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

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SUMMARY OF CONTENTS

Highlights in the field of air analysis included: a new focus on measuring tyre-wear particle emissions; an interest in using unmanned aerial vehicles for sampling purposes and an increased use of ICP-MS for measuring halogenated volatile organics, metals sampled directly from air and single particles.

Workers have explored further the full capabilities of ICP-MS/MS, which continued to dominate water analysis, including the speciation analysis of non-metallic elements in environmental samples. By far the largest number of papers on water analysis involved preconcentration. The growing interest in reagents for green chemistry was evidenced by the publication of several reviews. Novelties included the direct introduction of magnetic nanoparticles into FAAS to boost sensitivity, and the simultaneous dual-drop preconcentration of oxidation state species that avoided the need for a sequence of elution steps by preconcentrating the analytes into specific reagents contained in the drops. Although the total reflection XRFS and LIBS techniques are close to achieving the detection limits needed to screen contaminated waters, users of these instruments often neglect to validate their methods adequately through the use of reference materials.

In methods for the analysis of soils, plants and related materials, sustainable digestion, extraction and preconcentration methods featured strongly. The development of AAS, AES and AFS methods for the direct analysis of solid samples and for increasing sensitivity through analyte enrichment continued to be of considerable interest. The nitrogen-microwave inductively coupled atmospheric-pressure plasma showed promise for ICP-MS analyses. Applications of LIBS have increased dramatically in number with noteworthy developments including single-chamber laser-ablation LIBS and the analysis of plant leaves without the

need for grinding and pelleting. However, many published studies lacked validation through e.g. analysis of CRMs or comparison with results obtained by other techniques.

Efforts have continued on the characterisation of natural and synthetic materials that are sufficiently homogeneous to act as reference materials (RMs) in the analysis of geological materials. Application of microanalytical techniques, such as LA-ICP-MS and SIMS, led to the availability of a variety of new RMs for in situ isotope ratio determinations. The application of portable LIBS instrumentation to mineral prospecting and ore processing has received much attention, with the development of new chemometric models to improve data quality. The enormous amount of analytical data produced by modern instrumentation prompted the development of software, most of which has been made freely available, for facilitating the processing and reduction of isotopic data.

1 Introduction

This is the 39th annual review of the application of atomic spectrometry to the chemical analysis of environmental samples. This Update refers to papers published approximately between August 2022 and June 2023 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 Review papers

A comprehensive review (143 references) on *tyre-wear particles*, an emerging atmospheric pollutant of interest, covered[7] the mechanisms of their formation, factors that can influence their emissions (*e.g.* road surfaces, environmental conditions, tyre specifications and vehicle loads) and their emission characteristics (*e.g.* concentrations and particle size distributions). Particle sampling systems and their placement on vehicles were also usefully covered. A timely paper by Harrison and Alghamdi[8] (64 references) reviewed the relative merits of various inorganic and organic tracers characteristic of species present in tyre particles as exemplified in a study[9] that used ICP-MS and pyrolysis GC-MS to measure elemental and organic tracers and in another study[10] that used MC-ICP-MS, XAFS and μ-XRF techniques to measure the isotopic and speciated forms of a Zn marker element contained in size-segregated airborne particles. A review paper (263 references) by Zuo *et al.* [11] is recommended for a wider oversight on the use, challenges and future perspectives of stable isotope tracers (Cu, Fe, Hg, Nd, Pb, Si, Sr and Zn) for the source tracing of APM.

2.2 Sampling techniques

An evaluation[12] (55 references) of test reports published between 1994 and 2021 that detailed the *performance testing of personal air samplers* highlighted a lack of pertinent experimental information from which conclusions regarding comparative performance could be drawn. Another identified gap was the lack of reported testing over time to ascertain whether changes in the manufacturing process could contribute to changes in sampler performance. The preparation of a standardised test protocol and its subsequent adoption by producers was recommended.

Developments in *aerosol sampling media* included new nanofibrous filter substrates, fabricated[13] by layering nanofibrous polymers (for improved particle capturing performance) on top of microfibrous media (for mechanical support). The substrates achieved particle collection efficiencies of 99.4 - 99.9% for a 0.3 µm particle size at a face velocity of 10 cm s^{-1}. The resultant drop in pressure was 0.5-2.2 kPa. This new approach was suitable for designing bespoke filter media for specific chemical or toxicological measurement requirements. A new high-flow-rate impactor sampler operating at a flow rate of 100 L min^{-1} employed[14] a gelatin substrate that dissolved completely in water thereby allowing the easy extraction of sample particles for subsequent toxicological analysis. However, inorganic contaminants in this substrate could hinder certain chemical assays.

A reassessment of e*ndogenous contaminants in sampling media* is required as measurements become more sensitive. In a source-identification study that involved[15] the measurement of Sb isotopes in APM, one particular QF filter brand was preferred because it possessed the lowest Sb blank and so did not unduly influence the isotopic measurements. The precleaning of MCE filter media by ultrasonication in 0.07 M HCl before use enabled[16] the successful determination of soluble Pt in workplace air particles at 0.02 ng m^{-3} in a nominal 1 m^3 sample. The selection of a clean activated-carbon sorbent for trapping gaseous iodine enabled[17] LODs as low as 0.3 ng m^{-3} for ^{127}I by ICP-MS and 0.05 x 10^5 atoms m^{-3} for ^{129}I by AMS to be achieved.

