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: a review paper of developments in new personal air samplers for workplace air measurements; *a new passive air sampler for* Hg^0; *new filter-based RMs; a new field-deployable carbon analyser for speciation measurements of carbonaceous aerosols and advances in the measurement of RCS using vibrational spectroscopic techniques.*

The maturity of AAS methods for the analysis of waters was highlighted this year by the lack of significant developments. All the novelty was in sample preparation as reflected in Tables 1 *and 2. The tables also reflect the large interest in the use of graphene oxide as a solid phase for preconcentration and the continued use of magnetic nanoparticles. There are now enough methods and application to warrant the inclusion of the analysis of nanoparticles as a separate section rather than as a subsection in speciation. This trend is set to continue as instrumental improvements allow lower size LODs and the determination of lower particle numbers. Notable advances in the analysis of soils and plants included work on the preparation of new RMs as alternatives to NIST soil SRMs that are now in short supply. There was increased interest in the development of miniaturised AES instruments with the potential for field deployment. In the analysis of soil by LIBS, more studies included some form of external validation e.g. comparison with results of an established analytical method, which is most welcome.*

The availability of well-characterised matrix-matched reference materials continues to be a limitation in the production of high-quality geoanalytical data, particularly when exploring the fine structure of geological materials by microanalytical techniques such as LA-ICP-MS and SIMS. It is heartening to see that many of the researchers working in this area appreciate the importance of making new RMs available to the wider geochemical community.

Although the development of portable LIBS systems continues to attract much interest, the current generation of instruments do not appear to be able to match the capabilities of techniques like pXRFS, particularly for the quantification of minor and trace elements in geological settings. Some of the LIBS calibration issues highlighted are reminiscent of those encountered in the early days of pXRFS and should be overcome in time.

Many of the reported improvements to in-situ measurements of isotope ratios were in support of geochronological studies. Likely future trends include the increased use of imaging in U-Pb *geochronology given that LA-ICP-QMS mapping is now capable of acquiring all the required compositional and U-Pb age information at high-spatial resolution.*

1 Introduction

This is the 37th annual review of the application of atomic spectrometry to the chemical analysis of environmental samples. This Update refers to papers published approximately between August 2020 and June 2021 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 significant advances in the use of atomic spectrometry in the environmental sciences.

All the ASU reviews adhere to a number of conventions. An italicised word or 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.

2 Air analysis

2.1 Sampling techniques

Highlights in a *review*[7] **(**102 references) of developments in new personal air samplers for workplace air measurements were a new disposable device for sampling inhalable-sized particles and a device that collected a <300 nm particle size fraction. There are challenges in comparing exposure datasets because different designs of personal samplers can possess different sampling efficiencies. A review (54 references) of studies published between 2004 and 2020 compared[8] different samplers but, alas, found no discernible trends. The authors recommended that a standardised testing protocol be adopted to aid future comparisons. Following a review (29 references) of procedures for measuring surface contamination in workplaces, it was concluded[9] that, whilst undertaking quantitative measurements remains problematical because of challenges in sample collection, such measurements nevertheless were useful in assessing contamination routes and in validating efficacy of cleaning procedures. In a review (79 references) of methods for measuring reactive Hg in air, it was concluded[10] that future research should focus on developing both better sampling substrates for collecting Hg species and new MS-based methods for their subsequent identification. Methods for the collection of ambient air particles, characterising their physicochemical properties and ascertaining their *in-vitro* toxicities were summarised[11] (243 references).

A new *ambient air* sampler[12] made it possible to collect sufficient size-segregated ambient air particulate matter in 1 h for improved time-resolved speciation analysis to be carried out. Complementary to this was the development of an agitator sampler for re-suspending and collecting representative road dust samples, thereby enabling both direct (airborne) and indirect (re-suspension) sources of emissions from vehicles to be assessed. A new online integrated $PM_{2.5}$ measurement system developed for improved chemical mass-closure and source apportionment studies consisted[13] of: an aerosol MS for determining molecular species; an XRF system for determining elemental species; an aethalometer for black carbon measurements and a combined nephelometer with beta attenuation for mass measurements. Key to the success of this instrument was the development of a single isokinetic sampler inlet that, under conditions of laminar flow, ensured particles were transported to these various analyser components with a transmission efficiency of close to 100%.

Modification to an air-sampling cassette facilitated**[14]** the rapid *workplace analysis* of RCS by portable FTIR spectroscopy for timely exposure intervention studies. Particles of <300 nm size can penetrate deep into the lung so use of a new deposition sampler that collects these small particles was proposed**[15]** to provide better estimates of biologically relevant exposures to welding fume than achievable with traditional penetration-based samplers.

A new *passive air sampler* (PAS) for Hg^0 consisted**[16]** of a sulfur-impregnated activated-carbon sorbent contained in the body of a Radello® radial diffusive sampler. It had a sampling uptake rate of 0.07 m^3 per day and operated over a useful 1-10,000 ng m^{-3} concentration range so reliable time-weighted exposure averages could be determined in either ambient, residential or occupational air settings. Now commercially available, this sampler was used**[17]** in a study to determine airborne Hg^0 concentrations in and around residential settings. The indoor levels (2 - 10.8 ng m^{-3}) were higher than those (1.8 - 2.5 ng m^{-3}) measured outdoors so it was concluded that emissions from the households in this study were a net contributor of Hg to the wider atmosphere.

Sampling *gases* into cylinders or flasks for subsequent compositional and/or isotopic analysis is well established but measurement challenges still exist: these include the need for large air volumes and for dealing with condensable interferences such as water vapour. In a new field-deployable system[18] that employed a Nafion™ air drier for sampling CO_2, the requisite dry purge-air was usefully provided by initially feeding the spent-exhaust flow from the flask sampling-system through a molecular-sieve cartridge. Sampling requirements for ^{14}CO measurements were reduced**[19]** from 500 - 1000 L to *ca.* 90 L at STP by using air compression in conjunction with a small-volume electro-polished stainless-steel cylinder for sample collection. Embedded in this system was a CO scrubber that facilitated the production of a procedural blank for assessing the potential for extraneous ^{14}CO sample contamination that could occur during transportation of samples back to the laboratory. Sources of this contamination could be ingress of air due to leakage or *in-situ* ^{14}CO formation due to bombardment of samples with cosmic radiation.

2.2 Reference materials, calibrants and interlaboratory comparisons

The development of *RMs for air analysis* is to be encouraged given that the availability of such materials is poorer than that for other environmental matrices. Newly available single-element-on-PTFE-filters (Al, Ca, Ce, Cl, Cr, Cu, Fe, Na, Pb, S, Si, Ti, V and Zn at mass loadings of 0.2 – 70 µg cm^{-2}, uncertainties <10%) met**[20]** the need for appropriate filter media at suitable mass loading values and so will benefit future aerosol measurements by XRFS. A procedure for the repeatable spiking of reference filters with fly-ash was reported**[21]**. Individual filters were spiked sequentially and a target mass-loading of 2.5 mg achieved by the judicious selection of the volume of fly-ash-laden air sampled through each filter. This volume was calculated from real-time aerosol concentrations derived from continuous TEOM readings and from sampling-flow-rate data derived from continuous MFC readings. Candidate filters so produced were distributed to three laboratories for analysis by ICP-MS in accordance with procedures stipulated in EN 14902. The RSD was <20% for As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn. Reference filters containing a carbonaceous matrix that mimics particles derived from combustion-derived processes are desirable. Relative differences of 1 – 17% between measured and certified elemental values were obtained[22] when sample masses of 1 mg rather than the recommended 10 mg of either HSL RM MSWF-1 (elements in mild steel welding fume) or RM SSWF-1 (elements in stainless steel welding fume) were analysed. New data were provided on the elemental solubility in a phosphate buffer, an extractant often used in procedures to estimate metal bioaccessibility, and the oxidative potential of these RMs, as determined using a dithiothreitol-based assay, given that exposure to transitional metals in such materials can induce the formation of reactive oxygen species in human cells. Development of µm-sized U-containing reference particles for nuclear safeguarding purposes involved[23] generation of an aerosol using a VOAG and a drying step that produced spherical particles homogeneous with respect to their size, volume and U-content. The U content (3.56 ± 0.08 pg, k = 1) determined using ID-MC-ICP-MS, a technique widely used in nuclear facilities, agreed with certified values (3.58 ± 0.31 pg, k = 1) by the RM producer, who used ID-TIMS.

Performance testing of *calibration systems for generating Hg gas standards* was reported in three publications. A system developed at VSL for production of Hg^0 gas standards traceable to the SI was based[24] on a diffusion process described in ISO 6145-8. Standards could be prepared with a relative expanded uncertainty of 3% (k = 2) for concentrations between 0.1 and 2.1 $\mu g\ m^{-3}$ and 1.8% for concentrations between 5 and 100 $\mu g\ m^{-3}$. The so-called “bell-jar” calibration, which involves the analysis of a saturated head space of Hg^0 vapour kept at a defined temperature, is widely used but a discrepancy of 8% was noted[25] between the calibrant gas output from this approach and the output from the new SI-traceable approach. This indicated a problem with the former that is a concern because of its wide use. It was planned to measure Hg^0 with a new laser-absorption spectroscopic method (see section 2.4.5) and to use transfer standards, prepared by dosing sorbent tubes with defined amounts of Hg^0, in order to calibrate instruments previously calibrated using the "bell-jar" approach. The output from two generators that produced an oxidised Hg calibrant gas was analysed[26] online by ICP-MS. Use of a customised PTFE connector inserted into the ICP-MS torch to *ca.* 1 cm before the end of the quartz injector improved analyte transfer and so enabled standards of up to 10,000 ng m^{-3} to be measured in <5 min without significant memory effects.

Diesel engine emissions are best mimicked by soot particles with a high EC/TC ratio and a small size. A new prototype *particle generator* with a novel premixed-flame mode generated**[27]** such particles with an EC/TC ratio of 0.85 and mobility diameter of 50 nm without recourse to a thermal after-treatment process that had previously been required for generation using a diffusion flame. A new laboratory-based facility[28] for producing particles that mimic those found in ambient air employed: a generator for production of a carbonaceous particle fraction; a smog chamber to coat these particles with organic compounds and thereby simulate aged particles; a nebuliser to produce an inorganic-salt-particle fraction; and a rotating brush generator to produce a mineral-dust-particle fraction. It is anticipated that this facility will be used for: performance testing of new air sensors; measurement intercomparison studies; and health-related aerosol studies.

In an *interlaboratory comparison* (ILC) organised**[29]** by JRC Ispra, $PM_{2.5}$ filter samples that contained elements regulated under the EU air quality directive (As, Cd, Ni and Pb) were sent to laboratories for analysis by either ICP-MS (using EN 14902) or EDXRFS. Whereas there was good agreement amongst the ICP-MS results, it was concluded, unsurprisingly, that EDXRFS analysis was not sufficiently sensitive for the determination of As or Cd at concentrations typically encountered in such particles in ambient air. Reliable EDXRFS Ni and

Pb measurements that met data quality objectives prescribed in the EU directive were possible if the concentrations were >25 and >8 ng m^{-3}, respectively. Results from an ILC carried out in 2014 and then repeated in 2019 for the determination of metals (using EN 14385) and Hg (using EN 13211) in stack gas emissions showed**[30]** that participants' performance had improved but that better consistency and more transparency were still required in the calculation and reporting of LOQs and associated MU values. Blank Hg concentrations in sorbents can sometimes cause inaccuracies. Following a field trial of three different Hg^0 passive sampler designs, it was concluded**[31]** that the MerPAS® sampler performed better than the CNR-PAS and IVL-PAS alternatives because it possessed a superior sampling uptake of Hg^0 and gave a better S/N.

2.3 Sample preparation

The BCR *sequential extraction* protocol was automated**[32]** using a new FI-based ICP-MS system so that leachates from 5 mg test samples could be analysed for 17 elements in 80 min. The summed elemental recoveries for a road dust sample of only 72% of those obtained using the established but manually operated protocol was a reflection on the lower extractant concentrations and shorter extraction times used in the new automated approach. The measurement repeatability of 1-48% (RSD) is influenced, no doubt, by the heterogeneity arising from the small sample masses.

Measuring PGEs and Re at trace levels in road dust samples remains problematical because of severe isobaric and polyatomic interferences that can arise in ICP-MS analysis. In a new procedure, dust samples were digested**[33]** in inverse *aqua regia* in a HPA and the PGEs separated from the matrix by CEC for ID-ICP-MS/MS analysis. The use of a mass filter to select only ions of interest in conjunction with the use of ion-reaction chemistry meant that spectral interferences derived from residual elements remaining after clean-up could be avoided.

Analysis of IRMM BCR CRM 723 (road dust) gave values that were 71% (Ir), 91% (Os), 100% (Pd), 100% (Pt), 98% (Re), 81% (Rh) and 79% (Ru) of the certified values.

2.4 Instrumental analysis

2.4.1 Atomic absorption and emission spectrometries

Direct solid-*analysis of PM_{10} atmospheric particles by CS-AAS* involved**[34]**: quartering of glass-fibre filters; homogenisation by ball-milling; and analysis of 0.08-0.6 mg sample aliquots. Impressive LODs of 0.001, 0.001 and 0.004 ng m^{-3} for Be, Cd and Pb, respectively, could be achieved. An aqueous calibration was deemed sufficient as the calibration curves obtained were close to those obtained when a matrix-matched calibration that involved spiking of 0.30 mg aliquots of powdered glass-fibre was employed. Results for five air samples were in statistical agreement with results obtained using a solution-based assay that involved MAD of 100 mg sample aliquots in a HNO_3-HCl-H_2O_2 (4+1+1) acid mixture and analysis by CS-AAS and by ICP-MS. Although, undoubtedly, this assay is very sensitive and so has potential applications in studies in which masses are limited, one suspects that the preparatory step involving ball-milling is too time-consuming for routine applications. Use of water as a solvent to determine both soluble S (by ICP-AES) and SO_4^{2-} (by IC) in $PM_{2.5}$ filter extracts made[35] the rapid, cost-effective screening of air samples for water-soluble organic atmospheric-S-species possible. These are important indicators of the formation of secondary organic aerosols for which complex and expensive analytical tools such as field-based aerosol-MS or laboratory-based LC-MS were previously required.

Evaluation of a new Cyrotrap-GC-AED system for the determination of *atmospheric trace-organic gas species* at pptv levels focused**[36]** on calibration linearities, LODs and the generation of compound-specific response factors for 64 VOCs. The emission lines of Br (163 nm), C (197 nm), I (178 nm), N (174 nm) and S (181 nm) were used. Although quantification with VOC gas standards was preferable, the authors suggested that these new response factors made semi-quantitative analysis to an accuracy of *ca.* 30-40% possible for those compounds present in a chromatogram but not present in the gas standard. Furthermore, they suggested that this new instrument with its simultaneous CCD detection had potential for detecting other volatile species such as organo-metallic species emitted from volcanoes.

2.4.2 Mass spectrometry

2.4.2.1 Inductively coupled plasma mass spectrometry. A summary of progress in the *determination of elements in* $PM_{2.5}$ *by ICP-MS* discussed[37] (91 references) advantages and disadvantages of various filter media and of digestion procedures as well as developments in isotopic and speciation analysis. A bespoke sample-aerosol introduction-device in which sampled air was replaced with argon was used[38] with a desolvating HEN system for the online ICP-MS determination of ^{239}Pu in the air at a nuclear fuel reprocessing plant. The LOD was 2.24 x 10^{-5} Bq m^{-3} and the LOQ 7.45 x 10^{-5} Bq m^{-3} when 0.8 L of air was sampled. Rapid discrimination[39] of gunshot residue containing Ba, Pb and Sb from other particles such as those from brake pads and fireworks that can contain the same elements was possible by LA-ICP-MS analysis and interrogation of the resultant elemental distribution patterns using data-visualisation software. Samples were collected by swabbing hands with carbon adhesive tape. The analysis time of as little as 33 min was considerably less than that required for SEM-EDS analysis. Measurement of ^{194}Pt/^{195}Pt ratios in individual particles was possible by sp-MC-ICP-MS analysis[40] with a newly developed fast data-acquisition system for capturing transient signal events. The measurement precisions (2SD) for 30, 50 and 70 nm-sized particles of *ca.* 40, 20 and 10%, respectively, were comparable to those estimated from counting statistics.

2.4.2.2 Other mass spectrometry techniques: The *soot-particle aerosol-mass-spectrometer* is an instrument that combines the attributes of HR-aerosol-TOFMS with those of a soot particle photometer (SP2) for unrivalled measurements of both the chemical and size compositions of aerosols at high time-resolution. Studies to date using this technique were summarised[41] (89 references) and potential applications proposed. Latest versions of the instrument employ both a resistively-heated tungsten filament for vaporising non-refractory PM and an intracavity laser for vaporising refractory particles such as black carbon and metal particles. Increases in non-refractory PM ion signals observed when a dual-ionisation mode was used instead of a single-ionisation mode were[42] attributed to differences in either particle collection efficiencies or in the relative ionisation efficiencies for the same species vaporised from these two sources rather than to the laser heating.

The *aerosol chemical speciation monitor* (ACSM) is a field-deployable mass spectrometer for measuring the mass and chemical composition of non-refractory sub-µm PM in real-time. In order to validate ACSM measurements, data from laboratory measurements of aerosol PM_1 and $PM_{2.5}$ samples were compared[43] with results for samples collected at the same time on filters. Data for particle number and size distributions and black carbon concentrations taken at the same time were also used in the comparison. Systematic deviations between the results for a PM_1 fraction obtained using ACSM and those obtained from the offline weighing of filters were attributed to a lower transmission efficiency of the particle-focusing inlet lens for smaller particles than for larger particles. Better correlations were obtained for SO_4^{2-} (slope 0.96, R^2 0.77) and for total particle mass (slope 1.02, R^2 0.90). Studies like this are valuable for QA purposes and for identifying potential biases between old and new measuring approaches. Particulate chloride is an important PM component in marine air masses. A revised calibration procedure for improved chloride quantification by ACSM involved[44] modifying the standard ion fragmentation data held within the software and adopting a specific calibration for NH_4Cl.

The s*ingle-particle aerosol-mass-spectrometry* of samples from pristine environments with low concentrations of aerosol particles was made[45] possible by using a new aerodynamic lens system inlet in conjunction with use of a delayed-ion-extraction protocol. Detection efficiencies of 50% for 230-3240 nm-sized particles and 95% for 350-2000 nm-sized particles were possible for PSL and NaCl test particles. Use of this procedure improved the ion-yield from the ablation, ionisation and extraction processes and resulted in a 7-fold enhancement in signal intensities for cationic species.

2.4.3 X-ray spectrometry

The relative merits of sampling onto either polycarbonate or quartz-fibre filters were explored[**46**] for the *measurement of metals in* PM_{10} *particles by TXRFS***.** The direct analysis of flat filters such as polycarbonate was demonstrated by the determination of elements in NIST SRM 2783 (air particulate on filter media), for which measured values were within 8% of certified values. The procedure involved: punching out a 0.5 cm^2 area of filter; spiking with ISs (Ga and Y) together with 5 µl of HNO_3; and evaporating on a hotplate for 10 min at 80 °C. The MDLs for many elements were *ca.* 1 ng cm^{-2} but were higher for Ca and Zn because these were contaminants in the polymer material. The use of MAD with a HNO_3-HCl mixture was preferable for quartz filters because particles were embedded in the media: the MDLs were similar to those achieved with the flat filter but Ba, Ca, K and Ti were noticeable contaminants.

Adoption of a procedure widely employed in the PLM analysis of asbestos fibres ensured[47] that the requisite thin-layer sample was presented for TXRFS analysis by placing a segment of a cellulose-based air filter sample directly on a quartz reflector and dissolving it with a few drops of acetone. As remarked earlier, whilst there is sometimes merit in using sensitive techniques such as TXRFS or SS-AAS for the ultra-trace analysis of aerosol samples, routine use remains hampered by the often laborious and time-consuming sample preparation involved. Developments in automating filter preparation would therefore be welcome.

