR programme, two new calibrant systems were evaluated[24]. In both systems, a Hg^{2+} solution was dosed into a heated chamber at a constant rate and the resultant gaseous Hg^{2+} species diluted with air to provide the required gas calibrant standard. If there were no Hg losses within the system, the resultant Hg concentrations could be calculated from the Hg concentration in the starting solution, the liquid dosing rate and the gas dilution flow rates. Further tests were planned, in which defined volumes of gas standards would be collected on sorbent traps and analysed, to check the accuracy of the theoretical outputs for these two prototype devices.

In an innovative approach, NO *calibration gas* was generated[25] on demand by the photolysis of N_2O, which is readily available in disposable gas cartridges used, for example, in the catering industry as an aerosol propellant for generating whipped cream. By combining this new device with an existing O_3 calibrant generator, NO_2 gases could be generated using the stoichiometric gas-phase reaction of NO with O_3 to result in a new portable device that could calibrate NO, NO_2 and O_3 air monitoring instruments up to 1000, 500 and 1000 ppb respectively.

2.3 Sample preparation

The *solubility of trace metals* deposited into the oceans from aerosols is a key factor in phytoplankton growth. In an evaluation (97 references) of published leaching protocols, it was concluded[26] that harmonised testing guidelines were required to better understand the biogeochemical impacts of such depositions because comparing solubility data generated in different studies by different research groups using different analytical protocol remained difficult.

Sample *losses or contamination* are omnipresent challenges when preparing air filter samples for trace element analysis. A substantial 6-10x increase in Hg recoveries from air filter samples was noted[27] when lithium tetrathiafilvalene carboxylate (LICTTF) was added prior to MAD. The average airborne particulate Hg concentration determined for filter samples by ICP-MS was 0.4 ng m^{-3} with addition of LICTTF and 0.05 ng m^{-3} without. The BCR sequential extraction procedure, originally devised for soil samples, was adapted[28] for the fractionation of PTEs in airborne particles collected on air filter samples. Simulant test samples were prepared by spiking air filters with small test portions (*ca.* 63 mg) of IRMM BCR CRM 701 (*lake sediment*), a CRM certified for its extractable analyte content using the BCR protocol. An endogenous Zn contaminant was noted, consistent with air sampling by glass-fibre based filters, which are notorious for being contaminated with Cu, Fe and Zn. After subtraction of results for blank filters, elemental fractionation patterns mirrored the certified patterns, and total elemental recoveries (combining elemental data from each of the 4 leaching steps of the BCR protocol) were 84 – 113% of the certified values.

A new *automated system* enabled[29] radiocarbon analysis of carbonaceous aerosols collected on filters to be performed more efficiently. The initial step involved combustion, in which organic or elemental carbon moieties were converted to CO_2 by heating filter pieces to defined temperatures in a stream of either He or O_2 carrier gases, with on-line verification of complete combustion by NDIR spectroscopy. Combustion impurities such as NO_X, SO_2 and halogens were removed together with H_2O. The purified CO_2 was then cryogenically collected in glass ampoules under N_2 and sealed for future off-line ^{14}C measurement. The system was capable of preparing very small samples of 10–50 μg C. The rapid $^{235}U/^{238}U$ analyses of material deposited on cotton swabs was possible[30] using an Advion® plate express reader on an Orbitrap® MS instrument equipped with a liquid-sampling GD microplasma ionisation source. Rapid (30 s) desorption of U species from swab samples into a stream of 2% (*v/v*) HNO_3 was possible. The measured $^{235}U/^{238}U$ ratios (0.053-1.806) were accurate to within <10%. The system portability had potential application in nuclear non-proliferation survey exercises.

For air sampling purposes, a stretching ring is required to keep a *PTFE filter* taut and hence flat, but the thickness of the ring can subsequently impede the irradiation of a filter by X-rays when analysed. It would be preferable to remove this ring, but the PTFE filters would then deform and so present an uneven surface for analysis. A new sample preparation device, termed the Smart Store®, enabled[31] a PTFE air sampling filter to be prepared for TXRFS analysis by removing this support ring and encapsulating the filter between two sheets of laminated polythene film to keep it flat. There was some signal attenuation due to absorption of X-rays by this film, but nevertheless this device offers potential for labour-saving in the preparation of delicate air filters for analysis.

2.4 Instrumental analysis

2.4.1 Atomic absorption and emission spectrometries

Two approaches for the *speciation analysis of mercury* in flue gases were evaluated[32]. In the off-line approach, a gold-coated alumina sorbent for trapping Hg^0 and an alumina sorbent for trapping oxidised forms of Hg were coupled in sequence for analysis by TD-AAS. In the on-line approach, flue gases were introduced directly into a quartz atomiser *via* a heated transfer line from the stack. The ability to vary the cell temperature enabled Hg^0 to be determined selectively at ambient temperature, but the determination of oxidised Hg species required 900 °C to facilitate dissociation to Hg^0. The former approach offers better sensitivity because preconcentration is involved, useful for benchmarking against regulatory emission limit requirements, but the latter approach offers speed because near instantaneous measurements were possible, useful for checking performance of Hg trapping technologies installed on stack.

The rapid elemental profiling of individual particles sampled from air was possible[33] by combining bright-field microscopy with *LIBS*. An ultra-thin polythene film had the following advantages: it usefully immobilised selected particles for interrogation, vaporisation of the thin film was rapid so quenching effects were minimised, and the simple polymer composition minimised the potential for spectral artifacts. Measurement of unburnt C in fly ash can be a useful indicator of combustion efficiency within coal-fired power plants. A new two-stage cyclone enabled[34] better C measurements by on-line LIBS. Fly ash and CO_2 were separated effectively from a combustion gas stream. Application of a plasma-temperature correction-protocol that involved interrogation of Mg II/I emissions provided results that agreed well with those for ash samples tested off line.

2.4.2 Mass spectrometry

2.4.2.1 Inductively coupled plasma mass spectrometry. A new *ICP-MS/MS* procedure for determining 67 elements in size-segregated particulate matter collected on air filters was reported[35]. Of particular interest was the successful determination of S as SO^+ at *m/z* 48 by using mass-shift ion chemistry involving O_2. The S recoveries were 96±4% when aliquots of NIST SRM 1648 (urban particulate matter) were analysed. A new method for determining $^{236}U/^{238}U$ isotope ratios also employed[36] O_2-mediated mass-shift ion chemistry to reduce significantly the $^{235}U^1H^+$ isobaric interference on ^{236}U. By cleverly exploiting the fact that the hydride form of UO^+ (UOH^+) is less prone to formation in the plasma than UH^+, together with the use of a desolvating nebuliser, it was possible to constrain the $^{235}U^{16}O^1H^+/^{235}U^{16}O^+$ formation rate to *ca.* 10^{-7} so $^{236}U/^{238}U$ ratios of $<10^{-8}$ could be determined successfully for material deposited from the Fukushima Daiichi nuclear incident.

Siloxanes in *gaseous fuels*, even at low concentrations, can be problematic because, upon combustion, amorphous Si can deposit and cause damage within combustion systems or fuel cells. The LOQ for Si of *ca.* 0.01 mg m^{-3} for a new GC-ICP-MS approach to the analysis of fuels was[37] below the benchmark limit of ≤0.1 mg m^{-3} designed to protect machinery. The Hg^0 concentration output from the NIST prime calibrator (see section 2.1) was certified[38] using ID-CV-ICP-MS at selected span points over the range 0.25 to 38 µg m^{-3}. Two procedures were used, a direct gas analysis approach and a preconcentration method that involved trapping defined gas volumes on activated carbon. The direct measurement approach yielded expanded MU ranging from 5.5% at 0.5 µg m^{-3} to 1% at 38 µg m^{-3} with a LOQ of 0.06 µg m^{-3}, whereas sample preconcentration yielded an expanded MU of 1% across this range with a LOQ of 0.001 µg m^{-3}.

The *single particle ICP-MS* analysis of atmospheric particles deposited in ice-core samples was performed[39] for the first time using CFA coupled to ICP-TOF-MS. The fact that Al and Mg signals were associated with Fe signals emanating from Fe-rich particles suggested that clay minerals such as illite were the dominant components in the particles being examined. Use of a dry aerosol provided[40] a significant gain in ion extraction from a plasma thereby making it possible to now size silver and titanium NPs at 3.5 and 12.1 nm, an improvement of 29 and 37% over that achievable under wet plasma conditions.

In the *LA-MC-ICP-MS* determination of isotopic ratios in sub-μm sized UO_x particles a new small-dead-volume ablation-cell produced[41] a better S/N, but alas a comparable improvement in precision was not achieved, suggesting that there was an unknown source of measurement imprecision. Upon investigation, the authors found that some sample ions were not being detected within a measurement window, which they called detector “blind time”. This issue was traced to the design of the instrumental data acquisition system, originally conceived to integrate the steady state ion signal arising from a continuous liquid sample nebulisation process, rather than rapid transient signals arising from the laser ablation process. By setting a signal integration window of 500 ms, this “blind time” effect was minimised. Development of new fast data acquisition systems for LA applications can therefore be anticipated.

2.4.2.2 Other mass spectrometry techniques: A novel *real-time* system employed**[42]** an extractive ESI source coupled to a HR TOF-MS instrument for determining water-soluble metals present in aerosols. Laboratory experiments involved nebulisation of simultant metal-EDTA-chelate test samples as dry aerosols using either an in-house fabricated nebuliser with a silica gel drier or a commercially available desolvating HEN. The resultant ions were detected using negative ionisation. Preliminary results were encouraging with good linear mass responses, low ng m^{-3} LODs and a fast single-second response. An ultrafine-particle concentrator employed**[43]** a water-based condensation tube to increase the size of small 10 nm-sized particles with a solvation shell so ensuring their effective capture prior to analysis by aerosol MS. Inlet sampling was configurable between 1 and 1.7 L min^{-1} with a resultant output flow into the aerosol MS of between 0.08 and 0.12 L min^{-1}. As a consequence, aerosol samples were concentrated 8 to 21 times. Initial field experiments were carried out with an aerosol MS set-up equipped with a switching valve, so that aerosols could be sampled either through this new preconcentrator inlet or through a standard inlet. No alterations in the particle chemistry were observed for the new system.

2.4.3 X-ray spectrometry

Collection of size-segregated PM_{10} particles directly onto quartz reflectors acting as impaction plates facilitated[44] subsequent analysis by *TXRFS*. Absolute mass-response calibration was performed using Si wafers impregnated with 4 or 8 ng Cr (±5%). Analysis of a Si wafer spiked with known aliquots of a multi-elemental standard allowed RSFs (relative to Cr) to be determined thereby alleviating the need, common with many TXRFS applications, for an IS to be spiked into each sample. The LODs of, for example, 0.09 (As), 0.24 (Ni) and 0.20 (Pb) ng m^{-3} for a 1 m^3 sample volume and 3000 s integration made the procedure suitable for EU ambient air regulatory measurement purposes, for which the limit values (yearly averages) are 6 (As), 20 (Ni) and 500 (Pb) ng m^{-3}. Furthermore, this inherent method sensitivity made it possible to monitor short-lived pollution episodes at high time-resolution. Further planned developments included a portable TXRFS instrument for measurements in the field.

2.4.4 Combustion-based techniques

Thermal-optical combustion-based measurements are widely used to classify *carbonaceous aerosols* captured on filters from measurements of their organic (OC) and elemental (EC) carbon moieties and, by summation, their total carbon (TC) content. Whereas, in general, results are in agreement for TC measured using various combustion protocols and/or instruments, results for

EC can vary greatly because OC can be misclassified as EC. Accurate EC measurements are required because EC-containing particles contribute to climate change through radiative forcing effects. In addition, EC in the workplace is used as a marker of exposure to diesel fumes. An interesting comparision[45] of EC and OC mass measurements was conducted concurrently by three long-term monitoring networks (the US IMPROVE and the Canadian CAPMoN and CABM networks) at one North American ambient-air monitoring site. Whereas the values for EC, OC and TC measured by IMPROVE were 5-75% higher than those measured by CAPMoN, they were 15-80% lower than those for CABM. The authors concluded that regular inter-comparisons between monitoring networks should be made and, additionally, that there is a need for new filter-based RMs because different operationally-defined procedures used in these networks give different answers. The formation of so-called pyrolysed carbon arising from OC charring during the combustion process is one reason why such measurement challenges exist. Upon further heating, pyrolysed carbon can be oxidised to CO_2 and contribute to measured CO_2 values arising from EC combustion, hence generating a false-positive EC value. A detailed report[46] described the structural changes in simulant carbonaceous samples prepared with a soot generator during a typical thermal-optical measurement cycle.

A two-step *thermal-oxidative analysis* enabled[47] EC and TC species emitted from turbine engines to be determined. The established NIOSH 5040 thermal-optical method requires filters to be sectioned so the ability of this new procedure to analyse a complete filter was a distinct advantage as it eliminated any potential sample-heterogeneity issues. Another advantage over the NIOSH approach was the ability to analyse filters with high carbon mass loadings (> 90 $\mu g/cm^2$) such as those expected from the direct sampling of engine exhausts. A constraint, however, was that OC was not measured directly but by the difference between TC and EC. For many tailpipe measurements, this may not be an issue as freshly emitted particles typically contain high EC/OC ratios (e.g. 9:1), but it would be a disadvantage for studies of aged carbonaceous emissions with lower EC/OC ratios (e.g. 1:1) that can occur over time upon mixing with other organic pollutants in the atmosphere, resulting in an increased potential for the formation of a pyrolytic carbon artifact.

Optical methods are attractive for measuring black carbon in carbonaceous aerosols because they can be faster alternatives to the laboratory-based combustion approaches and can be made portable. For quantification purposes, however, knowledge of the light-absorption properties of black carbon are required, so tabulation[48] (63 references) of reported mass absorption cross-sectional values was timely. Lower cost alternatives to the expensive black-carbon sensors currently available were based on the use of cameras. In one approach, black carbon on filters was estimated[49] using a smartphone camera and a calibration algorithm facilitated by the analysis of 1,878 filter samples for which reference black carbon values were available. When used in the field, this smartphone approach demonstrated good predictability against reference black carbon on filter measurements with an R^2 of 0.904 and a coefficient of variation (RMSE) of 25.3%. In another study, black carbon values estimated from filter images taken with a digital camera correlated[50] well (normalised RMSE <10%) with data derived from two reference black carbon measurement approaches (smokestain reflectance and hybrid integrating plate and sphere methods) and from an EC measurement method.

The *measurement of workers' exposure* to carbonaceous aerosols remains topical. Aethalometer-derived black carbon measurements of large-diameter (50-80 nm) CNTs sampled onto filters were[51] comparable to reference EC on filter measurements by NIOSH method 5040, but black carbon measurements were lower than EC measurements when small-diameter (<8 nm) CNTs were assessed. Instrumental drift also occurred when the aethalometer was challenged with elevated CNT airborne concentrations (>30 $\mu g\ m^{-3}$) that could arise from activities such as cleaning and powder bagging. Continuous monitoring of diesel particulate matter (DPM) in underground mine air is desirable to assess workers' exposure to pollution. An evaluation[52] of four DPM monitoring devices (the FLIR Airtec monitor, the Magee Scientific AE33 aethalometer, the Sunset Laboratory OC-EC field analyser and Airwatch, a new prototype continuous-monitor based upon the Airtec monitor) in a laboratory and in a mine setting concluded that both the AE33 and the Sunset instruments had potential for unattended monitoring underground provided that there was reliable access to power and that periodic routine maintenance was performed. The prototype Airwatch instrument had potential but required further development to achieve reliable and consistent measurements.

2.4.5 Other techniques

Advances in *vibrational spectroscopic techniques* offer potential for measuring airborne pollutants. An innovative optical-trapping Raman method examined[53] single suspended CNTs, an approach that eliminates measurement artifacts arising from sampling onto filters. A Raman method for the analysis of respirable crystalline silica (RCS) collected on silver filters had[54] a LOD of 0.26 μg, which was an order of magnitude better than that achievable by established XRD and FTIR approaches. In a continuation of work, reported in last year's ASU[1], on measuring mine workers' personal exposure to RCS by portable FTIR, researchers at NIOSH demonstrated[55] that results for filter samples analysed by four commercially available instruments varied by <5%. Variations in average filter measurements, conducted over an extended time period, were not statistically significant.

3 Water analysis

3.1 Certification of reference materials and metrological investigations

An *interlaboratory comparison* assigned[56] values for B, Cs, Ga, Ge, Hf, Li, Nb, P, Rb, Re, Rh, S, Sc, Se, Si, Sn, Th, Ti, Tl, W, Y, Zr and REEs in the NRCC CRM SLRS-6 (river water) together with an indicated Sr isotopic composition by mainly ICP-AES and ICP-MS. The concentrations were generally lower than those reported previously for the SLRS-5 RM.

A *full validation approach* was applied[57] to the ID-cold vapour-ICP-MS determination of Hg in marine biota, sediments and coastal waters. The blanks, selectivity, working range (1.2-240 ng kg^{-1}), linearity (0.9991), recovery (97-103%), repeatability (<2.5%), intermediate precision (<3.5%), LOD (0.72 ng kg^{-1}) and LOQ (1.10 ng kg^{-1}) were systematically assessed following ISO/IEC 17025 and Eurachem guidelines. The relative expanded uncertainty of the total Hg mass fractions in coastal seawater samples was 27.2-32.8%. Recovery correction for the ID spike contributed 60-75% to the uncertainty budget because the spiked IRMM CRM BCR 579 (coastal seawater) itself had a relative expanded uncertainty of 26%. Another significant contribution (10-35%) to uncertainty was correction of the procedural blanks, which was particularly important for the low Hg-mass-fractions typically found in coastal seawaters. The repeatability of the CVG ICP-MS measurements in seawater samples was 5-10%.

3.2 Sample preconcentration

The use of DGT samplers as passive *solid-phase preconcentration devices* in the measurement of labile trace metal concentrations in marine environments was reviewed[58] (50 references). These devices have even been successfully mounted on autonomous underwater vehicles to probe labile metal concentrations in coastal and open ocean waters. Other uses of DGT samplers and significant advances in the SPE of trace elements from water samples are summarised in Table 1.

[Table 1]

In their review (265 references) on the use of ionic liquids for *liquid-phase extraction* of trace analytes, Pletnev *et al.*[59] defined ionic liquids as “salts being liquid at room temperature or not very high temperatures”, “not very high” was considered to be ≤100 °C. For water analysis only those that are liquid at room temperature are of interest. The expanding use of ionic liquids was confirmed[60] by a review (130 references) on the use of ionic liquids and ionic-liquid-modified sorbents for the preconcentration of heavy metal ions and organic pollutants from water samples.

The most significant advances in the use of liquid-phase extraction, published in period covered by this ASU are summarised in Table 2.

[Table 2]

3.3 Speciation analysis

A *comprehensive review of arsenic speciation* (240 references) in environmental samples, including surface, ground, and geothermal waters, covered[61] the period 2004-2018. Although LC-ICP-MS was by far the most widely used technique, other techniques such as those involving XRF detection were increasingly reported. The review covered the analytical process from sample preparation to measurement and is recommended for all workers in the field of environmental analysis.

Aluminium complexes in water were investigated[62] using CE with ESI-MS and ICP-MS detection. Both detectors were most sensitive at pH 3. Peaks were identified by ESI-MS. Using ICP-MS under cool plasma conditions, the peaks were baseline resolved so an Al LOD of 0.037 μM was achievable for a 35 nL injection.

The capabilities of modern instrumentation for *arsenic speciation analysis* in waters was demonstrated[63] using a standard Hamilton PRP-X100 SAX column with diluted-phosphate-buffer gradient-elution to decrease blank values. The LODs were as low as 0.01 ng L^{-1} for arsenobetaine and 0.35 ng L^{-1} for As^V when the ICP-MS instrument was operated in KED mode. Analysts from the US EPA solved[64] the problem of thioarsenite detection in groundwater by matching the pH of the eluent to that of the sample to minimise species transformations due to proton transfers. It was possible to resolve the differences between previous XAS and chromatographic data, thereby progressing our understanding of arsenic behaviour in sulfate-reducing environments.

The *detection of perchlorate in river water* by HPLC-ICP-MS was improved[65] 10-fold by using ICP-MS/MS instead of a single quadrupole instrument. The instrumental LOD for Cl was 0.3 µg L^{-1} when freeze drying was used to preconcentrate the sample. A method LOD of 50 ng L^{-1} for Cl was possible in the absence of large concentrations of carbonate, making the technique competitive with the standard HPLC-ESI-MS/MS method whilst avoiding the need for isotopically labelled ISs.

In order to make the US EPA Method 1630 for *methyl mercury in water* more easily applicable to several Hg species in petroleum production waters, it was modified[66] by including an ultrasonic CPE step with an acidified solution of Triton X-114 (0.5% *w/v*, pH 3) and by using propylation rather than ethylation for derivatisation. This sample preparation eliminated reagent interactions with oil-based constituents in the matrix thereby preventing artefact formation during derivatisation and distillation. With GC-cold vapour-AFS detection, the LODs for mercury species were 5 (Hg^{2+}), 8 (CH_3Hg) and 11 (CH_3CH_2Hg) pg L^{-1} in this type of sample, which is generally difficult to analyse.

It is pleasing to note progress in the determination of *marine biogenic activity tracers* and their reaction products in environmental matrices, as they are used extensively as proxies for past sea ice cover. Low-pressure IC was coupled[67] with MC-ICP-MS to follow the oxidation of ^{129}I spikes in seawater to iodate. Use of a commercially available sparging interface, in which volatile I_2 was generated after the addition of HNO_3 as an oxidant, increased I transport to the plasma ten-fold in comparison to that for pneumatic nebulisation, thereby making it easier to monitor the ^{129}I/^{127}I isotope ratio. An HPLC-ICP-MS/MS method was developed[68] to determine the oxidised breakdown products of dimethylsulfide in seawater after reaction with HOBr. Use of a Hypercarb™ mixed-mode column with a formic acid gradient made it possible to separate dimethylsulfoniopropionate, dimethylsulfoxide, dimethylsulfone, dimethylsulfide, methanesulfonic acid and methanesulfinic acid in under 12 minutes. Detection by ICP-MS/MS with H_2 and O_2 as reaction gases resulted in LODs that ranged from 1.7 (dimethylsulfide) to 136 (methanesulfinic acid) nM. The reaction rate constants determined could be incorporated in models of the ocean-atmosphere interface.