The potential offered by advances in *unmanned aerial vehicles* include the collection of APM in hazardous environments and provision of a lower-cost alternative to manned flight. However, new miniaturised and lightweight air samplers are required because of the inherent lower loads and available power associated with drones. An impactor-based microsampler, operated[18] at a nominal flow rate of 1 L min^{-1}, weighed only 63 g yet had a particle collection efficiency of *ca.* 50% for *ca.* 1 µm particles. Volcanic eruptions such as the Icelandic Eyjafjallajökull eruption in 2010 can ground aircraft because of concerns over potential damage to engines due to ingress of volcanic ash. Such disruption could be avoided if there were better assessments of concentrations and particle size distributions of volcanic ash emitted into the atmosphere thereby facilitating the production of more accurate metrological dispersion models that can assist in the potential rerouting of flights. Development of a prototype airborne sampler to collect ash particles on a stub for subsequent SEM analysis involved[19] simulating its performance at an altitude of 4000 m using computational fluid dynamics modelling. Deployment on an electric-motor-powered UAV was envisaged because such engines are less susceptible to ingress of ash particles than internal-combustion engines. The STAC (automated size and time-resolved aerosol collector) sampler employed:[20] a suite of P/RH/T sensors to monitor ambient conditions; an OPC to measure aerosol size distribution; a micro-aethalometer to measure the black-carbon mass concentration; and a four-stage impactor operating at 3 L min^{-1} and with particle cut-off sizes of 2.3, 0.62, 0.42 and

0.12 μm to collect particles for offline analysis. This system was attached to a tethered balloon system deployed at various heights to undertake a vertical profiling of the atmosphere.

Passive air samplers require no power and are low cost and so are suitable for deployment in large numbers, especially in remote locations where power supplies are lacking. The performance of a GEM sampler that used a Radiello^{TM} diffusive barrier with an activated carbon sorbent was assessed[21] by deploying multiple units at remote locations in the Southern Hemisphere and the Antarctic, for which until now there has been a paucity of available GEM data. The development of this sampler and its validation were described[22] in a previous paper. The authors concluded that a greater emphasis on controlling sampling blanks was required if future deployments were to be considered because the GEM concentrations were <1 ng m^{-3}. In addition, more investigative work into sample uptake kinetics and sampling rate at sub-zero temperatures was needed. A new PAS employed[23] quartz wool discs for collecting black carbon particles for subsequent EC analysis by a TOT procedure in which disc segments were loaded into the combustion analyser using a modified quartz sampling boat. The intra-sample coefficient of variation of <11% indicated a good degree of sampling (deposition) homogeneity. The inter-sample coefficient of variation derived from deploying six samplers concurrently was <17%. Measured EC in field blanks was <1.8% of that collected in samples. The concurrent deployment at two sampling locations and subsequent measurement of pumped air filter samples allowed an average PAS sampling rate of 1.1 ± 0.2 m^3 per day to be calculated.

2.3 Reference materials and instrumental intercomparisons

Aviation is a significant source of *ultrafine soot* (<100 nm) and measurements are required to understand better its impact on health and the climate. The performance of measurement systems can be tested under controlled conditions using laboratory-based soot generators to generate simulated atmospheres. However such generators typically burn ethylene or propane fuels in air to produce black-carbon particles with a GMD of 150–200 nm which are larger than those emitted from gas turbine engines (20 – 50 nm). Other fuels (acetylene, dimethyl ether, ethylene, methane and propane) were mixed[24] with oxygen-enriched air in an attempt to produce substantially smaller and more realistic soot particles, but alas none of the gas combinations tested was able to produce particles <95 nm in size. In contrast, by running their prototype soot generator on liquid Jet A1 fuel rather than gas fuels, researchers at ETH Zurich did produce[25] realistic soot with a controllable GMD of 15 – 153 nm in sufficient quantities (up to 255 mg m^{-3}). This facilitated the routine measurement of the soot-specific surface-area and pore-size distributions, measurands required in health and climatic studies. An additional benefit was that this generator could also run on the greener paraffins and cycloparaffins and so could be used in future studies on more sustainable aviation fuels.