2.4.4 Combustion-based techniques

Carbonaceous aerosols captured on filters are classified by their organic (OC), elemental (EC) and, by summation, their total (TC) carbon content. Whereas there is, in general, good agreement in TC results from the different combustion protocols used for this classification, results for EC can vary between protocols because OC can be misclassified as EC due to the formation of so-called pyrolysed carbon that can sometimes arise from OC charring during the combustion process. Reference filter materials with certified OC and EC contents are therefore desirable but their production remains elusive. Therefore, practitioners typically use spiked simulant filters for calibration, method performance checks and QC purposes. One such approach involved[48] the preparation of two starting materials: a 1 mg mL^{-1} suspension of Cab-o-Jet 200 (19.92% mass fraction) in water as an EC surrogate; and a 4.0 mg mL^{-1} solution of sucrose as an OC surrogate. Binary working mixtures were prepared from these starting materials so that filters could be spiked with defined EC:OC mass ratios. Use of a new field-deployable carbon analyser enabled[49] speciation measurements of carbonaceous aerosols to be performed at high time resolution. The TC content of an aerosol sample collected on a quartz-fibre filter was determined as CO_2 following combustion. The LOD was 0.3 $\mu g\, m^{-3}$ C when hourly samples were collected at a 16.7 L min^{-1} flow rate. The system comprised of two identical sampling channels so continuous operation was possible with one channel used for sampling whilst the other was used for analysis. Equivalent black carbon concentrations were concurrently measured using an aethalometer so the OC aerosol content could be calculated by difference. The advantages of this instrumental approach were: carbon speciation at a high time resolution; avoidance of pyrolytic effects prevalent with conventional OC/EC combustion-based analysers; and elimination of the need for speciality gases because only filtered-air was required for combustion. Carbonaceous aerosols are typically measured either as EC or as equivalent black carbon mass concentrations but, increasingly, determination of a refractory black carbon component using instruments such as a SP2 are becoming more commonplace. In an informative study of colocation data from five European air sampling sites**,** the median ratio of refractory black carbon to EC ranged[**50**] from 0.53 to 1.29 with a GSD of 1.5. Whilst there were deviations of up to a factor of 2 in individual paired values, the correlation between refractory black carbon and EC (determined using the EUSAAR-2 TOT protocol) fitted a linear relationship with a constant ratio indicating that both methods were measuring the same carbonaceous aerosol component.

2.4.5 Other techniques

There is growing interest in assessing the contribution of windblown *mineral dusts* to air pollution because of their role in climatic radiative forcing and their impact at ground level on air quality. A rapid, inexpensive and non-destructive semi-quantitative method involved[51] use of UV-VIS DRS to measure the colour of collected air filter samples. The finding that a redness in filters was due to the presence of hematite, a major mineral in Saharan dust, correlated well with Fe-on-filter measurements by PIXE. Measurements in real-time are preferable but can be challenging. In the aethalometer analysis of mineral dusts in Crete, determining the optical absorption was[52] difficult because small black-carbon particles such as diesel fumes possess a much larger mass absorption cross-section and so can obscure the much smaller absorption from larger mineral particles. The larger mineral dust particles could be preferentially sampled by using a high-volume virtual impactor. A mass absorption cross section value of 0.24 ± 0.01 m^2 g^{-1} at 370 nm for a $PM_{10-2.5}$ particle size fraction was established by determining the mineral dust concentrations in filter samples taken concurrently. These dust concentrations were calculated from the measured Ca content and by assuming an average Ca concentration (12%, *m/m*) in the mineral dust previously established for this particular sampling site.

Advances in *vibrational spectroscopic techniques* offer new potential for measuring RCS at low airborne concentrations within occupational settings. Emissions from the cutting and polishing of natural and artificial stones, a workplace activity that can give rise to substantial inhalation exposures if uncontrolled, were measured[53] using a new Raman-based procedure. An established XRD-based assay was used in parallel. Results correlated well for both respirable-sized (R^2 values of 0.95-0.98, slope of 1.11) and thoracic-sized (R^2 values of 0.95-0.98, slope of 1.07) RCS particles tested. The LOD of *ca.* 0.2 µg was an order of magnitude better than that achievable by XRD analysis. An alternative, QCL-based, IR method involved[54]: collection of aerosol on a filter; filter treatment using a low-temperature O_2-plasma asher to remove the matrix; redeposition of the RCS as a dried 1 mm^2 diameter spot on a secondary filter for direct-on-filter analysis; and measurement of α-quartz at its characteristic 798 cm^{-1} peak. The LOD was 0.12 µg and results for samples taken from workplaces agreed to within 3-28% with those determined using a reference XRD method.

The reliability of *monitoring mercury in stacks* is constrained by the availability of accurate and metrologically traceable calibrant Hg^0 gas standards which are typically generated on demand using either controlled gas diffusion or permeation processes. Verifying the output from generators is therefore important. Researchers at NIST compared[55] results obtained using a previously reported[56] high-resolution laser-absorption spectroscopic instrument with those obtained by sampling defined volumes of Hg^0 onto sorbent tubes and analysing following desorption using an accurate and precise ID-CV-ICP-MS method[57]. The output from a calibrator unit was split so that the two methods could be performed simultaneously. Agreement between the two techniques was within 1-1.8% for Hg^0 concentrations of 41-287 $\mu g\ m^{-3}$ thereby confirming the suitability of this new approach as an alternative primary measurement method.

3 Water analysis

A review (144 references) of *metals in waste waters associated with advanced technologies* included[58] consideration of current analytical methods for determining Gd, PGE and REEs in waste waters. Whereas Gd came mainly from MRI contrast agents and personal care products, the PGEs and REEs probably came from materials used in modern technologies.

Two interesting papers on the *release of trace elements into water* have been published. The first looked[59] at the release of Ag from two types of PET water bottles doped with Ag: one with porous glass containing Ag_3PO_4 and the other with Ag NPs. The PET bottles (500 mL) doped with 300 mg kg^{-1} of Ag (as Ag_3PO_4 glass) released enough Ag after 10 days to reach a concentration of 2 $\mu g\ L^{-1}$ when stored at 21 °C. This increased to 72 $\mu g\ L^{-1}$ when stored at 43 °C, thereby exceeding the European Food Safety Authority migration limit of 0.05 mg L^{-1} for 10-day storage at >40 °C. In contrast, the bottles doped with Ag NPs at a higher concentration

(400 mg kg^{-1}) released hardly any Ag: the test solutions concentrations were below the ICP-MS LOD (0.1 µg L^{-1}) under all conditions. In an extremely relevant article, given the current Covid-19 pandemic, the leaching of trace elements into water from disposable face masks was measured[60]. Seven types of face masks were immersed in 250 mL of deionised water for 24 h. The test solutions were then acidified with 1 mL of 1 M HNO_3 and analysed by ICP-MS. It was thought that the Cd, Co, Cu, Pb, Sb and Ti found in some of the solutions came from additives in fibres used to manufacture the masks.

3.1 Certification of reference materials and metrological investigations

A *candidate seawater CRM* from the Turkish National Metrology Institute was analysed[61] by ID-ICP-MS/MS to determine the Cd, Cr, Cu, Ni, Pb and Zn concentrations after trimethylamine-assisted $Mg(OH)_2$ co-precipitation. The results were validated by analysis of the NRCC CRM CASS 6 (nearshore seawater) and the NMIA CRM MX014 (trace elements in sea water).

3.2 Sample preconcentration

The *affinity of DGT samplers for PGE in aged samples* was determined[62]. Whereas DGT samplers loaded with the Purolite S914, S920 and IONQUEST® MPX-317 chelating resins had an unchanged quantitative affinity for Pt in spiked waters, even after ageing for 17 days, the sampling efficiency for Rh decreased by 70% because Rh was hydrolysed to $Rh(OH)_3(s)$ which is not taken up by the resin. Fortunately though, this effect was much less pronounced when sea water was sampled.

Other significant advances in the SPE of trace elements from water samples are summarised in Table 1 and those in the use of LPE in Table 2.

3.3 Speciation analysis

The reaction kinetics of the transformations of the *arsenic species* As^v, AB and AC in aqueous solutions during ultrasonic extraction were followed[63] in detail in order to obtain the optimum extraction conditions. A previous study by the same authors had shown that arsenic species were unstable. The transformation followed 1st-order reaction kinetics at different ultrasonic water bath temperatures (0–80 °C) and powers (150–750 W). Reasonable extraction efficiencies with relatively low interspecies transformation rates were considered possible if the ultrasonic bath conditions were 150–300 W and 40-60 °C with a 5–10 min extraction time. To separate As^{III} from As^V in Iranian mine waters, an As^V-specific IIP was prepared[64] and applied to an etched TLC plate to form a set of μTLC plates for subsequent LA-ICP-MS detection. Optimum separation for a 10 μL sample volume was obtained within 10 min with a 1:1 acetonitrile:water mobile phase. The LOD for As in the μTLC plates was 0.06 μg L^{-1} for both species. Results for mine water samples compared well with those obtained using the standard HG-AAS method. Although this method is time-consuming and so provides little advantage for the analysis of waters, it would have an advantage for the analysis of crude oil samples because organic solvents cannot be transported to the plasma source during μTLC-LA-ICP-MS analysis.

The wider availability of ICP-MS/MS has made the *speciation of organo-halogen or halogen-tagged molecules* more accessible. For instance, a mix of chlorinated and brominated acetic acids was successfully separated[65] on a mid-bore C_{18} HPLC column and detected by HPLC-MS/MS. With an injection volume of 50 μL, the LODs of 0.8 and 1.4 μg L^{-1} for Br and Cl, respectively, were well below the US EPA maximum contaminant level of 60 µg L^{-1} for these compounds. The method was validated by analysis of spiked samples and the Sigma Aldrich RM EPA 552.2 (haloacetic acids mix). Mono- and di-iodoacetic acids were separated[66] by AEC and ICP-MS detection. No preconcentration was necessary. The results compared favourably with those from 5 control laboratories using Chinese standard methods for the analysis of raw waters with high I concentrations after disinfection with Cl and UV irradiation. The LODs of 0.06 and 0.04 µg L^{-1} for the mono- and di-iodoacetic acids, respectively, were comparable to those obtained by the control laboratories which used a sample preconcentration step before analysis.

Although not strictly atomic spectrometry, *the determination of* Fe^{2+} *by ESI-MS* is of interest[67]. Complexation with 1,10-phenanthroline resulted in peaks such as that at *m/z* 208 ($[Fe(phen)_2]^{2+}$) which could be used to determine Fe^{2+} concentrations in river waters. Results compared well with those obtained using a standard colorimetric method. Of the total Fe present in Japanese rivers, 40% was present as Fe^{2+}. Unfortunately, the authors did not report an LOD for comparison with current colorimetric and chemiluminescence methods.

The determination of *Gd-based contrast agents* in waters remains of interest because these agents can enter the environment from WWTPs. Gadolinium-containing compounds in seawater were successfully separated[68] from the matrix on micro SPE cartridges packed with graphitic carbon for analysis by HILIC-ICP-MS. A four-fold preconcentration factor was obtained by using a sample volume of 1 mL and an elution volume of 0.25 mL. It was possible to determine Gadoterate Meglumine (Gd-DOTA) and Gadobutrol (Gd-BT-DO3A) at concentrations of 180 and 140 ng L^{-1}, respectively, in Australian coastal seawater. As HILIC chromatography can be considered similar to normal-phase chromatography, it is not generally considered to be compatible with ICP-MS analysis. To overcome this problem, researchers developed[69] an aqueous mobile phase capable of separating the main 6 commercially available Gd-based contrast agents on a HILIC column before ICP-MS detection. The LODs were between 3.7 ng L^{-1} (Magnevist® Gd-DTPA) and 22 ng L^{-1} (ProHance® Gd-HP-DO3A) and so were sufficient for identifying these compounds in waters near the outfall from a WWTP. The method also allowed the preliminary quantification of unknown Gd compounds (suspected transformation products) in river water.

To widen the applicability of *mercury speciation methods in water*, a SPE method was adapted[70] to preconcentrate Hg and Pb species simultaneously for detection by HPLC-ICP-MS. A C_{18} SPE cartridge conditioned with 2-mercaptoethanol was used to separate species from coexisting ions in water with preconcentration factors ranging from 459 for Pb^{2+} to 2400 for Hg^{2+} for 10 mL samples. The LODs were 0.001 and 0.011 ng L^{-1} for Hg and Pb, respectively, in freshwater samples. The results were validated by analysis of the Chinese RMs GBW08603 (mercury in water) and GBW08601 (lead in water). A two-step CPE method was developed[71] to prevent peak overlap after extraction and thereby to improve the LOD of an HPLC-CV-AFS method for mercury species in water and soils. In the first step, the mercury species were preconcentrated into Triton™ X-114 micelles as DDTC chelates. To make the extract compatible with HPLC, this solution was then back extracted into a 0.1% m/v L-cysteine solution. The LOD of 4 ng L^{-1} for inorganic mercury and 16 ng L^{-1} for methylmercury were probably sufficient for the quantification of Hg species in soil samples but insufficient for the analysis of uncontaminated waters.

As chromatographic methods for elemental speciation mature, focus is shifting to *preconcentration methods for elemental species*. Methods developed for one specific oxidation state are included in Tables 1 and 2 whereas methods for one or more organometallic species are included in this section. Graphene oxide bound to silica NPs was modified[72] with sodium dodecyl benzene sulfonate to preconcentrate tetramethyl and tetraethyl lead from river waters. Enrichment factors of >1300 were obtained for both species in 10 mL samples. By using fairly standard HPLC conditions (buffered ion pairing agents) and ICP-MS detection, the method LODs were 0.018 for (tetramethyl lead) and 0.023 (tetraethyl lead) ng L^{-1}. Cytostatic Pt compounds used in chemotherapy were isolated[73] from a WWTP effluent using strong anion exchange cartridges. The ionic forms of Pt were adsorbed on the cartridge at pH 3 and then eluted at high pH with 5 - 10% *v/v* NH_3 solutions. Despite extensive optimisation, the adsorption and desorption efficiencies were quite low (44-68%). No HPLC-ICP-MS analysis was undertaken so the actual species being preconcentrated was not confirmed. The extensive body of literature on the separation and retention of this class of compounds on ion-pair-modified C_{18} silica phases contains the information needed for improving this method.

3.4 Analysis of nanomaterials

The analysis of *nanomaterials in waters* is becoming widespread and even routine, yet advances and challenges remain to be overcome as highlighted by a number of reviews. An article[74] (68 references) on the trends in sample preparation and analysis of nanomaterials in environmental samples covered: the sources of nanomaterials; their transformation products in aquatic environments; sampling; and analytical techniques. A helpful summary was provided with the aim of avoiding potential pitfalls. A more specific review[75] (159 references) covered the challenges in determining Ti NPs in aqueous samples. Focussing on the analysis of TiO_2 NPs from sunscreens, the authors reviewed the use of sp-ICP-MS and highlighted the need for improved sample pretreatment and better modelling of the fate of these materials. A review (186 references) on the use of asymmetric FFF in the analysis of engineered and natural NPs as well as colloids in aquatic systems covered[76] advances in this technique and the various challenges faced. Deviations from theoretical results were typically caused by sample losses, membrane-analyte interactions and overloading of the analytical system.

The performance of *single particle ICP-MS* continues to be improved. A total consumption nebuliser was proposed[77] as a means to avoid particle loss during nebulisation. As all the sample was nebulised at a liquid flow rate of 8 µL min^{-1}, there was no need for determining the transport and nebulisation efficiencies. Under these conditions, the size distributions of gold, platinum and silver NPs in known standards were determined successfully. The method was then applied to the determination of gold NPs in surface waters after dissolved-standard calibration to determine the NPs' average diameter. In the ICP-SFMS determination of CeO_2 NPs in Canadian waterways, the size LOD was improved[78] to <4 nm by using a 50 µs dwell time and gold and silver NPs as size RMs. The NP number and size were then successfully determined in samples of urban rainwater and river water. Up to 36% of the Ce-containing NPs in Montreal rain were engineered NPs. As mentioned in previous ASUs, sizing can be improved by eliminating the dissolved fraction signal. Cloud point extraction of dissolved Ag has once again been confirmed[79] as a suitable method for this task. By removing the dissolved Ag from the sample and then preconcentrating the silver NPs present, the size LOD was reduced from 20 to 4.5 nm.

The *coupling of asymmetric field-flow-fractionation with ICP-MS* continues to be a reference method for the sizing of particles within complex matrices. In a study of coated platinum-NPs in water samples, quantitative membrane recoveries for a 30 min run time allowed[80] 5, 30 and 50 nm NPs added to natural and artificial (humic acid added) surface water samples to be separated. As found in previous studies, complexation by OM in the water was a critical factor.

The *concentrations and metal loads of nanoplastics in the environment* are becoming of increasing concern. A method to detect microplastics by ICP-MS involved[81] functionalising polystyrene microspheres with gold NPs and detection with sp-ICP-MS. The functionalisation with gold NPs made it possible to count individual particles. The quantification limit was 8.4 x 10^5 particles L^{-1} and the response was linear up to 3.5 x 10^8 particles L^{-1} for particles of up to 1µm diameter. The size LOD was 135 nm. The LA-ICP-MS depth profiling and mapping of marine plastics was used[82] to discriminate between surface adsorbed metals (As, Cd, Cu, Fe, Sb, Sn, Pb, U and Zn) and additives (Cu, Pb or Sb) in the bulk polymer. Mapping of the plastics made it possible to estimate diffusion of the metals from the surface to the subsurface during weathering.

3.5 Instrumental analysis

3.5.1 Atomic emission spectrometry. A review (177 references) of *analytical applications of a commercially available MIP-AES instrument* found[83] that preconcentration and matrix removal were necessary for the analysis of seawater because this technique has a sensitivity somewhere between those of FAAS and ICP-AES. Some elements (Al, As, Ba, Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, Zn) were present at concentrations that could be determined directly in drinking water, effluent and wastewater. Better performance could be achieved by improving sample transport with HG or ultrasonic nebulisation.

The *use of heated spray chambers* was investigated[84] to improve the sensitivity of ICP-AES instruments at low flow-rates. An instrument operating with different heated spray chambers and nebulisers at sample flow rates between 50-75 μL min^{-1} had a sensitivity similar to that obtained using a normal cyclonic spray chamber with a nebuliser operating at 1 mL min^{-1}.

The development of *low-power discharges for water analysis* continues to be of interest and useful LODs are now being achieved. A solution cathode-glow-discharge was used[85] as an excitation source for the determination of Ga and In in water samples. Whereas few interferences were present in the determination of In, even when matrix components were present in a 20-fold excess over the analyte concentration, the determination of Ga suffered severely from interferences. As a consequence, the LOD for Ga (0.1 μg L^{-1}) was much higher than that for In (0.016 μg L^{-1}). The same type of excitation source was successfully coupled[86] with HG to determine Sb in water samples. Standard HG conditions for the generation of stibine gas gave an LOD of 0.36 μg L^{-1}, good spike recoveries and results for real samples comparable with those obtained by ICP-MS. The use of low power means instruments can be made portable. An instrument with a DBD to generate a microplasma was used[87] in the field to determine As and Sb in environmental water samples. The solid reagent sulfamic acid was used instead of HCl when possible in order to reduce liquid waste. The LODs of 0.5 and 0.2 μg L^{-1} for As and Sb, respectively, were impressive for an instrument that weighed only 15 kg in total and operated at <60 W total power consumption.

3.5.2 Vapour generation. The *vapour generation of Cd* remains a key method for improving instrument sensitivity. Use of an electrochemical cell to generate volatile forms of Cd using graphite electrodes and a DC power supply removed[88] the need for an ion exchange membrane to separate the electrolyte solutions. An AFS LOD of 0.05 µg L^{-1} was achieved and good results were obtained for the analysis of the Chinese IERM CRMs, GBW0806, GSBO7-3186-2014 and GSB07-1185-200 (environmental water). The PVG-SQT-AAS LOD for Cd in waters of 2.5 µg L^{-1} was[89] significantly better than the 0.14 mg L^{-1} achieved when using AAS alone. Use of PVG improved analyte transport to the flame where atoms were trapped in the quartz tube with a lean flame for 6 min before introduction of H_2 to release the trapped atoms.

The *chemical vapour generation of Cr^{VI}* was enhanced[90] by the addition of sodium diethylaminodithioformate to the reaction mix of KBH_4 and HCl. The total Cr concentration was determined after oxidation of the sample with $KMnO_4$ so the Cr^{III} concentration could be calculated. The chemical VG efficiency of 28% resulted in an LOD of 0.2 µg L^{-1} for Cr^{VI} when using ICP-MS detection. The method was validated by spike recovery from tap water and analysis of the Chinese CRM GEW(E)080197.

A gold trap typically employed in the determination of Hg was used[91] for the *preconcentration of Se* after HG. The AAS LOD was improved from 0.23 to 0.013 µg L^{-1} by trapping at of 450 °C for 300 s and desorbing at 970 °C. This device could not be used with ICP-MS because of losses of volatile Se species by condensation onto the cold tube walls between the amalgamation unit and the plasma torch. In an offline preconcentration procedure,[92] H_2Se generated by direct addition of the reagents to the sample was trapped in an aqueous ammonium solution that was then analysed directly by AAS. Recoveries of spikes from tap water samples were 99 ± 3% and the LOD was 1.3 µg L^{-1}.