Tin species were separated[69] by TLC on a glass slide coated with an ion-imprinted polymer created by copolymerising N-allylthiourea and ethylene glycol dimethacrylate in the presence of Sn^{II}. The two tin species (Sn^{II} and Sn^{IV}) were completely separated using a mobile phase of 1:1 (*v/v*) acetonitrile-ethanol at pH 6. After deposition of 10 µL of standard (0.8-900 µg L^{-1}), the plate was scanned using LA-ICP-MS with a 50 µm spot size and a 20 Hz shot frequency. The method LOD was 0.3 µg L^{-1}, sufficient to quantify Sn species in samples from the Caspian Sea, a local river and waste waters.

Although *GC-MS methods for the determination of elemental species in water samples* have existed for many years, only recently has modern instrumentation been capable of LODs at the level routinely achievable by GC-ICP-MS. Selenocyanate was quantified[70] in waste water by GC-MS/MS after derivatisation with triethyloxonium tetrafluoroborate, to generate volatile ethylSeCN, and by back extraction into chloroform. The LOD for Se was 0.1 ng g^{-1}. Using $^{80}Se^{13}C^{15}N$ as an IS, spike recoveries from sea and river waters were quantitative at the ng g^{-1} level. Selected organoarsenic compounds were determined[71] in mining and waste waters by SPME-GC-MS using 1,3-propanedithiol as a derivatising agent and a 65 µm polydimethylsiloxane divinylbenzene SPME fibre. The LODs of 0.4 to 5.9 µg L^{-1} were achieved after a 30 minute fibre equilibration time. Mercury species (Hg^{2+}, EtHg and MeHg) were derivatised with sodium tetraphenylborate[72] and trapped on a polydimethylsiloxane-coated SPME fibre in the headspace for subsequent GC-MS/MS analysis. For thermal desorption in the injection port at 250 °C, the LODs were 0.03 (MeHg and EtHg) and 6 (Hg^{2+}) ng L^{-1}.

Although most published articles concern known compounds, there is still scope for *untargeted and fractionated analysis* of trace elements and their compounds. An important example of this approach was[73] the determination of perfluorinated compounds in surface and groundwaters. Current control methods for the nearly 5000 per- and polyfluoroalkyl substances with related CAS numbers measure only a limited number of these compounds, so an untargeted screening method for the measurement of total organic F extracted from ground and surface waters was developed. After extraction by SPE and the addition of Ga, F was detected in a CS-ETAAS instrument as molecular GaF, probably at 211.248 nm but this important information was not given. The method LOD was 5.3 ng L^{-1}. Accuracy was verified by analysis of the EC CRMs MISSIPPI-03 and Battle-02 (both river water) certified for total F. Although NPs and colloids can be fractionated by size and easily and routinely detected by FFF-ICP-MS, the dissolved fraction is lost in the cross-flow across the membranes. An FFF instrument was modified[74] with an interface designed to convert the discontinuous cross-flow into a continuous flow suitable for ICP-MS analysis. Results for the dissolved fractions of Al, Ca, Mg, P and Si in aqueous standards and water samples compared well with those obtained from discrete sampling and ultrafiltration.

3.4 Instrumental analysis

3.4.1 Atomic absorption spectrometry. The advent of the xenon short-arc lamp as a *continuum source for a high-resolution atomic-absorption spectrometer* has been the main advance in AAS in recent years. Eskina *et al.*[75] reviewed (173 references) use of this instrumentation and included the analysis of waste and drinking waters amongst all applications considered. The HR scanning ability of this ETAAS instrumentation was exploited[76] to remove matrix interferences in the determination of Pb directly in seawater. A mixed $Ba(NO_3)_2$-HF modifier suppressed the sulfate interference (by formation of refractory barium sulfate) and removed the chloride interference (by formation of volatile HCl), thereby allowing an LOD of 0.3 $\mu g\ L^{-1}$ to be achieved. Unsurprisingly, the recovery error was only 6% when the accuracy was estimated at the rather unrealistic spike concentration of 50 $\mu g\ L^{-1}$, some 1000 times higher than the level expected in seawater.

3.4.2 Vapour generation. Photochemical reduction of As^V and DMA to As^{III} was used[77] in the VG-FAAS *speciation analysis of arsenic* in soils, sediments and surface waters from a heavily contaminated area of Brazil. The LODs of 3.2 (As^{III}) to 6.7 (DMA) $\mu g\ L^{-1}$, obtained using ZnO NPs as photocatalysts and optimisation of the pH and formic acid concentration, were considered fit for purpose for waters impacted by mine waste leakage.

There is an increasing focus on *bismuth in the environment* as it becomes more widely used in industrial processes. The sensitivity of ICP-MS determination of this element was improved[78] 70-fold for the PVG of volatile $(CH_3)_3Bi$ after reaction with formic and acetic acids in the presence of Co^{2+} ions compared with that of pneumatic nebulisation. The LOD was 0.3 ng L^{-1}. A different approach for improving the sensitivity of AFS for Bi involved[79] modification of the flame atomiser, optimisation of the optical path of the spectrometer and addition of a 307.1 nm interference filter. The LOD was 0.9 ng L^{-1} in water. The Bi concentrations of 22 and 24 ng L^{-1} determined for the NRCC CRMs NASS-7 and CASS-6 (seawater), respectively, for which there are no certified or indicative values, were within the range of expected values for seawater. Accuracy was demonstrated by analysis of NIST SRM 1643f (trace elements in natural water) for which the measured value of 12.8±0.1 ng L^{-1} ($n = 3$) was in close agreement with the certified value of 12.62±0.11 µg L^{-1}.

The AFS *determination of lead in water samples* was achieved[80] by forming volatile Pb chelates with ammonium O,O-diethyldithiophosphate. Although the reported VG efficiency of 12% doesn't seem an advance on the efficiency of traditional HG, the LOD of 1.1 µg L^{-1} was sufficient to determine Pb in river water samples successfully.

3.4.3 Inductively coupled plasma mass spectrometry.

A *correction for M^{2+} interferences* is required when determining As and Se in REE-rich waters by the US EPA method 200.8. Smith *et al.*[81] considered that corrections based on the "half mass" interferences generated by alternative, non-interfering isotopes (*e.g.* m/z 71.5 for $^{143}Nd^{2+}$) could be more effective than estimating the "whole mass" interference (*e.g.* on m/z 75 for $^{150}Nd^{2+}$) because other, non-REE-related interferences, could lead to an overcorrection in the latter approach. The new approach using single-quadrupole instrumentation reduced the number of overcorrected measurements and gave results closer to those obtainable by ICP-MS/MS or ICP-SF-MS. An additional advantage was that the measured intensities could be used simultaneously to correct for drift and differences in matrix composition.

The *boron memory effect during isotope ratio measurements* by MC-ICP-MS was significantly reduced[82] by adding NaF to the wash solution. A solution of NaF (0.6 mg g^{-1}) in 1% *v/v* HNO_3 was as effective as a 0.3 M HF rinse solution but had no damaging effects on the instrumentation. The B counts returned to baseline levels in <4 minutes after sample analysis.

A method for the *preconcentration of mercury from waters* without causing any isotope fractionation used[83] a 3 L bubbler for CVG before analysis. The sample was transferred to the bubbler and a BrCl solution added to oxidise the Hg species to Hg^{2+}. The subsequent addition of $SnCl_2$ produced Hg^0, which was then purged with an Ar stream and trapped on a Cl-impregnated activated-carbon cartridge to give an enrichment factor of 1000. The trapped Hg was desorbed thermally and detected by MC-ICP-MS. Analysis of test samples spiked with either NIST SRM 3133 (mercury (Hg) standard solution) or NIST RM 8610 (mercury isotopes in UM-Almaden mono-elemental secondary standard) gave results that were not significantly different in isotopic composition to that of the original spike. Repeat analyses (n = 16) of real samples gave analytical precisions of 0.06‰ ($\Delta\ ^{199}Hg$) to 0.13‰ ($\delta\ ^{202}Hg$).

Accurate determination of the *sulfur isotope ratios* of sulfite, sulfate and thiosulfate in waters was achieved[84] in one analytical run by coupling IC to MC-ICP-MS. An S-containing IS (trimethylsulfoxide) was added to correct for mass bias, and on-column fractionation was corrected by external calibration. Use of a linear regression slope to calculate the isotope ratios of the transient signals resulted in a combined uncertainty of <0.25‰ for $\delta^{34}S$ in solution and a reproducibility of 0.5‰ for an injection of 1 µg of S. An anion-exchange membrane was evaluated[85] for the extraction of S from fresh and marine pore waters before determination of S isotope ratios by MC-ICP-MS. Recoveries were >90% when concentrations of competing ions (bicarbonate, carbonate, chloride, nitrate and phosphate) were limited to <0.5 mM per cm^2 of membrane. The lowest S concentration detectable without fractionation was 0.5 µM, but the recovery dropped at concentrations >0.01 mM probably as a result of reaching the breakthrough volume for the disc membrane.

3.4.4 Laser methods. A new mercury-specific matrix containing mefenamic acid and thymine allowed[86] the detection of *mercury ions in solution by MALDI-MS*. The Hg^{2+}-containing ions were generated so specifically that there was little background signal from other ions. The stated LOD in water of 1 nM is equivalent to 0.2 µg L^{-1} yet it was presented erroneously by the authors to be equivalent to 2 µg L^{-1}.

Preconcentration is required to determine *trace elements in water by LIBS*. By electrospraying aqueous samples onto a heated substrate to generate a detectable solid residue Ripoll *et al.*[87] achieved LODs of 17 (Ni)-57 (Cr) µg L^{-1}. However, the recoveries were poor due to strong matrix effects, so a standard additions calibration was required to improve the recoveries to 91 (Ni)-110 (Cd). Problems of water splashing and plasma quenching in the handling of liquid samples made it preferable to analyse solid samples. In a study into the effect of sample pH after deposition onto different substrates, a series of substrates was investigated[88] for the formation of surface precipitates. The formation of a fine uniform $ZnCl_2$ precipitate on the surface when the sample pH was 3.5 to 6.5 and HCl was used as an acidifying agent resulted in more laser energy being transferred to the sample in the precipitate and to improved LODs of 0.009 (Cd) to 0.0006 (Cr) mg L^{-1} at pH 6.5. The procedure was therefore suitable for the analysis of sewage discharge and other waste waters according to Chinese environmental standards.

3.4.5 X-ray fluorescence spectrometry. The *ISO Standard 20289 for total reflection X-ray fluorescence analysis of water* was based[89] on the analysis of a residue dried on an X-ray reflector and was intended for the routine analysis of large numbers of drinking, ground and surface waters samples. The method could also be applied to the analysis of waste waters after sample dilution.

The use of *hand-held or portable XRFS instruments* continues to be of interest. The LODs in the low mg L^{-1} range for 200 µL of mine waters dried onto a filter paper were[90] sufficient for screening in the field. Trapping the Pb present in 2 L of tap water onto a disc of carbon felt and detection with a hand-held XRF instrument gave[91] an LOD of 15 µg L^{-1}. It was suggested that the method could be used in the field and could be applicable to a wider range of elements (*e.g.* Ca, Cu, Fe, Mn and Zn).

4. Analysis of soils, plants and related materials

4.1 Review papers

Review articles featuring specific elements included a comprehensive overview of developments[61] (239 references) in As speciation analysis in atmospheric particulates, biota, sediment, soil and water published in the period 2004-2018, and a discussion[92] (144 references) of As content and speciation in Chinese mushrooms. Butcher[93] (60 references) summarised advances in atomic spectrometry methods for the determination of Ca, and also discussed the use of Ca as an IS. Ravipati *et al.*[94] (131 references) described trends in the measurement of Pb in biological and environmental samples from 2000 to 2018. Etteieb *et al.*[95] (128 references) included a comparison of analytical methods in their review of Se as an emerging contaminant in the mining industry, whilst Filella *et al.*[96] (122 references) highlighted that the lack of suitable analytical methods (with sufficiently low LODs) and of CRMs seriously limits current understanding of the environmental chemistry of Te.

An evaluation (75 references) of the scope and limitations of *analytical techniques for visualisation of elements in hydrated plant tissue* included[97] SEM-EDS, TEM-EDS, XFM, PIXE, ICP-MS, SIMS, autoradiography and confocal microscopy with use of fluorophores. This article provides a valuable introduction to these techniques for workers interested in applying them in their own research.

Nawar *et al.*[98] (151 references) showcased *developments in the exploitation of different types of spectral information obtained in the field* to estimate PTE concentrations in soil. The techniques considered were LIBS, pXRFS and MIR and VIS-NIR spectroscopies. Interest in multi-sensor data-mining has expanded rapidly in recent years, not only to obtain analyte concentrations but also to predict general soil properties such as texture, pH and cation exchange capacity.

4.2 Reference materials

New information on RMs included that for Ba isotope ratios determined[99] by MC-ICP-MS for 34 NRCGA geological RMs (rocks, soils and sediments). Methyl Hg concentrations were reported[100] for four RMs (one river sediment and three types of biological sample) already certified for their total Hg content. Measurements were performed using species-specific ID and HPLC-ICP-MS. Water-extractable concentrations of 18 elements in the NCS CRM DC 77302 (formerly GBW 07410 (soil)) and the Analytika RMs Metranal-31 (light sandy soil (metals)) and Metranal-33 (clay loam soil (metals)) were provided[101] as information values to aid future researchers. Similarly, information values were presented[102] for $\delta^{114}Cd/^{110}Cd$ in NIST SRMs 2709 and 2709a (San Joaquin soil), 2710 and 2710a (Montana I soil) and 2711 and 2711a (Montana II soil) and IGGE CRM GSS-1 (soil).

4.3 Sample preparation

4.3.1 Sample dissolution and extraction

Various *sample-milling methods* were compared[103] for the ICP-MS determination of Cu, Pb, Sb and Zn in soil from a small-arms range. Concentrations and precision were affected by both the method of milling and grinding time. Whereas puck mill grinding required only 5 minutes to obtain a homogeneous powder, ball mill grinding required 20 h. Ball mill, puck mill and ring and puck mill all gave RSD values <15%, whereas grinding by pestle and mortar or the analysis of un-milled samples gave high RSD values of 28-55% and 17-257%, respectively.

In the eternal quest for *improved reagents for digestion and extraction*, Santos *et al.*[104] compared acidic (HBF_4) and alkaline (NaOH) digestions of plants and fertilisers for the determination of Si by MIP-AES. The LOD of 0.03 g kg^{-1} obtained with acid digestion was superior to that (0.4 g kg^{-1}) obtained with alkaline digestion. However, the problems arising from the formation of highly corrosive HF had to be addressed through the use of high dilution factors, addition of H_3BO_3 and an inert sample introduction system. Mokoena *et al.*[105] evaluated dilute HNO_3 hot-plate digestion as a means to avoid dilution prior to analysis by ICP-AES. Optimised conditions for 1.0 g of sample were 180 °C, 45 minutes and 10 mL of 5 M HNO_3. Accuracies for As, Cd, Cr, Cu, Fe, Pb and Zn ranged from 98 to 111% for Supelco CRMs CRM015 (trace metals – fresh water sediment 2) and CRM052 (trace metals - loamy clay 1). Precision was 1.4 to 5.8%.

The *use of mathematical models for optimisation of extraction parameters* has increased. Nuapia *et al.*[106] applied response surface methodology to evaluate pressurised hot water for the extraction of nutrients from dried *Moringa oleifera* leaves for ICP-AES determination. The main factor that influenced the extraction of macronutrients was extraction time, whereas extraction of micronutrients was more markedly affected by increasing temperature, at a constant flow rate (0.3 mL min^{-1}) and pressure (105 bar). The optimum extraction for 5 g samples was achieved at 90 °C for 60 minutes. Recoveries ranged from 22% for Cr to 98% for Ca and K when results were compared with those obtained by MAD in HNO_3/H_2O_2. In an ultrasound-assisted extraction procedure for the determination of Cu, Fe, Mn and Zn in plants by FAAS, the extractant composition was optimised[107] by applying a simplex centroid design and the time, power and temperature optimised by applying the Box-Behnken design. Optimum extraction from a 250 mg sample was obtained with 10 mL of a 0.5 M HNO_3 + 1.1 M HCl mixture at 40 °C for 10 minutes. Recoveries for the analysis of NIST SRM 1515 (apple leaves) were between 89 and 98%, RSDs were <6.7% and LOQs were 0.95 (Cu) to 2.42 (Fe) mg kg^{-1}. A central composite design was used[108] to optimise (3.0 mL HCl + 3.6 mL HNO_3 + 2.78 mL HF) an ultrasound-assisted extraction method for the determination by FAAS of Al, Cd Cu, Ni and Zn in 0.1 g soil samples. Method LODs ranged from 1.3 (Zn) to 230 (Al) mg kg^{-1}. Analysis of IRMM CRM BCR 142 (light sandy soil), RM-Agro E2002a (tropical soil) and RS-3 (river sediment) gave results that were mainly within 10% of certified values. The Box-Behnken design was applied[109] in the optimisation of a closed block digestor for determination of elements in tobacco products (cigar, shredded and rope) prior to analysis by ICP-AES. For an extraction solution of 3.0 M HNO_3 + 3.5% H_2O_2, the optimum conditions were 180 °C and 120 minutes. Accuracies for up to 17 elements in three CRMs INCT CTA-OTL-1 (oriental tobacco leaves), NIST SRM 1515 (apple leaves) and Agro C1003a (tomato leaves) were in the range 91±4% (V) to 117±4% (Sr). Product types could be classified according to element concentrations.

A novel *microscale sample pretreatment method* was proposed[110] for the multi-element analysis of plants. Laser-capture microdissection was used to isolate as little as 400 ng tissue samples which were digested under a pressure of 40 bar in 50 µL of 2:1:1 HNO_3-H_2O_2-H_2O. The digests were aspirated into an ICP-MS instrument at a low flow rate of 50 µL min^{-1}. Accuracy was assessed by analysis of 500 µg portions of NIST SRM 1515 (apple leaves) and ranged from 84% (Mo) to 128% (Ni). Precision (RSD, n=8) was ≤11% for Al, B, Ca, Cu, K, Mg and Mn but poorer for Mo, Ni and Zn (32, 62 and 19%, respectively). The authors did not explain why sample microdissection and digestion might be preferred to direct mapping of tissue samples by established techniques such as LA-ICP-MS, XFM or LIBS.

Methods for assessment of trace element availability in soil included[111] a procedure for the measurement of B isotopic composition as a means of assessing B availability. The B was extracted into hot water (100 °C, 30 minutes), recovered using three stages of ion exchange chromatography and analysed by MC-ICP-MS. The isotopic composition of B extracted within the first 50 minutes was constant; then $\delta^{11}B$ values increased, indicating that less available forms of B were being released. The chemistry of I in soil solution was investigated[112] using microdialysis for *in-situ* passive sampling, HPLC-ICP-MS for speciation analysis and SEC coupled to both UV spectroscopy and ICP-MS for determination of molecular weight. The optimised microdialysis approach was particularly recommended for soils with low moisture content. More conventional methods such as centrifugation and soil-squeezing may require soil wetting, which can alter redox conditions in the soil solution.

A dual-frequency ultrasonic enzymatic procedure allowed[113] fast, efficient extraction of *As species* from powdered herbs used in traditional Chinese medicine. Using cellulase in Tris-HCl buffer at 30 °C, samples were irradiated simultaneously at 40 kHz in an ultrasonic bath and at 20 kHz by insertion of an ultrasonic probe. A 95% extraction efficiency was achieved in just 6 minutes. There were no significant differences between measured and certified values for BMEMC CRMs GBW(E)090066 (*Salvia*) and GBW(E)090067 (*Paeoniae Radix Rubra*). The overall LODs were 0.7 and 2.5 µg kg^{-1} for As^{III} and As^{V}, respectively.

Estimating the *human bioaccessibility of As species in soil and plant-based foods* is important for accurate exposure assessment. Tokalioglu *et al.*[114] assessed species stability during application of the popular BARGE UBM by applying it to simulated saliva spiked with As^{III}, As^{V}, DMA, MMA and a mixture of these spikes. There was no species interconversion in either gastric or gastrointestinal phases when analysed by HPLC-ICP-MS.

The operational nature of *sequential extraction procedures* was highlighted[28] by an attempt to scale-down the well-established BCR protocol. Soil samples with masses as low as 0.0625 g were extracted in 2-3 mL of reagents. Although the fractionation patterns obtained were similar to those obtained using the full-scale protocol, they were significantly affected when the size of the extraction vessel was reduced from 50 to 15 mL. Klotzbucher *et al.*[115] investigated the mechanisms underlying the Hedley fractionation procedure. They spiked pure mineral phases (ferrihydrite, goethite, amorphous aluminium hydroxide, allophane, montmorillonite and kaolinite) with different forms of P (NaH_2PO_4, phytic acid and RNA), mixed these with silt-sized quartz and then carried out the extraction. They concluded that the protocol characterised neither mineral sources nor binding strengths of P in soil and that it was therefore unsuitable for studying P bioavailability.

Optimisation of extraction procedures for the *determination of NPs by sp-ICP-MS* has continued to be of interest. Gao *et al.*[116] found sodium pyrophosphate to be a more effective extractant than water, sodium carbonate or sodium chloride for the isolation of gold NPs from soil and sediment. Their optimised method was evaluated for gold NPs with different diameters and coatings. The extraction efficiency was improved by destruction of SOM with UV irradiation. Li *et al.*[117] decreased the sample SOM content in their optimisation and validation of a previously published method for silver NPs in soil by diluting their samples with SiO_2 prior to extraction. In a study on the persistence of foliar NP pesticides on lettuce, Laughton *et al.*[118] recommended methanol digestion rather than the standard enzymatic procedure to prevent the dissolution of copper NPs.

Ermolin *et al.*[119] compared a microcolumn to a rotating coiled column (RCC) for estimating *the mobility of* CeO_2 *nanoparticles in spiked soil*. Although the microcolumn simulated the structure of a real soil more closely, the RCC was useful for estimating maximum NP mobility.