It is encouraging to see *comparisons of analytical instrumentation* for air pollution measurements being undertaken. Certified U particles were used[26] in a comparison of AMS, SIMS and TIMS for the determination of isotope ratios in individual U particles, an application important for nuclear provenance and safeguarding purposes. The relative error in the determination of $^{234}U/^{235}U$ and $^{234}U/^{236}U$ in NBL CRM U200 (uranium isotopic standard) by AMS was <10 and <20%, respectively, whereas the results obtained by fission track-TIMS and SIMS were within ±5% and ±10% of the certified values, respectively, for both techniques. The relative error and external precision of $^{234}U/^{238}U$ and $^{235}U/^{238}U$ in the analysis of NBL CRM U850 (uranium (U_3O_8) isotopic standard, 85% U-235) by AMS, SEM-TIMS or SIMS were <10% and <5%, respectively. The average values of the relative error and external precision for $^{236}U/^{238}U$ were both <5% for AMS analysis but <10% for SEM-TIMS or SIMS analyses. The EDXRFS and SF-ICP-MS analyses in an inter-laboratory comparison of $PM_{2.5}$ filters from the IMPROVE air monitoring network gave[27] results that agreed within ±20%. Major-axis regression-analysis between the techniques revealed very strong correlations ($r^2 > 0.9$) for Al, Ca, Cu, Fe, K, Na, Mg, Mn, Sr, Ti, V and Zn, strong correlations ($0.8 < r^2 < 0.9$) for Cr, Ni and P, a weak correlation ($r^2 = 0.69$) for Zr and very weak correlations ($r^2 < 0.4$) for As, P and Rb. Highly correlated elements yielded regression slopes within ±20% of unity, except for Zn, indicating that absolute element determinations by the two techniques agreed. This exercise is timely because as air becomes cleaner, lower measurement LODs are required so the use of ICP-MS could supersede that of XRFS. In a similar study, a comparison of ICP-MS/MS and PIXE measurements of Al, As, Br, Ca, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, Pb, Rb, S, Se, Sr, Ti, V, Zn and Zr in $PM_{2.5}$ and $PM_{2.5-10}$ filter samples demonstrated[28] that paired-data ratios were mostly *ca.* 1 except for those of Br, Mg, Na and Zr. Increased use of ICP-MS/MS is welcome because its enhanced capability in resolving isobaric interferences makes the determination of elements such as S, hitherto not possible with older ICP systems, feasible.

2.4 Sample preparation

Undertaking *acid digestions* remains a laborious task and so a robotic system was developed[29] for processing large numbers of samples of house dust by MAE. Liquid handling steps such as dispensing acids into digestion vessels and diluting samples were automated thus freeing up operator time to perform other required laboratory tasks.

In the determination of the *in-vitro bioavailable fraction* of metal(oid)s in $PM_{2.5}$, filter samples were leached[30] in ALF (pH = 4.5 ± 0.1), and SBF (pH = 7.4 ± 0.1) was used as an acceptor solution for the leachates. A dialysis membrane system (8 kDa MWCO) designed to mimic what occurs at the gas-exchange region in the deep lung was assembled in 50 mL glass flasks. Samples were incubated in batches at 37 °C for 24 h and SBF samples diluted and analysed by ICP-MS. Any remaining undissolved residues were subjected to MAE with HNO_3/H_2O_2 following the EN 14902 standard protocol. When aliquots of ERM CRM CZ120 (fine dust (PM_{10}-like) elements) were tested, the mean relative errors for As, Cd, Ni and Pb were -12, 12, -3, and -6%, respectively. The mean bioavailable fractions (C_{SBF}/C_{MAE}) determined in $PM_{2.5}$ samples were 0.52, 0.06 and 0.36 for Cd, Ni and Pb, respectively. It was not possible to calculate a bioavailable fraction for As because concentrations were below the LOQ. Data were reported for 26 elements in total. It was claimed that inclusion of the dialysis membrane simulated more realistically the process that occurred in the human lung and so provided a better estimation of the health risk posed by inhaled metal(oids)s in $PM_{2.5}$. In the assessment of a procedure for extracting metallic NPs from air-filter samples, simulant samples spiked with 50 nm-sized gold and 70 nm-sized platinum NPs were subjected[31] to either MAE or UAE using various solvents. Interestingly, an alternative extraction system, termed “hard cap espresso extraction”, used a coffee machine with disposable coffee capsules modified in-house for achieving the desired high temperatures and pressures. The NPs were extracted quantitatively in 2.0 % (*m/m*) NH_4OH within 4 min by MAE, but for the other procedures tested either incomplete NP recoveries or sample degradation occurred. Soluble P leached from APM deposited into the oceans from the atmosphere is a crucial nutrient source for the marine ecosystem and bioavailability assessment studies generally involve extractions into pure water. However in a study in which both 18 MΩ water and seawater were used[32] to leach TSP and $PM_{2.5}$ particles collected on filters, the P concentrations determined in water leachates were on average *ca.* 25% higher than those measured in seawater leachates. This led the researchers to conclude that marine phytoplankton productivity rates were being overestimated.

2.5 Instrumental analysis

2.5.1 Atomic absorption emission and fluorescence spectrometries

Coal-fired powered stations can be a major industrial source of *mercury emissions* that contain GEM (Hg^0), GOM (Hg^{n+}, n = 1 or 2) and particulate-bound Hg. The latter two species are readily scrubbed from flue emissions by air pollution control devices such as electrostatic precipitators that capture fly ash particles or by flue gas desulfurisation (FGD) scrubbers that remove SO_x. The volatile Hg^0 species is, however, insoluble in the FGD limestone slurry-scrubbing agent and binds poorly to fly ash particles and so can readily escape to the atmosphere if additional controls, such as carbon injection, are not implemented. More recently, the installation of additional clean-up technologies, such as NH_3-based selective catalytic reduction (NH_3-SCR) systems designed to convert NO_x to harmless N_2 and H_2O emissions, has raised the question of whether such systems affect Hg emission and speciation. In a simulation study, a commercially-available CV-AAS instrument was modified[33] to facilitate real-time Hg^0 measurements in harsh experimental conditions that involved passing various gas mixtures over an operational SCR bed. Whereas 66% of GEM was converted to GOM in the presence of 10 ppmv HCl, the conversion was minimal in the presence of NO and NH_3. A furnace was attached[34] to a GC-AFS system to identify those Hg species that were thermally released from solid by-products, such as fly ash and gypsum, produced by an SCR-equipped power station. The dominant Hg species were $HgCl_2$ and HgO in fly ash and Hg_2Cl_2 and HgO in gypsum.