The *dielectric barrier discharge*, an up-and-coming addition to VG systems, was successfully coupled[93] with ICP-MS for the detection of PGEs in river, lake and rain waters. The sample was nebulised into the DBD in the presence of formic acid to improve the generation of volatile PGE species. The LOD was reduced 10-fold when compared to normal nebulised sample introduction and the spike recoveries from the water matrices ranged from 80% (Pd in rainwater) to 110% (Pt in lake water). The typical use of DBDs in AAS and AFS is as atomisers and atom traps for hydrides, as exemplified[94] by the determination of Sb in bottled water. An LOD of 5 ng L^{-1} was achieved with a 50 s accumulation time followed by atomisation and AFS detection. The instrumental response was linear up to 50 µg L^{-1}. A seven-fold improvement in sensitivity over that achievable by standard HG-AFS was obtained and the recoveries of spikes from bottled tap water samples were quantitative.

3.5.3 Inductively coupled plasma-mass spectrometry. An extensive review (126 references) of *the determination of REEs in waters* by ICP-MS covered[95] sample introduction systems and the reduction or elimination of interferences in the analysis of surface, ground and rain waters and Antarctic ice. Tables of assigned or published values were presented for many available water CRMs.

Sample stabilisation before the determination of mercury by ICP-MS is always important. A mixture of thiourea and HCl stabilised[96] Hg in humic-acid-rich waters before direct analysis without the need for further sample preparation. The LOD of 0.4 ng L^{-1} indicated that the researchers had managed to maintain low Hg blank levels. The method was validated by analysis of the IRMM CRM ERM®-CA615 (groundwater) and by recoveries of spikes from waters with artificially enriched humic-acid contents.

Matrix separation remains an important strategy for ICP-MS analysis of samples such as seawater that have challenging matrices. An online desalination device removed[97] Ca, Mg and Na from seawater samples during analysis. A helical coil packed with an element-specific ion-imprinted-polymer removed the matrix ions but did not retain the analytes (As, Cd, Cu, Mn, Ni, Pb, Sb, Tl). The desalination device was effective for at least 9 h. Removal of the matrix improved the LODs for all analytes. Trueness and repeatability of the method were determined to be <3 and <5%, respectively, by analysis of the NRCC CRM CASS-5 (nearshore seawater) during the analytical run. Because analyte preconcentration from WWTP effluents was impeded by the presence of EDTA in samples, it was destroyed[98] by digestion with a mix of HNO_3 and H_2O_2 prior to preconcentration of Fe, Cu and REEs on a chelating resin. The method was validated against the JSAC CRM JSAC 0302-3c (river water) with ICP-MS detection.

It has been demonstrated[99] through analysis of the NMIJ CRM 7202-c (river water) that Ne can be used successfully as a *collision gas for ICP-MS analysis* of river water. Helium was considered[100] the collision gas of choice for the quantification of REEs in fresh and slightly saline waters and digested sediments but the interference of Ba on Eu and the difficulties in determining Sc remained. The method was validated by the recovery of spikes from 5 commercial mineral waters and by the analysis of the NRCC CRMs SLRS-6 (river water), SLEW-3 (estuarine water) and AQUA-1 (drinking water). Oxygen was used[101] as reaction gas in the ICP-MS/MS determination of REEs in order to form REE monoxide ions and thereby displace the analyte peaks from those of the interferences. The LOD for the direct analysis of waters were from 0.004 (Er) to 0.26 (Nd) ng L^{-1}. The method was validated against the NRCC CRM SLRS-4 (river water). The REE concentrations in various Japanese lake and river water samples were determined.

Addition of methane to the plasma improved[102] the *detection limit for P in water* as determined by ICP-SFMS. The addition of a flow of 6 mL min^{-1} resulted in a 3-fold sensitivity increase and a LOD of 7 ng L^{-1}. That methane did not generate any spectral interferences was verified by scans in medium resolution mode. The method, validated by analysis of the Chinese RM GBW(E)081215 (phosphate in plant root water), was considered sensitive enough to determine P in Arctic glacial meltwaters and lake, river, rain and sea waters.

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The *determination of* ^{226}*Ra* was simplified[103] by replacing the standard R=10000 medium resolution slit of an ICP-SFMS instrument with a R=2000 slit to ensure spectral peak separation from known interferents whilst maintaining a flat topped peak for good isotope ratio determinations. As the concentrations in seawater were expected to be between 0.03 and 0.1 fg g^{-1}, the ^{226}Ra was initially preconcentrated from 1 L of seawater by coprecipitation with MnO_2 and then isolated using a 2 column clean-up procedure (strong CEC followed by extraction chromatography). The extraction efficiency was 90-99% and the method LOD 0.033 fg g^{-1}. The results for samples taken at one of the cross reference stations used in the GEOTRACES cruises compared well with those obtained by alternative methods.

The *isotope ratios* of Sr (^{87}Sr/^{86}Sr and $\delta^{88}/^{86}$Sr) in sediment pore waters were determined[104] by MC-ICP-MS following a single miniaturised extraction protocol that used 30 μL of Sr Spec resin. The matrix was removed with three 1 mL aliquots of 3M HNO_3 and the Sr by three volumes (0.25, 1.25 and 1.5 mL) of deionised water. Indicative values measured for the NIST SRM 1640a (trace elements in natural water) were $^{87}Sr/^{86}Sr = 0.708790 \pm 0.000062$ and $\delta^{88}/^{86}Sr = 0.07 \pm 0.10‰$ (2SD, n = 6). All of the various analytical methods compared[105] for the MC-ICP-MS determination of Pb isotopes in seawater involved Pb separation by either SPE with the Nobias Chelate PA-1® resin or coprecipitation with $Mg(OH)_2$. Mass bias was corrected using either a Pb double-spike or external normalisation to Tl. For the analysis of seawater with Pb concentrations of 1-7 ng, all the ICP-MS methods gave results comparable to those obtained by TIMS analysis but with a higher sample throughput. The use of resin extraction gave the highest analytical throughput and was most suitable for high-silicate waters but the low cost of precipitation made it an attractive alternative for waters with low concentrations of silicates.

3.5.4 Laser methods. The *detection of molecular species* in water samples is now generally undertaken by LIBS rather than AAS. To determine Cl and F in water, 100 µL samples of water were deposited[106] onto a calcite absorbent. The LODs of 0.38 mg L^{-1} for F and 1.03 mg L^{-1} for Cl were obtained using the molecular emission spectra of CaCl and CaF. The method was verified against results obtained by an IC standard method and was deemed sufficiently sensitive as a screening method for WHO action levels of Cl and F in drinking water. The dissolution of isotopically enriched B powders in water followed by deposition onto a Cu sputtering plate demonstrated[107] that LIBS can distinguish between B isotopes by detection of BO molecular species. The measurement uncertainty of *ca.* 10% and mediocre accuracy when carrying out IDA analysis at concentrations of 1000 mg L^{-1} demonstrated that further method development is required before the technique becomes the method of choice.

The *oxidation state speciation of Fe* using LIBS detection was achieved[108] by preferentially trapping Fe^{2+} and Fe^{3+} on an iminodiacetic acid functional group resin at different pH values. After species-specific trapping, the resin was ground and tabletted before LIBS measurement of the Fe content. The LODs were 0.120 (Fe^{2+}) and 0.142 (Fe^{3+}) mg L^{-1}. The method was validated by spike recovery and comparison with ICP-AES results.

3.5.5 X-ray fluorescence spectrometry. Depositing a 200 µL *single water drop* onto a hydrophobic support that was then agitated prevented[109] the formation of a coffee-ring type drying effect and so resulted in a more uniform deposit for the direct TXRFS analysis of mineral waters. The potential of this method was demonstrated by the improvement in emission intensity for V in a mineral water sample from 1005 counts to 3709 counts. Direct determination of Se in a single drop of mine water[110] by TXRFS was possible in unfiltered and unacidified samples when a 600 s counting time was used. Increasing this time to 1800s allowed Se detection in all the samples down to the ng g^{-1} concentration range. The method was verified by comparison with results obtained by ICP-MS analyses of the same samples and of NIST SRM 1640a (trace elements in natural water). The detection of trace elements at the µg L^{-1} level in a 5 µL drop by EDXRFS was made possible[111] by modifying the instrument so that the entire Bremsstrahlung spectrum emitted from the tube was focussed into a 35 µm spot using polycapillary optics. The LODs of between 0.38 (Cr) and 4.11 (Bi) µg L^{-1} were obtained without the need for any preconcentration or complicated sample preparation. The results were validated using the NIST SRM 1640 (trace elements in water).

4 Analysis of soils, plants and related materials

4.1 Review papers

A review (132 references) on *methods for the separation and characterisation of environmental nano- and micro-particles* included[112] useful information on the typical range of particle sizes than can be investigated using different separation methods and on the scope and limitations of techniques such as FFF-ICP-MS.

4.2 Reference materials

The *preparation and characterisation of new RMs* was the goal of a collaboration[113] between the IAG and the USGS. Sediments and soils from six locations in the Western USA were combined to produce three RMs with the same elemental compositions as NIST SRM 2709a (San Joaquin soil), 2710a (Montana I soil) and 2711a (Montana II soil). Analysis in more than 80 laboratories of the candidate RMs, SdAR-H1 (metalliferous sediment), SdAR-M2 (metal rich sediment) and SdAR L2 (blended sediment) as part of the Geo*PT* proficiency testing scheme, produced reference values for 41, 48 and 49 elements, respectively. The new RMs, whose elemental compositions are close to (correlation coefficients > 0.85) those of the existing NIST SRMs, are alternatives for use in monitoring studies.

A ^{111}Cd-^{113}Cd double-spike ICP-MS procedure was used[114] to determine *Cd isotope ratios* in 34 RMs that covered a wide range of environmental matrices. The method precision of better than ± 0.074‰ (2SD) was determined from analysis of RMs using an optimum mixing ratio of ^{111}Cd$_{spike}$/^{112}Cd$_{sample}$ of 2.0. The $\delta^{114/110}$Cd values of -0.001 to +0.287‰ for rock and -0.806 to +0.142‰ for biological samples provided a useful database for monitoring studies. The Cd mass fractions and isotope compositions in NIST SRMs 1566b (oyster tissue), 1573a (tomato leaves) and 1575a (pine needles), IRMM CRM BCR 482 (lichen) and ERM CE278k (mussel tissue) were determined[115] by TIMS using a ^{116}Cd-^{106}Cd double-spike. Based on analysis of

NIST SRM 3108 (Cd standard solution), the precision of the procedure was high at $\delta^{114/110}$Cd = -0.005 ± 0.029‰ (2SD, n = 47). Variations in $\delta^{114/110}$Cd ranged from -0.52‰ ± 0.03 (2SD, n=5) for mussel to +0.24‰ ± 0.04 (2SD, n=6) for pine needles. This study highlighted the potential for using natural mass-dependent Cd fractionation in biogeochemical studies.

Isotopic ratios for Mg were determined[116] following digestion in HNO_3 + H_2O_2 for a range of RMs: IRMM CRMs BCR-383 (green beans) and BCR-380R (whole milk); NIST SRM 1577c (bovine liver); ERM-CE464 (tuna fish); and NRCC CRMs DORM-2 and DORM-4 (fish protein) and TORT-3 (lobster hepatopancreas). The separation of Mg from the sample matrices involved a three-column procedure: the first column contained AG1-X8 anion-exchange resin for removal of Fe; the second contained AG50W-X12 cation-exchange resin, which was eluted with 1 M HCl for removal of Ca, Na, P and S; and the third was a another AG50W-X12 column, which was eluted with 0.4 M HCl for removal of other matrix elements, in particular K. The isotopic analysis was performed in two laboratories on three MC-ICP-MS instruments. The measured δ^{26}Mg values for three USGS basalt RMs and IAPSO (standard sea water) were not significantly different from published values. Measured relative to the value for the RM DSM-3 (nitrate solution), δ^{26}Mg ranged from 0.52‰ ± 0.29 (2SD, n=7) for the bovine liver to -1.45‰ ± 0.2 (2SD, n=5) for the tuna fish with a precision of 0.03‰ (2SD, n=85). Accurate Mg isotopic determinations would be of value not only in environmental but also in human health studies as variations have recently been reported in patients with type 1 diabetes.

4.3 Sample preparation

4.3.1 Sample dissolution and extraction

Alternative digestion procedures were investigated with the aim of avoiding the use of HF. These included[117] the use of HBF_4 as a HF substitute in a method that involved MAD (room temperature to 60 °C in 9 min; 60–125 °C in 25 min; 125–160 °C in 12 min; 160–240 °C in 14 min; 20 min hold) using 200 mg of sample with double distilled HNO_3 (3 mL) and incremental volumes (0, 0.1, 0.5, 1.0, 1.5, and 2 mL) of HBF_4, followed by ICP-MS. For IAEA CRMs Soil-7 (soil) and SL-1 (lake sediment), HNO_3 alone gave extraction efficiencies of 87–120% for Cd, Co, Cr, Fe, Mn, Pb, V and Zn. Addition of HBF_4 was necessary to recover Ba, Sb, and Sr adequately; the highest recovery (>85%) was achieved on addition of 1.5 mL HBF_4. The elements Th, Ti, Y and Zr could not be recovered by this procedure so HF would still be needed.

A *protoype IR sample digestor* developed[118] as a simple and inexpensive means for digesting soils consisted of a wooden box that housed two commercial IR lamps and had a metal lid with 18 holes to accommodate 50 mL PTFE microwave-digestion vessels. For digestion, HNO_3 (2 mL) was added to the sample (150 mg) and heated to dryness, followed by addition of H_2O_2 (2 mL), also heated to dryness. The total heating time was 30 min. Triplicate MIP-AES determinations of Ca, Cd, Cu, Fe, K, Mg, Mn, P, Pb and Zn in NIST SRM 2711 (Montana soil) and EMBRAPA RM Agro E2002a (tropical soil) gave extraction efficiencies of 80% (Mg) to 99% (Pb) and of 83% (Ca) to 99% (Mg), respectively.

Various *digestion methods for the determination of Cd isotope ratios* in a range of soil and plant materials were studied[119]. High pressure bomb digestion at 195 °C for 72 h with a 1+3 mixture of HNO_3 and HF did not lead to Cd loss and $\delta^{114/110}$Cd values for the four soil and two plant RMs tested gave reproducible results within reported values. On the other hand, dry ashing, performed at 550 °C for between 12 and 24 h with 25-700 mg sample, followed by heating at 120 °C for 24 h with a 1+3 *v/v* mixture of HNO_3 and HF, resulted in Cd loss and perturbation of Cd isotope ratios to varying degrees in all sample types. That dry ashing was unsuitable for Cd isotope ratio measurements was demonstrated by the 2.69‰ deviation in $\delta^{114/110}$Cd obtained for NIST SRM 1570a (spinach leaves). The values of -0.07 ± 0.09‰ and 0.26 ± 0.05‰ for $\delta^{114/110}$Cd in NIST SRM 1573a (tomato leaves) and NRCCRM RM GSD-30 (drainage sediment), respectively, were the first that had been reported.

The drive for *improved reagents for extraction* led[120] to the synthesis of three stable ILs derived from substituted benzothiophenes. The relatively time-consuming process involved thiophene metalation, performed at -30 °C, followed by α substitution with an ethyl, butyl or dodecyl group to produce the 2-alkylbenzothiophene. This was reacted with silver tetrafluoroborate (0.44 mM) and methyl iodide (2.8 mM) for 12 h and cooled to -18 °C overnight to obtain the final salt. The products were characterised spectroscopically and by DSC. The 1,2-dimethylbenzo[b]thiophenium tetrafluoroborate salt (10 mM) for the MAE (250 W, 120 °C) of metals in spiked estuarine sediments (pH=2) extracted the same amounts of Cd, Cu, Cr, Ni, Pb and Zn (paired t-test, $t_{calc.}<t_{crit.}$) as the first two fractions of the BCR protocol together. However, the reaction time of only 30 s was much shorter than the 32 h required for the BCR procedure. Based on simulations of solvent efficiency, nine natural DESs were prepared[121] and water content, reaction time and temperature optimised for the extraction of Cu, Mn, Mo and Zn from powdered barley grass (*Hordeum vulgare L.*). Metal concentrations were determined by ICP-MS/MS. Maximum extraction efficiency was obtained when the water content was above 50% for all solvents. Optimum extraction durations and temperatures were DES-specific. The Cu, Mn and Mo contents determined in ERM CD281 (rye grass) were accurate but there was an overestimation of the Zn content that was attributed to contamination. A methanol-based solvent-extraction-procedure was proposed[122] to overcome the problem of changing particle size distribution observed in enzymatic extraction protocols for NP analysis. It involved sonification of homogenised NP-treated leaves, addition of 50% *v/v* MeOH+deionised water and shaking of the resultant solution (150 rpm, 1 h). Tween 80® (1% *v/v*) was added for NP

stabilisation prior to filtration and dilution for sp-ICP-MS or sp-ICP-TOFMS analysis. The method was tested on corn, lettuce and kale samples spiked with Au, CuO and ZnO NPs. The total metal recoveries of 70 - 100% were influenced by both the NP and the leaf type. The procedure has potential for the monitoring of nanoparticulate agrichemicals.

A HNO_3-based leaching method for the *determination of radionuclides of Am and Pu in soils and sediments* employed[123] several clean-up steps to remove interfering elements and to reduce matrix effects. The method combined several traditional steps: sample ashing; HNO_3 leaching; coprecipitation with $Fe(OH)_3$ for the removal of alkali and alkaline metals; a two-stage chromatographic separation, firstly with UTEVA and DGA resins for separation of Am and Pu and removal of interfering elements (Bi, Hf, Hg, Pb, Pt, Th, Tl and U) and then with TEVA® resins for further purification; and ICP-SFMS quantification. Concentrations of Am and Pu measured in IAEA CRMs 447 (moss-soil), 384 (Fangataufa lagoon sediment) and 385 (Irish Sea sediment) and NIST SRM 4357 (ocean sediment) ranged from 83.6 ± 8.0% to 88.4 ± 2.4% and 70.6 ± 6.4% to 91.1 ± 0.5% of the certified values, The LODs for 2 g samples of 0.039 mBq g^{-1} (0.31 fg g^{-1}), 0.94 μBq g^{-1} (0.41 fg g^{-1}), 2.33 μBq g^{-1} (0.28 fg g^{-1}) and 1.35 mBq g^{-1} (0.35 fg g^{-1}) for ^{241}Am, ^{239}Pu, ^{240}Pu and ^{241}Pu, respectively, made the method suitable for simultaneous determination of ultratrace quantities of the nuclides from global fallout or nuclear accidents.

A novel online protocol for *sequential extraction from small samples* such as fine dusts was based[32] on the BCR and Tessier schemes but with a more relevant reduced sample-size of 5 mg. Traditional solvents were diluted with 3% HNO_3 to enable direct online introduction of extracts for ICP-SFMS analysis. Optimal pump-flow-rate was 0.3 mL min^{-1} with a transfer-line diameter of 0.25 mm. Mobility patterns were determined in the multi-element (Al, Ba, Ca, Cd Co, Cr, Cu, K, Mg, Mn, Na, Ni, Pb, Rb, Sr, V and Zn) characterisation of soils, coals and mine- and road-dusts. The total mass recovery was 72% of that obtained by conventional offline extraction because lower extractant concentrations and shorter extraction times were used. To determine the physico-chemical partitioning of PTEs in airborne PM, Sagagi *et al.*[124] developed two non-specific flow-through sequential extraction procedures with chemometric identification of substrates and element distribution (CISED) methodology. One method was based on reduction of sample requirement (2 g of sample and 10 mL of extractant) for a standard CISED extraction to 0.1 g of sample and 3 mL extractant. The other method employed an in-line quasi-flow-through system in which the sample was supported on a TX40 filter in a 47 mm polycarbonate filter holder. When applied to IRMM BCR CRM 701 (lake sediment), the extractions gave recoveries comparable to those of the well-established BCR extraction steps 1-3. The CISED data processing identified seven distinct geochemical components including carbonates, oxyhydroxides and species dominated by Fe and Si. The flow-through method is potentially useful for identification of the geochemical components of urban air pollution and the assessment of associated health risks.

In the *element-specific extraction of Hg* from surface sediments, de Jesus *et al.*[125] demonstrated that Hg could be extracted without digestion by using dithiothreitol as a chelating agent. The relatively simple procedure involved sonication (250 mg sample, 30 min) with dithiothreitol solution (4 mL, 0.1 M, pH 9) and CV-AAS analysis. Method LODs and LOQs were 6 and 19 ng g^{-1}, respectively. Results obtained for analysis of NRCC marine sediment CRMs MESS-3 and PACS-2 were 0.112 ± 0.014 and 3.11 ± 0.36 mg kg^{-1} (certified values 0.091 ± 0.009 and 3.04 ± 0.20 mg kg^{-1}). A method for the microcolumn-based leaching of bioaccessible Pb for online ICP-AES analysis allowed[126] near-real-time monitoring of Finnish shooting-range soils under various physicochemical conditions. The custom-made 5 × 0.8 cm column consisted of a Teflon cylinder with three cotton buds positioned at the column inlet and outlet for eluate filtration. The sample mass of 2.5 g, larger than that usually packed in microcolumns, gave more representative sampling. The column was positioned upright and an eluent flow rate of 0.3 mL min^{-1} used to deliver eluate to the ICP-AES instrument through polyurethane tubing. A range of solutions was tested. For soil samples containing *ca.* 500 mg kg^{-1} Pb, extractant efficiency was 55% for 0.11 M acetic acid, 58% for 1 M $MgCl_2$, 61% for 0.1 M $NH_2OH.HCl$, 93% for 0.1 M citric acid and 96% for 0.1 M HCl. Analysis time was under 5 h. A slurry sampling procedure followed by HR-CS-ETAAS analysis, proposed for the determination of Yb in road dust samples, involved[127] ultrasonic homogenisation for 34 min with 0.24 M HNO_3. The analysis of NIST SRM 2586 (trace elements in soil containing lead from paint), NCS DC 73301 (rock) and CCRMP TILL-1 (geochemical soil) using pyrolysis and atomisation temperatures of 1200 °C and 2700 °C, respectively, gave accuracies of 99 ± 4 to 104 ± 2%.