4.3.2 Analyte separation and preconcentration

A review (93 references) on the *preconcentration of radionuclides* considered[120] fully and partially automated flow methodologies for ICP-MS or radiometric analysis. Particular emphasis was placed on determination of Ra, Sr, Tc, Th, U and Y nuclides as required under the auspices of REVIRA, the Spanish Network of Radiological Surveillance. Methods developed[121] for the simultaneous determination of ^{237}Np and Pu isotopes employed ^{242}Pu as a yield tracer for all the nuclides measured. A new type of extraction resin, TK200, was used[122] for the isolation of Pu isotopes. The Pu recovery was 81-91% and the LOD was 0.13-0.24 pg kg^{-1} for a 2 g soil or sediment sample.

An on-line preconcentration device for Mn in tea leaves based on two knotted reactors and FAAS was automated[123] using four solenoid valves controlled by an Arduino board to switch sample streams and reagents. Multivariate optimisation of the method resulted in an LOD of 0.070 mg kg^{-1}, spike recoveries of 95-105% and a Mn concentration of 52.0±5.0 mg kg^{-1} for NIST SRM 1515 (apple leaves) for which the certified value is 54.0±3.0 mg kg^{-1}.

Tables 3 (liquid-phase extraction methods) and 4 (solid-phase extraction methods) summarise other methods for the analysis of soils, plants or related materials as well as those developed for other sample matrices using soil or plant CRMs for validation.

[Tables 3 and 4]

4.4 Instrumental analysis

4.4.1 Accelerator mass spectrometry

Progress has been made to address various *challenges in the use of AMS*. The Fe isotopic compositions of sediments are used by astrophysicists to gain insight into processes such as stellar evolution, so the availability of new ^{60}Fe standards[124] should allow greater accuracy to be achieved in such studies. Two new materials, one wood and one mammoth bone, were characterised[125] and made available to fulfil the need for appropriate, radiocarbon ‘dead’, procedural blanks in dating applications. An analytical procedure was successfully adapted[126] to allow ^{242}Pu to be used as a yield tracer in the determination of ^{237}Np in clays. Although not yet proven through the analysis of real environmental samples, the proposed new method[127] for the preparation of calcium- or neodymium-fluoride-based targets for the determination of ^{236}U is welcome because the higher ion yields obtained, relative to those of traditional iron oxide-based targets, should improve sensitivity.

4.4.2 Atomic absorption spectrometry

A method for *the determination of Cd* in lichens by SS-ETAAS involved[128] pipetting 10 µL of a mixed matrix modifier (2 g L^{-1} Pd + 1 g L^{-1} $Mg(NO_3)_2$ + 0.1% Triton X-100) over 2 mg of sample. The LOD of 0.9 µg kg^{-1} was considerably better than that (2.1 µg kg^{-1}) for conventional solution analysis. Results obtained for four plant CRMs were in agreement with certified values (t-test at 95% CI). In the analysis of mint, a molybdenum-coated T-shaped SQT atomiser for FAAS gave[129] signals 75% higher than those for an uncoated quartz tube. The optimal trapping time was 360 s. Trapped Cd was released by introducing H_2. Recovery from spiked mint leaves was 98% and a concentration of 1.56±0.16 mg kg^{-1} was determined for NIST SRM 1573a (tomato leaves), for which the certified value is 1.517±0.027 mg kg^{-1}.

In the development of a low-cost method for *arsenic speciation analysis,* a heterogeneous photocatalysis procedure was optimised[77] by using ZnO/UV irradiation to reduce As^{V} and DMA to As^{III} prior to HG-FAAS detection. Spike recoveries from soil, sediment and water samples were 89-104% and the LODs were 3.2, 3.9 and 6.7 µg L^{-1} for As^{III}, As^{V} and DMA, respectively. The method is particularly suitable for studying environmental contamination in resource-poor regions of the world where techniques such as HPLC-ICP-MS are not widely available.

4.4.3 Atomic emission spectrometry

Developments in element-specific analysis included[130] a multicomponent spectral-fitting algorithm that could reduce interference from Cu in the determination of P in soil extracts. A new method[131] for the measurement of Hg and MeHg in biological tissue and sediment by ETV-CCP-AES was based on a prototype system previously proven for other analyses. Following sample digestion or extraction, 10 µL of solution was pipetted onto a Rh filament for atomisation into an argon microplasma. In a procedure for the determination of Si in plants by MIP-AES, the introduction of 1 L min^{-1} of air to the N_2 plasma overcame[104] matrix interference associated with the presence of high levels of Na resulting from use of alkaline digestion.

In *multi-element analysis*, the performances of Bi and Pt as ISs were compared[132] for the determination of 17 elements in IRMM CRMs BCR 482 (lichen) and BCR 670 (aquatic plants) and NIST SRM 1515 (apple leaves) by ICP-AES with an axially viewed plasma. In general, best accuracy was obtained with Pt as the IS but the use of Bi also gave better results than analysis without an IS. An investigation into interference effects in the analysis of sediment extracts obtained by the BCR sequential extraction procedure highlighted[133] the need for reagent-matched calibrants, robust plasma conditions and use of an IS.

Improvement in *glow discharge emission sources* included[134] a new HG-APGD system for the determination of As and Se in environmental samples. Optimised GD conditions were: 10 mm electrode gap; He plasma gas flow rates of 65 (As) and 55 (Se) mL min^{-1}; and discharge currents of 30 (As) and 25 (Se) mA. The LODs were 0.087 and 0.13 ng mL^{-1} for As and Se, respectively. Results for analysis of BMEMC CRM GBW 07381 (stream sediment) were within 6% (RPD) of certified values. A novel tantalum porous-cage-carrier improved[135] signal stability and sensitivity in the determination of trace elements in soil. The fabricated device gave reasonable accuracy (relative error 0.7-17%) for the determination of 21 (mainly REE) analytes in BMEMC CRM GBW 07430 (soil). The LODs were 0.04-1.31 mg kg^{-1}.

Arc emission spectrometry was recommended[136] as an alternative to pXRFS for the direct determination of Cd in soil because its LOD (0.01 mg kg^{-1}) was far superior than that of pXRFS (*ca.* 20 mg kg^{-1}). Accuracy, estimated as RPD with respect to certified values for three BMEMC soil CRMs (GBW 07311, GBW 07308a, and GBW 07446) was better than 13% and the precision (n=10) was <15%. This approach was therefore considered fit-for-purpose for rapid screening analyses.

The renewed interest in the use of *the two-jet argon plasmatron emission source* was highlighted[137] by the publication of a method for the multielement analysis of powdered plant samples using a powder-introduction device in which a spark between zirconium electrodes agitated the sample for transport to the plasma in a stream of argon. Calibration was based on the trace element content in graphite powder CRMs. Whereas leaf and grass samples could be analysed directly, analysis of matrices with higher starch content (maize, potato, rice and wheat) benefitted from heating in a furnace for 15 minutes at 250 °C followed by 30 minutes at 350 °C.

In *the direct analysis of solid samples* by ETV-ICP-AES, Al Hejami and Beauchemin[138] showed that addition of a small amount of H_2, N_2 or water vapour as a sheath gas around the sample aerosol increased sensitivity and lowered LODs for 13 elements in soil. Best performance was obtained with N_2. This work was extended by Scheffler *et al.*[139] who recommended addition of 0.4 L min^{-1} of N_2 to the plasma gas flow and 20 mL min^{-1} of N_2 sheath gas to the central channel of the ICP in order to form a mixed gas plasma. Results obtained for three soil CRMs were within 20% of certified values. There were[140] no significant differences (student t-test at 95% CI) between results obtained for Ca, Cd, Cu, Fe, Mg, Mn, Sr and Zn when determined by either ETV-MIP-AES or LA-MIP-AES when the same spectrometer system was used with both sample introduction methods. The LODs for ETV-MIP-AES of 0.1-1.2 µg kg^{-1} were similar to those of

LA-MIP-AES but the precision (n = 3) of 2-4% was slightly better than that (3-7%) of the latter technique. Accuracy was tested through analysis of NIST SRM 2711 (Montana soil) and NRCC CRMs PACS-2 (marine sediment) and TORT-2 (lobster hapatopancreas). For most of the elements a t-test (at 95% CI) showed no statistically significant difference between found and certified values. In an ETV-ICP-AES method for multielement analysis of plants, a high plasma operating power (1600 W) increased[141] sensitivity, thereby allowing smaller sample masses to be analysed.

4.4.4 Atomic fluorescence spectrometry

Liu *et al.*[142] reported the first combination of PVG (20 s UV irradiation at 12 W from a mercury lamp) and gas-phase analyte preconcentration on the surface of a dielectric barrier detector (DBD) for *the determination of trace Se in water and soil* by AFS. A detailed mechanistic study indicated that, in the presence of 10% (*v/v*) formic acid and 0.2% (*m/v*) $NaNO_3$, the species generated by PVG were SeCO and H_2Se which reacted under the Ar/O_2 atmosphere inside the DBD and were trapped on the quartz surface as SeO_2 or selenite. Subsequent introduction of Ar/H_2 generated H radicals that released a pulse of Se atoms from the surface for quantification. The LOD was 0.004 μg L^{-1} and the precision was 4% (RSD) at 20 μg L^{-1} (n = 11). Results for the analysis of BMEMC soil CRMs GBW 07449 and GBW 07405 were within 10% of certified values or results obtained by ICP-MS.

4.4.5 Inductively coupled plasma mass spectrometry

The determination of Ra by ICP-MS is challenging because the presence of polyatomic interferences on ^{226}Ra (the longest-lived isotope of Ra with $t_{1/2}$ 1600 y) dictates purification of samples prior to analysis. Ben Yaala *et al.*[143] successfully developed a method for ^{226}Ra measurement in sediments that did not require pre-treatment. Either the signal at *m/z* 226 from a matrix-matched blank was subtracted or a mathematical interference correction was used. The LOD was 0.11 ng kg^{-1} and results obtained were in broad agreement with those obtained by α-particle- or γ-ray-spectrometry.

The capabilities of flow FFF-UV-ICP-MS and sp-ICP-MS to obtain information on *particle size distribution of colloidal iron oxyhydroxides in soil solution* were compared[144] with approaches such as DLS, TEM, filtration, centrifugation and dialysis. Flow FFF-UV-ICP-MS was recommended due to its ability to measure smaller particles than sp-ICP-MS (down to 5 nm hydrodynamic diameter) and because of the wide size range detectable.

Chromatographic separation coupled to ICP-MS is becoming more routine but new or improved methods continue to be reported. Worthy of note were: an HPLC-ICP-MS method[145] for As speciation in seaweed, sediment and seawater; a SEC-ICP-MS method[146] to study Cd and Cu complexation by humic acids in soil; an IC-SF-ICP-MS method[147] for determination of lanthanides, Pu and U in spent nuclear fuel and soil; SEC-UV-ICP-MS and HPLC-ICP-MS methods[112] that were used together for identification of I species in samples of soil solution obtained by microdialysis; a HPLC-ID-ICP-MS method[148] for Hg speciation in marine sediment; and an IC-ICP-MS approach[149] for S speciation in foodstuffs based on orange daylily and wolfberry.

In an ETV-ICP-MS method for the direct determination of *iodine in rocks, soils and sediments* the use of pre-reduced Pd prevented[150] analyte loss during ashing and improved analyte transfer into the plasma. Subsequently, ionisation efficiency was improved with sodium citrate. The method LOQ was *ca.* 10 µg kg^{-1} and results similar to certified values were obtained for a suite of geological CRMs.

Researchers successfully developed[151] a *slurry nebulisation ICP-MS method for screening 16 elements in plant-based foods*. A mean particle size of 0.8 µm was achieved in 90 s by wet milling with 1.5 mL 0.5% polyethylene imine in water. Results for eight CRMs were within 10% of target values when aqueous calibration standards were used

An attempt was made[152] to obtain *2D images of U distributions across oak tree rings* by HR-LA-ICP-MS using pressed-pellet calibrants prepared from both U-doped cellulose and NIST SRM 1570a (spinach leaves). The IS was ^{13}C. The high uncertainty and poor agreement with results obtained by HR-ICP-MS analysis of solutions was attributed to heterogeneous distribution of the analyte within the sample.

Interest in the measurement of isotope ratios has led to *the development and application of new MC-ICP-MS isotope methods* for the measurement of the following: ^{11}B/^{10}B in irrigation water and bell pepper plants to study B fractionation during uptake and translocation[153]; ^{114}Cd/^{110}Cd in rock, soil and manganese nodule CRMs[102]; ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb in soil and wine as a potential geographic tracer for authentication of Lambrusco PDO wines from Modena[154]; ^{130}Te/^{126}Te in mine tailings, soil and sediment by HG-MC-ICP-MS as indicators of Te mobility and environmental redox conditions[155]; and ^{234}U/^{238}U and ^{235}U/^{238}U in soils from Odisha, India and Fukushima, Japan[156]. Although it was reported[157] that MC-ICP-MS was not necessary for measurement of ^{67}Zn/^{66}Zn in soil-fertiliser-plant systems as the precision obtained with standard quadrupole ICP-MS was adequate, this study featured the addition of a nutrient solution containing highly enriched ^{67}Zn and so did not concern the measurement of natural isotopic variations.

New ICP-MS/MS methods continue to be developed as instrumentation becomes more widely available. Key features of a procedure for determination of $^{236}U/^{238}U$ isotope ratios below 10^{-8} in lake sediments potentially affected by the Fukushima Daiichi nuclear power plant accident were[36] O_2 as the reaction gas and use of the $^{234}U/^{235}U$ ratio measured by MC-ICP-MS to correct for bias in the ICP-MS/MS measurements. The combination of chemical separation and use of a CO_2-He reaction gas mixture allowed[158] accurate measurement of trace Pu in soil samples containing high levels of U (U/Pu atom ratios up to 10^{12}). A method for the measurement of non-metallic elements in herbal teas used[159] O_2 and H_2 sequentially as reaction gases. First, O_2 was introduced to the cell and Br, I, P and S measured as their oxide ions; then H_2 was introduced and Cl measured as $H_2{}^{35}Cl^+$ and Si as $^{28}Si^+$. Results for NIST SRMs 1515 (apple leaves) and 1547 (peach leaves) agreed (95% CI) with the certified values. The development[160] of an approach to distinguish engineered zero-valent iron NPs from naturally-occurring Fe-rich colloids by ICP-MS/MS trace element profiling is welcome as it may help in the development of optimised strategies for the remediation of contaminated soils and waters.

4.4.6 Laser-induced breakdown spectroscopy

Useful *two-part LIBS reviews* have been published this year. One featured research in the period 2010-2019 on agricultural materials, with part 1[161] (76 references) covering soils and fertilisers and part 2[162] (82 references) crop plants and food products. Another two-part review focussed exclusively on soil. Part 1[163] (74 references) covered the principles of LIBS and its use to estimate soil properties including pH, degree of humification of SOM and texture. Part 2[164] (97 references) covered elemental analysis, trace element mapping and soil classification.

Improvements in the LIBS analysis of soil were achieved through study and optimisation of the laser energy[165, 166], pressure[167], lens-to-sample distance[166] and time delay between irradiation and signal acquisition[165-167]. Application of a magnetic field perpendicular to the plasma increased[168, 169] plasma temperature and hence analyte emission intensities and thereby lowered LODs. Spatial confinement of the plasma within a cylindrical cavity achieved[170] the same result. Ablation of the sample generated a shock wave, reflection of which from the cavity wall compressed the plasma plume, increased collision probability and thereby enhanced the number of atoms in excited states.

Numerous publications featured *LIBS methods for the determination of trace elements in soil.* This is a challenging field and genuine improvements are welcome. However, unfortunately, not all proved their accuracy through analysis of CRMs or by comparison of results with those obtained by an established technique. It cannot be emphasised strongly enough that taking a soil sample, spiking portions with different concentrations of analyte, dividing these into a training set and test set and then demonstrating that, with appropriate chemometric processing the model can accurately predict the analyte concentrations in the test set, does not necessarily lead to a robust analytical method widely applicable across a range of different soil types because the nature of the sample matrix markedly affects the signal obtained. Sun *et al.*[171] illustrated the differences in the slope of calibration curves obtained for Ag in spiked CRMs and soil samples before using machine-learning algorithms based on BPNN to propose a soil-independent multivariate model with REP in the range 5-6%. Wu *et al.*[172] developed a standard addition method for quantification of Pb in soils from the vicinity of a Pb/Zn smelter. Addition of uncontaminated soil taken from 3 m depth at each of the individual sampling locations facilitated production of a standard addition curve (perhaps more accurately a "matrix dilution" curve) for each sample analysed. Results were generally within 18% of those obtained by ICP-AES so the method was considered suitable for screening analysis. Other studies that used ICP-AES data for comparison included a multivariate LIBS method developed by Lu *et al.*[173] for Sr and V and a method for the determination of Ca, Fe, K and Mg developed by Costa *et al.*[174]. Guo *et al.*[175] measured 13 elements in 17 BMEMC 'GBW' soil CRMs to compare univariate calibration with PLSR and SVR. The PLSR model gave more accurate predicted concentrations than did the SVR model when GBW07448 was analysed as an 'unknown'. An article with an eye-catching title apparently offered[176] rapid detection of Cr in different oxidation states in soil by LIBS. Disappointingly, however, no solid-state speciation was performed. Instead, a soil was mixed with a solution containing Cr^{III} and Cr^{VI} and the filtrate analysed directly (2.5 µL on a zinc target) to give total Cr concentration. The Cr^{VI} in a 1 mL aliquot was preconcentrated on 0.1 g of anion-exchange resin which was then attached to a glass slide for analysis. The Cr^{III} concentration was estimated from the difference between the total Cr and Cr^{VI} concentrations. At best, the method is therefore applicable to Cr speciation analysis in the soil solution provided this can be recovered without species interconversion.

There has been continued interest in *the prediction of soil properties based on chemometric processing of LIBS data*. Methods were reported for cation exchange capacity[177] based on PLSR, soil pH[178] based on the RF model, and soil texture[179] (proportions of sand, silt and clay) based on PLSR and the elastic net algorithm.

The same research group that applied a magnetic field to increase plasma temperature in the analysis of soil, as already described in this section, also carried out[180] a similar study for plants by using *an external electrical field for enhancement of emission line intensity*. Results for Ca, Cr, K, Li, Mg and Na were broadly similar to those obtained by LA-TOF-MS in the root, stem and leaf of *Euphorbia indica.*

Notable for the *determination of trace elements in plants* was a method[181] for measurement of Ca, K, Mg, Na and P concentrations in edible seeds that combined LIBS, ICP-AES, hyperspectral imaging and PCA to explore analyte correlations. A calibration-free LIBS procedure produced[182] results within 5% of ICP-AES values for Ca, K, Fe, Mg, Mn, Na, P and S in *Moringa oleifera* leaves. Agreement for Cu and Zn was, however, poorer. The addition of copper powder and the use of Cu emission lines to correct for self-absorption effects in the determination of Ca in fennel, bay, dandelion, spinach and parsley leaves improved[183] markedly the agreement with ICP-AES data. Without correction, the LIBS results were almost four times the ICP-AES values but with correction they were within 3% of the ICP-AES results. A slope ratio calibration procedure used successfully for the determination of major and trace elements in plant leaves was based[184] on the relationship between emission intensity, ablated sample mass and number of laser pulses. A key advantage of the approach was that it required only a single solid calibrant. An optimised collinear dual-pulse LIBS method for the determination of Cr in rice leaves used[185] an inter-pulse delay of 1.5 μs, energy ratio of 1:3 and a total energy of 80 mJ. Further work was carried out[186] to visualise the distribution of Cr in the leaves.

There was continued interest in *chemometric processing of LIBS data for plant classification*. Liu *et al.*[187] successfully determined the geographical origin of *Mentha haplocalyx* from five provinces in China by a LS-SVM method. Feng *et al.*[188] discriminated between leaves of three types of plant growing at the same site (*Ligustrum lucidum*, *Viburnum odoratissinum* and bamboo) using PLS-DA.

The use of a secondary laser for *excitation of the analyte atoms in the ablation plume for quantification by AFS* can improve both selectivity and sensitivity in LIBS analysis. An optimised LIBS-LIF method incorporated[189] a tuneable dye laser for the determination of Pb in medicinal herbs. Results for analysis of five samples of *Rheum officinale* were within ±15% of those obtained by ICP-MS. The LOD was 0.13 mg kg^{-1}. An LA-LEAF procedure for As based on excitation by an ArF excimer laser was intended[190] primarily for the analysis of steel but a successful preliminary analysis of Japanese seaweed was also reported with a LOD of 1.0 mg kg^{-1}.

4.4.7 X-ray spectrometry

An informative IUPAC technical report (170 references) on advances in *X-ray techniques for trace element analysis* included[191] recent applications involving atmospheric particulates, geological samples, living organisms, sediments, soils, waters and waste materials. A useful review (110 references) highlighted[192] the scope and limitations of pXRFS when applied to soil analysis. Users were cautioned to be cognisant of the sources of uncertainty and of the influence of the matrix.

In the *analysis of soils*, She *et al.*[193] selected calibration standards for samples of unknown composition based on $K\beta/K\alpha$ ratios. The $K\beta/K\alpha$ ratios for Al, Ca, Fe and Si measured in 14 CRMs deviated 1.5% (Si) to 21% (Al) from expected values according to sample type. More accurate results were obtained for "unknown" samples when the $K\beta/K\alpha$ ratios for sample and CRM were similar. A TXRFS method for the chemical classification of clays was developed[194] and optimised using a full factorial experimental design. Optimised conditions for a data acquisition time of 1000 s were: sample size 50 mg; 2.5 mL 1% Triton X-100 solution as dispersing agent; deposition of 5 µL of the slurry on a siliconised quartz reflector; and drying at 50 °C for 5 – 10 minutes. Validation was performed using the SARM-CRPG RM ZW-C (zinnwaldite). Recoveries were 80-100% for 12 out of 15 elements. Another TXRFS study explored[195] different calibration strategies for the determination of Cd, Pb and Zn in soil suspensions. Whereas the analysis of a suite of CRMs gave an accuracy of 80-100% when using an IS of Ga (for the Mo X-ray tube) or Pd (for the W X-ray tube), results for environmental samples from a mining area were <70% of the values obtained by ICP-AES. Accuracy was not improved when spiked soils were used as external calibrants. However, when results were normalised using a calibration curve obtained by the ICP-AES analysis of a set of soils with similar matrix composition to that of the unknown samples, accuracies were in the range 95-98%. Mitsunobu *et al.*[196] developed a 'live soil imaging chamber' for simulation experiments to observe metal(loid) behavior at the redox layer of waterlogged soils. The chamber consisted of a thin (6 mm) rectangular box made of corrosion-resistant titanium with a low permeability quartz glass window to allow observation and prevent oxidation. The chamber was mounted directly on the sample holder in the μXRF-μXAFS beamline. In paddy-field simulation experiments, As-spiked soil was incubated in the chamber for one month at 24-26 °C and then the chamber was mounted directly into the synchrotron allowing element abundance and speciation to be determined *in situ*.