The measurement of *particle number, mass, shape and size in harsh industrial environments* is challenging but aspirational because *in-situ* measurements are needed to support process automation. A unique set of instruments with potential for the characterisation of APM during metal smelting processes was assessed[35] for interrogating simulant Al_2O_3 and chalcopyrite particles aerosolised in a dust chamber. The instrumentation, all contactless and working in real-time, included: stroboscopic imaging for confirming particle sphericity and measuring particle number density; LIBS for estimating particle number density and compositional analysis; and LII for classifying particles based upon their tendency to incandesce. Whereas a LIBS setup for aerosol measurements typically involves high fluences and low repetition rates, in this study low pulse energies (3 or 10 mJ) with high repetition rates (up to 500 Hz) were used for the rapid measurements required for process monitoring. The resultant plasma, captured by CCD imaging, allowed the detection volume and the particle hit rate to be measured and hence the particle-number-density values to be calculated. Results were consistent with values derived from stroboscopic measurements. Performing LII measurements at very low particle-number-densities was possible because of the large sample volume deployed. A sensitive and robust photodiode was able to count all light-emitting events because it was operated at a repetition rate of 100 kHz and so responded quickly at the ns scale.

Further developments in application of LIBS to the analysis of air samples are summarised in Table 1.

Insert Table 1

2.5.2 Mass spectrometry

2.5.2.1 Inductively coupled plasma mass spectrometry. Two complementary *sp-ICP-MS* review papers[36, 37] (137 and 107 references, respectively) presented overviews of the benefits and limitations of the technique and summarised future trends, which included hardware developments such as ICP-TOF-MS for multielement measurements and microdroplet generators for calibration. Topics covered included: use of hyphenated techniques to provide complementary particle information; use of enriched isotope tags to track NP transformation and bioaccumulation processes in the environment; and real-time monitoring of NPs using an IS calibration approach.

Application of *ICP-MS as an-online detector for atmospheric measurements* continues to be of interest. A gas-exchange device for exchanging air with argon was coupled[38] to an ICP-MS instrument so that $PM_{2.5}$ particles could be sampled directly from air into the plasma thereby making possible trace measurements at a temporal resolution of 5 min. This novel approach, together with TEM analysis of particles collected on impactor samplers, assisted in identifying the sources of air pollution episodes that contained metallic particles. In a similar study, the elements As, Cd, Cs, Cu, Fe, Mg, Mn, Pb, Rb, Sn, Tl and V in $PM_{2.5}$ could be determined[39] with LODs of 0.001 – 6.30 ng m^{-3} and a temporal resolution of 3.3 min. Calibrant metallic aerosols containing Cr, Mo and W were produced by a spark generator. A comparison with the more conventional ICP-MS analysis of filters in the laboratory gave elemental correlations (r^2) of 0.19 – 0.84 with slopes of 0.12 – 0.80 suggesting that further development is needed.

A new *automated method for the determination of volatile organic carbon compounds containing Br, I, Se and S* involved[40] trapping on a sorbent, desorption and analysis by TD-GC-ICP-MS. Volatile species were stable in sorbent tubes stored at −20 °C for at least 28 days. Measurements were performed in <15 min, and the absolute LODs for the various species were in the fg to pg mass range.

Further ICP-MS applications for air analysis are summarised in Table 2.

Insert Table 2

2.5.2.2 Mass spectrometry techniques other than inductively coupled plasma mass spectrometry: Applications of MS to air analysis are summarised in Table 3.

Insert Table 3

2.5.3 X-ray spectrometry

Both NIST SRM 2783 (air particulate on filter media) and reference filters produced by the University of California at Davies were used[41] in the *calibration* of a new hand-held XRFS instrument for the determination of 24 elements (Al, As, Br, Ca, Cl, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Rb, S, Se, Si, Sr, Ti, V and Zn,) in $PM_{2.5}$ and PM_{10} samples. By illuminating samples with a wide 8mm-diameter X-ray beam, the effects of heterogeneity caused by variable deposition of particles on filters was minimised. The instrument was operated under vacuum or helium rather than in air when low-Z elements were analysed. The reanalysis of filters previously analysed using a benchtop EDXRFS instrument demonstrated comparable performance and gave similar LODs. Differences between measurements pairs was <40% with well-correlated data of $r^2 = 0.88 – 0.99$. Although TXRFS is inherently sensitive, its use for aerosol measurements has been somewhat hindered up to now by the lack of suitable filter RMs. A new, simple and effective method for producing RMs that mimic aerosol samples obtained using a cascade impactor sampler design involved[42] fabricating flexible reusable and low-cost shadow masks by photolithography. Once produced, the masks were placed on acrylic sampling substrates and a Ti calibrant deposited on top by an e-beam evaporation technique. The removal of the masks revealed the desired Ti deposition pattern, an arrangement of thin circular dots that mimicked the pattern obtained when APM was collected on the cascade impactor sampler. This method was versatile and had potential for preparing other customised calibrant-filters for specific air sampler devices.