4.3.2 Analyte separation and preconcentration

Methods for the *separation of specific elements from soils and plants* continue to be developed. The treatment of PUF by boiling with 5% NaOH, washing and immersion in 10% HCl improved[128] Au adsorption and minimised adsorption of Ca, Fe, K, Mg, Na and Si in comparison to the use of untreated foam. Following hotplate digestion of soil containing between 0.5 and 1000 ng g^{-1} Au, adsorption was 92.6 - 98% for treated foam but only 77.1 - 86% for the untreated sorbent. Although the LOD of 0.02 ng g^{-1} was better than that (0.04 ng g^{-1}) achievable using MAD, the latter was considered a more attractive option for routine trace level determination because of the shorter extraction time. A single-step procedure for the separation and purification of Sb in soils and plants used[129] a thiol-functionalised mesoporous silica powder. Following sample digestion (microwave with various acid mixtures depending on sample) and Sb reduction, samples were loaded onto SPE columns containing 0.2 g of the porous sorbent. Sorbed elements were released with increasing concentrations of HCl, Sb being eluted with 6 M HCl. Quantification was by HG-MC-ICP-MS. The method was tested by the analysis of 14 CRMs. Interfering elements were removed with >97% efficiency and Sb recovery after purification was 100 ± 7% of the Sb concentration determined without purification. A two-step purification process for the separation of Cd involved[130] AG-MP-1M and TRU resins. The method was validated by the analysis of NIST SRM 3108 (Cd standard solution) and secondary RM BGEG-Cd. The $\delta^{114/110}$Cd measured for a range of geological standards were in good agreement with reported values. Common water hyacinth (*Eichhornia crassipesas*) can be used[131] as a biosorbent for Pb. By applying factorial design, SPE conditions were optimised at 0.02 g of dried and milled leaves as sorbent, with sample inlet and eluent (0.1 M HCl) flows of 5.6 and 6.8 mL min^{-1}, respectively. This low-cost and environmentally friendly method was validated with NIST SRM 1515 (apple leaves). The mean Pb value determined by FAAS was not statistically different from the certified value.

Other methods for the analysis of soils, plants or related materials, or those developed for other sample matrices that used soil or plant CRMs for validation, are summarised in Tables 3 (liquid-phase extraction methods) and 4 (solid-phase extraction methods).

4.4 Instrumental analysis

4.4.1 Atomic absorption spectrometry

Optimised ETAAS methods were reported for the determination of As, Cd and Pb in hemp products[132]; Cd and Pb in boron minerals and boron-rich waste[133]; and Cr in cigarette tobacco, filters and ash[134]. All of these methods were validated by analysis of soil, sediment or plant CRMs.

Interest in the use of *HR-CS-ETAAS and its variant HR-CS-ETMAS* continued. An optimised method for the quantification of Yb in road dust involved[127] sonication of the sample in 0.24 M HNO_3 for 34 min, injection of 20 µL of slurry into a graphite furnace pre-conditioned with 250 µg of W permanent chemical modifier, pyrolysis at 1200 °C and atomisation at 2700 °C. The LOD was 22 ng g^{-1} and results for analyses of three CRMs were not significantly different from the certified values according to a Student t-test at 95% CI. Germanium could be measured[135] directly in 0.1-0.2 mg solid plant and soil samples by using a mixed-matrix modifier (0.1% w/w $Mg(NO_3)_2$ + 0.2% w/w $Pd(NO_3)_2$ + 0.1% Triton X-100) and pyrolysis and atomisation temperatures of 1500 and 2550 °C, respectively. The LOD of 0.5 mg kg^{-1} made it possible to quantify Ge in tissue samples from a range of plants but some discrepancies were noted with respect to results obtained by ICP-MS following acid digestion. A method for quantification of P in solid samples based on the PO molecular species involved[136] pyrolysis at 1500 °C and vaporisation at 2200 °C. The preferred chemical modifier was 10 µg of Au which promoted conversion of P to PO. The method was validated by the analysis of NIST SRMs 1547 (peach leaves), 1573a (tomato leaves) and 1570a (spinach leaves) which contain 1371 ± 82, 2161 ± 28 and 5187 ± 67 mg kg^{-1} of P, respectively.

4.4.2 Atomic emission spectrometry

Novel developments in sample introduction included[137] the first use of ETV-ICP-AES for the determination of F in solid samples of plant materials. The optimised temperature program (pyrolysis at 250 °C and vaporisation at 2200 °C) took just 70 s to complete. Calibration involved increasing amounts of either NRCC CRM DUWF-1 (durum wheat flour) or F standard solutions. A previously reported multimode sample introduction system that interfaced two HPLC instruments to an ICP-AES system was adapted[138] to allow simultaneous separation and detection of both hydride-forming (anion-exchange column and in-spray chamber HG) and non-hydride-forming elements (cation-exchange column and conventional pneumatic nebulisation).

Aerosol dilution was demonstrated[139] to improve the tolerance of *MIP-AES* to samples with high total-dissolved-solids content. The signal suppression that occurred at NaCl concentrations > 0.9 g L^{-1} when using conventional nebulisation was less severe with aerosol dilution: indeed, the emission intensity for some lines was greater in solutions containing 5 g L^{-1} NaCl than in those containing 0.1 g L^{-1}. A PVG-SPME-TD manifold was optimised[140] for the determination of Hg by MIP-AES. Sample solution containing 5% *v/v* formic acid was pumped through a quartz reactor where it was exposed to UV radiation (100-280 nm) to generate Hg vapour. This vapour was preconcentrated onto a SPME fibre in the gas-liquid separator under stopped-flow conditions and the fibre then transferred to the TD port of the MIP-AES instrument. The results of 133 ± 5 mg kg^{-1} obtained for CRM ERM CC580 (estuarine sediment) was in agreement with the certified value of 132 ± 3 mg kg^{-1}.

There has been considerable interest in developing *miniaturised atomic emission spectrometers* as alternatives to pXRFS and LIBS instruments for field analysis. Different approaches have been chosen to improve analytical performance. He *et al.*[141] developed a novel cross double-point discharge incorporating four electrodes that produced a larger microplasma than previous single-point discharge devices, thereby ensuring that a higher proportion of analyte (introduced as the hydride) was excited. The LODs of 2.4, 0.15 and 1.9 μg L^{-1} for As, Hg and Pb, respectively, were about a third of those previously reported. Yuan *et al.*[142] optimised a GD-

AES method using a HG-solution anode for determination of Hg with an LOD of 0.03 µg L^{-1}. Deng *et al.*[143] designed a compact device integrating a tungsten coil ETV atomiser and a conventional (two electrode) point-discharge microplasma in a single quartz tube. The unusually close proximity of the atomiser and plasma (optimal distance 12.5 mm) had improved transport efficiency and, hence, better LODs than devices that incorporate an interface. Results for Ag, As, Bi, Cd, Cu, In, Pb, Sb and Zn in a selection of 14 environmental CRMs were not significantly different from certified values at 95% CI. Liu *et al.*[144] explored the use of an electromagnetically-heated tungsten boat for direct analysis of solid samples as an alternative to the use of a tungsten coil atomiser and liquid sample introduction. The excitation source was a DBD. The LODs for analysis of a 5 mg sample were 0.018, 0.008 and 3.5 mg kg^{-1} for Cd, Hg and Pb, respectively. Accurate analysis of 10 soil CRMs was demonstrated (t-test at 95% CI).

The optimum conditions in the first demonstration[145] of *LA-APGD-AES for direct determination of Cd, Pb and Zn in soil* were: 28 mA discharge current, 14 mm discharge distance, 140 mL min^{-1} gas flow rate (3% H_2 + 97% He), 60 mJ laser energy and 10 Hz laser repetition rate. Samples were presented as pressed pellets without binder. Calibration curves were obtained by analysis of CRMs covering a range of concentrations. The LODs were 0.31, 2.7 and 0.68 mg kg^{-1} for Cd, Pb and Zn, respectively. Results for two soil samples from different parts of China were similar to those obtained by ICP-AES but no statistical comparison was reported.

4.4.3 Atomic fluorescence spectrometry

A novel method for simultaneous preconcentration and speciation of Se and Te involved[146] online IL-formation, microextraction and HG-AFS. Mixing of the IL $[C_8mim]Cl$ and KPF_6 to yield non-soluble $[C_8mim]KPF_6$ extracted Se^{IV} and Te^{IV} from soil and sediment extracts as their

APDC complexes at pH 4. These were retained on a cotton microcolumn before elution with 5 M HNO_3 in methanol into a miniaturised external hydride generator. Pre-reduction of analytes allowed total Se and Te concentrations to be determined so that Se^{VI} and Te^{VI} concentrations could then be calculated by difference. Acceptable ($p<0.01$) accuracy was demonstrated by analysis of IRMM CRM BCR 402 (white clover) containing 6.7 ± 0.25 mg kg^{-1} Se. Recoveries of spikes from soil and sediment samples were 96-102% for Se species and 95-108% for Te species at a spike concentration of 0.5 mg kg^{-1}.

4.4.4 Inductively coupled plasma mass spectrometry

The sources and types of *interference effects* commonly encountered in geochemical analysis by quadrupole ICP-MS were discussed[147] in an excellent tutorial review (178 references) along with means by which these can be overcome. Although not specifically for the analysis of soil and plants, the publication[148] of a searchable database of ions that can cause spectral overlap in ICP-MS was a valuable contribution likely to be of interest to analytical geochemists.

A comparison of *calibration strategies for the determination of Cd, Co, Cu, Fe, Mn, Ni and Pb in soil by ICP-SFMS* concluded[149] that there was generally little difference between results obtained using IDA, gravimetric external calibration with gravimetric internal standardisation, and gravimetric standard addition with gravimetric internal standardisation but noted that the volumetric preparation of standards could lead to loss of accuracy.

A *flow-injection slurry-sampling ICP-MS method* used[150] a mixed-gas plasma to achieve a high-throughput determination of Al, Cd, Cu, Fe, K, Mo and Zn in wheat flour. Sample slurry (1% *m/m)* in a surfactant solution (Aerosol-OT) was stable enough to be introduced without continuous agitation during sampling. The plasma gas was made up of 462 mL min^{-1} N_2 + 18.5

L min^{-1} Ar and the sheath gas was 4 mL min^{-1} H_2. Results for analysis of NIST SRM 8437 (wheat flour) were statistically similar to certified values (95% CI) for all elements except Al, which was overestimated due to polyatomic ion interferences, in particular $^{1}H^{12}C^{14}N^{+}$, caused by addition of the H_2 and N_2,

The *coupling of chromatographic separation with ICP-MS* continues to be of interest because of the insight it can provide into trace element speciation. Of particular note for As were two HPLC-ICP-MS methods. The first was used[151] not only for speciation analysis in different tissues of rice plants but also to explore associations between As and DNA fractions. The second was applied[152] together with UHPLC/ESI-MS/MS to identify As species in marine algae and algae-based foodstuffs. Another HPLC-ICP-MS method could resolve[153] Cr^{III} and Cr^{VI} in rice extracts in <4.5 min and had a LOD of 0.012 ng mL^{-1} for both species. An unknown Cr compound was detected that required further investigation. A novel online microdialysis-HPLC-ICP-MS system was developed[154] for continuous sampling and measurement of Cr^{VI} in soil solution, thereby minimising Cr species interconversion which is the bane of conventional extraction procedures. Because the Hg^{I} species is also prone to redox instability, it is difficult to explore its role in biogeochemical processes. A new method based on 2-mercaptoethanol extraction and HPLC-ICP-MS was used successfully to detect[155] Hg^{I} in plant and soil samples. The application of SEC-ICP-MS and AEC-ICP-MS aided[156] the identification of new Ni-containing proteins in water extracts of *Arabidopsis* root.

Advances in FFF-ICP-MS included[157] the first successful use of a preparative rather than an analytical asymmetric FFF instrument, thereby increasing the injection volume and sensitivity for the detection of particulate P in soil extracts. The capabilities of FFF-ICP-TOFMS and FFF-sp-ICP-TOFMS for analysis of soil spiked with engineered NPs (CeO_2, Fe_2O_3 and TiO_2 at concentrations of 0.05, 0.5 and 5 mg kg^{-1}) were explored[158]. An increase in Ce, Fe and Ti signals with increasing spike concentrations was observed when using FFF-ICP-TOFMS. However, the magnitude of the increase did not correspond to the amounts of NPs added and the signals for a range of other elements also increased. The explanation proposed was enhanced extraction of natural particles caused by introduction of residual surfactants left over from NP synthesis. It was not possible to distinguish the NPs, at least at the concentrations added, from the high background of soil particles containing Ce, Fe and Ti. However, the study demonstrates the importance of multi-element screening to avoid misinterpretation of results.

Other *developments in sp-ICP-MS* included[159] a method for the analysis of CeO_2 NPs extracted from soil with 2.5 mM tetrasodium pyrophosphate that had LODs of 15 nm particle size and 194 NPs mL^{-1}. An assessment of aging on NP in soils found that no marked change occurred in particle size, size distribution or particle concentration over a period of one month. A LA-sp-ICP-MS study initially ablated[160] Au NPs deposited on a flat polyether sulfone membrane in order to check particle size preservation and linearity of response. Subsequently, NP-doped soils were analysed. A key finding was that particle recovery was affected by the nature of the substrate on which the particles were presented to the laser. In a procedure for the sp-ICP-MS/MS analysis of TiO_2 NP in plant digests, O_2 was added[161] to the collision/reaction cell to overcome spectral interferences on $^{48}Ti^{+}$. Quantification of Ti was based on the $^{48}Ti^{16}O^{+}$ ion at *m/z*=64. The size LOD was 15 nm. The method was used to study NP uptake in radish.

Studies involving *elemental imaging by LA-ICP-MS* included[162] a cold plasma method for studying the distribution of Na in roots of *Arabidopsis thaliana* grown in a cultivation medium containing 0.05 nM Na. Plasma cooling was achieved by reducing the plasma power to 670 W and delivering an additional wet aerosol (dilute HNO_3) to the ICP. This improved the LOD for Na two-fold. When a laser spot size of 4 µm was employed, it could be seen that Na was located in a narrow band of cells. This finding supported the hypothesis that the root epidermis may act as a diffusion barrier. The first application of LA-ICP-MS to the study of the spatial distribution of major (Ca, K, Mg and P) and trace (Co, Fe, Mn, Na and Zn) elements in the rhizosphere through analysis of soils cores (0-15 cm depth) provided[163] useful information on the effects of different soil amendments and agronomic practices.

An investigation of *the utility of CaF_2 as a dominating matrix for quantitative analysis by LA-ICP-MS* used[164] NIST SRM 2719a (Montana soil) as its test substrate. A mixture of 0.3 g NH_4HF_2 + 0.65 g $CaCl_2$ + 0.05 g soil was heated in an electric furnace, ground and pressed into a pellet for analysis. Although promising results were obtained for Al, Fe, Mg and Mn using $^{44}Ca^+$ as IS, there is a need to prove this approach for analytes present at lower concentrations.

New methods for *the precise measurement of isotope ratios by MC-ICP-MS* included[165] a procedure that used a single cation-exchange column to separate K from sample matrix elements with a 99.5 ± 0.6% yield. That K isotopes may have greater potential as environmental tracers than previously thought was highlighted by the analysis of 23 geological and biological RMs. Whereas the $\delta^{41}K$ values for rocks were similar to each other and consistent with published data, those for soil, sediment and plants were more varied. A single-step purification method for Sb based on a thiol-functionalised mesoporous silica powder was used[129] to determine the $\delta^{123}Sb$ values in a wide variety of CRMs with complex matrices. A double-spike MC-ICP-MS method for Cd provided[130] $\delta^{114/110}Cd$ values in four soil, nine sediment and two manganese nodule CRMs that fell within the range of published data. A value (−0.08 ± 0.04 (n=6)) for $\delta^{114/110}Cd$ in IGGE GSD-3a (sediment) was reported for the first time.

Radionuclides in soil were a focus of *ICP-MS/MS research*. In a method for the determination of ^{236}U, 0.6 mL min^{-1} CO_2 and 7 mL min^{-1} He were introduced[166] to the collision/reaction cell to remove interferences, in particular by converting $^{235}U^1H^+$ to $^{235}U^{16}O^+$. This allowed determination of $^{236}U/^{238}U$ ratios as low as 3 x 10^{-10}, an order-of-magnitude better than previously achievable. A study conducted using NH_3 and He cell gases demonstrated[167] that the determination of Pu was relatively insensitive to the sample preparation method used. However, removal of Pb and U was more challenging following lithium metaborate fusion than following digestion in either *aqua regia* or 8 M HNO_3. A procedure for the measurement of ^{241}Am, also using He-NH_3 collision-reaction gas, had[168] a LOD of 0.091 fg g^{-1}, three times better than that achievable using other types of ICP-MS. The results for the analysis of the IAEA CRMs 375 (soil) and Soil-6 of 0.758 ± 0.078 and 0.528 ± 0.055 mBq g^{-1} were not significantly different from the certified values of 0.71 ± 0.16 and 0.48 ± 0.10 mBq g^{-1}, respectively. The method was applied to seven surface soils from China and a sediment from Denmark. A key step[33] in a ID-ICP-MS/MS method for simultaneous determination of PGEs and Re was removal by CEC of the majority of elements likely to form isobaric or polyatomic ion interferences. The reaction gas in the collision cell was 10% NH_3 in He.

4.4.5 Laser-induced breakdown spectroscopy

A competition organised under the auspices of the 10th Euro-Mediterranean Symposium on LIBS involved[169] *processing of soil spectral data* with the aim of correctly classifying the highest possible number of unknown spectra (the test set) using a training set of labelled spectra. The classification approaches employed by the five most successful teams were discussed in detail. This type of exercise is very much to be encouraged as it leads to sharing of knowledge and good practice across the community.

Efforts have continued with the aim of improving the performance of *LIBS for soil analysis*. A 532 nm monomode and a 1064 nm multimode laser were compared[170] using the same spectrometer system and laser fluence (460 J cm^{-1}). A larger mass was ablated at 532 nm but the plasma temperatures and electron densities were similar for the two lasers. The superior S/N obtained for C, Fe, Mg and K in a test soil meant that use of the 1064 nm laser was recommended. The importance of optimising the energy ratio and inter-pulse delay time in DP-LIBS was demonstrated[171] and the enhancement in emission line intensity, and hence sensitivity, that can be achieved by plasma spatial confinement (discussed in last year's ASU[1]) was confirmed[172]. The beneficial effects of using a heated target in soil analysis were demonstrated[173] for the first time. When a sample spiked with Pb powder (80 ppm) was analysed at 100 and 200 °C, emission intensities for matrix elements such as Al, Ca, Fe and Si increased and spectral lines of the Pb became visible. None was visible at room temperature. The LOD for measurement at 200 °C was 3.8 ppm.

In LIBS-LIF, a second, tuneable laser is used to pump analyte atoms in the primary laser ablation plume to excited states from which emission can occur, thereby increasing emission intensities and S/N. When *a LIBS-LIF method for micronutrients in soil* was applied[174] to a suite of 12 GBW CRMs, a linear response was obtained with LODs of 0.36, 0.48, 23, 1.2 and 1.2 ppm for B, Cu, Fe, Mn and Zn, respectively. The approach showed promise but application to CRMs not used in calibration would have been desirable.

Numerous *LIBS methods for the determination of specific elements in soil* have been reported and it is pleasing to note that several researchers evaluated performance by comparison with results obtained by other techniques. Noteworthy was a procedure for the determination of Cd with an LOD of 7.8 mg kg^{-1} that gave[175] a relative error of <6.1% for analysis of soil samples previously tested by the Chinese Institute of Environmental References Materials or the Ministry of Environmental Protection. A method for estimating available-K involved[176] immersing a cation-exchange membrane in a soil suspension in deionised water, shaking for 10 min, recovery of the membrane, removal of adhering soil particles by sonication, drying at 40 °C and LIBS analysis. Results agreed within 2.6% with ammonium-acetate-extractable K values. A study combined[177] LIBS and VIS-NIR data from various wavelength regions using different models to estimate P concentration in 147 Danish agricultural soils. Results were compared with data for water-extractable P; available P as defined by the method of Olsen; oxalate-extractable P; and total P obtained by wet chemical methods. The combined LIBS and VIS-NIR models with variable selection generally produced the results most similar to the reference method for all four P pools. In an improved method for the determination[178] of soil C, overestimation of the analyte at 247.8561 nm due to interference from the Fe II line at 247.8572 was overcome by use of a high resolution spectrometer and a LS interference-correction method.