Chemometric processing of pXRFS data to infer information on general soil properties continues to attract attention. Numerous researchers[197-202] employed different machine learning algorithms in their proximal sensing approaches for investigating various soil fertility parameters. Mancini *et al.*[203] compared RF, SVM and LDA models, built with and without PCA, to predict soil parent material. In an evaluation of the RF, SVM and GLM models for prediction of soil texture, the RF algorithm predicted[204] sand content best but the SVM model was superior for predicting silt and clay contents.

Developments in WDXRFS included a study on As bioavailability in soil by An *et al.*[205] who analysed directly the sorbent material (chelex and TiO_2) recovered from a DGT device and dried at room temperature for 2 h before analysis. A LOQ of 0.06 μg As was achieved. Li *et al.*[206] prepared samples of rock, soil or sediment by high-pressure (2000 kN for 30s) pelleting followed by coating of the pressed pellets with a 3.6 µm film of polyester. The determined Cl content was stable under repeat analyses whereas the content of pellets prepared without a film was not. Accuracy, assessed using pellets prepared from 8 CRMs, was within 10% for major elements and 25% for trace elements.

Methods for the analysis of plant samples continue to evolve. Shao *et al.*[207] used the argon fluorescence peak in air as a normalisation standard in a low-power TXRFS method for the rapid determination of the low-Z elements Ca, K, P and S and the medium-Z element Fe. The procedure required only a small amount a sample (20 mg) and a short measurement time (10 minutes). Results were in good agreement with those obtained using Ge and V as ISs. For the Chinese CRMs GSB 11 (citrus leaves), GSB 14 (porphyra), GSB 16 (spirulina), and GSB 19 (astragalus), recoveries were in the range 80–120% and RSDs were <10%. The spatial resolution (down to 5 µm) of µXANES was[208] sufficient to differentiate leaf tissues in a method for the assessment of cell-specific metal speciation in plants. Metal coordination was determined by comparing the spectra with the XANES information for relevant reference compounds. Use of shock-frozen hydrated samples in a cryostream reduced the sample degradation observed for other sample preparation methods. Cell-specific changes in Zn ligands could be observed in infected plants.

5 Analysis of geological materials

5.1 Review articles

Several reviews covered the *analysis of geological materials by a variety of techniques*. That of Balaram *et al.*[209] (207 references) on the REEs, critical components in a range of modern technologies, not only reviewed methods for the determination of the REEs but also summarised the whole life cycle of these metals. Tjabado and Mketo[210] (176 references) outlined the spectrometric, chromatographic and electroanalytical techniques that have been applied over the past decade for the determination of total elemental S and the halogens in various matrices including environmental materials. The challenges and merits of analytical techniques in which samples could be analysed directly were compared with those for methods requiring sample pretreatment.

A special issue of Chemical Geology (volume 537, March 2020) devoted to *calcium isotope geochemistry* is essential reading for anyone interested in this subject. It contained contributions that highlighted a range of applications and identified interesting and fundamental problems that could be the subject for future work. The introduction[211] (63 references) to this special issue provided a brief historical perspective on the analysis and interpretation of stable Ca isotopes in the geosciences and identified future directions and approaches for their increased utility and broader acceptance by the geosciences community.

Reviews that focussed on a specific type of instrumental analysis can be found in the relevant sections.

5.2 Reference materials and data quality

The *synthesis and characterisation of microanalytical RMs* is an ongoing priority for matrix-matched calibration and QC for *in situ* microbeam technologies such as SIMS, LA-ICP-MS, LIBS and EPMA. A set of three new synthetic reference glasses with an andesitic major element composition (ARM-1, 2 and 3) was prepared[212] by fusing mixed-oxide powders containing 54 trace elements at levels of 500, 50, and 5 µg g^{-1}. Because the material was viscous, a prolonged melting procedure was needed. This involved maintaining the melt at 1550-1600 °C for 4 h and then stirring for 5 h. The ARM glasses were considered to be homogeneous for all major elements at a spatial resolution of 10 μm for EPMA and for trace elements at a spot size of 50 μm for LA-ICP-MS. Reference and information values were presented for 56 elements, including major elements. Ke *et al.*[213] developed a new method for preparing a matrix-matched RM for the LA-ICP-MS analysis of scheelite, an accessory mineral common in various hydrothermal deposits. Single crystals of $CaWO_4$ doped with several REEs were grown from a polycrystalline material synthesised from a solid-state reaction at 1200 °C over four days between $CaCO_3$, WO_3, Na_2CO_3 and REE oxides. The structure and matrix composition of the crystals were verified by XRD and EMPA and the homogeneity of the REE distribution assessed by methods such as LA-ICP-MS and solution ICP-MS. The variations in REE concentrations were of the order of 4% RSD. The $CaWO_4$ single crystals were deemed to satisfy the requirements of a matrix-matched RM for LA-ICP-MS measurements of REEs in natural scheelite. Hydroxyapatite pellets spiked with Co, Mn, Ni, Sr and V were synthesised[214] using a co-precipitation procedure in which the dried precipitate was calcined at 450 °C for 3 h prior to pelletisation. These potential RMs for LIBS mimicked the ablation properties of biogenic hard tissues such as bones and teeth much better than other pressed powder pellets of comparable composition. Although the pellets were chemically homogeneous, only 50 to 60% of the expected analyte concentrations were recovered after calcination so solution ICP-MS analysis was necessary to characterise the materials. In a feasibility study on the production of RMs suitable for SIMS and EPMA, ^{47}Ti or ^{48}Ti were implanted[215] into synthetic, ultra-high-purity silica glass. This technique of high-energy ion implantation generated a known concentration of the implanted isotope in three dimensions, a so-called 'box-profile'. The procedure involved multiple implantation steps with varying ion energies, thereby producing several 'box-profiles' with mass fractions ranging from 10 to 1000 $\mu g\ g^{-1}$ Ti and homogenous Ti distributions to depths of 200 nm to 3 μm. The SIMS depth profile measurements demonstrated that the Ti distribution in the 'box-profile' was within the target uncertainty of ±5%. This multi-energy approach was considered promising also for the production of RMs for EPMA; 1000 µg g^{-1} Ti at an implant depth of 3 µm could be determined accurately by EPMA. An added advantage was that all elements from H to U could be implanted individually, with no restrictions regarding the matrix.

As well-characterised *carbonate reference materials* for *in situ* Sr isotope analysis by LA-ICP-MS were only available with Sr concentrations >1000 µg g^{-1}, Weber *et al.* **[216]** prepared a new RM with a Sr mass fraction of *ca.* 500 µg g^{-1}. This nanopowder RM, called NanoSr, had a ^{87}Sr/^{86}Sr ratio of 0.70756±0.00003 (2SD) as determined by TIMS and MC-ICP-MS and was homogeneous at the tens of µm scale. A study by Jochum *et al.***[217]** investigated whether the homogeneity of several $CaCO_3$ RMs could be improved by further processing to produce fine grained nano-powders. Analysis of nano-pellets of USGS RM MACS-3 (synthetic $CaCO_3$) and the natural GSJ RMs JCp-1 (coral) and JCt-1 (giant clam) by ns- and fs-LA-ICP-MS clearly showed that the nano-pellets were 2-3 times more homogeneous than pellets of the original material, so making them much more suitable as microanalytical RMs for LA-ICP-MS. For MACS-3, the mass fractions determined for all certified elements in the nano-pellets except that for Si agreed with those in the original sample within the LA-ICP-MS repeatability of several percent. However, for JCt and JCp very small but significant differences were found for some trace elements at low concentrations, indicating the need for a re-certification of these materials. The study proposed more robust reference values for MACS-3 and Sr isotope data for all three materials.

Several contributions focused on *natural mineral RMs for in situ trace element and isotope analysis*. Batanova *et al.***[218]** characterised the olivine MongOL Sh11-2 from central Mongolia by EPMA, LA-ICP-MS, SIMS, ID-ICP-MS, XRFS and ICP-MS at six institutions worldwide. The homogeneity was sufficient for reference and information values to be reported for 27 major, minor and trace elements. An examination of the chemical composition and homogeneity of two

Mg-rich olivines (355OL and SC-GB) by EPMA, LA-ICP-MS and solution ICP-MS concluded[219] that these olivines could be used as primary standards. Unfortunately, these materials are in limited supply so can only be distributed for characterising new olivine RMs in other laboratories. The importance of matrix-matched calibration was emphasised but, if this was not possible, settings for LA-ICP-MS parameters such as spot size, fluence and number of total shots were recommended to minimise fractionation effects when using a non-matrix-matched silicate glass RM. An apatite RM (Eppawalla-AP) for high precision Cl isotope measurements was obtained[220] from a mega-crystal from the Eppawalla carbonatite (Sri Lanka) and characterised by IRMS and SIMS. Neither technique showed any variation in the δ^{37}Cl values within the analytical uncertainties, so Eppawalla-AP was considered to be homogeneous at the 10 μm scale. The recommended δ^{37}Cl value for Eppawalla-AP was -0.74±0.15‰ (2SD) as determined by IRMS. It was proposed that this apatite could be used as a matrix-matched RM for *in situ* Cl isotope studies of apatites and as a QC material for bulk analysis. Various microanalytical techniques were used[221] to confirm a uraninite from Utah, USA as a potential RM for the determination of REEs in U-rich matrices. The CaO content determined by EPMA was sufficiently homogeneous (2.70±0.38 *m/m*%, 2SD) for Ca to be employed as an IS for LA-ICP-MS. Major element and REE compositions were homogeneous at the cm and μm scales, respectively. Ma *et al.*[222] investigated various natural titanite crystals with ages ranging from *ca.* 20 Ma to *ca.* 1840 Ma as potential RMs for *in situ* U-Pb and Sm-Nd isotopic measurements by LA-(MC)-ICP-MS. The RMJG rutile from Hebei Province, China was introduced[223] as a new RM for U-Pb dating and Hf isotope determinations by LA-ICP-MS. This rutile has very low Th (<0.003 μg g^{-1}) and common Pb proportion of <0.5% but has high contents of Hf (102 μg g^{-1}), radiogenic Pb (20 μg g^{-1}) and U (61 μg g^{-1}). Isotopic homogeneity was established by ID-TIMS, LA-MC-ICP-MS, LA-SF-ICP-MS and LA-ICP-MS; the recommended U-Pb age was 1750±8.4 Ma and the ^{176}Hf/^{177}Hf value 0.281652±0.000007 (2SD).

Several *natural zircons* have been characterised to assess their potential as microanalytical RMs. Huang**224** proposed a zircon megacryst (SA01-A) as a new RM for microbeam U-Pb geochronology and Hf and O isotope geochemistry. A mean ^{206}Pb/^{238}U age of 535.08±0.32 Ma was determined by CA-ID-TIMS, a δ^{18}O value 6.16±0.26‰ of by laser fluorination and a mean ^{176}Hf/^{177}Hf ratio of 0.282293±0.000007 by solution MC-ICP-MS. Although the megacryst was homogeneous for these measurements, it had significant spatial variations in Th/U and Li isotope ratios. A huge dataset of more than 10,000 analyses of the well-known Mud Tank zircon (MTZ), consisting of trace element, U-Pb and Hf isotope data was compiled**225** from QC measurements made between 2000 and 2018. Based on the U-Pb data, a Concordia age of 731.0±0.2 Ma (2SD, n = 2,272) was proposed as the age of crystallisation for MTZ. It was noted that some grains had lower concordant to slightly discordant ages, probably reflecting minor Pb loss. It was concluded that MTZ is a suitable RM for the QC of U-Pb and Hf-isotope analyses if care is taken to select grains that have been tested for homogeneity.

To assess their potential as *matrix-matched RMs for the calibration of O isotope measurements by SIMS*, five olivine, three clinopyroxene and three orthopyroxene mineral samples were studied**226**. Homogeneity at the µm scale was investigated on multiple grains using SIMS and the O isotope compositions determined by laser fluorination IRMS. All eleven minerals were considered suitable as RMs. A calcite from the Oka carbonatite complex (Quebec, Canada) was presented**227** as a new Chinese national RM (GBW04481) for carbonate C and O isotopes microanalysis by SIMS. Homogeneity was demonstrated by hundreds of SIMS analyses and the recommended values of $\delta^{13}C_{VPDB}$ = -5.23±0.06‰ and $\delta^{18}O_{VPDB}$ = -23.12±0.15‰ were established by conventional IRMS. After measuring O isotope ratios in a range of zircon RMs with high-precision using SHRIMP, Avila *et al.*[228] concluded that Temora 2 was a highly satisfactory RM for O isotope determinations if the provenance of the grains was well established. Repeated analyses over nine sessions and seven different mounts agreed within analytical uncertainty for zircons Temora 2, FC1, R33, QGNG, Plešovice and 91500 when normalised to Mud Tank zircon, which was regarded as a useful QC material with typical repeatability of ≤0.3‰ (2SD). Caution was sounded when using other zircons from the Duluth Complex (FC1, AS57 and AS3) as RMs for this purpose as they had an excessive scatter of $\delta^{18}O$ values associated with low-U zircon grains. Yang *et al.*[229] assessed the O isotope homogeneity of six well-known apatite RMs and two in-house apatites by SIMS. The O isotope data for all the apatites studied were normally distributed with precisions of between 0.38 and 0.47‰ (2SD), only slightly worse than the precision of 0.36‰ (2SD) for the Durango 3 apatite which was used for QC during the study. Application of a homogeneity index (H, the ratio of the measurement uncertainty to the expected total combined uncertainty) showed that none of the apatites had significant O isotopic heterogeneities. However, on consideration of all the evidence, the three apatites GEMS 203, Kovdor and McClure were considered to be the most suitable to act as RMs for *in situ* oxygen isotope analysis.

Four new *selenium-rich rock RMs* (GBW07397 to GBW07400) with Se mass fractions from 38.5 to 1030 μg g^{-1} were prepared[230] by the China University of Geosciences following ISO guidelines and analysed in 10 laboratories by a variety of methods. Certified values were assigned for As, Cd, Cu, Mo, Pb, Se, V and Zn and the materials were approved as national CRMs.

Many RMs with established total elemental contents continue to be characterised for *specific isotope systems*. For example, the Ba isotopic compositions of 34 geological RMs encompassing a wide range of matrices (silicates, shale, carbonates, river and marine sediments, and soils) with Ba mass fractions between 6.4 and 1900 μg g^{-1} were determined[99] by MC-ICP-MS. The variation of $\delta^{138}Ba/^{134}Ba$ in these RMs was up to 0.7‰. The highest ratio was in a shale that had been subjected to a high degree of weathering. An interlaboratory comparison[231] involved measuring all currently available Mg isotope RMs and artefact standards with natural Mg isotope compositions with the aim of establishing SI traceability and the comparability between different Mg δ-scales. The RMs were cross-calibrated with expanded measurement uncertainties of <0.03‰ for $\delta^{25/24}$Mg and <0.04‰ for $\delta^{26/24}$Mg. The authors recommended retaining the established scale based on DSM3 (Mg solution) and anchoring it with European RM ERM-AE143 (Mg solution) at -1.681‰ for $\delta^{25/24}\text{Mg}_{\text{DSM3}}$ and -3.284‰ for $\delta^{26/24}\text{Mg}_{\text{DSM3}}$. This would allow a laboratory to use any of the Mg isotope RMs in its research and convert the δ values obtained to any other scale. The Ga isotope ratios of 10 geological RMs (silicates, shales and ferromanganese nodules) and two pure Ga RMs were measured**[232]** by MC-ICP-MS with the aim of providing data to improve interlaboratory calibration. Difficulties encountered were the lack of consistency in the use of RMs by each laboratory for defining the Ga δ zero and the paucity of reliable uncertainties in published Ga isotope data for geological RMs. Following normalisation of all available δ^{71}Ga data for geological RMs to a single RM, the results were in agreement with previously reported values. Kuessner *et al.***[233]** demonstrated the effectiveness of their automated IC separation method by obtaining a δ^{7}Li value of 30.99±0.50‰ (2SD) for NRCC RM NASS-6 (seawater) and then reported the first δ^{7}Li values for CRPG RM GS-N (granite) and NIST SRM 2709a (soil). The δ^{65}Cu values for 10 geological and biological RMs were determined**[234]** for the first time using MC-ICP-MS. In addition, δ^{65}Cu values measured for the USGS RMs BIR-1 (Icelandic basalt) and W-2a (diabase) agreed with previously published values. These RMs had complex and varied matrices with Cu mass fractions between 32.2 and 53.3 µg g^{-1} and δ^{65}Cu values relative to NIST SRM 976 (copper isotope) ranging from -0.10‰ to 0.29‰. Molybdenum stable isotope compositions (δ^{98}Mo relative to NIST SRM 3134 solution) and Mo mass fractions in a suite of NIST, USGS, GSJ and BAS geological RMs were determined**[235]** by MC-ICP-MS using a double-spike method. The study focussed on low-temperature sedimentary silicate and carbonate sedimentary materials for which Mo isotopic information can be a useful geochemical tool. These RMs had Mo contents between 0.076 and 364 µg g^{-1} with δ^{98}Mo in the range -1.77 to 1.03‰.

Chinese reference materials have featured in the continuing search for suitable matrix-matched RMs for isotope ratio measurements. The homogeneity of a set of Chinese Geological Standard Glasses (CGSG-1, CGSG-2, CGSG-4 and CGSG-5) for the isotopic analysis of Hf, Nd, Pb and Sr was assessed**[236]** by TIMS and MC-ICP-MS over a period of almost three years. It was concluded that all four glasses were sufficiently homogeneous for these analyses and would be suitable RMs for related geochemical measurements. Differences between the isotopic composition of the glasses and the powdered RMs from which they had been prepared resulted from the addition of flux during the glass preparation. Yang *et al.***[237]** provided the first comprehensive study of Hf and Lu mass fractions and Hf isotopic data for 13 Chinese rock RMs (GBW07 103–105, 109–113 and 121–125) representing a broad compositional range of volcanic, plutonic and ultramafic rocks. Values determined were in agreement with the limited data available from previous studies, so the RMs were considered suitable for Lu-Hf isotopic analysis. In order to expand the number of geological RMs available for Ni isotope ratio measurements, high-precision δ^{60}Ni/^{58}Ni values were determined**[238]** by double-spike (^{61}Ni-^{62}Ni) MC-ICP-MS on 16 IGGE RMs for the first time. The intermediate precision for NIST SRM 986 (Ni isotope solution) was 0.05‰ (2SD, n = 69) and typically 0.06‰ for geological RMs. The δ^{60}Ni/^{58}Ni values of the 16 IGGE RMs varied from -0.27‰ to 0.52‰. Because of their characteristic Ni isotope compositions, GSS-1, GSS-7, GSD-10 and GSB-12 were proposed as potential RMs for QC and interlaboratory comparisons. Wu *et al.***[239]** measured the δ^{53}Cr values of 22 geological RMs with values in the range −0.44‰ to 0.49‰. They suggested that IGGE RMs GSS-7 (soil), GSS-4 (soil) and GSD-10 (stream sediment) were suitable RMs for interlaboratory comparisons as their Cr isotope compositions complemented existing RMs, most of which had isotopic signatures similar to that of bulk silicate Earth.

To address the problem of there being no internationally-recognised *sulfur isotope RM* available for $\Delta^{33}S$ and $\Delta^{36}S$ data normalisation, essential for interlaboratory comparisons, two sodium sulfate materials (S-MIF-1 and S-MIF-2) artificially enriched in ^{33}S were synthesised**[240]. **Four of the five laboratories that characterised these materials used conventional IRMS whereas the fifth used a newly-developed MC-ICP-MS method. Isotopic homogeneity and consistency of data led to the conclusion that the $\Delta^{33}S$ values derived for S-MIF-1 (9.54±0.09‰) and S-MIF-2 (11.39±0.08‰) could be adopted to calibrate $\Delta^{33}S$ measurements. In particular, they could be used to establish a calibration curve spanning a large $\Delta^{33}S$ range (0-11‰) by mixing them with other sulfur RMs with zero $\Delta^{33}S$, such as IAEA-SO-5 and IAEA-SO-6 ($BaSO_4$).

In an informative editorial, Meisel**[241]** discussed the *use of the δ and* Δ *notations to express variations in isotope ratios*. In order to express the very small variations in stable isotope ratios relative to a reference isotope ratio ($\delta = 0$), notations such as ε and μ were introduced into the scientific literature. However, Meisel argued that there is no need for these when expressing isotope ratio differences because δ is a relative difference and therefore dimensionless. Thus it could be expressed in±, ‰, parts per ten thousand or ppm, depending on how large the variation is; it should not be automatically assumed that δ values are ‰.

Participation in *proficiency testing programmes* enables laboratories to monitor, assess and improve the quality of their analytical data. In addition, proficiency tests can also provide a route to characterising RMs and CRMs. Potts *et al.***[242]** discussed how the Geo*PT* proficiency testing scheme, established about 25 years ago, could meet the requirements of ISO Guide 35:2017 for the certification of geological RMs. Following a detailed assessment of the metrological properties of Geo*PT*-assigned values in relation to Guide 35 recommendations, they demonstrated that these values may be regarded as certified values, provided a number of criteria were met. A related study provided**243** a critical comparison of results from two rounds of the Geo*PT* proficiency testing scheme*,* in which the same material, an andesite, was distributed 18 years apart. A comparison of consensus values for over 50 determinands measured in the two rounds of testing showed remarkable consistency. This demonstrated not only the stability of the material but also the robustness of the procedures adopted by the scheme, given the changes in laboratory practices over the intervening 18 years. The paucity of geological RMs with reliable data for As, Bi, Sb, Se and Te at the µg g^{-1} level prompted**244** a study of 34 samples from various Geo*PT* rounds and 10 geological RMs covering different rock types. Precautions were taken during the *aqua regia* digestion to avoid loss by volatilisation before measurement by HG-AFS. Although there were no assigned or even provisional values for many of the Geo*PT* materials because of the wide range of results reported, the authors calculated a medium value from the data submitted to the Geo*PT* scheme. Where the As, Bi, Sb and Te mass fractions were above their respective LODs, their HG-AFS results agreed with the calculated Geo*PT* median values suggesting that these *GeoPT* medians could be considered as information values. This was not the case for Se, for which it was noted that for Se mass fractions <0.5 µg g^{-1} many of the results reported to Geo*PT* may be systematically high.