The *improved characterisation of aerosols in their native state* was[43] the goal of researchers at the Swiss Light Source beam-line facility. Test aerosols, generated by nebulising salt solutions and dried using a diffusion drier, were directed into a measurement chamber for *in-situ* interrogation by XAS. This approach was preferable to alternatives that employed lenses to focus test aerosols as thin jets into a low-pressure chamber because ambient pressure conditions were maintained throughout ensuring that the thermodynamic state of the particles was controllable from generation to analysis. At the ATOMKI accelerator centre in Hungary, a new PIXE setup, equipped with a large angle SDD detector installed in an external beam-line, made it possible[44] to process batches of 100-200 aerosol filter samples in 10-12 h.

Analysis of NIST SRM 2783 (air particulate on filter media) gave results within ± 5% of certified values. The LODs were <10 ng cm^{-2} for many elements of interest when samples were deposited onto quartz, polycarbonate or PTFE filter media. Developing new mapping capabilities at <mm resolution was proposed as the next development.

2.5.4 Other techniques

The *thermal optical determination* of TC and its components EC, OC, water-soluble OC (WSOC) and water-insoluble OC in aerosol samples is used in conjunction with radiocarbon (^{14}C) analysis to identify the origins of carbon emissions from the combustion of fuels. Rauber *et al.*[45] extracted WSOC from filter samples and dried and oxidised the residues to generate CO_2 for radiocarbon analysis by AMS. If the presence of inorganic carbonate particles on filters was suspected, residues were initially acidified to liberate this C as CO_2. Removal of WSOC was beneficial as it can interfere in subsequent determinations of OC and EC because it chars and forms so-called pyrolytic carbon that can then be misclassified as EC in TOT analysis thereby leading to positively biased results. The use of a hyphenated TOT-AMS system facilitated the straightforward transfer *via* a zeolitic trap of the CO_2 generated for isotopic analysis. A new data extrapolation protocol, developed to automatically calculate EC amount and yield after every TOA, had the advantage over earlier protocols of requiring less sample material because the quantities of collected aerosol samples were small.

Suitable OC / EC split points in *TOT assays* can be chosen by measuring the transmission of a beam of light through a filter sample during its combustion and by exploiting the fact that different carbonaceous compounds possess different light absorption properties. The fact that other aerosol species also absorb light was exploited[46] in the determination of Fe in mineral dust samples collected on filters. Calibrant samples, prepared by doping filters with suspensions containing either Fe_2O_3 or NIST SRM 2709 (San Joaquin soil), enabled linear calibrations to be made over the 10 to 100 µg cm^{-2} range. When PM_{10} samples containing hematite particles were analysed, the Fe results agreed with those obtained by ICP-AES or ICP-MS analyses following MAE. However, results did not agree for filter samples collected from railway tunnels because the Fe content and morphology of particles were different. This highlighted a matrix dependency in this new methodology. More disconcertingly, deciphering a suitable OC / EC split point for air filter samples that contained both C and Fe (loadings of >10 µg cm^2) became challenging because of overlaps in optical absorption spectra and resulted in underestimations in EC and overestimations in OC values. In a worst-case scenario, EC determination was not possible at all. This has serious implications if the use of TOA is contemplated for air environments such as those in vehicle repair shops, where diesel (carbonaceous) fumes and (Fe-containing) welding fumes can potentially co-exist.

Further measurements of carbonaceous particles are summarised in Table 4

Insert Table 4 here

Development of a new two-stage semi-dry electrostatic precipitator (SDEP) sampler for use in *on-line IC systems* that measure water-soluble inorganic ions in $PM_{2.5}$ was reported[47]. The number-based collection efficiency was >95% for particles in the 14 nm – 11 µm size range, the mass-based $PM_{2.5}$ collection efficiency was 94 – 98% and the ion recovery rates were 93 ± 10% for Na^+, 103 ± 15% for NH_4^+, 96 ± 8% for NO_3^- and 92 ± 6% for SO_4^{2-}. In field trials, results obtained with this new SDEP-IC system agreed with those obtained using the established (particle in liquid sampler) PILS-IC system with linear regression slopes of 0.84–0.97 and r^2 values of 0.90–0.96. Results for NH_4^+ by the PILS-based system were, however, *ca.* 16% lower than those obtained using this new prototype. This loss was attributed to volatilisation when aerosol samples were mixed with high-temperature steam in the PILS-based system to extract water-soluble ions for analysis but which did not occur with the SDEP-based prototype because it used a parallel plate wet denuder to extract water-soluble ions for analysis. It was established[48] that the main sources of uncertainty in online IC measurements were variations in LOD, measurement repeatability, fluctuations in sampling flow rates, variabilities in liquid sample volumes and the representativeness of sampled air. The poor LOD for NO_3^- (*ca.* 0.6 µg m^{-3}) was attributed to impurities in the eluent but it was noted that cleaner alternatives were available. A preconcentration IC column was recommended for measurements undertaken in more pristine air environments because the LOD term, not surprisingly, dominated the measurement uncertainty budget. The uncertainties in flow and volume measurements were dictated by the performance of the MFC and the syringe pump, so it was important to keep instrumental components in good working order. Loss of HNO_3 by reaction with the walls of the inlet sampling line was problematical, so it was recommended to keep the length of the sampling line short to minimise reaction time and thereby improve sampling representativeness. In summary, regular instrumental maintenance, use of appropriate consumables and regular cleaning were recommended to decrease uncertainties in measurements.