A Design of Experiments approach was used[179] to optimise a multi-element *LIBS method for analysis of river sediments*. Both single-pulse LIBS at 1064 nm and DP-LIBS using 532 and 1064 nm lasers were studied. Parameters considered were laser energy, delay time, gate width and number of pulses accumulated (plus inter-pulse delay for DP-LIBS). The selection of optimal conditions was based on S/N contour graphs. Single- and DP-LIBS methods for determination of P were developed[180] and used to analyse samples taken from sediment cores collected in two rivers in Brazil. Although results sometimes differed from those obtained by ICP-AES following HNO_3 digestion, overall trends in P concentration with depth were similar.

Research on *elemental analysis of plants by LIBS* is generally less advanced than the analysis of soils. Although the field is advancing rapidly, method performance assessment still tends to focus on model development and internal validation using training and test sets rather than on comparison with results obtained by established methods. Procedures have been reported for the determination of: Cr and Cu in mulberry leaves[181]; Al, B, Ca, Fe, K, Mg, Mn, N and P in vegetables[182] and Al, Ca, Cu, Fe, K, Mg, Na, P, Si and Zn in different parts of the rice plant[183].

A method for *the determination of Pb in rhododendron leaves by LIBS-LIF* involved[184] direct analysis of solid samples following grinding, spiking with different amounts of $Pb(NO_3)_2$ solution (for standard addition calibration), drying and mounting on adhesive tape. An alternative sample preparation method, described as "solid-liquid-solid transformation" (SLST) had an intriguing name but was in fact a conventional UA digestion in 0.03 M HCl followed by spiking with the $Pb(NO_3)_2$ and drying onto glass slides. Results were compared with those obtained by ICP-AES following MAD. Unsurprisingly, the two methods involving total sample digestion gave similar results! However, the conclusion that this proves the superiority of SLST-LIBS-LIF over ICP-AES in terms of overall speed and efficiency is based on an unfair comparison, since the extracts prepared for LIBS analysis could easily have been analysed by ICP-AES without the need for MAD. It is also unclear why, given that one of the key strengths of LIBS is the ability to analyse solid sampled directly, the introduction of sample digestion and extraction steps to analytical protocols should be desirable.

In *spark discharge-LIBS*, electrodes are positioned just above the sample surface and held at a voltage below the spark-gap self-breakdown potential. When the laser is fired at the sample, the ablation plume expands in the gap and triggers the spark discharge which reheats the plasma and increases signal intensity. A further potential advantage is the ability to calibrate the analysis by using a single solid standard with a matrix composition similar to that of the samples and by varying the voltage applied to the electrodes, thereby avoiding the need to produce a set of solid standards with different analyte concentrations. Multi-voltage calibration was investigated[185] for the determination of Al in plants and P in fertilisers, together with two other strategies that involved just one standard: (a) multi-line calibration and (b) slope ratio calibration based on accumulation of multiple laser shots. Accurate results were obtained at 95% CI for Al in NIST SRMs 1570a (spinach leaves), 1515 (apple leaves) and 1573a (tomato leaves) using all three approaches. Whereas results for P in fertilisers based on multi-voltage and slope-ratio calibration were in agreement with those obtained by HR-CS-FAAS, those based on multi-line calibration were not.

4.4.6 Thermal ionisation mass spectrometry

A novel extraction method allowed[186] quantitative isolation of water-soluble Cl from soil for measurement of δ^{37}Cl values by TIMS. Soil was dried, sieved, ground, treated with H_2O_2 to decompose OM and then extracted with high purity water. The extract was purified using a four-step ion-exchange-chromatography procedure. Although soil samples from Weifang, China were affected by seawater intrusion and were highly contaminated with Cl (up to 531 mg kg^{-1}), δ^{37}Cl values (−2.40 to 1.16) indicated the presence of Cl from multiple anthropogenic sources in addition to that from seawater.

4.4.7 X-ray spectrometry

A *review* (100 references) (in Chinese with English abstract) focused[187] on recent advances and limitations in the use of X-ray spectrometry for the study of element translation in plants. A review by Feng *et al.*[188] (76 references) on the application and limitation of XRFS studies of plants and soils included assessments of food safety and nutrition and concluded that development in detectors, beamline capability and scanning systems would improve performance and application.

Developments in the *XRFS analysis of soils* focused on sample preparation and spectral interpretation. Croffie *at al.*[189] compared sample presentation using loose powder, pressed pellet and pressed pellet with wax binder for the EDXRFS determination of 13 elements in four international soil exchange RMs ISE 952 and 961 (clay), 992 (sandy clay), and 995 (sand). Recoveries were highly dependent on both the element and the preparation method and ranged from 87% for Al in clay prepared with binder to 710% for Si in sand with pressed pellet preparation. A general overestimation (>20%) of recoveries was attributed to large particle sizes in Si-containing samples and peak overlap. Wu *et al.*[190] corrected the overlap of As and Pb peaks by applying a Gaussian mixture statistical model and chaotic-particle-swarm optimisation, thereby providing a mechanism for more accurate element quantification. In a paper in Chinese, spectra obtained in the field in the determination of Pb were corrected[191] for noise by applying harmonic analysis at different Pb concentrations and smoothed pseudo Wigner-Ville distribution.

A measuring chamber developed[192] for fluorescence kinetic measurements was modified[193] for the *μXRFS imaging of trace elements in living plants*. The measuring chamber provided the humidity and nutrients needed for continued plant growth during analysis so that the health of the pepper plant could be maintained during 20 h of irradiation with a dwell time of up to 600 ms per spot. The customised bench-top XRFS instrument was modified with a multilayer mask on the detectors to minimise spurious counts and result in cleaner spectra. The system was used for whole-leaf mapping (rather than spot measurements) of Zn in the hyperaccumulator *Noccaea caerulescens* and, as a result of the long irradiation time possible, was also successfully used to study the distribution of Cu, Fe, Ni and Zn in pepper leaves and soy bean roots.

5 Analysis of Geological Materials

5.1 Review articles

In a review (63 references) of the advances in ICP-MS technology and their impact on the *mineral exploration sector*, the ability of multi-element ICP-MS data to reveal significant ore bodies was demonstrated[194] in a series of case studies. However, not all the developments in ICP-MS have been widely implemented by exploration geochemists and reasons for this were examined. A review (87 references) on advances in exploration geochemistry between 2007 and 2017, particularly in relation to ore deposits under relatively young cover, considered[195] four key areas: understanding metal mobility and mechanisms; rapid geochemical analyses; data access, integration and interoperability; and innovation in laboratory-based methods. It was noted that a common problem in the geosciences was the poor availability of suitably-trained geochemists for industry, although this had started to be addressed by recent initiatives at various universities at graduate level. A short paper (41 references) on advances in the use of isotopes in geochemical exploration focussed[196] on developments in instrumentation and the application of isotopes for the understanding of geochemical processes. Although it was felt that isotopic compositions were unlikely to become a standard tool in exploration, they were considered important for tracing the origin of key elements and as indicators of dispersion processes.

Photo-induced force microscopy is a cutting-edge technique that combines the advantages of AFM with IR spectroscopy to acquire simultaneously 3D topographic data and molecular chemical information at high spatial (*ca.* 5 nm) and spectral (*ca.*1 cm^{-1}) resolution. A comprehensive review[197] (80 references) of the technical aspects of this technique and its application to geosciences through nanoscale chemical imaging had the aim of introducing this new analytical development to a broader geochemical audience. Examples of its application included the visualisation of growth zonation in zircons and the identification of fluid speciation in high-pressure experimental samples and of nanoscale organic phases in biominerals.

An annual bibliographic survey provided[198] a summary of *RMs used in geochemistry and related fields*, such as paleoclimate and environmental research, that featured in papers published in 2019. This review examined 6850 papers from more than 20 scientific journals and used data from nearly 700 articles. All the RM data are freely available in the GeoReM database (http://georem.mpch-mainz.gwdg.de) and all the articles are listed in an appendix. A review in Chinese (115 references) discussed[199] progress in the production of geological RMs with ultrafine particle sizes in China since 2003 and their role in improving analytical accuracy.

Field-portable geochemical techniques have seen rapid development over the past two decades, so a review[200] (61 references) of handheld and site-portable instruments used for mineral exploration is timely. It covered a range of techniques including core scanners, XRFS, XRD, LIBS, IR, FTIR, μRaman and gamma spectroscopies and discussed the benefits, challenges and pitfalls of field measurements as well as the balance between data quality and quantity. A comprehensive review (121 references) of field-portable and handheld LIBS provided[201] an historical overview of the technique and a comparison with its main competitor, pXRFS. A detailed description of the current status of LIBS instrumentation and a wide variety of applications was presented. It was concluded that although the future for this technique was very promising, important technological advances were still required to maximise its potential.

The limited availability of matrix-matched calibrants was also a major impediment to environmental applications.

Those engaged in research on *mineral-hosted melt inclusions* are directed to a series of recommendations[202] (279 references) for sample preparation, analysis and data presentation. The paper was dedicated, by the participants and organisers of the melt-inclusion workshop held in 2018 at Woods Hole Oceanographic Institution, to Erik Hauri in recognition of his contributions to the *in-situ* analysis of melt inclusions. The intention of these guidelines was to bring some uniformity to the characterisation of melt inclusions and to systematise data collection and reporting, thereby facilitating the comparison and evaluation of published data.

A review (250 references) of the *analysis of geological materials by a wide variety of techniques* provided[203] a basic introduction to sample decomposition and analysis. The merits and limitations of 11 commonly used techniques for geochemical applications were discussed and some practical examples given. The same author summarised[147] (178 references) the technical advances in ICP-MS made over the last three decades aimed at reducing the different types of interferences encountered. Developments discussed included the use of cool plasmas, collision/reaction cell technology, HR-ICP-MS and ICP-MS/MS. The contribution of approaches such as internal standardisation, ID, standard addition and matrix-matching calibrations to the improvement of data quality were also discussed.

Advances in *laser-assisted techniques* such as LA-ICP-MS and LIBS were the focus of several review papers. Recent developments related to isotopic fractionation, matrix effects and isobaric interferences in LA-MC-ICP-MS were considered[204] (149 references) as well as methods for their mitigation. It was emphasised that the selection of appropriate correction methods was critical to obtain accurate and precise isotope ratios. There was, however, no universal solution and each isotope system required its own procedure dependent on the hardware available and the samples of interest. A review[205] (123 references) on recent developments in LIBS analysis combined with machine learning for geochemical and environmental resources exploration, covered instrumentation, sample preparation, spectral fusion technology, field-portable and remote LIBS, machine learning methods and applications to various geological and environmental materials. The accuracy, precision and LODs of LIBS analysis constrained current applications, and substantial improvements were required to achieve potential applications.

5.2 Reference materials and data quality

There is an ongoing interest in the *synthesis and characterisation of microanalytical RMs* for *in-situ* microbeam technologies such as SIMS, LA-ICP-MS, LIBS and EMPA. One study described[206] the production of PGE RMs from sub-µm-size PGE-doped silica particles. These doped particles were used as feedstock materials for electrophoretic deposition followed by thermal processing to fabricate two cm-sized materials with PGE concentrations between 0.5 to 3 $\mu g\ g^{-1}$. Excellent homogeneities of 2-5% RSD were confirmed by LA-ICP-MS, provided that the rims of the materials (outer 1 mm) were not used. These materials could represent some of the most complete and homogeneous PGE RMs synthesised with a silicate matrix. The process of ‘additive manufacturing’ clearly has great potential in the production of matrix-matched RMs. The incorporation of Pb, REEs and U into calcite involved[207] heat- and pressure-induced crystallisation from amorphous calcium carbonate that had been precipitated from an element-doped reagent solution. The doped elements in the resulting calcite RMs were homogenously distributed (<12%, 2RSD). As the $^{207}Pb/^{206}Pb$ ratio varied by <1% and the

$^{238}U/^{206}Pb$ ratio by 3–24%, depending on element mass fractions, these synthetic RMs were considered to be a promising alternative to natural calcite RMs for U-Pb geochronology. Courtney-Davies *et al.*[208] used ID-TIMS and LA-ICP-MS to characterise cm-sized chips of a synthetic haematite RM called MR-HFO. A comparison of this MR-HFO and a zircon RM (GJ-1) for the calibration of LA-ICP-MS analyses of natural haematite samples, ranging from Cenozoic to Proterozoic in age, indicated that MR-HFO yielded more concordant U-Pb ratios that were in better agreement with independently acquired ID-TIMS data from the same natural haematite grains. It was concluded that MR-HFO was a suitable RM for LA-ICP-MS haematite U-Pb geochronology despite there being some heterogeneity in U/Pb ratios detected by ID-TIMS. Four iron sulfide RMs for LA-ICP-MS analysis were prepared[209] by hydrothermal synthesis, in which doped elements in solution entered the synthetic sulfide lattice as isomorphs during crystal growth. The resulting nanosulfide pressed-powder-pellets had a typical grain size of 500-600 nm and their excellent cohesion allowed them to be prepared without the addition of a binder. Good homogeneity was demonstrated for most trace elements (<3% RSD for PGEs, Au and Pb) and S isotope compositions (<0.23‰).

Several studies examined *natural minerals as RMs for in-situ isotope ratio analysis*. After screening a large number of apatite specimens from several mineral collections, Wudarska *et al.*[210] focussed on a set of six apatite RMs with Cl mass fractions spanning a range within the apatite solid solution series. Their Cl isotope homogeneity was evaluated using SIMS and $\delta^{37}Cl$ measured by IRMS. All six apatite RMs were deemed suitable for the calibration of *in-situ* $\delta^{37}Cl$ measurements. In addition, major and key trace element compositions as determined by EPMA were reported. In a related study, three Harvard tourmaline RMs (schorl 112566, dravite 108796 and elbaite 98144), already used for the calibration of *in-situ* B isotope measurements, were characterised[211] for their Li and O isotope compositions by SIMS. The Li mass fractions of these tourmalines vary over three orders of magnitude. Homogeneity tests by SIMS demonstrated that the ^{7}Li/^{6}Li and ^{18}O/^{16}O isotope ratios were constant within ±2.2 and ±0.2‰ (1SD), respectively, at sub-ng test portion masses. Reference values reported for δ^{18}O, Δ^{17}O and δ^{7}Li in these tourmaline RMs were based on results for bulk mineral analyses undertaken at several independent laboratories. Any inter-laboratory bias was assessed. A new set of six tourmalines presented[212] as potential RMs for *in-situ* B isotope ratio measurements by SIMS covered an extended compositional range of tourmaline supergroup minerals, including Fe-, Li- and Mg-rich end-members. Bulk MC-ICP-MS analysis yielded B isotopic compositions ranging from -15.5‰ to -9.2‰ with uncertainties of 0.1 – 0.7‰ (2SD). Four existing tourmaline RMs were also re-evaluated for their major element and B isotopic compositions. For two of the RMs, a discrepancy of *ca.* 1.5‰ in δ^{11}B values was observed between the previously published reference values and those determined in this study. It was concluded that a multi-analytical comparison study between different laboratories was required to elucidate fully the reasons for the differences in these results. Two materials, a natural crystallised quartz (Qinghu-Qtz) and a fused quartz (Glass-Qtz), were described[213] as new RMs for *in-situ* O isotope analysis by SIMS. Variations in δ^{18}O of 0.50‰ (n=1083, 2SD) for Qinghu-Qtz and 0.22‰ (n=283, 2SD) for Glass-Qtz, indicated that both materials were homogeneous at the scale of *ca.* 20 µm. In comparison, NBS 28 quartz RM, a well-established quartz O-isotope RM designed for bulk analysis, was less homogeneous at this scale. Two new natural iron sulfide RMs – pyrrhotite JC-Po and pentlandite JC-Pn – were characterised[214] for their Fe and S isotope compositions. Homogeneity was demonstrated by EMPA (major elements), SIMS (S isotopes) and LA-MC-ICP-MS (Fe isotopes). Recommended values for δ^{56}Fe were based on solution MC-ICP-MS analysis whereas δ^{33}S and δ^{34}S were determined by IRMS. Li[215] proposed a natural chalcopyrite (HTS4-6) as a RM for *in-situ* S-isotope-ratio microanalysis after examination by SIMS and LA-MC-ICP-MS. The measurement precision for ^{34}S/^{32}S from both techniques was <0.39‰ (2SD). The recommended $\delta^{34}S$ value determined by IRMS was +0.63 ± 0.16‰ (2SD, n = 23). Another chalcopyrite RM (TC1725) was described[216] for *in-situ* Cu isotope ratio measurements by LA-MC-ICP-MS. Homogeneity was evaluated by solution MC-ICP-MS analysis of bulk material and single grains as well as by fs LA-MC-ICP-MS. Results from all analytical methods agreed within uncertainties. It was concluded that chalcopyrite TC1725 was texturally and chemically sufficiently homogenous to be used as a Cu isotope RM. The recommended mean $\delta^{65}Cu$ value for TC1725 was given as -0.06 ± 0.03‰ (2SD, n = 132) as determined by bulk solution MC-ICP-MS. It is pleasing to note that all the authors of the papers cited in this section appreciated the importance of making these new RMs available to the wider geochemical community.

New reference minerals for *U-Pb geochronology* studies are of continuing interest. More than 100 grains of a bastnaesite K-9 were analysed[217] by EMPA, LA-ICP-MS, SIMS, ID-TIMS and ID-MC-ICP-MS to establish its credentials as a RM for element concentration and U–Th–Pb dating measurements. The homogeneity of major elements (<5 wt% RSD) was demonstrated by EPMA and that of the U-Pb and Th-Pb systems (<2% RSD) by SIMS. The recommended age data (a $^{206}Pb/^{238}U$ age of 116.80 ± 0.13 Ma and a $^{208}Pb/^{232}Th$ age of 116.59±0.11 Ma) were determined by ID techniques. A natural zircon megacryst SA02 was studied[218] as a potential RM for micro-beam U-Pb geochronology and Hf-O isotopic analysis. A mean ID-TIMS $^{206}Pb/^{238}U$ age of 533.7 ± 3.7 Ma (2SD, n = 8) was recommended as the working value when using untreated grains for calibration. Results obtained by SIMS and LA-ICP-MS were in agreement with the ID-TIMS data within the uncertainties of these techniques. The recommended reference value for $^{176}Hf/^{177}Hf$ was 0.282287 ± 0.000016 (2SD, n = 31) based on solution data measured by MC-ICP-MS. Homogeneity was assessed by LA-MC-ICP-MS.

A mean $\delta^{18}O$ value of 6.03 ± 0.28‰ (2SD, n = 13) determined by laser fluorination was in agreement with data obtained by SIMS.

New isotope RMs for solution-based analyses have been developed by several laboratories, particularly with the aim of comparing data for non-traditional stable isotopes. For example, the isotope RMs often used as zero-δ scale for Fe (IRMM-014) and Mg (DSM3) are either out of stock or not readily available so RM IRMM-524A (Fe solution) and ERM-AE143 (Mg solution) have been produced as alternatives by IRMM and BAM, respectively. The Fe and Mg isotope ratios for these two new materials, determined by MC-ICP-MS, were reported by de Vega *et al.*[219] to be $\delta^{56}Fe_{IRMM\text{-}014} = -0.004 \pm 0.014$‰ (2SD) and $\delta^{57}Fe_{IRMM\text{-}014} = +0.005 \pm 0.024$‰ (2SD) for IRMM-524A (Fe), and $\delta^{26}Mg_{DSM3} = -3.295 \pm 0.040$‰ (2SD), and $\delta^{25}Mg_{DSM3} = -1.666 \pm 0.043$‰ (2SD) for ERM-AE143 (Mg). Based on these values, Fe and Mg isotopic compositions for 21 geological RMs were determined. In a parallel study, Bao *et al.*[220] characterised GSB-Mg, a large volume (9.5 L) of a pure, concentrated and homogeneous Mg standard solution for use as a secondary RM for Mg isotope analysis. Its Mg isotope composition was determined by MC-ICP-MS at five different laboratories and quoted relative to DSM3 (a 0.3 M HNO_3 solution of Mg). The reference values for the GSB-Mg standard solution were given as $\delta^{26}Mg_{DSM3} = -2.049$‰ and $\delta^{25}Mg_{DSM3} = -1.056$‰, with a combined expanded (k = 2) uncertainty of 0.049‰ and 0.028‰, respectively. Three new Mo isotope RMs have been developed[221] by the National Institute of Metrology (China). One of these, GBW 04504, has natural isotope abundances whereas the other two are enriched in either ^{97}Mo (GBW 04505) or ^{100}Mo (GBW 04506). The mass bias of the MC-ICP-MS measurements was accurately corrected using five gravimetric isotope mixtures. It was claimed that these three RMs are the first with absolute Mo isotope amount ratios traceable to SI units. Another contribution[222] described the development, uncertainty evaluation and certification of a set of eleven new Zn isotope RMs (GBW04465-04475) with ^{64}Zn/^{66}Zn ratios ranging from 0.02 to 13. They were gravimetrically prepared from enriched isotopic materials whose composition had been accurately determined by total evaporation TIMS. Traceability to the mole SI unit was claimed and reference values were validated by a between-laboratory comparison.