5.3 Sample preparation, dissolution, separation and preconcentration

An authoritative *review***245** (180 references) of recent advances in sample preparation for elemental and isotopic analysis of geological samples focussed on: (1) acid digestion methods in open vessels, high-pressure bombs and microwave ovens; (2) alkali fusions; (3) high-pressure ashing; and (4) bulk analysis by LA-ICP-MS. Limitations and applications of the different sample digestion methods were discussed, with special emphasis on sample digestion with NH_4F and NH_4HF_2, both of which are currently attracting much attention. Although LA-ICP-MS is a powerful *in situ* microanalytical technique, it is frequently used for bulk analysis and this review provided a balanced discussion of procedures for the preparation of pressed powder pellets and fused materials for this purpose.

Various contributions offered *improvements in digestion and combustion techniques*. He *et al.*[246] developed a method based on NH_4HF_2 digestion and subsequent dilution with NH_4OH for the simultaneous SF-ICP-MS determination of Br, Cl and I in geological materials. The halogens were retained during digestion in open Teflon vessels at temperatures of 200−240 °C for 0.5 to 12 h because the alkaline atmosphere produced during the digestion process suppressed their volatilisation. Most of the results for the 12 geological RMs analysed were consistent with literature values, for which, however, there is a significant spread. For the quantification of REEs in geological samples by ICP-AES, a digestion method using condensed phosphoric acid instead of HF was re-evaluated[247]. Results for six international RMs and three Brazilian ore samples indicated that although many potential REE-bearing minerals were dissolved by this method, zircon and xenotime remained in the undigested residue so the method should be used with caution depending on the sample mineralogy. Rondan *et al.*[248] developed a digestion method for the ultra-trace determination of Se and Te in coal by ICP-MS using microwave-induced combustion under O_2 at 20 bar without the use of HF. Of the various combinations of mineral acids evaluated as the absorbing solution, a mixture of HNO_3-HCl (1 + 1) gave the most accurate results. Negligible blank levels resulted in very low LOQs of 0.002 mg kg^{-1} for Se and 0.007 mg kg^{-1} for Te. To test whether desilicification with HF improved the extraction of elements with variable chalcophile affinities (Ag, Cd, Cu, In, PGEs, Re, S, Se and Te) from geological RMs, digestion procedures involving HF-HNO_3 in bombs were compared[249] with those using HNO_3-HCl in Carius tubes. The extraction efficiency of HF-desilicification varied for different elements in different RMs; whereas a significant increase (30–70%) was observed for Cd and In mass fractions after HF-desilicification, there was negligible increase for other strongly chalcophile elements in many of the samples. The variabilities of the host matrix and of the chalcophilic nature of the elements were thought to influence the efficiency of element release from the matrix.

Developments in *sample purification* included**[233]** a robotic pipetting arm to automate analyte separation by IC in the determination of Li isotope ratios in geological matrices. When compared with manual sample processing, the robotic system reduced sample processing time without compromising accuracy, precision and effectiveness of the chromatographic purification. Another semi-automated procedure, for the measurement of stable and radiogenic isotopes of alkali and alkaline-earth elements in silicate rocks, involved**[250]** decomposition by borate fusion and purification with an IC system equipped with a fraction collector. Each analyte was completely separated from other elements in the elution profile without isotope fractionation and resulted in the complete removal of interference matrices from reagents and samples. Values for δ^{7}Li, δ^{26}Mg, δ^{88}Sr, ^{87}Sr/^{86}Sr determined for various GSJ geochemical RMs were consistent with published values.

A modified method**[251]** for determining *very low concentrations of gold in rocks* (<0.01 ng g^{-1}) involved Carius tube digestion with reverse *aqua regia*, chromatographic separation to remove most of the sample matrix and measurement by SF-ICP-MS. Quantification was by external calibration with internal standardisation using Au/Pt ratios, which were precisely determined by ID. Procedural blanks were very low (<6 pg) and the LOD was <0.8 pg L^{-1}. The results were indistinguishable (<5–10%, 2SD) from those obtained by a standard addition technique on the same solution. Reverse *aqua regia* was an efficient reagent for Au extraction under the high temperature conditions (240–270 °C) employed and was preferable to HF-*aqua regia* because it only released limited amounts of Hf and Ta, whose oxides would otherwise cause significant interferences. Daniel *et al.***[252]** evaluated procedures for preparing gold ores using various types of mills in common use. Optimal performance required the use of a grinding aid such as silica flour or bauxite to avoid caking; a 1 + 1 mixture of silica and bauxite proved to be as effective as grinding in 100% silica. The grinding charge mass was limited to ≤50% of the nominal capacity of the mills. Under these modified conditions, gold particles of mm size could be comminuted to ≤100 µm in <5 minutes; particle sizes of <50 µm could be achieved for 95% of the material with extended grinding times. These results made it viable to reduce the sample masses from the commonly used 25-50 g to 5 g or less for the routine determination of Au in geological samples, thereby decreasing reagent consumption in the subsequent *aqua regia* digestions or fire assay.

5.4 Instrumental analysis

5.4.1 Laser-induced breakdown spectroscopy

This technique has a wide variety of applications and a short tutorial *review* (58 references) summarised[253] issues related to sample preparation, qualitative and quantitative approaches, signal enhancement, calibration strategies and data processing. Because LIBS is often regarded as only a semi-quantitative technique, Syvilay *et al.*[254] (23 references) published some guidelines for improving the quality of LIBS analyses. Their recommendations such as the use of control charts, optimisation of measurement conditions and evaluation of the various data processing models available are in fact nothing more than good analytical practice. The authors, rather optimistically, claimed that based on their "rigorous" methodology, "it will become possible to compare the LIBS results obtained by different analysts and pave the way towards inter-laboratory comparison."

Reviews of the LIBS analysis of geological samples included[255] a critical account (127 references) of its application to the sourcing and discrimination of minerals and gems and the analysis of slurry and drill cores in mineral exploration. The determination of elements of economic importance such as Ag, Au, the REEs and several light elements (C, F, Li) were also highlighted. Coal analysis by LIBS was the subject of a comprehensive review[256] (206 references) which will be invaluable to any reader working in this area. It offered up-to-date information on the progress of LIBS analysis from the fundamentals to industrial developments. The experimental and instrumental challenges that need to be addressed to realise the wide commercialisation of LIBS for coal analysis were also identified. A review (126 references) on advances in the remote detection capability of LIBS considered[257] three basic configurations: stand-off LIBS, remote LIBS with optic fibre and compact-probe LIBS. The characteristics of these techniques were described together with a range of applications which included geological investigations and planetary exploration.

Handheld LIBS instruments are becoming increasingly popular. A recent application was the fast quantification[258] of F during the purification of fluorite (CaF_2) from low-grade and fine-grained ores. Particle size played a key role as there were significant differences in LIBS intensities exhibited for the 10-150 µm and <20 µm powders, with no discernible correlation between the particle size and magnitude of the signal. Matrix effects displayed a non-linear relationship with the F contents measured independently by ISE. By adopting a multi-variate approach based on the signal intensities at two CaF molecular bands to overcome the matrix effects, the on-line LIBS analyser was able to meet the target of a ≤2% error in the F content of CaF_2-rich samples. Handheld LIBS was also evaluated[259] in a field laboratory for measuring Ag in gold as a rapid method for gold provenance studies. Based on the results for nine training samples of commercial gold alloys (five distinct populations) from French Guiana, the best calibration model was a quadratic univariate model. Subsequently, the origins of four "unknown" samples of gold from the same region were correctly identified in this preliminary study.

Several contributions investigated *the use of LIBS in the mining and ore processing industries*. A total of 162 sulfide rocks were analysed[260] by LIBS and chemometric methods to identify and classify minerals relevant to the copper industry. Of four different chemometric methods assessed for sensitivity, precision and accuracy, the nonlinear classifier artificial neural networks (ANN) proved to be the most reliable method for the identification of seven sulfur minerals (bornite, chalcopyrite, covellite, chalcocite, enargite, molybdenite and pyrite) in untreated rock samples. Another study demonstrated[261] that LIBS combined with laser-induced fluorescence (LIBS-LIF) had great potential in the search for high-grade uranium deposits because of the selectively enhanced intensity of the U spectrum which minimised spectral line interferences. Parameters such as the slope of the calibration curve, coefficient of determination (R^2) and precision (average RSD) were all significantly better than those of conventional LIBS. This was the first report of a U LOD of <100 $\mu g\ g^{-1}$ in an ore matrix being achieved using LIBS. A multi-energy calibration strategy was successfully applied[262] to the fully quantitative LIBS determination of Al_2O_3, Fe_2O_3 and TiO_2. Two calibrants were required: (1) a mixture of the sample and a RM; and (2) a mixture of the sample and a blank; both in the same proportions. The NIST SRMs 679 (brick clay) and 2703 (sediment for solid sampling) were used as the RM and sample, respectively, and were prepared as fused discs by borate fusion to minimise sample heterogeneity. Boron and Li were used as ISs to compensate for matrix effects. The relative differences from the reference values were -4 to 15%, with LODs between 0.4 and 0.6% for all analytes.

Analysis by LIBS has great potential for the *determination of coal properties* such as calorific value, ash, volatile content and C and H contents. Zhang *et al.*[263] developed a set of calibration schemes with the aim of improving the figures of merit of such measurements to meet industrial needs. The selection of an appropriate spectral pre-processing method combined with multivariate calibration models improved the accuracy and precision of each index of coal properties. Two methods of sample preparation were compared[264] for the LIBS analysis of semi-coke (a special coal with relatively high C content and low volatility). Although painting semi-coke powders onto a tape was a simple way of presenting the samples for on-line monitoring, mixing the coal powder with a binder and pressing into a 'slice' for ablation improved the measurement precision significantly, reduced matrix effects and enhanced the stability of the spectrum. A new algorithm that combined SVM with PLSR was utilised to obtain an effective prediction model for determining the C content in this type of coal sample with high accuracy.

The *shapes of LA craters* produced by a LIBS system employing different numbers of laser shots and pulse energies were studied[265] using high resolution X-ray CT. Accurate measurements of crater volume, width, depth and cone angle in aluminium and rock (gold ore) samples closely agreed with those produced by a theoretical simulation model. This method of 3D characterisation of LIBS crater geometry was considered useful for optimising LA setups to produce a constant ablation rate or known depth profile resolution.

5.4.2 Dating techniques

In recent years, *in situ U-Th-Pb geochronology* has been applied to a range of different minerals. Five allanite samples with significant variations in Fe and Th contents were analysed[266] by SIMS to address the issue of matrix effects caused by variable amounts of Th that had been observed in a previous study. Changes in calibration parameters evident for allanites with a large range of Th contents were overcome by applying the power law relationships both between Pb^+/U^+ and UO_2^+/U^+ and between Pb^+/Th^+ and ThO_2^+/Th^+. No matrix effects were evident using this strategy for SIMS U-Th-Pb dating on allanites with FeO contents ranging from 12.8 to 16.1% and ThO_2 contents between 300 μg g^{-1} and 2%. It was concluded that the accuracy was mainly controlled by the proportion of common Pb in the analysed material. Luo *et al.*[267] assessed the potential of

LA-ICP-MS for U-Pb dating of wolframite minerals which often occur in tungsten deposits and other hydrothermal ore deposits. Lack of a matrix-matched high-quality wolframite RM was a major limitation; the ages determined for wolframite samples when calibrated against the well-characterised zircon 91500 were *ca.* 12% younger than the corresponding ID-TIMS ages. If water vapour were added to the He carrier gas before the ablation cell, this discrepancy was eliminated and accurate wolframite U-Pb ages were obtained using ns-LA-ICP-MS. Several of the wolframite samples analysed in the study were promising candidate RMs. Bastnäsite is the end member of a large group of carbonate-fluoride minerals whose LREE contents make them important commercially. A study of 47 bastnäsite samples by LA-(MC)-ICP-MS emphasised[268] the importance of a correction for the presence of common Pb in order to obtain reliable U-Th-Pb ages. The relatively high Th contents in most bastnäsites meant that Th-Pb ages were preferred to U-Pb ages as they could be determined more precisely. It was suggested that some of the bastnäsites analysed could be potential RMs for calibration or QC. Fission track dating of apatites by LA-ICP-MS is susceptible to small but systematic variations in apatite U contents so Cogné *et al.*[269] adopted a zeta-based approach to correct for this bias. Instead of counting fission tracks in large numbers of zeta-standard grains (*e.g.* Durango apatite) for every LA-ICP-MS session – clearly a time-consuming procedure – they determined a single, high-precision zeta factor ζ_{ICP} in an initial LA-ICP-MS session. This factor was reused for subsequent LA-ICP-MS sessions during which the unknowns were analysed and some of the Durango grains were reanalysed. In this way, a session-specific zeta fractionation factor could be calculated to account for differences in ^{238}U/^{43}Ca fractionation resulting from variations in LA-ICP-MS tuning between sessions.

To reduce fractionation effects in *U-Pb age determinations of zircons by LA-ICP-MS*, Corbett *et al.* [270] applied multiple 1 Hz shots to a single sample location in a standard ablation cell (volume *ca.* 8 cm^3). A short washout time (3 s) maintained an elevated signal between laser pulses. The extremely shallow craters (aspect ratio of <<1) significantly reduced the effect of 'downhole' fractionation and allowed age determinations to be made on a µm to sub-µm scale. This ability to integrate and collate signal pulses for a small number of consecutive laser shots rather than pulsing the laser continuously at 5-20 Hz produced precise age determinations (*ca.* 1% reproducibility, 2 RSD) often indistinguishable from those determined by ID-TIMS for the same zircon. In addition, this approach reduced thermally induced effects such as substrate melting, plasma loading and signal mixing with depth in a heterogeneous sample. Liu *et al.*[271] introduced a 2% *v/v* ethanol solution into the ICP to increase the sensitivity and to suppress any isotopic fractionation during the dating of zircons by LA-ICP-MS at high spatial resolution. In combination with a shielded torch system, the mixed gas plasma significantly improved the precision, accuracy and uncertainty of ^{206}Pb/^{238}U ages for small (10 and 16 µm) spot diameters. However, the effect was insignificant for intermediate (24 and 32 µm) spot diameters. Mean weighted ^{206}Pb/^{238}U ages of zircon RMs (Plešovice, GJ-1 and 91500) determined by this method agreed within 2SD with literature values obtained by ID-TIMS and LA-ICP-MS. Anderson *et al.*[272] showed that Raman spectroscopy could be used to produce maps of radiation damage in zircon crystals as an aid to the interpretation of (U/Th)/He dates obtained by LA-ICP-MS. These Raman spectroscopy maps could be used to visualise intracrystalline variations in zircon properties, which had implications for the analytical strategy adopted when dating ancient, zoned zircons by LA-ICP-MS.

One of the challenges faced in the *isotopic analysis of single grains* of zircon is the small amounts of U they contain. By improving dissolution, purification and measurement methodologies previously developed to determine ^{238}U/^{235}U ratios in small samples, Tissot *et al.*[273] demonstrated that it was possible to measure this ratio in single zircon crystals by MC-ICP-MS with a precision (±0.04 to ±0.25‰) sufficient to resolve U isotopic differences between grains from the same location. It was proposed that this method could be used to improve the accuracy and precision of U–Pb and Pb–Pb dates and to enable accurate re-evaluation of U decay constants. The *in situ* U-Pb dating of the U-rich mineral uraninite by SIMS or LA-ICP-MS is hardly ever carried out because a matrix-matched RM is required to correct for Pb/U fractionation. A procedure developed[274] for U-Pb dating of single-grain uraninite by ID-TIMS had the advantage that no matrix-matched RM was necessary. Because <1 µg of material was required for the determination of ages with high precision, this method provided the basis for the highly spatially resolved analysis of uraninite grains in samples such as thin sections. Prior to the ID-TIMS analysis, it was important to use EPMA and LA-MC-ICP-MS to identify minerals, to determine chemical composition and to check age homogeneity.

In the context of *dating speleothem carbonate* samples, Perrin *et al.*[275] proposed an integrated petrographical and geochemical approach for optimising the subsampling of speleothems for U/Th dating. Non-destructive *in situ* trace element screening by portable EDXRFS was combined with petrographical and mineralogical information to produce elemental distribution maps which were used to identify growth discontinuities and primary and secondary (diagenetic) carbonate phases on the sample surface and thereby facilitate the selection of areas suitable for subsampling for radiometric dating. A rapid procedure for extracting Pb and U from carbonate minerals combined[276] the commonly used extraction of Pb on AG1-X8 anion-exchange resin with that of U on Eichrom TRU-resin to create a single-column sequential extraction. Experiments with large speleothem calcite samples showed that it was possible to process 200 mg of material in only one day, half the time required for separate sequential extractions based on the same chemistry. Because low blanks (*ca.*10 pg Pb) could be maintained, the procedure was ideally suited for high-precision U-Pb dating of speleothems.

Acid leaching is widely used in Pb-Pb geochronology to separate radiogenic Pb from non-radiogenic Pb in samples. A study of acid-leached minerals from meteorite samples demonstrated[277] the potential pitfalls of acid leaching for this purpose. High-Ca lamellae within single pyroxene grains were more affected by leaching with dilute HF than were low-Ca lamellae so inaccurate Pb-Pb age estimations and scattered Pb isotopic data resulted. It was considered that leaching with HF should be utilised with great caution for Pb-Pb dating of pyroxenes and pyroxene-bearing materials.

Improvements in the $^{40}Ar/^{39}Ar$ *dating* of samples rich in volatile elements were achieved[278] by modifying the gas purification protocol so that suppression of the Ar signals caused by incomplete cleaning of the gases extracted from the sample by a laser heating device was minimised. The modified preparation configuration improved the precision of the age determinations by MC-noble gas MS by an order of magnitude resulting in geologically plausible ^{40}Ar/^{39}Ar ages for small masses of rocks of Quaternary age. In a quest to find suitable RMs for inter-laboratory and inter-technique comparisons of ages produced by the ^{40}Ar/^{39}Ar and U-Pb geochronometers, sanidine and zircon crystals from the Carboniferous Fire Clay tonstein, a large ash bed in the Appalachian Basin (USA), were assessed[279]. The preferred mean ^{40}Ar/^{39}Ar date from the sanidine crystals of 315.36±1.10 Ma (2SD) was consistent with the weighted mean ^{206}Pb/^{238}U zircon age of 314.629±0.35 Ma (2SD). Based on the good single-crystal reproducibility of the sanidine data and the overall consistency between the two geochronometers, the Fire Clay tonstein was considered to hold promise as a RM of Palaeozoic age.

5.4.3 Inductively coupled plasma mass spectrometry

5.4.3.1 Instrumentation. A new micro-flow liquid sample *introduction system* developed for the direct nebulisation of small samples into the plasma at flow rates as low as 5 µL min^{-1} consisted[280] of a demountable direct injection high efficiency nebuliser (dDIHEN), a FIA valve and a gas displacement pump connected to a mass-flow controller to deliver a very stable liquid flow. The µ-dDIHEN plugged directly into the ICP torch in place of the injector. The system was successfully tested on four different types of ICP-MS instrument with sample loops of 10 and 50 µL and flow rates of 5-50 µL min^{-1}. Signal sensitivity increased with the liquid uptake rate up to 30 µL min^{-1} but poor aerosol quality and reduced ionisation under wet conditions affected performance at higher flow rates. Three different applications were demonstrated: B isotope ratio measurements in geological samples; trace element analysis of natural water samples; and gold NP characterisation by single particle ICP-MS.

5.4.3.2 Trace element determinations. *New approaches to trace element determinations by LA-ICP-MS* included**[281]** the use of single-shot measurements (200 nm, 1 Hz repetition rate) to determine Mg/Ca in µm-sized calcareous chambers of foraminifera using a fs-LA system and SF-ICP-MS. Precision of the Mg/Ca ratio was improved through almost simultaneous measurement of doubly charged $^{44}Ca^{2+}$ ($m/z = 22$) and singly charged $^{25}Mg^{+}$ ($m/z = 25$) ions. Low fluence settings of 0.3–0.6 J cm^{-2} enabled a high depth resolution of 50–100 nm per pulse down to a depth of 10–20 µm. The precision was *ca.* 5% RSD. The procedure was applied to the detailed analysis of single chambers and shell-depth profiles in planktic and benthic foraminifera shells for paleoclimate reconstruction studies. In a novel approach to the analysis of geological samples, solutions of digested material were ablated**[282]** to produce an aerosol for measurement by ICP-MS. In the procedure, 50 mg of material was first digested in NH_4HF_2 in a screw-top PFA vial at 230 °C for 3 h; then 15 µL of digest was pipetted into tiny pits on a Teflon sheet which was sealed with parafilm and ablated with a 193 nm ArF excimer LA system. Water-related interferences were reduced by 1–2 orders of magnitude compared to those for solution aspiration and were similar to those for sample introduction *via* a desolvating nebuliser. Other advantages were greatly reduced matrix effects and signal sensitivities improved 70-250 times. The NIST SRM 610 (silicate glass) was employed as the calibration material and a multi-element standard solution for QC. Using In as the IS, the concentrations obtained for major and trace elements in geological RMs ranging from mafic to felsic rocks were within 10% of the reference values for 45 elements; precisions were <7%. This method was regarded as comparatively environmentally friendly because the consumption of acid and ultrapure water during sample preparation was 20–100 times less than that of conventional liquid nebulisation. It would be interesting to see how the performance criteria and green credentials of this method compare with those of ablating a pressed pellet.

Matrix effects that can arise when elemental abundances in sulfides are determined by ns-LA-ICP-MS using non-matrix-matched silicate RMs for calibration were quantified[283] using three different ISs (Cu, Fe, Ni). Individual fractionation indices (F_i values) for Fe-rich sulfides were significantly different from those derived for Fe-rich metal alloys. Nickel was the preferred IS for the measurement of volatile elements, whereas Cu or Fe was recommended for transitional and/or refractory elements. As shown in previous studies, the magnitude of the matrix effects for sulfides was strongly correlated with elemental volatility but remained constant for each element with increasing concentrations. This finding was used to derive a new model for predicting F_i values for Fe-rich sulfides and to assess any discrepancies between measured and true sulfide liquid–silicate melt partition coefficients which may be under- or over-estimated by up to 0.15 and 0.2 log units, respectively, if matrix effects were not taken into account.