3 Water analysis

3.1 Reviews

Two *reviews on mono-elemental analysis of water* covered F[49] (82 references) and Pb[50] (61 references). Both papers considered atomic spectroscopy and other detection methods, such as spectrophotometry and electrochemical techniques, both with and without preconcentration.

A less-specific review (102 references) on *instrumental methods for the quantification of potentially toxic elements* in environmental and other matrices included[51] nine papers on water analysis.

In an overview (88 references) of *the preservation of mercury in water samples*, King *et al.*[52] evaluated trapping on SPE phases as an alternative to the current practice of using preservatives in bottles. The authors noted that, when using SPE, various species can be preserved in the field without the use of hazardous reagents. Further advantages are decreased transport costs and elimination of the need to maintain the cold chain. However, the current lack of standardised methods is a drawback.

3.2 Sample preconcentration

A review (120 references) of *solid- and liquid-phase microextraction* for the determination of Hg in environmental samples included[53] the treatment of air, soil, water and biota samples. The authors concluded that sample preparation in the field and, eventually, full *in situ* analysis will simplify the determination of Hg. A review in Chinese (74 references) on recent advances in the use of graphene for sample preparation covered[54] metal ions and organic compounds in biological and environmental matrices.

The increasing interest in *green chemistry and deep eutectic solvents* was reflected in the publication of three reviews. The first (88 references) covered[55] homogenous LLME with solvent-, pH- or temperature-driven phase-separation prior to the extraction of organic compounds and inorganic ions. The second[56] (178 references) was an overall review of DESs for the extraction of organic or inorganic species from water and food samples. The third (150 references) covered[57] green solvents, including DESs, and ILs for the extraction of trace analytes from various matrices. These three reviews highlight the importance and possibility of removing traditional volatile and toxic solvents from analytical methods.

Tables 5 and 6 present the most significant advances in analyte preconcentration using SPE or LPE for water analysis.

Insert Tables 5 and 6

3.3 Speciation analysis

The *multi-elemental speciation* of As, Cr and Mo in rainwater leachates of geotechnical composites was achieved[58] by compacting the composites into a lysimeter and collecting the leachates after rainfall events. The oxyanions AsO_4^{3-}, CrO_4^{2-}, and MoO_4^{2-} were separated by fast SAX LC on a high porosity column with a linear gradient from 18 MΩ water to 0.7 M NaCl at a flow rate of 1.5 mL min^{-1}. The LODs for a 100 µL injection and ICP-MS detection ranged from 0.16 (As and Cr) to 0.31 (Mo) ng mL^{-1}. Spike recoveries from the sample were

100-103%. The poorer LOD for Mo was probably as a result of contamination from the pump. The results could possibly have been improved through use of an inert pump and an ion suppressor unit. Volatile organo-Br, -I, -S and -Se species in aquatic samples were collected[40] on board ship by purge and trap on a mixed Tenax TA® /Carbograph 5TD sorbent cartridge, which gave optimum trapping and storage stability with analyte recoveries of 100 ± 9% after storage at -20 °C for 28 days. The analytes were thermally desorbed at 200 °C in the laboratory and quantified by GC-ICP-MS. The MDLs were 88 x 10^{-3} (DMDSe) to 122 (DMS) fM for a 0.5 L aquatic sample. The complete analytical cycle of desorption, separation and quantification lasted 15 min for each sample.

Three methods for *the determination of Gd-based contrast agents* for MRI were compared[59]. The first two of the methods were based on HILIC with a binary eluent gradient of acetonitrile and 12 mM ammonium formate (pH 9) at a flow rate of 0.3 mL min^{-1}. In the first method the column was coupled to an ICP-MS instrument whereas in the second method it was coupled to an ESI-MS/MS system. Perhaps unsurprisingly, the HPLC-ICP-MS combination gave the lowest absolute LODs with all analytes detectable at sub pg levels, whereas the HPLC-ESI-MS/MS system achieved absolute LODs in the order of tens to hundreds of pg. The third method involved IC with conductimetric detection and was only able to separate unambiguously three of the seven contrast agents. The other agents had split peaks that the authors ascribed to dissociation caused by the OH^- eluent. The LODs for the three agents that could be separated were in the ng range. The HPLC-ICP-MS method was successfully employed to determine Gd agents in Chinese municipal wastewater. It would have been interesting to see what improvement could have been made by coupling the IC with ICP-MS.

The standard manual method for *the determination of dimethyl and elemental mercury in seawater* was automated[60] to overcome the instability of these species after collection and to reduce sample handling of the extremely toxic methylated mercury. Dissolved volatile species were separated from the water sample with a CF water-collection cell sparged with Hg-free air. The Hg species were trapped on Carbotrap® sorbent packed in tubes and were subsequently desorbed thermally and fed by a flow of Ar into a GC set-up for separation and AFS detection of the Hg peaks. The improved reproducibility of the automated process resulted in a reduction in sampling time from 2 h to 30 min and an improvement in LODs from the 2 - 25 fM achieved in previous studies to 0.2 fM. The method was successfully applied in a sampling programme off the Eastern Coast of the USA.