It is difficult to obtain marine *carbonate RMs* such as JCp-1 (*Porites* coral) and JCt-1 (giant clam) because of their animal origins so NIST prepared**[223]** RM 8301 (boron isotopes in marine carbonate (simulated coral and foraminifera solutions)). This consists of two synthetic solutions produced to imitate typical coral and foraminifera in terms of their $\delta^{11}B_{SRM951}$ values and trace element contents. Seven leading research laboratories contributed B isotope data to the characterisation of this new SRM. The assigned NIST reference values for $\delta^{11}B_{SRM951}$ were 24.17 ± 0.18‰ (NIST RM 8301 (coral)) and 14.51 ± 0.17‰ (NIST RM 8301 (foram)). Use of these new solution RMs should assist the palaeoceanographic community in evaluating the quality of their analyses. A new high-purity $CaCO_3$ isotopic RM, designated USGS44, was developed**[224]** as a secondary isotope RM to normalise stable-C-isotope measurements to the $\delta^{13}C_{VPDB\text{-}LSVEC}$ scale. The $\delta^{13}C_{VPDB\text{-}LSVEC}$ value was 42.21 ± 0.05‰ measured by both EA and DI IRMS. Although $\delta^{18}O$ values were reported, this new RM was not considered suitable for $\delta^{18}O$ measurements because its fine grain size (<63 μm) may result in exchange with atmospheric water.

The development of new RMs is important for *mineral exploration and environmental contamination* studies. Three sediment-based RMs (SdAR-L2 (blended sediment); SdAR-M2 (metal-rich sediment); SdAR-H1 (metalliferous sediment)) described by Wilson *et al.***[113]** were designed to mimic NIST SRMs 2709-2711 for selected element mass fractions while retaining a natural mineralogy essential for matching matrix and dissolution characteristics. The reference values for over 40 elements in each material were determined as part of the IAG Geo*PT* proficiency testing programme.

Further characterisation of existing RMs can be helpful when there is a paucity of suitable RMs for analyses. For instance, Druce *et al.*[225] reported δ^{66}Zn values for 18 geological and biological RMs, some for the first time. Similarly, N mass fraction and δ^{15}N data were published[226] for 14 silicate RMs chosen to span the range of crustal signatures. The δ^{15}N values of these RMs ranged from -0.5 to +19.8‰. Of these, USGS RM BHVO-2 (basalt) and CPRG RMs UB-N (serpentine), FK-N (feldspar) and Biotite-Fe (biotite) were considered to the most appropriate for use as QC materials as they were most reproducible in terms of N mass fraction (<10% relative error) and isotopic composition (<0.6‰, 1SD). New δ^{114}Cd/^{110}Cd values were reported[114] for 34 geological and biological RMs. Analyses were performed with a precision of <0.074‰ (2SD) using a ^{111}Cd-^{113}Cd double spike technique and MC-ICP-MS.

5.3 Sample preparation, dissolution, separation and preconcentration

Preconcentration methods for the determination of noble metals in geological samples included[227] the use of alumina as a sorbent to preconcentrate Ag, Au, Ir, Os, Pd, Pt, Re, Rh and Ru prior to their simultaneous determination by ICP-MS. After loading the target elements as chloro-complexes onto alumina columns, most determinands could be recovered by using 2 M HCl as eluent. However, for the determination of Au all HNO_3 had to be removed from the sample digests and the eluent needed to contain 3% thiourea. Tin powder was used[228] as an alternative to SnO_2 as the collector in a fire assay procedure for the determination of Ir, Pd, Pt and Rh. This enabled the melting temperature to be reduced from 1250 to 1050°C. The tin bead produced was dissolved in HCl and the insoluble $PtSn_4$, $PdSn_4$, $RhSn_4$ and Ir_3Sn_7 compounds separated by filtration before microwave-assisted digestion with *aqua regia*. The ICP-MS LODs were 0.003 - 0.057 ng g^{-1}. The accuracy of this procedure was confirmed by the analysis of 11 Chinese geological CRMs, including two chromites.

New *sample purification procedures for the determination of REEs in geological materials* continue to be reported. Liu *et al.*[229] developed a simple method using polyurethane foam to determine ultra-low amounts of REEs in iron-rich mineral samples by HR-ICP-MS. About 10–20 mg of sample powder were dissolved and then reacted with 0.14 g of foam by shaking vigorously for three hours. Under optimised conditions, over 98% of the iron was removed while recoveries for REEs and Y were between 98% and 104%. Analysis of two CCRMP RMs (iron formation FER-1 and FER-2) and one from NRCGA (GBW07267 (pyrite)) yielded results that agreed within uncertainties with previously reported values. In a chemical separation procedure for the determination of REEs and Y mass fractions in carbonates by ICP-MS, significant amounts of Ba and other alkaline earth elements were removed[230] using DGA resin (TODGA) after addition of a Tm spike. Three carbonate RMs (BEAN, CAL-S, JLs-1) were used to validate the method. This procedure could be applied to other rock types or organic-rich matrices for which quantitative removal of Ba is necessary.

5.4 Instrumental analysis

5.4.1 Laser-induced breakdown spectroscopy

As in previous years, various regression models were proposed for the *processing of data generated by LIBS*. These included a hybrid random-forest algorithm[231] combined with wavelet transformation applied to the quantitative determination of the K content in potash, and automatic preprocessing[232] of LIBS signals using machine-learning techniques.

A comprehensive review (193 references) on *elemental imaging using LIBS* covered[233] the technical requirements and data processing involved for successful LIBS imaging measurements. It also provided an overview of potential applications in life sciences, geosciences, cultural heritage studies and materials science. Janovszky *et al.*[234] demonstrated the potential of LIBS mapping for classifying minerals such as biotite, feldspar, quartz and amphibole and for assessing the distribution of Be and Li within these minerals in granitic rock samples. The three statistical approaches evaluated were: classification tree based on indicator elements; linear discriminant analysis; and random forest. The results indicated that biotite and amphibole were good targets when mining for Be and Li in granitic rocks. The presentation of a method for rapid and qualitative geochemical imaging of rocks and minerals using handheld LIBS included[235] an open source workflow for processing LIBS data to merge multiple raster grids and so produce cm-scale geochemical images.

The *accuracy and detection limits of elemental rock analysis by LIBS* are heavily dependent on the availability of robust calibration models. This is particularly true for pLIBS. Ytsma *et al.*[236] assessed the quality of data produced by a commercial pLIBS instrument using various calibration strategies which included univariate calibration, multivariate regression modelling, the default pLIBS model predictions supplied with the instrument and an in-house calibration method based on rock RMs. Quantification of trace and minor elements with multivariate regression yielded more accurate results than with univariate models. Calibration using the new in-house method had lower prediction errors than the default models. Whereas the accuracies for major elements based on measurements of over 2000 geological RMs were satisfactory, the authors concluded that another spectroscopic technique, such as XRFS, may be preferable for *in-situ* quantification of minor and trace elements in rocks since the errors for all calibration strategies were often greater than the average concentration of these elements in the test materials.

The potential of vacuum UV-LIBS for *the quantification of S on planetary bodies* without an atmosphere such as the Moon was investigated[237]. Experiments were conducted in high vacuum (10^{-3} Pa) with a moderate laser pulse energy (25 mJ), conditions realistically achievable under the mass, size and power constraints of space flight instrumentation. An LOD of 0.5 at% S was an improvement over that achievable for lunar rocks by LIBS in the more commonly used UV/VIS/NIR spectral range.

Accurate determination of S content plays a vital role in the *evaluation of coal quality*. Double-pulse LIBS in a helium atmosphere enhanced[238] the intensity of S spectral lines and reduced the interference from oxygen emissions. The best LOD of 0.038 wt% represented an improvement of two orders of magnitude compared to previous literature values so it was concluded that this technique had an enormous potential for online detection of S in the coal industry. Zhan *et al.*[239] developed a simple and fast method of sample preparation for online analysis of coal by LIBS. Pulverised coal was confined in a closed cavity in the form of a "coal pillar" with a narrow opening in the side of the device through which the plasma could target the sample. The flatness of the sample surface and stability of the ablation provided good spectral quality with respect to signal intensity, RSD and S/N.

5.4.2 Dating techniques

Although a number of improvements *related to in-situ measurements for the U-Pb geochronology of zircons* were reported, not many were particularly novel. Lin *et al.*[**240**] investigated Pb/U downhole fractionation effects at different laser (193 nm ArF excimer) settings in LA-MC-ICP-MS using small spot sizes (≤10 μm) and their effect on accuracy and precision of U-Pb age determinations in zircons. The aim of this study was to develop a method for high-spatial-resolution U-Pb dating because natural zircons often contain μm-scale heterogeneities, inclusions, cracks and narrow growth zones. Applying Iolite software to correct for downhole fractionation yielded accurate and precise U-Pb ages for four zircon RMs (Plešovice, 91500, GJ-1 and Temora-2). Another study investigated[**241**] the effect of the laser focus position on the accuracy and precision of routine U-Pb isotope analysis of several reference zircons, titanite and rutile by LA-ICP-MS. Varying the focus of an excimer laser (193 nm) by 30 μm could result in a systematic 4-6% shift in the ^{206}Pb/^{238}U ratio in zircons. This effect was smaller for larger diameter-to-depth ratios. It was concluded that, if the laser focus was accurate to within 5 μm, the influence of the focus offset was smaller than the analytical uncertainty and repeatability was improved. The importance of checking the laser focus during setup was stressed and users were encouraged to record focus positions in their laser log file as a matter of routine. Wu *et al.*[242] improved the sensitivity of *in-situ* zircon dating measurements by LA-ICP-SFMS at high spatial resolution (5-16 μm) by replacing the standard cones in the ICP-MS instrument interface with a Jet sample (1.2 mm orifice diameter compared to 0.8 mm) and X skimmer cones, and adding small amounts of N_2 to the plasma. Downhole fractionation was corrected by normalisation to zircon 91500. The overall accuracy of the age determinations was 1.5%. A method for the analysis of detrital zircons[243] demonstrated rapid sample throughputs of 120, 300, 600 and 1200 h^{-1}, equivalent to 30, 12, 6 and 3 s per analysis. These were achieved largely through modifications in data acquisition and reduction software and only minor adjustments to the LA-MC-ICP-MS hardware. In a comparison[244] of the analytical performances of IR (1030 nm) and UV (257 nm) lasers for U-Pb zircon dating by fs-LA-ICP-MS, the measured ages were in agreement with the reference ages at both wavelengths but the IR laser produced larger uncertainties. Imaging by HR synchrotron X-ray micro-tomography showed that there was a link between the evolution of crater morphology and size with the analytical performance of each laser. Although the IR fs laser was capable of producing accurate U-Pb ages, it required higher fluence, had a greater sample consumption and yielded poorer statistics in comparison with use of the UV fs laser. Thompson *et al.*[245] assessed the potential benefits of ICP-TOFMS for LA zircon geochronology by comparing data for various zircon RMs with those acquired by ICP-QMS. Some of the data were acquired in a split stream configuration. In general, the two techniques produced similar levels of precision and accuracy for most U-Pb ages despite the significantly lower sensitivity of ICP-TOFMS. However, the simultaneous detection capability of TOFMS made significantly longer integration times possible without compromising the range of elements determined, thereby providing greater geological context for interpretation of the U-Pb isotopic ages and better identification of mineral inclusions. Reduced accuracy due to the limited linear dynamic range of the TOF detector at higher count rates was mitigated by the use of ^{235}U instead of ^{238}U.

A method for the ^{238}U–^{206}Pb dating of young *zircons by SIMS* in studies of the pre-eruptive history of magma reservoirs included[246] corrections for common Pb and initial ^{230}Th disequilibrium based on theoretical considerations. An evaluation of the advantages and limitations of ^{238}U–^{206}Pb age determinations compared to the widely-used ^{238}U–^{230}Th dating of young zircons concluded that the ^{238}U–^{206}Pb method was more appropriate for zircons older than 150 ka but required high U and low common Pb contents. On the other hand, the ^{238}U–^{230}Th method was more suited to samples younger than 150 ka but it relied on a large Th/U fractionation between the zircon and magma and a high U content. A combined geochronological and geochemical study employed[247] SIMS to determine the U-Pb age and REE compositions of zircons simultaneously with a spatial resolution of <10 µm. Whereas previous methods used energy filtering at relatively low mass resolution, in this procedure the SIMS instrument was operated at a high mass resolution of *ca.* 15000 to separate the target isotopes from complex isobaric interferences. Operation in a dynamic MC mode reduced the measurement time to 18 min per analysis. The analysis of six well-characterised zircon RMs gave U-Pb ages within *ca.* 1% of the recommended values and REE data consistent with those determined by SIMS and LA-ICP-MS.

Investigations of *in-situ dating techniques for minerals other than zircon* included a study[248] of the U-Pb geochronology of a collection of 11 wolframite minerals by LA-ICP-SFMS. Significant interference effects from tungsten-oxide polyatomic ions on Hg and Pb made it inappropriate to use the ^{204}Pb correction procedure for common Pb contribution so alternative procedures using ^{207}Pb and ^{208}Pb were recommended. Specimens with a relatively high U content and negligible common Pb content typically gave a ^{206}Pb/^{238}U age precision of around 1%. Thompson *et al.*[249] developed a LA-ICP-MS methodology for the analysis of the mineral ilmenite for major, minor and trace element concentrations and U-Pb isotopic compositions. Modifications to a typical LA-ICP-MS geochronology protocol used for other mineral phases were required because of the challenges presented by low U (tens of ng g^{-1}) and low radiogenic Pb (<10 ng g^{-1} for ^{206}Pb) contents. Results obtained using a rutile RM for calibration yielded ages comparable to ages published for other minerals from the same sample. Mercury interferences need to be taken into account when correcting for common Pb in minerals such as apatite and titanite. Gilbert and Glorie[250] utilised LA-ICP-MS/MS to demonstrate that the ^{204}Hg interference on ^{204}Pb can be removed effectively using NH_3 gas to induce a charge transfer reaction in the reaction cell, thereby making additional corrections for this interference unnecessary. Another paper on detrital apatite geochronology promoted[251] the use of (U-Th-Sm)/He dating by LA-ICP-MS as a possible solution to some of the problems associated with bulk measurements of whole grains of apatite in such studies. As well as having high sample throughput and increased analytical efficiency, the spatially resolved He extraction method removed the sampling bias inherent in whole-grain methods and allowed the dating of imperfect grains with inclusions, fractures and unusual morphologies. A LASS-ICP-MS method for the rapid *in-situ* Sm-Nd characterisation of scheelite grains acquired[252] the isotope and trace element (Mo, REEs, Sr) data simultaneously. Despite some large error bars, it was concluded that this technique could be used as a rapid reconnaissance tool to constrain the age of mineral deposits when no other suitable minerals were present to characterise pathways of ore-forming fluids. Monazites often occur as minute crystals with fine textures that limit the use of analytical techniques. In the APT of nanoscale domains of monazite (0.0007 μm^3 analytical volume), application of a new protocol to correct for fractionation between $^{232}ThO^{2+}$ and $^{208}Pb^{2+}$ resulted[253] in analytical uncertainties of 15-20% on the corrected $^{208}Pb/^{232}Th$ age. This was considered to be sufficiently precise for addressing geological questions on an unprecedented small scale.

Although the *Rb-Sr isotopic system* has been widely employed in geochronology for decades, the advent of ICP-MS/MS instruments now makes it possible to achieve reliable *in-situ* dating using quadrupole instruments by removing the spectral interference of ^{87}Rb on ^{87}Sr. Gorojovsky and Alard[254] assessed laser and mass spectrometer parameters associated with *in-situ* Rb/Sr dating by LA-ICP-MS/MS and concluded that the most accurate and reproducible results were obtained using N_2O as the reaction gas in conjunction with shorter laser wavelengths (193 nm) and lower frequencies (5 Hz). Matrix-matched RMs were also recommended for obtaining accurate Rb/Sr ages. Redda *et al.*[255] assessed matrix effects and downhole fractionation in the *in-situ* Rb-Sr dating by LA-ICP-MS/MS of phlogopite minerals using 193 and 213 nm laser systems. They too recognised that the general lack of matrix-matched RMs was a major obstacle that affected both precision and accuracy, so they prepared a nano-powder pellet from a phlogopite RM (Mica-Mg). However, this Mica-Mg nano pellet was not ideal for use as a primary calibrant because of differences in ablation properties between it and the natural phlogopite mineral. Ages with an accuracy of 3% or better could be achieved through regular analysis of a secondary, matrix-matched, standard to assess the accuracy of the *in-situ* Rb-Sr ages. A novel mass spectrometer with a quadrupole mass-filter and collision cell fitted to the front-end of a MC-ICP-MS/MS instrument had[256] better ion transmission than that achievable with a single collector ICP-MS/MS instrument for Rb-Sr dating. The simultaneous collection of all Sr isotopes on FCs provided more precise $^{87}Sr/^{86}Sr$ ratios. The importance of mass-filtering before the collision cell for LA $^{87}Sr/^{86}Sr$ measurements was emphasised. Because only atomic ions with *m/z* from 82 to 92 were transmitted, accurate $^{87}Sr/^{86}Sr$ measurements could be made without any corrections for atomic or polyatomic isobaric interferences.

Developments in *Re-Os isotope dating* methods included[257] an improved alkaline fusion procedure for the decomposition of molybdenite in a study of hydrothermal ore deposits. Powdered samples were mixed with a 50% NaOH solution, carbonised flour and an enriched Re-Os isotope spike before digestion in a Zr crucible at 700 °C. Less NaOH was required than in previous fusion methods so procedural blanks were lower at 2 and 62 pg for Os and Re, respectively. The Os and Re isotopes were measured by ICP-MS following separation of Re by absorption on an anion-exchange resin and purification of Os by distillation. This simplified procedure yielded Os blanks comparable to those of methods involving Carius tube and high-pressure ashing and had the advantages of being simpler, quicker and safer. Another paper reported[258] modifications to the Carius tube digestion scheme for the NTIMS determination of the Re-Os geochronology in organic-rich sedimentary rocks. It was essential to maintain a low Re blank for samples with low Re and Os mass fractions, so the new method employed H_2SO_4–Na_2CrO_4 rather than H_2SO_4–CrO_3 for the digestion because the purification of Na_2CrO_4 using an acetone extraction method was easier. The procedural blanks for Os (0.6–1 pg) and Re (1–2 pg) were an order of magnitude lower than with H_2SO_4–CrO_3 digestion and comparable to those obtained with an inverse *aqua regia* digestion. Results obtained for black shale samples were consistent with those obtained following digestion with inverse *aqua regia*.

5.4.3 Inductively coupled plasma mass spectrometry

An Excel-based searchable and filterable database for identifying potential *spectral overlaps* from elemental, doubly charged and polyatomic ions was compiled[148] from a literature search (with citations) combined with experimental determinations on 74 single elements solutions. More than 50 ions had not been identified previously. However, no information was provided regarding the relative severity of the spectral overlaps. The database was accessible as an appendix in the Electronic Supplemental Materials to the published paper.

High signal intensities and minimised spectral interferences are necessary for precise and accurate measurements of *REEs in geological samples at ultra-trace concentrations* if preconcentration procedures are to be avoided. A novel method for the direct determination of REEs at very low concentrations in carbonates and peridotites involved[259] the construction of an in-house heating-condensing system. This was based on a Scott double-pass spray chamber heated with an IR lamp inside an aluminium box and connected to another double-pass spray chamber covered with a Peltier-cooler device to prevent too much solvent vapour from entering the plasma. At a temperature of 180 °C, signal intensities were improved 5–8 or 6–24 times depending on the type of skimmer cone employed. The geometry of the skimmer cone was crucial to achieving higher sensitivities and the addition of N_2 to the central channel of the plasma reduced oxide formation rates considerably. Wu *et al.*[260] used a multi-REE spike and ICP-MS analysis to generate high-quality REE data that were claimed to be comparable to those obtained using high-precision ID-TIMS but within a few minutes rather than a couple of days. To facilitate calculation of the final data, a "REE Calculation Workbook" based on Microsoft Excel was made available. For the spike elements, concentrations were calculated using ID equations. Concentrations of the four monoisotopic REEs and the almost monoisotopic REEs La and Lu were calculated by comparing their intensities with intensities of unenriched isotopes of ID elements.