The majority of software programs for *elemental imaging by LA-ICP-MS* were developed to work with rastered data and so are limited in their ability to handle signals generated from individual laser shots of short duration (<10 ms). To process baseline-separated peaks produced by the latest generation of LA systems, a new standalone software application called “LA-ICP-MS Image Tool” was developed[284] for converting raw LA-ICP-MS data into images using a ‘pixel-by-pixel’ approach. This freeware tool located peaks within raw data files and used the peak locations to segment the data at appropriate intervals, converting the data into a matrix of colour-coded pixels. Raw data were converted into a 60,000 pixel image within 2 minutes making it a viable approach for high-throughput imaging tasks. Both continuous signals and baseline separated peaks could be processed. The software also had the capability to identify peaks in single-shot or single-particle ICP-MS experiments to assist in the alignment of line scans. The image matrix could be exported as an Excel-compatible file, allowing further processing to be carried out off-line if required. Van Elteren *et al.*[285] explored the strengths and weaknesses of LA-ICP-MS imaging when the data were generated in single or multiple pulsed ablation modes. Depending on the LA-ICP-MS instrumentation and imaging conditions applied, various imaging artefacts such as smear, blur, aliasing and noise can degrade the image quality. An understanding of the potential sources of these artefacts was used in the development of a computer simulation model and metrics for the objective assessment of the image quality to aid the optimisation of LA-ICP-MS imaging parameters for fast and high-quality 2D mapping.

Recent developments in the e*lemental analysis of individual fluid inclusions by LA-ICP-MS* were summarised[286] in a short review (68 references) in which strategies for improving the success rate of ablation, accurate quantification and selection of suitable fluid inclusions were discussed. Tuba *et al.*[287] addressed the problem of analysing assemblages of fluid inclusions in orogenic gold deposits in which the inclusions are often too small and densely populated to be measured individually by LA-ICP-MS. For this application, inclusion-rich areas of the quartz host were analysed using a single continuous LA profile. The signals generated were converted into time-slice datasets and plotted as element ratios in ternary diagrams to reconstruct specific major and trace-element ratios. The method had high spatial and chemical resolution and the estimated compositions were in good agreement with results from previous analyses of the same material. Separate inclusion populations could be distinguished on the basis of their major- and minor- to trace-element concentration ratios.

5.4.3.3 Isotope ratio determinations by ICP-MS. The considerable research effort to improve isotope ratio determinations by MC-ICP-MS and other techniques is reflected in Table 5. Because the range of elemental isotope ratios now being measured in geological materials is so diverse, a table is provided as a starting point for readers to explore the systems of most relevance to them. It is difficult to discern any major breakthroughs as many of the studies provided modest improvements to existing separation procedures or analytical protocols.

Reports of *advances in isotope ratio methodology by LA-ICP-MS* covered many different matrices and isotope systems. The determination of Hf isotopes in zircon is not trivial as it requires five corrections for mass bias and interferences and measurements accurate to the 5th decimal place. With this in mind, Spencer *et al.*[**288**] discussed the fundamentals of Lu-Hf analyses of zircon and provided some novel techniques for data visualisation, integration of geographic information and statistical evaluation. Their recommended workflow was proposed as best practice for assuring that steps taken in data correction and interpretation were robust and rooted in fundamental geological, isotopic and analytical constraints. A new isobaric interference correction model was proposed[**289**] for *in situ* determinations of Hf isotope ratios in zircons, especially those with high Yb/Hf ratios. This LA-MC-ICP-MS procedure employed a specified zircon RM to calculate the mass bias factors that were then applied to other samples. In contrast to previous correction models, it was not necessary to determine the "natural" Yb isotopic composition and the model was equally applicable to zircons with low as well as high Yb/Hf ratios. The practical lower limit for the ^{180}Hf intensity was set at *ca.* 1 V so that meaningful ^{176}Hf/^{177}Hf ratios and <1.5 ε unit internal errors could be achieved simultaneously. Zircon was also the focus of a study which reported[**290**] a protocol for *in situ* determinations of stable Zr isotope ratios by LA-MC-ICP-MS. Potential interferences from $^{89}Y^{1}H^{+}$ and $^{180}Hf^{2+}$ were insignificant. Addition of N_2 to the central gas flow increased the Zr sensitivity by a factor of *ca.*

2. The use of laser spot sizes of 16-32 µm and a low pulse frequency of 1 Hz, together with signal-smoothing, improved the analytical precision by a factor of *ca.* 61 times compared to that without signal-smoothing. Data were reported relative to the GJ-1 zircon and typical analytical precisions for δ^{94}Zr/$^{/90}$Zr and δ^{96}Zr/^{90}Zr were 0.11 and 0.18‰ (2SD). Accuracy was confirmed by comparison with δ^{94}Zr/$^{/90}$Zr data obtained by the well-established double spike solution method for zircon RMs 91500, Plešovice, Penglai and Mud Tank. Lugli *et al.*[291] provided a user-friendly tool for processing large outputs of Sr isotope data generated by LA-MC-ICP-MS. This Excel-based interactive data reduction spreadsheet could be easily customised for user-specific data-acquisition protocols. Raw data files in a specific folder could be imported and the background and analysis cycles selected before corrections for the main Sr isobaric and polyatomic interferences and instrumental biases were applied. The results were automatically exported into a table. The performance of the spreadsheet was demonstrated by application to analysis of materials such as teeth, shells, speleothems and mineral phases. Further developments and improvements of *in situ* isotope ratio determinations by LA-ICP-MS included Ca isotope measurements in $CaCO_3$ and $CaPO_4$ materials[292], Fe isotope analysis of glassy cosmic spherules[293], Li isotope analysis in tourmalines[294] and in glass RMs and zoned olivines[295], and Os isotope ratios in sulfides[296].

[Table 5]

Hydride generation MC-ICP-MS can be a valuable technique for isotope analysis because of the potential to isolate the element of interest from interfering species. A method to measure Te isotopes by HG-MC-ICP-MS utilised[155] a ^{120}Te–^{124}Te double spike for mass bias corrections. Sensitivities were similar to those achieved with a desolvating nebuliser, and δ^{130}Te/^{126}Te precisions of 0.09‰ (2SD) were obtained for <8.75 ng of natural Te. Although HG avoided the need for a Ba correction and allowed analysis of samples without chemical separation of Te for simple matrices, a modified ion-exchange procedure was nevertheless employed to make the approach more universally applicable. Analysis of a range of USGS RMs, mine tailings, ancient sediments and soils revealed the largest spread in terrestrial Te isotopic composition to date ($\delta^{130}Te/^{126}Te = 1.21‰$), indicating that isotopic fractionation of Te is prevalent in low-temperature marine and terrestrial environments. Selenium stable isotopes are regarded as having great potential as a tracer of redox processes and chemical cycling of chalcophiles and volatile elements. A procedure for the measurement of Se stable isotopes in samples with low Se contents employed**297** a novel $^{76}Se–^{78}Se$ double-spike with HG-MC-ICP-MS detection. Sample requirement was typically 25 ng of natural Se and the sensitivity was >1 kV per 1000 μg L^{-1} for the total Se signal. Corrections were made for interferences from Ar, As and Ge. The results were expressed as $\delta^{82}Se/^{78}Se$ relative to NIST SRM 3149 (Se solution). The long-term external reproducibility was 0.040‰ (2SD, n = 93) so the method should be applicable to the measurement of the Se composition of a wide variety of geological samples.

5.4.4 Secondary ion mass spectrometry

Although TOF-SIMS cannot achieve the same precision as SF instruments, it is possible to record secondary ions for all elements and achieve high sensitivity analysis of a sample surface with minimal damage. Impressive *new instrumentation* included**298** a TOF-SIMS instrument for the *in situ* microanalysis of geological materials with complex structural and chemical features. The aim was to achieve high spatial and mass resolution with an O_2^- beam of *ca.* 5 μm diameter and intensity of *ca.* 5 nA. The mass resolution was >20,000 and the LODs <0.2 μg kg^{-1}. The performance characteristics were demonstrated by the analysis of zircons to obtain REE and Ti compositional information. A group at the US Naval Research Laboratory combined**299** a full SIMS instrument with a molecule-filtering single-stage AMS instrument used as a “detector” to make a single unified instrument for spatially resolved trace isotope analysis. This instrument was called NAUTILUS and was capable of collecting molecule-free raster ion images for rapid analysis of trace elements in complex, heterogeneous matrices with a trace element sensitivity at least 10 times better than commercial SIMS instruments due to the near-zero background. The novel capabilities of NAUTILUS were described and its performance demonstrated with relevance to nuclear materials analysis, cosmochemistry and geochemistry.

Various *improvements in isotope measurements by SIMS* included[300] an investigation into how the so-called topography effect could be eliminated in order to obtain high precision Si isotope measurements in quartz samples. A tight linear correlation between measured δ^{30}Si values and a secondary-beam centring parameter (DTCA-X value) was observed so the external repeatability and accuracy could be improved by correcting for this parameter. An external precision of ±0.10‰ (2SD) was considered achievable by using high primary-beam intensities (10-14 nA), a long acquisition time (160 s), sample mounts prepared as flat as possible and a correction based on the DTCA-X parameter. Villeneuve *et al.*[301] measured Si isotopes in a set of 23 natural and synthetic olivine RMs and three natural low-Ca pyroxene RMs by SIMS using two quartz RMs as QCs. All results were normalised to data for NIST SRM 8546 (quartz). The Si ion yields and IMFs varied with the analytical settings and chemical composition of the samples. The magnitude of the IMF in olivine varied in a complex manner resulting from variations in MgO and FeO content so a comprehensive set of RMs was required to avoid inappropriate corrections. In contrast, ion yields and IMFs in low-Ca pyroxenes showed limited variations and were thus more predictable. Matrix effects in the determination of Mg isotopes in olivines and pyroxenes by SIMS were quantified[302] by analysing 17 olivine and 5 pyroxene RMs by MC-ICP-MS and MC-SIMS. For olivines, the magnitude of the SIMS instrumental mass bias in δ^{25}Mg was *ca.* 3.3‰ and was a complex function of the fosterite contents which ranged from 59.3 to 100%. A correction procedure based on a combination of Mg/Si ratios and fosterite content was proposed. On the other hand, the pyroxene RMs showed a smaller range of instrumental bias (*ca.* 1.4‰ in

δ^{25}Mg) but no smooth function with enstatite content (48.6-96.3%), indicating that additional factors such as minor element abundances may contribute to the matrix effects. Vho *et al.*[303] assessed the matrix effects on SIMS O isotope measurements in garnet which appeared to be correlated to the relative proportions of the grossular, andradite and spessartine components present. To supplement the available RMs, three new garnet RMs were characterised (GRS2, GRS-JH2 and CAP02) that had grossular contents of 88.3±1.2% (2SD), 83.3±0.8% and 32.5±3.0%, respectively. Micro-scale homogeneity in O isotope composition was established from multiple SIMS and reference δ^{18}O values obtained by CO_2 laser fluorination. A SIMS protocol for *in situ* B isotopic microanalysis of basaltic glass was developed[304] with the aim of identifying different degrees of alteration of basalt glasses during magma generation and evolution in the mantle. The USGS RM BCR-2G (basalt) was chosen as the calibration material as its B content and matrix composition were well matched to those of natural basalt glasses. Its δ^{11}B value of -5.44 ± 0.55‰ (2SD) was determined by solution MC-ICP-MS and the performance of the proposed method evaluated by the analysis of other USGS and MPI-DING glasses, for which the results were consistent with those obtained by other methods. For the natural glasses, distinct δ^{11}B values were obtained along profiles from the grain core towards the rim.

Xia *et al.*[305] investigated a suite of zircon RMs for their suitability for *water content determinations in zircon by SIMS* and described a modified analytical procedure to acquire data on the zircon water content and O isotopes simultaneously. Features of the method included mounting the samples in a tin-based alloy to reduce degassing and the introduction of liquid N_2 to cool the analysis chamber and improve the vacuum, thereby limiting the atmospheric water vapour background to <10 ppm. While $^{16}O^-$ and $^{18}O^-$ ions were collected in FCs, $^{16}O^1H^-$ was measured simultaneously with an EM. The $^{16}O^1H^-/^{16}O^-$ ratio was converted into water content using a calibration based on FTIR water content determinations. The reproducibility of the water content determination for the suite of zircon RMs was <5% (2SD) except for zircon 91500 for which it was 7.84% (2SD). Taking into account the large variation of water content in natural zircons (<55 to 1,212 µg g^{-1}) it was considered that the homogeneity of these zircon RMs was acceptable. A set of five natural white mica RMs was developed[306] for *in situ* measurements of water content by SIMS. The water content of the RMs was obtained independently by thermal combustion elemental analysis. It was suggested that a matrix effect which correlated with the FeO content (1.13 to 3.67 wt.%) of the RMs should be corrected by including at least two RMs with FeO contents that bracket those of the unknown white micas. It was argued that an analytical precision of 0.02-0.08% (1 RSD) was expected as the final uncertainty on measurements of water content in unknown white micas.

5.4.5 Other mass spectrometric techniques

Atom probe tomography (APT) is a TOF-MS technique capable of 3D nanoscale chemical mapping of individual atoms. An excellent review (257 references) described[307] its development and application to the geosciences. A significant advantage of APT was its ability to provide quantitative, 3D images of all elements with sub-nm spatial resolution without the need to specify in advance which isotopic peaks to quantify. Because APT involves the detailed analysis of a very small volume of material, typically <0.002 µm^3, the importance of characterising samples using other analytical techniques prior to APT was stressed. Since the development of laser-assisted APT around 2005, the technique has been applied to a broad range of geological materials, including the nanoscale analysis of accessory minerals, and has provided new insights into the processes by which trace elements may become mobile in geological systems.

A practical guide (50 references) on the *double spike technique* for correcting mass-dependent fractionation in isotope ratio measurements was written[308] particularly for researchers tackling new isotopic systems. The measurement of Ca isotopes by TIMS was used as an example of how to achieve high quality results. Emphasis was placed on points to consider when selecting the optimal pair of isotopes for the spike and the importance of accurate calibration of the spike pair. The technique's advantages and limitations were discussed.

A study of the determination of the stable isotope composition of C in carbonates by *isotope ratio mass spectrometry* compared[309] three different approaches: dual inlet (DI); elemental analyser (EA); and continuous flow (CF). All methods were considered to be suitable for the determination of $^{13}C/^{12}C$ but DI-IRMS offered the most precise, accurate and sensitive instrumentation for this purpose. Extensive off-line sample preparation was, however, required. The EA-IRMS approach provided rapid and cost-effective determinations that may be sufficiently precise to distinguish natural trends in some applications requiring high sample throughput. In contrast, CF-IRMS yielded more precise and accurate results but was considered to be very time-consuming and equally expensive as DI-IRMS. Velivetskaya *et al.*[310] developed an improved LA fluorination method for the GC-IRMS measurement of S isotopic anomalies in sulfides. The new gas purification system was based on temperature-controlled flow traps for the cryogenic separation of SF_6 gas from other fluorinated products. The new method was tested with IAEA RMs and a natural pyrite with known isotope composition. Overall precisions of ±0.2‰ for $\delta^{34}S$, ±0.27‰ for $\Delta^{36}S$ and ±0.03‰ for $\Delta^{33}S$ were obtained when the optimal amount of 12–13 nmol SF_6 was generated. These were significant improvements over results obtained using a previous purification system. The revised protocol was therefore considered suitable for measuring $\Delta^{33}S$ and $\Delta^{36}S$ in Archean sulfides.

New procedures were reported [311] for the extraction of Ne from different mineral phases (quartz, pyroxene, hematite, apatite, zircon, topaz, and fluorite) and measurement on a static vacuum *noble gas mass spectrometer*. Neon was extracted at 1100 °C by lithium-borate-flux fusion under vacuum and purified by a cryogenic method capable of separating Ne from He. The noble gas mass spectrometer was operated at its highest mass resolving power of *ca.* 10,300 thereby permitting isobar-free measurement of all three Ne isotopes, albeit at reduced sensitivity. Cosmogenic ^{21}Ne and ^{22}Ne concentrations obtained for two internationally distributed Antarctic RMs, Cronus-A quartz and Cronus-P pyroxene, were in excellent agreement with previously obtained results. The same was true for nucleogenic ^{21}Ne and ^{22}Ne concentrations in two other RMs. However, as had been found for He, U and Th concentrations in previous studies, the Durango apatite was heterogeneous in Ne concentrations.

A new high-performance laser ablation and ionisation mass spectrometer for the analysis of solid samples was based**[312]** on a fs LA ion source coupled to a TOF mass spectrometer, thus combining high mass and high spatial resolving powers in one instrument. With a mass resolution of 10,000, the instrument was capable of separating isobaric interferences from clusters, molecules and multiple charged ions, thereby significantly improving quantitative analysis of complex samples. The analysis of various NIST SRMs demonstrated LODs in the ppm range and quantitative isotopic analysis with accuracies at the per mil level. Advantages of the technique included acquisition of spectra over the full mass range in a fraction of a second and with minimal sample preparation.

5.4.6 X-ray spectrometry and related techniques

A novel method of *pellet preparation for the analysis of geochemical samples by WDXRFS* involved**[206]** weighing powdered samples (without any binder) into a polyethylene cup which was covered with a 3.6 µm thick polyester film before pressing at high pressure (2,000 kN). The polyester film prevented changes in the Cl content after multiple analyses of the same pellet and reduced contamination from external sources such as dust. The film was not damaged by exposure to irradiation from a 4 kW X-ray tube for 180 minutes. Sixty-two rock, soil and sediment RMs were used to create the calibration curves and the method was evaluated by analysis of another 8 IGGE CRMs for major and trace elements. The relative differences between the results obtained and the certified values were <10% for major elements and <25% for trace elements except for those elements with concentrations close to the LODs. This method of preparation was particularly suitable for samples with high chorine and sulfur contents to enable repeat analysis and preservation for future use.

Several calibration strategies for the *determination of element concentrations in carbonate matrices by portable XRFS* were proposed. Arena-Islas *et al.*[313] prepared 11 gravimetric mixtures of NRCC CRM PACS-3 (marine sediment) with reagent grade $CaCO_3$ in different proportions to act as calibration standards for the analysis of carbonate sediments. The $CaCO_3$ reagent and 11 mixtures were also analysed by FAAS and ETAAS after total digestion to check their trace metal contents. Of the 31 elements detected in the solid mixtures, only 20 exhibited significant linear regressions ($p < 0.001$). This calibration technique was cost-effective because only one RM was required. It was concluded that reliable determinations of Al, As, Ca, Cu, Fe, Hg, Mn, Mo, P, Pb, S, Si, Sr, Ti, Zn, K, V, Rb, Y and Zr concentrations in carbonate sediments could be made and that the method could be adapted for other mineral matrices. In a different approach for analysing carbonate rocks (limestones and dolomites), Al-Musawi *et al.*[314] used a pXRFS instrument which was calibrated using a set of 43 carbonate samples previously analysed by WDXRFS, ICP-MS and ICP-AES. This carbonate-specific calibration yielded more accurate results than the procedure provided by the instrument manufacturer and developed for siliciclastic mudrocks. The concentrations of 13 elements (Al, As, Ca, Cu, Fe, K, Mg, Mn, P, Rb, Si, Sr, Ti, Y and Zr) could be accurately quantified as long as the unknown samples were prepared using the same protocol as the calibration materials to minimise any matrix effects.

Core scanning XRFS is a well-established technique for rapid semi-quantitative analysis of sediment cores at sub-mm resolution. A valuable review (89 references) of current perspectives on the capabilities of high resolution XRF core scanners was published**[315]** as the editorial in a special issue of *Quaternary International* dedicated to advances in data quantification and applications of this technique. The review summarised the historical evolution of high resolution XRF scanners, approaches to calibration and validation and gave examples of applications related to environmental, sedimentological and seismological studies as well as mineral exploration and forensic geochemistry. Several existing calibration methodologies were assessed**[316]** in a study in which 100 freshwater sediment samples were analysed by core scanning XRFS and ICP-MS to determine which method gave data with the best accuracy and precision and was most cost-effective. Although calibration using multivariate analysis of elemental log-ratios provided the most accurate results relative to the ICP-MS data, this strategy was considered most appropriate for studies involving large numbers of sediment samples ($n > 100$) or when it was crucial to obtain absolute concentrations. Otherwise, either normalising core scanning XRFS data to the X-ray scatter signal or converting the results to dry mass concentrations were regarded as suitable strategies for studies for which absolute geochemical values were less important.

Synchrotron X-ray techniques are increasingly used to study processes at a molecular level, particularly with the advent of ultrahigh-brilliance fourth-generation synchrotron-light-sources. A review (221 references) of the application to studies of ore deposits of various synchrotron X-ray techniques emphasised**[317]** their importance as tools to study trace element distributions at μm and smaller scales, the structure and chemistry of poorly-crystalline ore materials and the chemical nature of the fluids that give rise to ore formation. In an assessment of the accuracy of synchrotron XRFS, quantitative elemental maps of pyrite samples were compared**[318]** to those obtained by LA-ICP-MS and EPMA. A well-characterised, highly homogeneous pyrite sample

(CX-15) was employed as the RM for quantification. The accuracy and reliability of the synchrotron-XRFS data were strongly dependent on careful data processing. An overall positive correlation with datasets produced by EPMA and LA-ICP-MS was demonstrated with any differences being attributed to the heterogeneous nature of some of the pyrite grains and the different spot sizes employed. It was concluded that synchrotron XRFS offered complementary capabilities to those of EPMA and LA-ICP-MS. The rapid acquisition of quantitative elemental distributions over a wide range of concentrations enabled large areas (tens of mm to tens of cm) to be studied, something that could not be achieved by either EPMA or LA-ICPMS independently.