The HPLC-ICP-MS/MS detection of two *organophosphorus pesticides and their metabolites* in water was made possible[61] by the use of an oxygen reaction mode in which P^+ ions were detected as PO^+. The organophosphorus compounds were separated, without any derivatisation, on an anion-exchange column packed with TSK gel Super IC-AZ, which has quaternary ammonium ion-exchange ligands bound to a 4 µm particle size hydrophilic porous polymer. The mobile phase was 70 mM ammonium acetate buffered to pH 3.7 at a flow rate of 0.8 mL min^{-1}. With a 50 µL sample loop, the analytes were detectable in filtered water samples with LODs ranging from 0.03 (3-methylphosphinicopropionic acid) to 0.17 (glufosinate) µg L^{-1}. Spike recoveries from river water ranged from 98.8 (glufosinate) to 122% (aminomethylphosphonic acid).

The *elemental fractionation* in suspended particulate matter from an artificial lake was investigated[62] by trapping the particulate matter in a 5 mL sample onto a PTFE filter treated with poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) in a small electrolytical cell constructed in-house. The electrochemical cell was then loaded with H_2O, methanol or 0.05 mM EDTA in sequence to extract the water-soluble, organic and insoluble fractions, respectively, at a voltage of +0.8 V. The liberated ions (Cu, Mn, Ni, Pb and tetramethyl Pb, and Zn) were detected as their EDTA chelates by ESI-MS. The authors suggested that this proof of concept could one day replace the Tessier and BCR sequential extraction protocols. Feasibility was demonstrated by ICP-MS analysis of the samples after water extraction and total digestion using the standard Chinese protocol (HJ 539-2015). The ESI-MS peak areas were in the same ratios as the concentrations found in the fractions obtained by the standard protocol.

3.4 Instrumental analysis

3.4.1 Atomic absorption spectrometry. *Methods for improving the sensitivity of the AAS analysis of waters* that did not involve chemical preconcentration included[63] the trapping of Hg^0 after CV generation on a tungsten coil. Coating of the coil with platinum and heating it to 60 °C during the trapping phase doubled the absorption signal obtained when trapping at room temperature. Under optimised conditions, the LOD of 8.8 ng L^{-1} was a significant improvement on the LOD of 44.8 ng L^{-1} obtained with conventional CV AAS detection of Hg. Analysis of the NIST SRM 1641e (mercury in water) gave results within the certified range. The sensitivity of using magnetic absorbents as preconcentration agents for trace elements was improved[64] 40-fold by inserting the absorbent directly into the flame of the FAAS instrument to eliminate the nebulisation step and thereby boost the signal. A graphene-oxide-aerogel solid-extraction-phase had the twin advantages of having a high adsorption capacity and of burning rapidly thereby resulting in narrow and reproducible absorption peaks and minimal background interferences. The LOD for Pb was 1.3 µg L^{-1}. The signal reproducibility ranged from 17% at a concentration of 10 µg L^{-1} to 8% at 180 µg L^{-1}. The method was validated by spike recovery (96-102% recovery for spike levels of 5 - 20 µg L^{-1}) and analysis of the NIST SRM 1643e (trace elements in water).

Bazo *et al.*[65] demonstrated the possibility of using a CS-AAS instrument as a *molecular absorption spectrometer for determining Sr isotope ratios* in spiked tap water. Using an Ar/CH_3F gas mixture as the fluorinating agent and an Ar/H_2 mixture as a purge gas, Sr isotopes could be detected as SrF molecules at 630.27 nm. Peak deconvolution was used to resolve spectral overlap between the isotopic signals. The authors stated that the method had potential for determining $^{87}Sr/^{88}Sr$ and $^{86}Sr/^{88}Sr$ ratios in naturally abundant Sr standards at concentrations above 100 mg L^{-1}, but clearly, for most samples, this approach is unlikely to replace TIMS or MC-ICP-MS procedures.

3.4.2 Vapour generation. The *detection of Cd by HG-AFS* was improved[66] by using 0.6 mM Cr^{3+} and KCN as reduction catalysts to enhance Cd vapour generation. Detection by AFS instead of FAAS allowed the KCN concentration to be lowered from 0.1 to 0.01 M, thereby considerably reducing the background signal and the toxicity of the reagents. Under optimised conditions, the LOD was 0.42 ng L^{-1}. The method was validated by the analyses of the NIST SRM 1643f (trace elements in water), the IRMM CRM ERM-CA713 (wastewater) and the NRCC CRMs CASS 4 (near shore seawater) and NASS 5 (seawater).

Although the *cold vapour generation of* Hg^0 *without using a reducing agent* could only give[67] an LOD of 0.09 µg L^{-1}, substantially poorer than that obtained when adding such a reducing agent, the finding that Hg^0 could be generated at a pH of > 11 without addition of a chemical reducing agent offers the intriguing possibility of a green-chemistry method for reducing Hg^{2+} and CH_3Hg^+ ions to Hg^0.

Some elements can be made volatile using *electrolytic vapour generation*. For instance, Os^{III} and Os^{IV} ions in solution were successfully oxidised[68] to the volatile Os^{VIII} compound OsO_4(g) (boiling point 130 °C) by using a RuO_2-coated dimensionally stable anode and a graphite cathode in the presence of H_2SO_4. The OsO_4 produced in solution was volatilised in a heated (>100 °C) gas-liquid separator for ICP-MS detection. The 12-fold increase in signal intensity compared to that obtained by pneumatic nebulisation resulted in a LOD of 5 pg kg^{-1}. A portable instrument for the determination of As in water employed[69] a large-surface-area Fe-coated lead oxide/lead cathode (Fe@PbO/Pb) to supply electrons for the reduction of As to AsH_3(g) before detection in a miniaturised atmospheric point-discharge plasma. The method was sensitive enough (LOD of 1 µg L^{-1}) to detect As in reservoir water.