The challenges and limitations in the *analysis of apatite by LA-ICP-MS* for *in-situ* determinations of Nd isotope ratios were summarised by Doucelance *et al.*[261] who evaluated the influence of laser parameters such as spot size, fluence, frequency and He/N_2 gas flows on measured ^{143}Nd/^{144}Nd, ^{145}Nd/^{144}Nd and ^{147}Sm/^{144}Nd ratios. The laser parameters had no influence on the ^{143}Nd/^{144}Nd and ^{145}Nd/^{144}Nd ratios and some cone geometries provided more precise data by MC-ICP-MS than others. For a laser spot of 40 μm, a precision of 125-150 ppm was obtained for the ^{143}Nd/^{144}Nd ratio. A systematic decrease in ^{147}Sm/^{144}Nd ratios during an analytical session resulted from a systematic instrumental drift so it was essential to normalise measured ratios to a matrix-matched RM measured under the same analytical conditions. Qian and Zhang[262] reported the simultaneous *in-situ* determination of REE concentrations (by ICP-SFMS) and Nd isotope ratio measurements (by MC-ICP-MS) in apatite by LASS-ICP-MS analysis. The measured Nd isotopic compositions for two apatite RMs (Durango and Otter Lake) agreed with their recommended values within analytical uncertainties as did the measured REE concentrations. A new microanalytical protocol was developed[263] for the determination of Br, Cl and I in apatite, scapolite and silicate glass RMs by LA-ICP-MS. Ablations were performed with a range of square spot sizes (30-80 μm) using high repetition rates (25 Hz) and extended dwell times (up to 250 ms) to improve signal intensity and stability. The method was rapid (1 min per analysis) with minimal sample preparation and straightforward offline data reduction. The calculated LOQs were 8, 360 and 0.75 μg g^{-1} for Br, Cl and I, respectively. Results obtained on test minerals were comparable to EPMA and SIMS data on the same materials. Well-characterised matrix-matched RMs spanning a broad range of concentrations were required to identify spurious contributions to measured signals.

Imaging by LA-ICP-MS is a rapidly expanding field in the geosciences because of the wealth of spatial information it provides on geological processes. In an invited review article, Chew *et al.*[264] (162 references) discussed advances in LA-ICP-MS methodology for this purpose and included a practical guide for setting up LA-ICP-MS multi-elemental mapping experiments. Consideration of the latest innovations in data reduction and image processing packages placed particular emphasis on quadrupole systems. Future trends included the increased use of imaging in U-Pb geochronology given that LA-ICP-QMS mapping is now capable of acquiring all the required compositional and U-Pb age information at high-spatial resolution. The LASS approach with both MC and single-collector detection showed great promise for obtaining high precision U-Pb isotope ratios and trace element data simultaneously. To support the great interest in elemental mapping by LA-ICP-MS an online app was developed[265] to assist the user in fine-tuning operational conditions to avoid aliasing, minimise blur and maximise the S/N. The app generated a list of optimised conditions from which the user may choose the most appropriate set based on requirements for single- or multiple-pulse LA-ICP-QMS mapping. Neff *et al.*[266] presented a control system for flexible LA-ICP-TOFMS imaging which synchronised movements of the translational stage, laser operation and data acquisition. The system could perform either in single pulse mode with high scanning speeds or hole drilling mode that provided lower LODs. Due to the synchronised and selective triggering in both modes, data were stored for each pixel individually to assist analysis data processing and image generation. As defined areas of interest could be ablated, imaging times shorter than those previously possible were achieved. That flexible adjustments of ablation modes could be made for specific analytical tasks was considered to be a significant advance towards fully automated element imaging.

The considerable research effort focussed on *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. In general, it is difficult to discern any major breakthroughs as many of the studies provided modest improvements to existing separation procedures or analytical protocols.

Isotope ratio measurements in biogenic carbonates is of great relevance to studies of climate change and geological processes. To assess the intercomparability of B isotope data generated in different laboratories, a group of researchers set up[267] the "Boron Isotope Intercomparison Project" in which two GSJ marine carbonate CRMs JCp-1 (*Porites sp.*) and JCt-1 (giant clam, *Tridacna gigas*) were analysed by 10 laboratories, mainly by MC-ICP-MS. The study included a comparison of different sample handling and mass spectrometric approaches. More consistent B isotope results were obtained if the carbonate CRMs were exposed to moderate oxidative treatment prior to sample dissolution. Overall, there was encouragingly good agreement of $\delta^{11}B$ values obtained by participating laboratories, with the distribution of laboratory mean values being close to commonly reported in-house intermediate precisions. A new analytical approach to the measurement of Mg isotopes in biogenic carbonates using LA-MC-ICP-MS demonstrated[268] that accurate δ^{26}Mg data could be achieved by avoiding scattered Na ions and removing interferences arising from the carbonate matrix. Analytical biases of up to 3‰ were observed when analysing carbonates with significant Fe or Mn content (*ca.*1%) but this could be limited to 0.2‰ in carbonates with low trace metal contents typical in many marine calcifiers. The method was applied in an assessment of the sub-µm diurnal variability of δ^{26}Mg in planktonic foraminifera and could be adapted for the analysis of other inorganic carbonates such as speleothems and carbonatites.

An investigation of instrumental mass bias resulting from oxide formation in the *measurement of Nd isotope ratios by MC-ICP-MS* looked[269] at several instrumental set-ups, including wet and dry plasmas, different introduction methods, the addition of N_2 and various sampler and skimmer cone geometries. A mathematical model was developed from this extensive dataset to describe the behaviour of Nd isotopic ratios for a range of oxide formation rates and different instrument settings. A qualitative model predicted the correction to Nd isotope measurements required to account for contributions from the major sources of mass bias. In addition, a series of recommendations was given for improving the data quality of Nd isotope ratio determinations by MC-ICP-MS.

Simultaneous determination of S isotope ratios and trace element chemistry by fs-LASS-ICP-MS was reported[270] for a range of sulfide and sulfate samples. Trace element quantification was performed by ICP-QMS and stable S isotope ratio measurements by MC-ICP-MS. The use of fs LA allowed matrix-independent calibration of the stable S isotope ratios to be made using IAEA-S-1 (silver sulfide) as the bracketing standard. However, the accuracy and precision of the trace element analysis were restricted by the limited availability of homogeneous RMs.

Quantification of major and trace elements at only the µg g^{-1} level was considered to be acceptable given the additional information on S isotope composition that could be obtained simultaneously.

New free software called Iso-Compass was developed[271] for *data reduction of isotope data measurements by LA-MC-ICP-MS*. Features highlighted included: a simple user-friendly interface for data input; manually defined selection of laser and background signals; corrections for background, interferences and mass bias; visual data presentation; and formatted data output for easier and more efficient processing of LA-MC-ICP-MS data. The flexible nature of the software enabled Iso-Compass to be used for various isotope systems.

5.4.4 Secondary ion mass spectrometry

The Sr isotope analysis of apatites using large geometry SIMS instruments is technically challenging because of the molecular isobars on the Sr isotopes. For this reason, Jeon and Whitehouse[272] evaluated all the theoretically possible interferences on masses 82 to 88. By carefully controlling the peak shape and applying precise mass centring at an intermediate mass resolution of about 4500, the only significant interferences were Ca dimers and $^{40}Ca^{31}P^{16}O$, both of which could be corrected for. Precisions of between 0.001 and 0.0002 (1 SE) were achieved for apatites containing <100 to 1500 µg g^{-1} Sr. A SIMS method developed by Gillespie *et al.*[273] specifically for the analysis of small apatite inclusions in zircon was capable of producing $^{87}Sr/^{86}Sr$ isotopic data with 1‰ precision at a spatial resolution of 15 µm or better. The several strategies investigated for overcoming the Ca dimer interference problem all involved peak-stripping algorithms, each tailored to different mass-resolution settings. The most accurate and precise $^{87}Sr/^{86}Sr$ ratios were achieved at a mass resolution of 3000 with appropriate energy filtering and use of a cold trap.

5.4.5 Thermal ionisation mass spectrometry

Several developments of *TIMS instrumentation* have been reported. The cavity thermal ionisation source is a specific type of thermal source with high ionisation efficiency that has been employed in nuclear physics for decades and is capable of producing 10-40 times more ions from a given amount of analyte than conventional flat filaments. Preliminary results for Nd isotope measurements demonstrated[274] that cavity ion sources may be the key to achieving isotope ratios precisions at the sub-ppm level by reducing the limits imposed by counting statistics. The key characteristics of new ATONA amplifiers fitted to FCson a TIMS instrument were[275] their low and stable noise levels similar to those of 10^{12} to 10^{13} Ω resistors, a response time of <0.5 s, an exceptional gain stability of <1 ppm and a vast dynamic range which theoretically would allow quantification of signals from 10^{-18} to 10^{-9} A. The U-Pb analysis of a set of Pb RMs, synthetic U–Pb solutions and natural zircons clearly demonstrated the advantages of using ATONA-FC detection over the use of Daly ion counting for ion currents of $>10^{-14}$ A. The authors concluded that ATONA-Faraday collection had the potential to increase both sample throughput and measurement precision for this type of application.

Table 5 includes a number of recent papers on *isotope ratio determinations by TIMS* listed by element as a starting point for readers to explore the systems of most relevance to them.

5.3.6 X-ray spectrometry and related techniques

In an intercomparison[276] of *XRFS core scanning* data designed to resolve some of the myriad of complexities of the technique, the same set of seven marine sediment sections (1.5 m each in length) was circulated to seven XRFS facilities around the world. Each laboratory was asked to use the element menus and instrument parameters they typically employed. Although the results expressed as raw element cps varied substantially between laboratories, there was better agreement for element ratios. Four of the laboratories also scanned a set of homogenised sediment pellets with compositions previously determined by ICP-AES and ICP-MS. A log-ratio calibration rather than a linear one proved to be an effective way to convert XRF scans to quantitative values and significantly improved the match between the profiles from different laboratories.

A method for the *preparation of fused glass discs* in the determination of major and minor elements by WDXRFS needed[277] only 30 mg of sample with a sample to flux ratio of 1:100 to produce normal-sized glass discs *ca.* 30 mm in diameter that could be measured in most laboratories. The fused discs were prepared using an automatic fluxer and their homogeneity evaluated using μ-XRFS mapping. Although the agreement with certified values was satisfactory for major elements, the 100-fold dilution factor resulted in unreliable data for many minor elements. A useful comparison of the advantages and drawbacks of this method with previously published fusion methods for small sample masses was presented.

A review (70 references) of the latest available *pXRF technologies* focussed[278] on the determination of light elements, in particular Al, Mg, Na and Si. Quantification through numerical modelling of the variables that attenuate X-ray energies identified the distance between the sample and the detector as the key limiting factor. The use of a helium flush significantly improved the X-ray transmission effectiveness for both Mg and Na. The combination of helium flush with a new graphene detector window assembly in place of a traditional beryllium one significantly reduced scanning times without compromising precision.

6 Glossary of Abbreviations

2D	two dimensional
3D	three dimensional
AAS	atomic absorption spectrometry
AB	arsenobetaine
AC	arsenocholine
ACGIH	American Conference of Governmental Industrial Hygienists
ACSM	aerosol chemical speciation monitor
AEC	anion exchange chromatography
AED	atomic emission detector
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
BAM	Bundesamt für Materialforschung und Prüfung (Germany)

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
C_{18}	octyldecylsilane
CA	Chemical abrasion
CABM	Canadian Aerosol Baseline Measurement
CAPMoN	Canadian Air and Precipitation Monitoring Network
CAS	Chemical Abstracts Service
CC	collision cell
CCD	charged coupled device
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
CISED	chemometric identification of substrates and element distribution
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
CV	cold vapour
CVG	cold vapour generation
Cys	cysteine
DA	discriminant analysis
DBD	dielectric barrier discharge
DDTC	diethyldithiocarbamate
dDIHEN	demountable direct injection high efficiency nebuliser
DDTP	diethyldithiophosphoric acid
DES	deep eutectic solvent
DGA	diglycolamide
DGT	diffusive gradients in thin films
DI	dual inlet
DLS	dynamic light scattering
DLLME	dispersive liquid liquid microextraction
DMA	dimethylarsinic acid
DNA	deoxyribonucleic acid
DP	double pulse
DPM	diesel particulate matter
DRS	differential reflectance spectroscopy
DSC	differential scanning calorimetry
DTPA	diethylenetriamine pentaacetate

EA	elemental analyser
EC	elemental carbon
ED	energy dispersive
EDS	energy dispersive (X-ray) spectrometry
EDTA	ethylenediaminetetraacetic acid
EDXRFS	energy dispersive X-ray fluorescence spectrometry
EM	electron multiplier
EMBRAPA	Empresa Brasileira de Pesquisa Agropecuária (Brazilian Agricultural Research Association)
EMPA	electron microprobe analysis
EMPIR	European Metrology Programme for Innovation and Research
EN	European Committee for Standardisation
EPMA	electron probe microanalysis
ERM	European reference material
ESI	electrospray ionisation
ETAAS	electrothermal atomic absorption spectrometry
EtHg	ethylmercury
ETMAS	electrothermal molecular absorption spectrometry
ETV	electrothermal vaporisation
EU	European Union
EUSAAR	European Supersites for Atmospheric Aerosol Research
FAAS	flame atomic absorption spectrometry
FC	Faraday cup
FFF	field flow fractionation
FI	flow injection

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
GSD	geometric standard deviation
GSJ	Geological Survey of Japan
HDEHP	bis(2-ethylhexyl)phosphoric acid
HEN	high efficiency nebuliser
HFSE	high field strength element
HG	hydride generation
HILIC	hydrophilic interaction liquid chromatography
HPA	high pressure asher
HPLC	high performance liquid chromatography
HPS	High Purity Standards (USA)
HR	high resolution
HSL	Health and Safety Laboratory (Health and Safety Executive, UK)
iHg	inorganic mercury
IAEA	International Atomic Energy Authority
IAG	International Association of Geoanalysts
IAPSO	International Association for the Physical Sciences of the Ocean

IC	ion chromatography
ICP	inductively coupled plasma
ID	isotope dilution
IDA	isotope dilution analysis
IEC	International Electrotechnical Commission
IERM	Institute for Environmental Reference Materials (Ministry of Environmental Protection of China, Beijing, China)
IIP	ion imprinted polymer
IGGE	Institute of Geophysical and Geochemical Exploration, China
IGGE	Institute of Geophysical and Geochemical Prospecting, China
IL	ionic liquid
ILC	interlaboratory comparison
IMF	instrumental mass fractionation
IMPROVE	Interagency Monitoring of Protected Visual Environments
INAA	instrumental neutron activation analysis
INCT	Institute of Nuclear Chemistry and Technology (Poland)
IR	infra-red
IRMM	Institute for Reference Materials and Measurements
IRMS	isotope ratio mass spectrometry
IS	internal standard
ISE	ion selective electrode
ISO	International Organisation for Standardization
JRC	Joint Research Centre (of the European Union)
JMC	Johnson Matthey Corporation
JSAC	Japanese Society for Analytical Chemistry

k	coverage factor
KED	kinetic energy discrimination
LA	laser ablation
LASS	laser ablation split stream
LC	liquid chromatography
LDA	linear discriminant analysis
LDPE	low density polyethylene
LEAF	laser excited atomic fluorescence
LGC	Laboratory of the Government Chemist (UK)
LIBS	laser induced breakdown spectroscopy
LIF	laser-induced fluorescence
LLE	liquid liquid extraction
LLME	liquid liquid microextraction
LOD	limit of detection
LOQ	limit of quantification
LPME	liquid phase microextraction
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
MFC	mass flow controller

MeHg	methylmercury
MIL	magnetic ionic liquid
MIP	microwave-induced plasma
MIR	mid infrared
MMA	monomethylarsonic acid
MOF	metal organic framework
MPI-DING	Max Planck Institute
MRI	magnetic resonance imaging
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 (China)
NBS	National Bureau of Standards (USA)
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
NIR	near infra-red
NIST	National Institute of Standards and Technology
NMIA	National Measurement Institute of Australia
NMIJ	National Metrology Institute of Japan
NP	nanoparticle
NRCC	National Research Council of Canada

NRCCRM	National Research Centre for Certified Reference Materials (China)
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
PET	polyethylene terephthalate
PFA	perfluoroalkoxy alkane
PGE	platinum group element
PIXE	particle-induced X-ray emission
pLIBS	portable laser induced breakdown spectroscopy
PLM	polarised light microscopy
PLS	partial least squares
PLSR	partial least square regression
PM	particulate matter
$PM_{0.1}$	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)
pptv	parts per trillion (by volume)
PSL	polystryrene latex (particles)
PTE	potentially toxic element
PTFE	polytetrafluoroethylene

PUF	polyurethane foam
PVG	photochemical vapour generation
pXRFS	portable X-ray fluorescence spectrometry
Q	quadrupole
QA	quality assurance
QC	quality control
QCL	quantum cascade laser
QMS	quadrupole mass spectrometry
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
SCX	strong cation exchange
SD	standard deviation
SEC	size exclusion chromatography
SEM	scanning electron microscopy
SF	sector field

SFMS	sector field mass spectrometry
SFOD	solidification of floating organic drop
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
TE	total evaporation
TEOM	tapered element oscillating microbalance
TEM	transmission electron microscopy
THF	tetrahydrofuran
TLC	thin layer chromatography
TIMS	thermal ionisation mass spectrometry

TOF	time-of-flight
TOFMS	time-of-flight mass spectrometry
TOT	thermal optical transmission
TXRF	total reflection X-ray fluorescence
TXRFS	total reflection X-ray fluorescence spectrometry
UA	ultrasound-assisted
UBM	unified bioaccessibility method
UHPLC	ultra high performance liquid chromatography
UNC	University of North Carolina
US EPA	United States Environmental Protection Agency
USGS	United States Geological Survey
UTEVA	uranium and tetravalent actinides
UV	ultraviolet
VAME	vortex-assisted microextraction
VIS	visible
VOAG	vibrating orifice mondisperse aerosol generator
VOC	volatile organic carbon
VPDB	Vienna Pee Bee Belemnite
VSL	Dutch Metrology Institute
WDXRFS	wavelength dispersive X-ray fluorescence spectrometry
WWTP	waste water treatment plant
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
Ag^{I}, Cd^{II}, and Pb^{II}	Drinking, swamp and waste waters	GO-Fe_2O_3 nanocomposites	3-mercaptopropyl trimethoxysilane	FAAS	3.2 (Cd) to 47.3 (Pb)	sample spike recovery	279
As^{III}	River, tap and waste waters	Magnetic GO nanocomposite	Glucamine	ICP-MS	0.05	sample spike recovery	280
As^{V}	Natural water	TiO_2 nanofibers	Graphitic carbon nitride	ICP-MS	0.6 ng L^{-1}	Institute for Reference Materials of SEPA, CRM GSBZ50004-88 (water)	281
As^{V}	Water	Quartz support	N-methyl-D-glucamine	TXRFS	0.05	sample spike recovery	282
As^{V}, Se^{VI}	Water	Cellulose filters	TiO_2	EDXRFS	0.25 (As) 0.4 (Se)	sample spike recovery	283
Au	Environmental waters, sediments, soils, coal, ores	Fe_3O_4 NPs	Poly(1-vinylimidazole) IIP	ICP-MS	0.002	sample spike recovery (water samples); National Research Center for Certified	284

						Reference Materials (China) CRM ZBK338 (ore)	
Be	Waters, alloy samples	Fe_3O_4 NPs	MIL-53(Fe) type MOF	FAAS	0.07	sample spike recovery	285
Cd	Drinking and river waters, fruit, meat	Magnetic GO	2-(3-hydroxy-1-methylbut-2-enylideneamino)pyridine-3-ol (acacapyrH_2)	FI-FAAS	0.06	sample spike recovery	286
Cd, Co, Cu, Ni, Pb	Water, food	Cellulose nitrate membrane filter	Quinalizarin	FAAS	0.1-0.7	sample spike recovery; analysis of CRMs	287
Cd, Co, Cu, Ni, Pb, Zn	Spring and sea waters	Cellulose membranes	Mixed GO and carbon CNTs	TXRFS	0.08 (Cd) - 0.21 (Co)	sample spike recovery; NIST SRM 1640a (trace elements in natural water) and Supelco CRM QC3163 (trace metals 1 in seawater)	288
Cd, Cu, Ni	Estuarine and sea waters	PVC and TBP polymeric membrane	Pyridine-2-acetaldehyde benzoylhydrazone	FAAS	0.33 (Cu)- 0.75 (Ni)	LGC CRM LGC6019 (Thames water); seawater spike recovery	289
Cd, Cu, Pb	Ground, river, and waste waters	GO membrane	Poly-aminophosphonic acid	ICP-AES	1.1 ng L^{-1} (all elements)	NIST SRM 1572b (citrus leaves), NIES	290