6. Glossary of abbreviations

2D	two dimensional
3D	three dimensional
AAS	atomic absorption spectrometry
ACGIH	American Conference of Governmental Industrial Hygienists
AEC	anion exchange chromatography
AES	atomic emission spectrometry
AF	atomic fluorescence
AFS	atomic fluorescence spectrometry
AMS	accelerator mass spectrometry
ANN	artificial neural networks
APDC	ammonium pyrrolidine dithiocarbamate
APGD	atmospheric pressure glow discharge
ASU	Atomic Spectrometry Update
BARGE	Bioaccessibility Research Group of Europe

APT	atom probe tomography
BAS	Bureau of Analysed Samples
BCR	Community Bureau of Reference (of the Commission of the European Communities)
BMEMC	Beijing Municipal Environmental Protection Monitoring Center
BPNN	back-propagation neural network
CA	Chemical abrasion
CABM	Canadian Aerosol Baseline Measurement
CAPMoN	Canadian Air and Precipitation Monitoring Network
CAS	Chemical Abstracts Service
CCP	capacitively coupled plasma
CCRM	Canadian Certified Reference Material
CE	cation exchange
CEC	cation exchange chromatography
CEN	European Committee for Standardisation
CF	continuous flow
CFA	continuous flow analysis
CI	confidence interval
CNT	carbon nanotube
CPE	cloud point extraction
cps	counts per second
CRM	certified reference material
CRPG	Centre de Recherches Pétrographiques et Géochimiques (France)
CS	continuum source
CT	computer tomography
CVG	cold vapour generation

DA	discriminant analysis
DBD	dielectric barrier detector
DDTC	diethyldithiocarbamate
dDIHEN	demountable direct injection high efficiency nebuliser
DDTP	diethyldithiophosphoric acid
DES	deep eutectic solvent
DGT	diffusive gradients in thin films
DI	dual inlet
DLS	dynamic light scattering
DLLME	dispersive liquid liquid microextraction
DMA	dimethylarsonic acid
DPM	diesel particulate matter
DTPA	diethylenetriamine pentaacetate
EA	elemental analyser
EC	elemental carbon
EDS	energy dispersive (X-ray) spectrometry
EDTA	ethylenediaminetetraacetic acid
EDXRFS	energy dispersive X-ray fluorescence spectrometry
EM	electron multiplier
EMPIR	European Metrology Programme for Innovation and Research
EPMA	electron probe microanalysis
ERM	European reference material
ESI	electrospray ionisation
ETAAS	electrothermal atomic absorption spectrometry
EtHg	ethylmercury

ETV	electrothermal vaporisation
EU	European Union
FAAS	flame atomic absorption spectrometry
FC	Faraday cup
FFF	field flow fractionation
FIA	flow injection analysis
FTIR	Fourier transform infrared
GC	gas chromatography
GD	glow discharge
GF	graphite furnace
GLM	generalised linear model
GO	graphene oxide
GSBZ	Institute for Environmental Reference Materials, Ministry of Environmental Protection of China, Beijing, China
GSJ	Geological Survey of Japan
HEN	high efficiency nebuliser
HFSE	high field strength element
HG	hydride generation
HPLC	high performance liquid chromatography
HPS	High Purity Standards (USA)
HR	high resolution
IAEA	International Atomic Energy Authority
IAG	International Association of Geoanalysts
IC	ion chromatography
ICP	inductively coupled plasma
ID	isotope dilution

IEC	International Electrotechnical Commission
IGGE	Institute of Geophysical and Geochemical Exploration, China
IL	ionic liquid
IMF	instrumental mass fractionation
IMPROVE	Interagency Monitoring of Protected Visual Environments
INCT	Institute of Nuclear Chemistry and Technology (Poland)
IRMM	Institute for Reference Materials and Measurements
IRMS	isotope ratio mass spectrometry
IS	internal standard
ISE	ion selective electrode
ISO	International Organisation for Standardization
JMC	Johnson Matthey Corporation
KED	kinetic energy discrimination
LA	laser ablation
LC	liquid chromatography
LDA	linear discriminant analysis
LEAF	laser excited atomic fluorescence
LIBS	laser induced breakdown spectroscopy
LIF	laser-induced fluorescence
LLME	liquid liquid microextraction
LOD	limit of detection
LOQ	limit of quantification
LREE	light rare earth element
LS	least squares
MAD	microwave-assisted digestion

MAE	microwave-assisted extraction
MALDI	matrix-assisted laser desorption and ionisation
MC	multicollector
MDL	method detection limit
MeHg	methylmercury
MIP	microwave-induced plasma
MIR	mid infrared
MMA	monomethylarsonic acid
MPI-DING	Max Planck Institute
MS	mass spectrometry
MS/MS	tandem mass spectrometry
MTZ	Mud Tank zircon
MU	measurement uncertainty
MWCNT	multiwalled carbon nanotube
m/z	mass to charge ratio
NACIS	National Analysis Centre for Iron and Steel
NCS	NCS Testing Co., Ltd. (China)
NDIR	non dispersive infra red
NIES	National Institute for Environmental Studies
NIOSH	National Institute of Occupational Safety and Health
NIST	National Institute of Standards and Technology
NMIA	National Measurement Institute of Australia
NP	nanoparticle
NRCC	National Research Council of Canada
NRCGA	National Research Centre for Geoanalysis (China)
NTIMS	negative thermal ionisation mass spectrometry

NWRI	National Water Research Institute
OC	organic carbon
PCA	principal component analysis
PDO	protected designation of origin
PFA	perfluoroalkoxy alkane
PGE	platinum group element
PIXE	particle-induced X-ray emission
PLS	partial least squares
PLSR	partial least square regression
$PM_{0.1}$	particulate matter (with an aerodynamic diameter of up to 0.1 μm)
$PM_{0.5}$	particulate matter (with an aerodynamic diameter of up to 0.5 μm)
PM_{1}	particulate matter (with an aerodynamic diameter of up to 1.0 μm)
$PM_{2.5}$	particulate matter (with an aerodynamic diameter of up to 2.5 μm)
PM_{10}	particulate matter (with an aerodynamic diameter of up to 10 μm)
PTE	potentially toxic element
PTFE	polytetrafluoroethylene
PVG	photochemical vapour generation
pXRFS	portable X-ray fluorescence spectrometry
QC	quality control
RCC	rotating coiled column
RCS	respirable crystalline silica
REE	rare earth element
REP	relative error of prediction
RM	reference material
RMSE	root mean square error
RNA	ribonucleic acid

RPD	relative percentage difference
RSD	relative standard deviation
RSF	relative sensitivity factor
SARM	Service d’Analyses des Roches et des Minéraux (France)
SAX	strong anion exchange
SD	standard deviation
SEC	size exclusion chromatography
SEM	scanning electron microscopy
SF	sector field
SFODME	solidified floating organic drop microextraction
SHRIMP	sensitive high resolution ion microprobe
SI	Système International (d'unités)
SIMS	secondary ion mass spectrometry
S/N	signal to noise ratio
SOM	soil organic matter
sp	single particle
SPE	solid-phase extraction
SPME	solid-phase microextraction
SQT	slotted quartz tube
SRM	standard reference material
SS	solid sampling
SSB	sample standard bracketing
SVM	support vector machine
SVR	support vector regression
TC	total carbon
TD	thermal desorption

TEM	transmission electron microscopy
TLC	thin layer chromatography
TIMS	thermal ionisation mass spectrometry
TOF	time-of-flight
TXRF	total reflection X-ray fluorescence
TXRFS	total reflection X-ray fluorescence spectrometry
UA	ultrasound-assisted
UBM	unified bioaccessibility method
UNC	University of North Carolina
US EPA	United States Environmental Protection Agency
USGS	United States Geological Survey
UV	ultraviolet
VAME	vortex-assisted microextraction
VIS-NIR	visible near infrared
VPDB	Vienna Pee Bee Belemnite
WDXRFS	wavelength dispersive X-ray fluorescence spectrometry
XAFS	X-ray absorption fine structure
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectroscopy
XFM	X-ray fluorescence microscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
XRFS	X-ray fluorescence spectrometry
Z	atomic number

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

Analytes	Matrix	Substrate	Coating or modifier	Detector	LOD in µg L^{-1} (unless stated otherwise)	Validation	Reference
Al^{III}, Co^{II} Cr^{III}, Cu^{II}, Fe^{III}, Mn^{II}, Ni^{II}, Pb^{II}, Zn^{II}	Water	0.1 – 0.2 mm particle size silica gel	Linear polyhexamethylene guanidinium and 1-nitroso-2-naphthol-3,6-disulfonic acid or 2-nitroso-1-naphthol-4-sulfonic acid	ICP-AES	0.75 (Cu) to 1.35 (Al)	Sample spike recovery	319
Ag^{I}, Cd^{II}, Co^{II}, Cr^{III}, Cu^{II}, Ni^{II}, Pb^{II}	Environmental water samples	Fe_3O_4-GO NPs	SiO_2	ICP-MS	2 (Co) to 14 (Ag) ng L^{-1}	Sample spike recovery and CRM GSBZ 50009–88 (environmental water)	320
Ag, Cd, Cr, Cu Pb	River water	Gold NPs	DDTC	LIBS	1.5 (Cu) to 4.5 (Cd)	Spike recovery and comparison with ICP-AES results	321
As^{III}	Ground, river, waste and drinking water	Carbon sheets	$MnFe_2O_4$ NPs	ICP-AES	0.03	Spike recovery and NIST SRM 2669 (frozen human urine)	322
As^{V}	River water	MWCNTs	Branched polyethyleneimine	ICP-MS	0.05	Spike recovery and comparison with HPLC-ICP-	323

						MS results	
Ba, Cd, Co, Cu, Mn, Ni	Lake and natural water samples	Silica gel	N,N'-bis(4-methoxysalicylidene)-1,3-propanediamine	ICP-AES	0.19 (Ni) to 0.36 (Cu)	NWRI CRM TMDA-53.3 (fortified Water) and IRMM ERM-CA022a (soft drinking water)	324
Cd	Petroleum production waters	Low-density polyethylene semipermeable membrane	DDTC complexes in solution	ETAAS	0.08	NMIA CRM MX014 (acidified coastal seawater)	325
Cd^{II}, Co^{II}, Cr^{III}, Cu^{II}, Fe^{III}, Mn^{II}, Ni^{II}, Pb^{II}	River water	SiO_2	Ta_2O_5	FAAS	5.3 (Cd) to 56.0 (Cu)	Spike recovery	326
Cd^{II}, Co^{II}, Pb^{II}, Pd^{II}	Well water, wastewater, soil	MWCNTs	Glutaric dihydrazide	FAAS	0.12 (Pb) to 0.19 (Cd)	Spike recovery	327
Cd, Cu, Pb plus carbamate and triazole pesticides	Water	In pipette tip polymer-based monoliths from allylthiourea and 1-allyl 3-methylimidazole difluoromethanesulfonylamide salt	-	ETAAS	0.13 (Cd) to 1.1 (Pb) ng L^{-1}	Spike recovery and comparison with ICP-MS results	328
Cr^{III}, Cu^{II} Pb^{II}, Zn^{II}	Lake, river, spring and mineral water as well as seawater	GO	Modified by reaction between *in situ* mixed phosphoric–carboxylic anhydrides and Na_2S with the	EDXRFS	0.06 (Cu) to 0.10 (Cr)	Spike recovery and NIST SRM 1640a (natural water)	329

			graphene oxide surface.				
Cr^{III}, Sb^{III}	Environmental waters	Carboxyl-functionalized organic-inorganic hybrid monolithic column	-	ICP-MS	0.004 (Cr^{III}) and 0.002 (Sb^{III})	Spike recovery	330
Dissolved Cu fraction	Seawater	Polypropylene Accurel® PP S6/2 hollow fibres	Di-2-pyridylketone benzoylhydrazone	ETAAS	0.62 nmol L^{-1}	IRMM CRM BCR-403 (Seawater (trace elements))	331
Hf, Nb, Ta, Zr	Seawater	NOBIAS® Chelate-PA 1	-	ICP-SF-MS	0.0008 (Ta) to 0.9 (Zr) pmol kg^{-1}	Spike recovery and NRCC CRMs CASS-5 and 6 (near shore seawater), and NASS 5 and 6 (seawater)	332
Hg	Lake and river water	Selective laser sintering 3D printing with a mixture of polyamide-12 powder with thiol-functionalized silica	-	ICP-MS	0.037 ng L^{-1}	Spike recovery	333
Hg	Seawater and river water	Quartz glass dip sticks coated with 3-aminopropyltrimethoxysilane and 300 nm diameter	Gold NPs	Thermal desorption AFS	0.18 ng L^{-1}	Spike recovery and IRMM CRM ERM-CA400 (Seawater (Hg))	334

		SiO$_2$ particles					
Hg, MeHg	Tap and river waters	Fe$_3$O$_4$ NPs	Nanocellulose	GC-pyro-AFS	5.6 pg mL^{-1} (Hg) and 4.0 (MeHg) pg mL^{-1}	Spike recovery	335
Hg, MeHg, EtHg	Tap and river waters	Silica particles	GO	HPLC-ICP-MS	5 (Hg^{2+}) to 9 (EtHg) pg L^{-1}	Spike recovery	336
Nd/Th ratio	Seawater	Nobias® Chelate-PA1	-	ICP-SF-MS	Blank reported as <10 pg of ^{232}Th for 10 L of sample	Internal RM BATS2000A	337
Pd	Environmental water	Mesoporous silica	3-Mercaptopropyltrimethoxysilane	ETAAS and ICP-MS/MS	0.06 (ETAAS) or 0.2 ng L^{-1} (ICP-MS/MS)	Spike recovery	338
Pd, Pt, Rh	Natural waters	DGT samplers	Comparison between Purolite® S914, S920 and S985 resins	ICP-MS	MDL (14 day deployment) 0.007 (Pt) to 0.153 (Pd) ng L^{-1}	Spike recovery	339
Se^{IV}, Te^{IV}	Environmental water	SiO$_2$-coated Fe$_3$O$_4$ NPs	Polyaniline	ICP-MS	1.2 (Te) and 5.3 (Se) ng L^{-1}	RM GBW(E)080548 (Te in water) and CRM GSBZ 50029-94 (environmental water)	340
Tl^{I} and Tl^{III}	River water	AG1-X8 SAX resin	DTPA (to complex Tl^{III})	ICP-MS	LOD not reported lowest sample concentrations reported 0.01 (Tl^{I}) and	Spike recovery	341

					0.22 (Tl^{III})		
U	Water and seawater	GO	-	TXRFS	0.04	Spike recovery	342

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

Analytes	Matrix	Method	Reagents	Detector	LOD in µg L^{-1}	Method validation	Reference
Cd	Ground water	DLLME	APDC and the DES $ZnCl_2$: CH_3CONH_2	FAAS	0.046	Spike recovery and NIST SRM 1643e (trace elements in water)	343
Cd, Co, Ni, Pb	High salinity oilfield production water	DLLME	DDTC, CH_3OH and CCl_4	ICP-AES	0.003 (Co) to 0.15 (Pb)	Comparison with ICP-MS results and NRCC CRM NASS-5 (seawater)	344
Cd, Pb	Ground and treated waters; hair	DLLME	L-Cysteine (2-amino-3-sulfhydrylpropanoic acid), 1-butyl-3-methylimidazolium hexafluorophosphate and hexafluorophosphate	FAAS	0.05 (Pb) and 0.13 (Cd)	NIST SRM 1643e (trace elements in water) and IRMM CRM BCR 397 (trace elements in human hair)	345
Cd, Zn	Water and fruit juice	Air-assisted LLME	Sorbitol, menthol and mandelic acid	FAAS	0.12 (Zn) and 0.15 (Cd)	RM SPS-WW2 Batch 108 (wastewater)	346
Cr	Water	LLME	Thiomalic acid and ferric chloride in ethylene glycol medium	FAAS	1.18	NWRI CRM TMDA-53.3 (fortified water)	347
In	Lake water	In syringe LLME	DDTC, chloroform	SQT-FAAS	19.2	Spike recovery and check against ICP-AES results	348

Ni	Water, food and tobacco	DLLME	1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate and quinalizarin	FAAS	0.6	NWRI CRM TMDA-51.3 and TMDA-53.3 (fortified water)	349
Pd, Pt	Tap, fresh, and saline waters	CPE	Triton X-114, 2-mercaptobenzothiazole and $SnCl_2$	ICP-AES	0.53 (Pd) and 0.75 (Pt)	Spike recovery	350
Ti, TiO_2 NPs	Water and swimming pool water	CPE	Triton X-114 and NaCl	ICP-MS	0.13	Spike recovery	351

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

Analyte(s)	Sample matrix	Method	Reagent(s)	Detector	LOD (µg L^{-1}, unless otherwise stated)	RMs or other validation	Reference
As^{III}, As^{V}	Carrot, coriander, radish spinach, and soil	VAME	Deep eutectic solvent based on choline chloride and citric acid, DDTP chelating agent	ETAAS	0.1	BMEMC CRMs GBW10014 (cabbage) and GBW10015 (spinach); spike recovery	352
As, Cd, Hg, Pb, Se, V	Fish, forage grass, peach leaves, liver	ultrasound-assisted extraction, MAE	Deep eutectic solvents based on citric acid, malic acid, and xylitol	ICP-MS	0.002-8.1 µg kg^{-1}	NIST SRM 1547 (peach leaves); NRCC CRM DORM-3 (fish protein)	353
Au	Soil, water	LLME	N-methyl-N,N,N-trioctylammonium chloride ion-pair forming agent, 1-octanol extraction solvent	FAAS	0.6	CRM-SA-C (sandy soil C)	354
Cd	Dust, seawater, soil, spring water, tap water, wastewater	Co-microprecipitation/flotation	KI complexation, cetyltrimethylammonium bromide/sodium perchlorate neutralisation	FAAS	0.18	Spike recovery	355
Cd, Cu, Mn, Ni	Water	Coprecipitation	Co(OH)$_2$	FAAS	0.07 for Cd, 0.2 for Cu, 0.3 for Mn, 0.2 for Ni	NIES CRMs No.1 (pepperbush) and No. 7 (tea leaves)	356
Co, Cu, Ni	Fish, oyster	SFODME	1-(2-thiazolylazo)-2-naphthol complexing agent, 1-undecanol extraction solvent	FAAS	0.03 – 0.04 mg kg^{1}	NIST SRMs 1573a (tomato leaves) and 1577 (bovine liver)	357
Cr^{III}, Cr^{VI}	Wild leafy vegetables	Tunable solvent system–DLLME	8-Hydroxyquinoline and APDC complexing agents,	ETAAS	0.048 for Cr^{III} 0.072 for	Spike recovery from an aqueous soup of *Digera arvensis*	358

			1,8-Diazabicyclo[5.4.0]undec-7-ene and decanol tunable solvent solution		Cr^{VI}		
Mo	Beef, grass	DLLME	Potassium ethyl xanthate chelating agent, acetonitrile dispersive solvent, carbon tetrachloride extraction solvent	ETAAS	0.03 µg kg^{-1}	NIST SRMs 1573a (tomato leaves) and 1577c (bovine liver)	359
Ni	Cabbage, potato, spinach, tobacco tomato, water	UA-IL-DLLME	Quinalizarin complexing agent, 1-hexyl-3-methylimidazolium tris-(pentafluoroethyl)trifluorophosphate solvent	FAAS	0.6	NWRI CRMs TMDA 51.3 (fortified water) and 53.3 (fortified water); NIST SRM 1570a (spinach leaves)	349
V	Apple, banana, mushroom, tomato, spinach, water	LLME	Deep eutectic solvent based on zinc chloride and acetamide, Triton X-114 non-ionic surfactant, ammonium pyrrolidine complexing agent	ETAAS	0.01	NWRI CRM TMDA-53.3 (Canadian lake water); NIST SRM 1573a (tomato leaves)	360
Te	Sediments, soils, water	IL-CPE	1-Octyl-3-methylimidazolium chloride and Triton X-114. APDC complexing agent	ETAAS	1.1 ng L^{-1} for Te^{IV} 1.7 ng L^{-1} for Te^{VI}	Spike recovery	361

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

Analyte(s)	Matrix	Substrate	Substrate coating	Detector	LOD ($\mu g\ L^{-1}$)	RMs or other validation	Reference
Cd, Co, Pb, Pd	Soil, water	MWCNTs	Glutaric dihydrazide	FAAS	0.12-0.19	NIST SRMs 2556 (used catalyst pellets) and 1570a (spinach leaves)	327
Co	Soil	Zirconium NPs		SQT-FAAS	2.2	Spike recovery	362
Co	Apple and orange juices, black tea, rice, saliva, urine, water, wheat	Magnetic graphene oxide		ETAAS	0.023	HPS RM TMDW (drinking water) and NIST SRM 1570a (spinach leaves)	363
Pb	Cigarette samples	Silica-coated magnetic nanodiamonds		FAAS	40.8	NACIS CRM NCSDC 73349 (bush branches and leaves)	364
Pd	Soil	Magnetic NPs		SQT-FAAS	6.4	Spike recovery	365
Te^{IV}, Te^{VI}	Sediment, soil, water	Ionic liquid nanocomposite based on Fe_3O_4@ SiO_2@NH_2 magnetic NPs		HG-AFS	1.9 ng L^{-1} for Te^{IV} 3.7 ng L^{-1} for Te^{VI}	Spike recovery	361
U	Rock, water	MWCNTs/ Cu_2O-CuO hybrid material		ICP-MS	0.52	NWRI CRMs TMDA-62.2 and TMDA-70.2 (water); BMEMC CRM GBW 07423 (soil)	366

Analyte	Matrix	Sample treatment	Technique	Analysis and figures of merit	Ref

Table 5. Methods used in the determination of isotope ratios in geological materials by solution ICP-MS and TIMS

Ag	Natural and processed gold	Dissolution of mg-sized gold samples in *aqua regia* and Au removed by AEC on AG1-X8 resin. Solutions doped with NIST SRM 3138 (Pd solution) to generate Pd/Ag ratios close to 1.9 (^{108}Pd/^{107}Ag *ca.* 1).	MC-ICP-MS	Combination of SSB method and Pd-doping for mass bias correction using the exponential law. δ^{109}Ag values expressed relative to bracketing NIST SRM 987a (Ag solution). Combined analytical uncertainty (2SD) was better than 0.016‰.	367
B	Boron RMs, loess, sediment	Fine-grained loess and sediment subjected to chemical leaching with acetic acid and B separated by ion chromatography using Amberlite IRA 743 resin. Procedural blank 0.25±0.03 ng and average recovery 99.1% B.	MC-ICP-MS	Different rinse solutions tested to minimise B memory effects; 0.6 mg g^{-1} NaF in 1% HNO_3 reduced B signals to blank levels within 4 minutes SSB method for instrumental drift and mass bias correction. Long-term reproducibility for NIST SRM 951a (B isotopes) was 0.01±0.06 ‰ (2SD, n = 27).	82
Ba	Barite RMs	Investigation of the effect of sample dissolution using the Na_2CO_3 reaction method on Ba isotope measurements. Ba purified by ion-exchange chromatography on AG50W-X12 resin; Ba yield >99%. A ^{135}Ba-^{136}Ba double spike was added to sample solutions prior to analysis.	MC-ICP-MS	^{131}Xe, ^{134}Ba, ^{135}Ba, ^{136}Ba, ^{137}Ba, and ^{140}Ce collected simultaneously. SSB and double spike used to correct for instrumental drift and mass bias. Ba isotope data reported relative to NIST SRM3104a (Ba isotopes), long-term external precision of δ^{137}Ba/^{134}Ba <0.05‰ (2SD).	368
Ca	Ca-rich minerals and geological RMs	Study to see if accurate Ca isotope ratios can be achieved by TIMS using ^{42}Ca-^{43}Ca double spike technique without column chemistry. All samples dissolved in 1.6 mol l^{-1} HCl. Two aliquots taken and mixed with ^{42}Ca-^{43}Ca double spike: one was measured directly and the other loaded onto Biorad AG MP50 resin to perform column chemistry.	TIMS	Samples were loaded on a single Ta filament and H_3PO_4 was added as activator. Monitored masses included ^{40}Ca, ^{41}K, ^{42}Ca, ^{43}Ca and ^{44}Ca. Instrumental mass bias correction by the double-spike technique and reported relative to NIST SRM 915a ($CaCO_3$). Insignificant differences (-0.04 to +0.07‰) between with and without chemistry, smaller than the measurement precision of ±0.12‰ over 6 years (2SD, n = 515). Conclusion: bias-free Ca isotope ratios can be achieved on Ca-rich materials	369

				without chemical separation.	
Ca, Mg	Geological and biological RMs,	Digested materials in 4 M HNO_3 purified in two-step CEC method using DGA and AG50W-X12 resins to separate Ca and Mg. Ca and Mg re-dissolved in 2% (v/v) HNO_3, for isotope analysis by MC-ICP-MS.. Effect of acidity and concentration mismatch as well as matric effects evaluated for Ca isotope analysis.	MC-ICP-MS	SSB method applied. Ions collected at $^{42}Ca^+$, $^{43}Ca^+$, $^{87}Sr^{2+}$ and $^{44}Ca^+$; ratios reported relative to NIST SRM 915a ($CaCO_3$). ^{24}Mg, ^{25}Mg and ^{26}Mg measured and Mg isotopic ratios based on the DSM3 standard. Repeated measurements of USGS BHVO-2 (basalt) and NIST SRM 1400 (bone) was better than ±0.08‰ and ±0.06‰ (2SD), respectively, for $\delta^{44}Ca^{/42}Ca$. For $\delta^{26}Mg$, the external precision was <0.11‰ (2SD).	370
Cd	Soil and rock RMs, Mn nodule RM	Different digestion schemes adopted according to sample matrix. All digested samples in 6 mol L^{-1} for one-step anion-exchange separation on AG1-X8 resin. Procedure blank <75 pg. Molecular and isobaric interferences studied.	MC-ICP-MS	A ^{111}Cd–^{113}Cd double spike used for instrumental mass bias correction. Signals for 6 stable Cd isotopes collected plus ^{117}Sn, ^{120}Sn, ^{105}Pd and ^{115}In for isobaric corrections. All Cd ratios normalised to NIST SRM 3108 (Cd solution). Intermediate measurement precision of a Cd solution was better than ±0.05‰ (2SD) for $\delta^{114}Cd^{/110}Cd$. Data for 15 RMs reported.	102
Cd	Geological RMs, Mn nodule RMs	Following digestion, ^{111}Cd-^{113}Cd double spike added to the samples, before improved Cd purification scheme for low-Cd samples using polypropylene mini column with AGMP-1M resin. Recoveries ≥90%, with blanks of ≤0.1 ng.	MC-ICP-MS	Cd isotope measurements on FCs using three different MC-ICP-MS instruments and data expressed relative to NIST SRM 3108 (Cd solution). External precision <0.064‰ (2SD). Cd isotope data for various geological RMs consistent with previously published results.	371
Ce	Geological RMs, uranium ore samples	After sample digestion, Ce separated by modified two-stage chromatographic procedure The LREE fraction eluted from AG50W-X12 resin in the first stage still contained some Ba. During the second step, $KBrO_3$ oxidised Ce^{III} to Ce^{IV}, which was	TIMS	Newly-developed film porous ion emitter (Pt/Re alloy with a porous structure) enhanced ionisation of Ce^+ ions and use of TaF_5 as an activator significantly suppressed Ba^+ interference signal. Mass fractionation factor determined using the exponential law.	372

		retained on LN resin. Ce yield was about 78%; blank <60 pg Ce.		Reproducibility of $^{138}Ce/^{140}Ce$ better by a factor of *ca.* 10 compared to previously published Ce^+ results and comparable with that of the CeO^+ technique.	
Cr	Geological RMs	Digested sample mixed ^{50}Cr-^{54}Cr double spike and heated overnight at 130 °C to homogenise. Modified two-step separation procedure on AG50W-X12 resin, which was preferred to AG50W-X8, as it gave a better separation efficiency.	TIMS	Cr loaded onto Re single filaments and high purity silica gel and saturated H_3BO_3 added to the sample drops. Cr double spike used to correct for isotopic fractionation during column chemistry and TIMS measurement. $^{53}Cr/^{52}Cr$ ratios expressed relative to NIST SRM 979 (Cr isotope solution). Long-term measurement precision for BHVO-2 ≤0.031‰ (2SD).	373
Cr	Geological RMs	Sample digests containing 200-300 ng Cr spiked with ^{50}Cr-^{54}Cr double spike before 3-step ion-exchange scheme.	MC-ICP-MS	Sensitivity improved by ≥1.5 times by cooling waste gas trap bottle of desolvating nebulizer to 5 °C. Empirical method to correct for effect of Fe interference on $\delta^{53}Cr$. Precision on $\delta^{53}Cr$ measurements <0.06‰ (2SD); $\delta^{53}Cr$ values reported on 19 new RMs ranging from -0.44‰ to +0.49‰	239
Cu, Zn	Geological RMs	New separation and purification procedure involving a single pass, triple-stack column. This reduced volume of acids required by *ca.* 50%, thus shortening duration of separation and lowering blanks.	MC-ICP-MS	Cu and Zn external normalisation in addition to SSB to correct for instrumental bias. New method of inter-calibrating Cu and Zn isotope fractionation coefficients by measuring mixed Cu-Zn solutions with enhanced mass bias variation generated by varying the sample gas flow rate.	374
Er, Yb	Rock RMs	New column chemistry separation technique to separate heavy lanthanoids using an ultra-fine-grained LN resin (20-50 µm) and flash column chromatography,	TIMS	Ta and zone-refined Re tested as filaments. Er and Yb isotopes acquired separately by dynamic multi-collection and multi-static methods with a two-line cup setting to reduce	375

		which accelerated the elution speed by 10 times compared to gravity flow. Recovery yields *ca.* 100%.		FC deterioration. Mass fractionation corrected with exponential law.	
Eu	Rock RMs	Two-step CEC using AG50W X-8 resin. Complete separation of Eu from other REE (>99.99% purity)	MC-ICP-MS	External mass bias correction using ^{150}Sm-^{154}Sm double spike and exponential law to estimate ^{151}Eu/ ^{153}Eu ratio. Method applied to five geological RMs and commercial Eu reagents.	376
Ga	Geological RMs	Two column separation method using AG MP-1M and AG 50-X8 resins; recoveries >99% Ga, procedural blanks ≤0.1 ng Ga.	MC-ICP-MS	Instrumental mass bias corrected using combined SSB and internal normalisation. Interlaboratory discrepancies in δ^{71}Ga data for geological RMs resolved by normalisation to a single Ga isotope RM. Highlighted the need for an internationally-agreed δ zero RM.	232
Hf	Geological RMs	Method developed for samples with very low Lu and Hf contents (Hf <0.1 µg g^{-1}). ^{176}Lu-^{180}Hf enriched spike added before digestion, one-step chemical purification on Ln Spec resin. Hf recovery >90%.	MC-ICP-MS	Lu and Hf concentrations also determined. Corrections for mass bias using enriched spike and normalisation to ^{179}Hf/^{177}Hf = 0.7325 using the exponential law. All data reported relative to JMC 475 Hf standard solution.	377
Li	Coal (also rock and seawater RMs)	Two-step microwave-assisted digestion with HNO_3-HF-H_3BO_3, Li separation on AG 50W X-12 cationic resin, recovery >99.3%	MC-ICP-MS	Precision better than ±0.30‰. Values for coal RMs SARM18, SARM19 and SARM20 reported relative to NIST L-SVEC (Li_2CO_3 powder).	378
Li	Geological RMs	Modified separation procedure on AG 50W-X12 cation-exchange resin using a micro column (to remove Ca and REE) and a long column (to separate Li from Na) arranged in series, to reduce time and volume of acid required for purification.	MC-ICP-MS	Collected eluent introduced directly into the ICP without further processing. SSB method employed with NIST L-SVEC (Li_2CO_3 powder) as the standard. Long-term precision <±0.47‰. Experiments to find the best zone in the ICP for Li isotope measurements.	379
Li	Geological and seawater RMs	Modified two-step column purification on 50W-X8 resin to completely separate Na from Li in complex matrices	MC-ICP-MS	SSB method employed with IRMM-016 (Li_2CO_3 powder) as the standard. δ^7Li values for a range of geological RMs consistent with published values.	380

Li	Geological and seawater RMs	Dual column system for Li separation on AG50W-X8 designed for high matrix tolerance (Na/Li <100). Procedural blank <0.004 ng Li and final Na/Li ratio <1.	Q-ICP-MS	SSB method with IRMM-016 (Li_2CO_3 powder) as the standard. Li concentrations in samples and standards matched to within 5%. Long-term precision 1.1‰ (2SD). Quadrupole ICP-MS method with hot plasma tolerant of Na/Li in samples up to 100:1.	381
Li	Geological RMs	Automated one-column separation using robotic pipetting with HCl and 2 mL resin (AGW50-X12) volume. Aqua regia digestion step to destroy any organic matter released from resin.	MC-ICP-MS	SSB method with NIST L-SVEC (Li_2CO_3 powder) as the standard. δ^7Li values for a range of geological RMs consistent with published values and first reported values for NIST SRM 2709a (soil) and CRPG GS-N (granite).	233
Mg	Carbonate RMs	Method for carbonates avoiding column chromatography. H_sSO_4 added to generate a $CaSO_4$ precipitate and $MgSO_4$ supernatant, which was diluted for Mg isotope measurements.	MC-ICP-MS	Matrix effects evaluated and method validated by repeat measurements of GSJ RM JDo-1 (dolomite); δ^{26}Mg of JDo-1 was -2.32±0.11‰ (2SD, n=34), consistent with recommended value of -2.35±0.15‰. The Ca/Mg ratio in solution should be <0.5 for accurate Mg isotope ratios.	382
Mg	Geological RMs	Three-step separation protocol designed especially for high-K and low-Mg rocks: (i) K removed by precipitation; (ii) Fe and Ca separated using 2 mL of AG50W-X12 resin; (iii) Al, Fe, Na and Ti separated on 0.5 mL of AG50W-X12 resin.	MC-ICP-MS	SSB to correct for instrumental mass bias, and normalised to DSM3 international Mg isotope solution. Long-term reproducibility was ±0.06‰ (2s).	383
Mo	Geological RMs	Single column extraction protocol using TRU Spec resin; Mo absorbed on resin in 1.5 M HCl while interfering elements are poorly retained. Time for separation procedure approx. 4 h.	MC-ICP-MS	^{97}Mo-^{100}Mo double spike combined with SSB methodology with NIST SRM 3134 (Mo isotope solution) for mass bias correction. Long-term precision of δ^{98}Mo was 0.082‰ (2SD, n=334).	384
Mo, W	Geological RMs	Microwave-assisted heating for rapid decomposition of rocks and sediments. Mo	MC-ICP-MS	For mass bias correction and determination of concentrations, SSB and an external correction	385

		and W separated from sample matrix using chelating resin NOBIAS Chelate-PA1 and anion-exchange resin AG1-X8.		method using Ru for Mo and Fe for W was employed. Reproducibilities (2SD) were 0.10‰ for δ^{98}Mo and 0.05‰ for δ^{186}W. Data for 12 geological RMs presented.	
Nd	Depleted basic and ultra-basic rocks	3 column purification scheme: (i) 1.5 mL of TRU resin to extract REE, Th and U; (ii) 1 mL DGA resin to separate Nd from Sm; (iii) 1 mL of LN2 resin for further purification from residual Ce and Pr. Takes about 12 h with blanks <50 pg and Nd recoveries >90%.	TIMS	Nd isotopes measured in static multi-collection mode. Within run precisions (2 RSD) 3-9 ppm for ^{142}Nd/^{144}Nd and 2-8 ppm for ^{143}Nd/^{144}Nd; external precisions within a factor of 2 of within-run precisions. USGS RM BIR-1 (ocean basalt) and CRPG RM UB-N (ultramafic rock) used to assess accuracy.	386
Nd	Nd isotope RM, rock RMs, U ores	Relatively simple two-stage extraction and ion-exchange chromatography using TRU resin and LN resin. Recoveries *ca.* 82% with blanks of 25 pg.	TIMS	^{143}Nd/^{144}Nd measured as Nd^{+} ions using a Pt/Re film porous ion emitter attached to the centre of a single Re filament ribbon; ion yields were 10x higher than those of traditional Nd^{+} ion analysis. External precisions of 35 ppm (2SD) achieved for 1 ng Nd samples. GSJ and USGS RMs used to validate procedure.	387
Nd	Rock RMs	Stable and radiogenic Nd isotope ratios obtained simultaneously by addition of ^{145}Nd/^{150}Nd, plus ^{149}Sm tracer for ID Sm concentrations. Standard chromatographic procedures on AG50W-X8 resin to separate REEs and Ln-Spec to collect Nd and Sm fractions.	TIMS	Nd double spike used correct for mass dependent fractionation. Ratios normalised to GSJ RM JNdi-1, long-term precision (2SD) better than ±0.015‰ for ^{146}Nd/^{144}Nd and ≤11 ppm for ^{143}Nd/^{144}Nd.	388
Nd, Sm	Rock RMs	Single column scheme based on TODGA resins for efficient separation of Nd from Ce, Pr and Sm. Yields >90% Nd and 95% Sm.	TIMS	Measurements as NdO^{+} and Sm^{+}. USGS Basalt RMs BCR-2, BHVO-2, BIR-1a, ultramafic RMs CRPG UB-N and IAG RM MUH-1 used to access accuracy of Nd and Sm isotope ratios and concentrations.	389
Ni	Geological RMs	Novel 4-step purification scheme on five	MC-ICP-MS	^{61}Ni-^{60}Ni double spike used to correct for	390

	and samples	columns (4 containing AG50W-X8 resin and one with AG1-X8) using only dimethylglyoxime and acetone as organic reagents. Ni yield >92%, blanks 0.4-1.2 ng		instrument mass bias and fractionation during purification. Long-term precision 0.06‰ (2SD, N = 18) for geological RMs; δ^{60}Ni values in good agreement with previous studies.	
Os	Geological RMs	Rock powder dissolved a 1 + 3 mixture of HNO_3-HCl (inverse *aqua regia*) and Os extracted by a conventional two-stage column separation.	NTIMS	Static FC collectors with 10^{13} amplifiers. Of the 6 RMs analysed, USGS RM BIR-1 (basalt) and CCRM WPR-1 (altered peridotite) were the most homogeneous with respect to Os isotopic composition for test portions of 0.5-1 g.	391
Re	Wide range of rock RMs (also waters)	Modified column chemistry involving loading dissolved sample onto AG1-X8 resin, removing the sample matrix in 3 steps, eluting the Re, evaporating and refluxing the Re fraction, and repeating the whole procedure twice. Samples doped with W to give W/Re ratio of 20.	MC-ICP-MS	Very low uptake rate nebulizer (*ca.* 37 µL min^{-1}) and detectors measuring Re isotopes fitted with 10^{13} amplifiers. SSB method with external normalisation to W. ^{187}Re/^{185}Re reported with precision of ±0.05‰ (2SD) for a mass of >3 ng Re.	392
Re, Os	Shale RMs	3 protocols for digesting organic shales in Carius tubes were compared; a 1 + 3 mixture of HNO_3-HCl (inverse *aqua regia*) preferred. ^{190}Os and ^{185}Re spikes added prior to digestion. Chemical separation and purification by published methods.	NTIMS, MC-ICP-MS	Os measured as OsO_3^- by NTIMS, Re by MC-ICP-MS. USGS black shale RMs SGR-1b and SBC-1 considered suitable matrix-matched RMs for the determination of Os and Re isotopes in organic-rich sedimentary rocks.	393
Sn, Cd	Meteorites, sediments	3-stage chromatography method: (i) Sn, Cd and Zn separated from matrix elements on AG1-X8 anion-exchange resin; (ii) Eichrom TRU resin used to separate Sn from Cd and remaining Zn; (iii) Eichrom Pre-filter resin to remove organic compounds introduced by TRU resin. Cd fraction further purified in 2-stage anion-exchange procedure.	MC-ICP-MS	Sn and Cd isotope ratios measured in dynamic mode, to allow isobaric interference corrections, using SSB method and normalised to either ^{116}Sn/^{120}Sn = 0.4460 or ^{116}Cd/^{11}Cd = 0.578505 using the exponential law to correct for mass bias. Removal of U shown to be critical because of interference from U^{2+}. Data for NIST SRM 3161a (Sn solution) in good agreement with previous data.	394

Sr	Geological RMs	Method developed for measurement of pg sample sizes (30-100 pg Sr). Digestion of 50 mg of silicate powder in HF-HNO_3-$HClO_4$ at 180 °C for 4 days. Purification on AG50W-X12 cation-exchange resin. Yields 75-81%, blanks <200 pg.	TIMS	Use of single Re filaments with silicotungstic acid as the ion emitter produced 3-fold enhancement of Sr ionisation efficiency compared to that for a classical Ta emitter. Analysis of NIST SRM 987 ($SrCO_3$ powder) gave precision of ≤0.013‰ (2RSD, n=8). Accuracy verified by analysis of a suite of geological RMs.	395
Sr	Geological RMs	To improve Sr yields and separate Rb satisfactorily from samples with high Rb/Sr, separation scheme devised involving HF coprecipitation combined with cation-exchange on AG50W-X12 resin. Method most suitable for samples with high Rb/Sr and low Ca and Mg contents.	TIMS	Sr isotope ratios determined using a double Re filament geometry and $^{87}Sr/^{86}Sr$ ratios normalised to $^{88}Sr/^{86}Sr$ using the exponential law for mass fractionation correction. Results for GSJ RM JR-2 (Rb/Sr=37.36) consistent with published data.	396
Te	Geological RMs, mine tailings, sediments	Samples digested in a 1 + 3 mixture of HNO_3-HCl (inverse *aqua regia*). Separation of matrix elements using AG1-X8 anion-exchange resin columns, then further purification on AG50W-X8 resin.	MC-ICP-MS	$^{120}Te/^{124}Te$ double spike used to correct for mass bias and any fractionation during sample preparation. HG sample introduction so no Ba correction required but correction of Sn-based interferences essential. Data normalised to NIST SSRM 3156 (Te solution). Precision of *ca.* 0.09‰ (2SD) for $\delta^{130}Te/^{126}Te$ similar to other methods.	155
Ti	Geological RMs, minerals	Purification using a dual-column loaded with Ln-Spec and AG50W-X12 resins, resulting in nearly 100% Ti recoveries with very low matrix element concentrations.	MC-ICP-MS	SSB method with NIST SRM 3162a (Ti solution), precision for $\delta^{49}Ti$ 0.047‰ (2SD, N=130). 14 geological RMs analysed and results in good agreement with published data.	397
U-Pb	Cassiterite	Dissolution in HBr in Parr bomb vessels with addition of ^{202}Pb-^{205}Pb-^{233}U-^{236}U tracer. After refluxing to ensure reduction of Sn^{4+} to Sn^{2+}, TRU-spec resin used to obtain U and Pb aliquots that were purified	ID-TIMS	U isotopes measured as UO_2^+ species, mass fractionation corrected online using the measured Pb and U isotope ratios in the tracer, an exponential fractionation law and assuming a $^{18}O/^{16}O$ of 0.0020485.	398

		separately using HBr-anion-exchange chromatography.			
W	W standard solutions	Regression model to obtain absolute isotope ratio measurements of an element by using an isotopic standard of another element, in this case NIST SRM 989 (Re isotope solution) was used to calibrate W in candidate RM WOLF-1.	MC-ICP-MS	Test solutions containing W and Re introduced into ICP and plasma power incrementally increased to induce a shift in the mass bias in a relatively short period of time, providing sets of W and Re isotope ratios within 10 minutes Regression model based on 159 sets of W-Re sets of data and traceable to SI units. W and Re in same solution so any matrix effect was eliminated.	399
Zn	Geological and biological RMs	Validation of SpinChem^{TM} technique, which involves placing loaded chromatographic columns in 50 mL centrifuge tubes into a large- volume centrifuge; the centrifugal force generated enhanced reagent flow rates of up to x10 faster than gravity protocols. Case study based on Zn isotopes purified using AG1-X8 resin in a two-pass protocol.	MC-ICP-MS	SSB employed to correct for instrument mass bias. Both δ^{66}Zn and δ^{68}Zn reported for USGS RMs BCR-2 and BHVO-2 (basalts). Figures of merit such as blanks, yields and analytical precision similar to those achieved by purification under gravity flow.	400
Zr	Geological RMs	Separation of Zr achieved using single Eichrom DGA resin column after addition of ^{91}Zr-^{96}Zr double spike. Purification procedure took <4 h. Compromise was to reduce Zr yield to *ca.* 95% to reduce Mo recovery to *ca.* 33%.	TIMS	Isobaric interference from Mo largely eliminated during filament heating and also off-line Mo correction. Long term precision for δ^{94}Zr ≤0.06‰ (2SD). Accuracy confirmed by analysing USGS RMs BHVO-2 (basalt) and AGV-2 (andesite).	401