						CRM 10C (rice flour); spike recovery	
Cd, Co, Cu, Fe, Mo, Ni, Pb, Ti, V	Ground and waste waters	Methacrylate resin	Carboxymethylated polyallylamine	ICP-AES	4 (Co) – 220 (Zn) ng L^{-1}	SCP Science CRM Enviromat EU-L-1 (wastewater low)	291
Cd, Co, Cu, Mn, Ni, Pb, Zn	Ground, river and sea waters	3D printed SPE cartridges with Lay-Fomm 40 porous filaments		ICP-MS	0.3 (Pb) to 6.7 (Zn) ng L^{-1}	NRCC CRMs CASS-4 (coastal seawater), SLEW-3 (estuarine water), NIST SRMs 1640a (trace elements in natural water) and 1643f (trace elements in water)	292
Cd, Hg, Pb	Environmental water	Fe_3O_4 NPs coated with SiO_2	Poly (ethylene glycol dimethacrylate-co-glycidyl methacrylate	ICP-MS	0.21 (Hg) to 2.9 (Pb) ng L^{-1}	Chinese GBW CRMs GSB 07-1185-2000 (water quality Cd), GSB 07-1183-2000 (water quality Pb) and GSB 07-3173-2014	293

						(water quality Hg)	
Cd, Ni	Water	Fe_3O_4 NPs	Polydopamine IIP	FAAS	25 (Cd) to 60 (Ni) ng L^{-1}	NIST SRM 1643e (trace elements in water)	294
Cd, Ni, Pb	Water	Granular activated carbon	Quercetin	FAAS	0.78 (Cd) to 8.1 (Ni)	NIST SRM 1643e (trace elements in water)	295
Cr^{III}	Drinking, spring and waste waters	Amberlite® CG-120 resin		FAAS	0.3	Environment Canada CRM TMDA-70.2 (high level fortified sample for trace elements of Ontario lake water)	296
Cr^{VI}	Water	Magnetic MWCNTs	3-aminopropyltrimethoxysilane	FAAS	3.2	spike recovery; comparison with ETAAS results	297
Cr^{VI}	Drinking and sea waters	GO	MoS_2	EDXRFS	0.05	Supelco CRMs QC1453 (chromium VI in drinking water) and QC3015 (chromium VI in seawater)	298

Hg	Water	Filter paper	Au NPs	head space portable Zeeman AAS	0.09	spike recovery	299
Hg^{2+}, $MeHg^{+}$ and $EtHg^{+}$	Ground, surface and sea waters; fish	Fe_3O_4 NPs coated with covalent organic frameworks	1,2-ethanedithiol	HPLC-ICP-MS	0.96 (Hg^{2+}), 0.17 ($MeHg^{+}$) and 0.47 ($EtHg^{+}$)	spike recovery (water); NRCC CRM DORM-4 (fish protein)	300
Hg	Spring and river waters; artificial seawater	Bi_2S_3 NPs		EDXRFS	0.06	Supelco CRM QC3163 (trace metals 1 in seawater)	301
In	water	Activated carbon	Sodium dodecyl sulfate	ETAAS	0.2 ng L^{-1}	spike recovery	302
Pb	Drinking, lake and spring waters	Amberlite® CG-120 resin		SQT-FAAS	0.23	Environment Canada CRM TMDA-70.2 (high level fortified sample for trace elements in Ontario lake water)	303
Pb	Contaminated water	MWCNTs	phenylenediamine	FAAS	1.5	NIST SRM 1640a (trace elements in natural water)	304
Ra^{226}	River water	AG® 50W-X8 resin		ICP-SFMS	0.46 fg L^{-1} (10 mBq L^{-1})	spike recovery	305
REE and Y	Sediment pore water	Nobias PA1® resin		ICP-MS	0.06 (Tm) to 1.47 (Y) pM	spike recovery and comparison with literature values found in NRCC CRMs	306

						CASS-5 (coastal seawater) and NASS-6 (seawater)	
Sb	Ground, surface and waste waters	Electrodeposition on microporous glassy carbon electrode		HG-HR-CS-AAS	0.1	NIST SRM 1640 (trace elements in natural water)	307
Sb^{III} and Te^{IV}	Lake, river, and environmental waters	Poly(glycidyl methacrylate-ethylene dimethacrylate) monolithic capillary	Cystamine	ICP-MS	3.9 (Sb) and 5.9 (Te) ng L^{-1}	GBW CRMs GSB 07-1376-2001 (water quality antimony) and GBW(E)080548 (tellurium in water)	308
Sr^{90}	Lake, ground, sea and radioactive waters	Eichrom DGA-B and Sr resins		ICP-MS	0.47 Bq L^{-1} (0.09 pg L^{-1}),	spike recovery and IAEA 2018 proficiency test exercise water	309
Th, U	Tap, river and lake waters	Fe_3O_4 NPs	Anoxybacillus flavithermus SO-15	ICP-AES	0.014 (Th) and 0.015 (U)	NWRI EC RM NWTM-15 (fortified lake water)	310
V	Water	Fe_3O_4 NPs and MWCNTs	4-(2-pyridylazo)resorcinol	ICP-MS	1.5 ng L^{-1}	NWRI EC CRM TMDA 51.3 (fortified lake water)	311

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

Analytes	Matrix	Method	Reagents	Detector	LOD in µg L^{-1} (unless stated otherwise)	Method validation	Reference
As^{III}, As^{V}	Water, soil, sediment	DLLME	APDC (chelating agent) and trihexyl(tetradecyl)phosphonium hexachlorodisprosiate (As^{III}) and trihexyl(tetradecyl)phosphonium tetrachloroferrate (As^{v})	ETAAS	17 (As^{v}) and 20 (As^{III}) ng L^{-1}	spike recovery	312
As^{III}, As^{V}, MMA, DMA, AB	Drinking, bottled, sparkling and sea waters	DLLME	Sequential extraction with the ionic liquid (IL) 1-octyl-3-methylimidazolium bis((trifluoromethane)sulfonyl)imide (DMA and MMA). Addition of APDC for As^{III}, reduction of As^{v} to As^{III} with sodium thiosulphate. Separate extraction of AB with sodium mercaptoethane sulphonate solution	ETAAS	0.02 (all species)	NRCC CRM NASS-6 (seawater), NIST SRM 1640a (trace elements in natural water) and SPS CRM SPS-SW2 (elements in surface waters)	313
Cd	Water, vegetables, hair	UA-DLLME	1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (IL) and 2-(6-methylbenzothiazolylazo)-6-nitrophenol (complexing agent)	FAAS	0.1	Environment Canada CRM TMDA-51.3 (fortified water)	314
Cd	Water, urban wastewater, molluscs	UA-LLME	1,2-dichloroethane and trichloroethylene (acceptor phase) and	FAAS	0.39	IRMM CRM BCR-713 (effluent	315

			2-(2-bromo-5-pyridylazo)-5(diethylamino)phenol (chelating agent)			wastewater) and NIST SRM 1566b (oyster tissue)	
Cd, Co, Cu, Ni, Pb, Zn	Waste and surface waters	LLE	Tetrabutylammonium bromide, $(NH_4)_2$SO4 and with 4-(2-pyridylazo)-resorcinol	ICP-AES	0.012 (Cd) to 0.4 (Zn)	spike recovery; SPS RMs SPS-SW2 (surface water) and SPS-WW1 (wastewater)	316
Cd, Cu, Ni, Pb	Food, water	carrier-free coprecipitation	3-benzyl-4-p-nitrobenzylidenamino-4,5-dihydro-1,2,4-triazole-5-thiol	FAAS	0.3-0.8		317
Co, Ni	Food, water	UA-DLLME with SFOD	Decanoic acid and DL-menthol (eutectic solvents) and). 2-(5-Bromo-2-pyridylazo)-5-(diethylamino) phenol (chelating agent)	FAAS	0.3 (Ni)- 0.4 (Co)		318
Cr^{VI}	Water, tea	UA-LLME	Choline chloride and phenylethanol (eutectic solvent) and APDC (complexing agent)	FAAS	0.8	spike recovery	319
Cu	Water, dialysis solution, sweat , urine	microextraction	THF and decanoic acid (supra molecular solvent) and 1-(2-pyridylazo)-2-naphthol (chelating agent)	FAAS	7.3	Environment Canada CRMs TMDA 53.3 (fortified lake water) and TMDA 64.2 (fortified lake water)	320
Fe^{III}	Water, wastewater	LLME	N, N-dimethyl-n-octylamine (solvent) and 2-(5-Bromo-2-pyridylazo)-5-(diethylamino) phenol (complexing agent)	FAAS	0.015	SPS RM SPSWW1 (wastewater)	321

Mn	River, ground, well and tap waters	LLME	Methanol and toluene (extraction solvent) (1-(2-pyridylazo)-2-naphthol (ligand)	ICP-MS	0.1 ng L^{-1}	spike recovery	322
Pb	Tap, lake and river waters; salted peanuts, chickpeas, roasted yellow corn, pistachios, almonds	LLME	Alpha-benzoin oxime and iron(III) chloride dissolved in phenol	FAAS	8 ng L^{-1}	Environment Canada CRMs TMDA 64.2 (Lake Ontario water), TMDA 53.3 (fortified lake water), and NACIS CRM NCSDC-73349 (trace elements in bush branches and leaves)	323
Pd	Stream, tap and sea waters	LLME	N-(3-chloro-4-fluorophenyl)-N-phenylthiourea	FAAS	2.3	spike recovery	324
Sb^{III}	Tap, dam, mineral, wetland, underground, rain and river waters	DLLME	Trihexyl(tetradecyl)phosphonium tetrachloroferrate (magnetic ionic liquid extractant) and ammonium diethyldithiophosphate (complexing agent)	ETAAS	0.02	spike recovery	325
Se and Te	Soils and sediments; sea, river, underground and tap waters	FI-LLME	1-octyl-3-methylimidazolium chloride and KPF_6 (ionic liquid), APDC (chelating agent)	HG-AFS	1.8 (Te) and 2.6 (Se) ng L^{-1}	spike recovery; IRMM CRM BCR 402 (white clover)	146

Th	Wastewater; phosphate rocks	CPE	2-(2,4-Dihydroxyphenyl)-3,5,7-trihydroxychromen-4-one (complexing agent) and Triton X-114 and KI (cloud point agents)	ICP-AES	0.11	spike recovery	326

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
Ag	Sediment, water	CPE	n-octanol, Triton X-100 (cloud point reagents), rhodanine chelating agent	FAAS	0.18	NRCCRM GBW 07301 (stream sediment), GBW 07311 (stream sediment); GBW 07312 (stream sediment)	327
As^{III}, As^{V}	Sediment, soil, water	MIL LLME	For As^{III}, APDC chelating agent and trihexyl(tetradecyl)phosphonium hexachlorodisprosiate MIL extraction solvent; For As^{V} trihexyl(tetradecyl)phosphonium tetrachloroferrate and magnetic rod separation	ETAAS	0.13 ng g^{-1}, 0.11 ng g^{-1}, 17 ng L^{-1}. for As^{III}; 0.14 ng g^{-1}, 0.13 ng g^{-1}, 20 ng L^{-1} for As^{V} in sediment, soil and water respectively.	Spike recovery	312
Cr^{VI}	Organic fertilisers	CPE	2% m/v NaCl, 0.3% v/v Triton X-100, and 0.05% (m/v) 1,5 diphenylcarbazide	FAAS or UV-Vis	0.55 μg g^{-1} for FAAS 0.41 μg g^{-1} for UV-Vis	NIST SRMs 2701, (hexavalent chromium in contaminated soil), and 695 (trace elements in multi-nutrient fertilizer), spike recovery	328

iHg, MeHg	Soil, water	Dual CPE	Sodium DDTC and Triton X-114 followed by displacement into L-Cys	HPLC-HG-AFS	0.004 for iHg and 0.016 for MeHg	Spike recovery	71
Mn	Soil	Switchable solvent LLME	N,N-Dimethylbenzylamine with deionised water switchable solvent; ((E)-2,4-dibromo-6-(((3-hydroxyphenyl)imino)methyl)phenol complexing agent	SQT FAAS	0.71	Spike recovery	329
Pd	Catalytic converter, road dust, water (tap, sea), wastewater	LLME	DES based on phenyl salicylate and menthol	ETAAS	0.03	Spike recovery	330
Se	Food, soil, water	VAME	APDC complexation, 1-butyl-3-methylimidazolium hexafluorophosphate IL, Triton X-114	ETAAS	0.07	NRCCRM GBW 07309 (stream sediment); NCS ZC73032 (celery)	331

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
As^{III}, As	Rice	tetra-n-butylammonium bromide		HG-AAS	0.01 $\mu g\ g^{-1}$	IRMM 804 (rice flour)	332
Cd, Co, Cu, Ni, Zn	Parsley, radish (black), quince, soil, water	Fe_3O_4 MNP	Polythiophene	Microsample injection system-FAAS	1.1 for Cd, 3.2 for Co, 1.4 for Cu, 9.6 for Ni, 1.2 for Zn	IRMM BCR 715 (industrial effluent waste water); SPS WW2 Batch 114 (wastewater); NCS DC 78302 (Tibet soil); LGC7162 (strawberry leaves)	333
Cd, Zn	Soil, water	Chemically-modified activated carbon with L-arginine		FAAS	1.6 for Cd, 2.4 for Zn	Spike recovery	334
Co, Cu	Soil, vegetable, water	Amberlite® XAD-4 resin	*Tricholoma populinum* fungal biosorbent	ICP-AES	0.019 for Co 0.034 for Cu	CNRC DORM-2 (dogfish muscle); NCS ZC73014 (powdered tea); NWRI NWTM-15 (fortified water); NIST SRM 1643e (trace elements in water)	335
Cu, Pb	Herbs	magnetic MWCNTs	1-(2-pyridylazo)2-naphthol	FAAS	18.9 for Cu 16.6 for Pb	SPS WW2 (wastewater); NCS DC73349 (bush branches and leaves)	336

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

Analyte	Sample matrix	Separation and purification	Detector	RMs and figures of merit	Ref
Ca, Fe	Geological materials	Matrix removal on single TODGA resin column	MC-ICP-MS, TIMS	Procedure validated with USGS RMs AGV-2 andesite), BCR-2 (basalt) and BHVO-2 (basalt)	337
Ca, K, Sr	Silicate rocks; calcium carbonate	1-step separation of Ca-K-Sr based on CEC with AG50W-X12 resin	MC-ICP-MS	External reproducibility on USGS RM BCR-2 (basalt): ±0.05‰ (2SD, n=9) for $\delta^{41}K/^{39}K$, ±0.04‰ (2SD, n=9) for $\delta^{44}Ca/^{42}Ca$, and 0.000012 (2SD, n=4) for $^{87}Sr/^{86}Sr$	338
Cd	Geological materials	2-step Cd purification using AG-MP-1M resin and TRU resin	MC-ICP-MS	Long term repeatability of 0.00 ±0.04‰ (2SD, n=45) for $\delta^{114/110}Cd$ in NIST SRM 3108 (Cd isotope solution)	130
Ce	Geological RMs	Separation on AG 50W-X12 resin and purification using Ln resin.	MC-ICP-MS	Typical reproducibility *ca.* ±0.030‰ for $\delta^{142/140}Ce$ in NIST SRM 3110 (Ce isotope solution).	339
Ce	Rock RMs	4-column ion chromatography using resins AG1-X8 (Fe removal), AG50W-X8 (REE separation), HDEHP (Ce separation) and G50W-X8 (Na removal)	MC-ICP-MS	Reproducibility of 0.03‰ (2SD) for $\delta^{142/140}Ce$ obtained for Ce Ames metal standard	340
Cu	Cu minerals	No chromatography after digestion in 4M HNO_3	MC-ICP-MS	NWU-Cu-A and NWU-Cu-B Cu solutions prepared from pure Cu used as RMs; results reported relative to NIST SRM 976 (Cu isotopes).	341
Cu, Pb, Zn	Geological RMs	AG MP1 resin for Cu and Zn separation and Cu purification, Eichrom Pb resin for Pb separation	MC-ICP-MS	Measurement precision <±0.03‰ (2SD) for $\delta^{65/63}Cu$ and $\delta^{66/66}Zn$. Validation using 5 USGS RMs for Cu and Zn, NIST SRM 981 (Pb isotopes) for Pb	342
Dy, Er, Yb	Geological materials	CEC on AG50W-X8 resin to collect REE followed by 2-column separation and purification on Eichrom Ln resin	TIMS	Validation using GSJ RMs JB-2 (basalt) and JG-2 (granite).	343
Fe	Geological RMs	Glasses prepared from geological RMs	fs-LA-MC-ICP-MS	Precision <0.15‰ (2SD) for $\delta^{56/54}Fe$. USGS and MPI-DING reference glasses	344
K	Geological and environmental RMs	Single column CEC with AG50W-X12 resin	MC-ICP-MS	Precision <±0.06‰ (2SD) for $\delta^{41/39}K$. Range of geological RMs.	165

K	Terrestrial and lunar rocks	2-step CEC on AG50-X8 resin	MC-ICP-MS	Precision *ca.* 0.05‰ (2SD) for $\delta^{41/39}$K. Range of geological RMs	345
Mg	Carbonates	Single step chromatography on Eichrom DGA resin	MC-ICP-MS	Precision *ca.* 0.13‰ for $\delta^{26/24}$Mg. Validation using GSJ RM JDo-1 (dolomite).	346
Ni	Igneous rocks	2-step AEC on AG1-X8 resin	MC-ICP-MS	Precision ±0.032‰ (2SD) for $\delta^{60/58}$Ni. Range of geological RMs; data reported relative to NIST SRM 986 (Zn isotopes)	347
Os	Os RM solution	No sample preparation	N-TIMS	Intermediate measurement precision of 85 ppm for ^{186}Os/^{188}Os (2SD) for IAG DROsS RM (Os isotope solution)	348
Pb	Geological RMs	AEC on AG 1-X8 resin	MC-ICP-MS	GSJ RMs JA-1 (andesite) and JMn-1 (manganese nodule). Reproducibility <±0.0032‰ (2SD) for ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb, <±0.0069‰ (2SD) for ^{208}Pb/^{204}Pb	349
S	Calcium sulfate and carbonates	S converted to sulfate and purified by AEC on AG1-X8 resin	MC-ICP-MS	Precision of 0.2‰ (2SD) for δ^{34}S; method validation assessed by comparison with EA-IRMS values on a variety of materials	350
Sb	Geological materials	2-step chromatography on AG 1-X4 and AG 50W-X8 resins	MC-ICP-MS	Reproducibility <0.04‰ for $\delta^{123/121}$Sb; data reported relative to NIST SRM 3102a (Sb isotopes). Standard addition with in-house synthetic solution for validation	351
Si	Silicate rocks	Laser fusion of rock powders to produce fused glasses	fs-LA-MC-ICP-MS	Measurement precisions of 0.06-0.11‰ for $\delta^{29/28}$Si and 0.10-0.17‰ for $\delta^{30/28}$Si. Five USGS RMs for method assessment	352
U	Zircon and titanite RMs	RMs mounted in resin and polished to obtain flat surface	LA-MC-ICP-MS	Typical precisions were 1‰ (2SD) for ^{235}U/^{238}U and 7‰ (2SD) for ^{234}U/^{238}U. Zircon RMs for validation	353
W	Terrestrial rocks, mainly basalts	Organic solvent extraction with 4-methyl-2-pentanone and purification by CEC (AG50W-X8) and AEC (AG 1-X8)	MC-ICP-MS	Reproducibility of 6-9 ppm (2SD) for $\mu^{182/184}$W. GSJ RM JB-2 (basalt) for validation	354
Zn	Geological and cosmochemical samples	2-step AEC using Eichrom AG1-X8 resin	MC-ICP-MS	Analytical precision of 0.02‰ (2SD) for ^{66}Zn/^{64}Zn in JMC-Lyon (Zn solution). Four USGS and one GSJ RM used to assess accuracy	355

Zn	Geological and biological RMs	2-step AEC using AG-MP1 resin	MC-ICP-MS	Measurement precision <0.02‰ for ^{66}Zn/^{64}Zn. IRMM-3702 used as the primary RM and values reported relative to JMC-Lyon (Zn solution)	225
Zr	Zoned zircons	Two-column purification procedure, Eichrom Ln-Spec and AG1-X8 resins	MC-ICP-MS	External reproducibility ±28 ppm for $\mu^{94/90}$Zr; RM zircon 91500 for validation	356
Zr	Zr standard solutions	Dilution of stock solutions in 1% HNO_3	MC-ICP-MS	Assessment of new Zr isotope RM (NRCC ZIRC-1) using the regression method with 2 NIST isotope SRMs 984 (Rb) and 987 (Sr)	357