Table 7 summarises the main advances in the application of *photochemical vapour generation*, a methodology not only widely used for hydride-forming elements but also commonly reported in the literature for producing volatile metal compounds from non-hydride forming elements under photochemical reaction conditions.

Insert Table 7

Microplasmas or discharges can replace pneumatic nebulisation and generate volatile species in a discharge in contact with the sample solution. A microplasma improved[70] the ICP-AES analytical signal intensities for Ag, Bi, Cd, Pb, Tl and Zn by 2-13 times and by over 30 times for Hg. The improvement was ascribed to the higher analyte fluxes and less water vapour produced by the microplasma. The LODs were 0.06 (Hg) to 0.4 (Ag) µg L^{-1} and the recoveries from spiked tap and seawater were 98-113%. A plasma electrochemical vapour generator was coupled[71] with MC-ICP-MS to improve Cd isotopic analysis. The VG improved the signal six-fold compared to that obtained with nebulisation, and removed the need for a desolvation unit before the ICP-MS unit. The matrix separation inherent with VG meant that only one step was required in the sample purification so the sample processing took only 3 h compared to the 72 h required for the method used previously. The $\delta^{114}Cd/^{110}Cd$ value of 0.00 ± 0.06 (2SD, n = 25) determined for the NIST SRM 3108 (Cd standard) at a concentration of 8 µg L^{-1} agreed well with results obtained after sample purification and isotope-ratio determination under dry plasma conditions.

3.4.3 Inductively coupled plasma atomic emission spectrometry. An *argentometric method for the determination of* Cl^- developed by Lerner *et al.*[72] was based on the classic precipitation of Cl^- with Ag^+ ions in acidic media. The Cl^- in solution was determined indirectly after the addition of a precipitation solution containing 300 mg L^{-1} Ag^+ and a 60 mg L^{-1} Y^{3+} IS. After filtration of the sample, the Ag^+ left in solution was inversely proportional to the Cl^- concentration. The working range was 0.2 to 16 mg L^{-1} and the LOD 0.075 mg L^{-1}. The method was verified by obtaining near quantitative spike recoveries from water, seawater, wine and urine samples. Results agreed with those obtained by IC analysis.

The intensities of analytical lines with low excitation energies are affected by the presence of easily ionisable elements in the *nitrogen plasma of MP-AES instruments*. This was overcome[73] by the addition to the sample of elements with low IPs, such as Al, Ba, Eu, Ga, In, La, Rb and Sm, at concentrations between 75-100 mg L^{-1}. Recoveries of 85 (Ba) to 99% (Mg) for Ba, Ca, K, Li, Mg and Na in lake sediment pore waters were achieved through the addition of In. The sensitivity of an MP-AES instrument was rather unsurprisingly improved[74] by addition of a commercially available enhanced nebulisation system with desolvation. Although the performance was still not as good as that achievable by ICP-AES, the three-fold improvement in LODs allowed detection of Al, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni and Pb in the NIST SRM 1643e (trace elements in water) (concentrations ranging from 6.5 (Cd) to 141.8 (Al) µg L^{-1}) and Cr, Cu and Mo in several Brazilian mineral waters.

3.4.4 Inductively Coupled Plasma Mass Spectrometry. The *direct determination of trace elements in water* remains an active research topic. Atmospheric precipitation was successfully analysed[75] for its dissolved Si content using an ICP-MS instrument equipped with a DRC to remove the $^{14}N^{14}N^+$ and $^{12}C^{16}O^+$ interferences at *m/z* 28. Use of CO_2 as a reaction gas and the addition of CH_4 to the plasma improved Si sensitivity. A significant decrease in the blank signal improved the S/N ratio from near zero to 113 when a 0.9 mL min^{-1} flow of CO_2 into the reaction cell was used. The addition of 2 mL min^{-1} CH_4 to the plasma gas doubled the instrument sensitivity for Si. Under these conditions the LOQ was 5 µg L^{-1}. The method was validated against the NRCC CRM SLRS-4 (river water) and the RM SPS-SW1 (trace elements in surface waters). Results for dissolved Si in ten rainwater samples ranged from 55 to 465 µg L^{-1}. It was possible[76] to determine 68 elements in filtered river water samples in one analytical run when ICP-MS/MS was used in all three acquisition modes (reaction, collision and mass shift using H_2, He and O_2, respectively) . It was not possible, however, to determine Au, I or Zr due to issues of sample stability. The method was validated against the RMs SPS-SW1 (trace elements in surface waters) and SPS-SW2 (surface water) and ECCC RM TMDA-51.5 (trace elements in water) as well as by spike recovery and analysis of in-house standards. The method was used successfully to fingerprint 12 German rivers and was recommended as a starting point for elemental monitoring of rivers and their catchments. Unfortunately, the authors didn't present the overall analysis time required for each sample when so many analytical modes were applied. This study demonstrated what is currently possible without resort to complex sample preparation methods.

The *interference-free ICP-MS/MS determination* of the radionuclide ^{129}I was made possible[77] by the addition of a flow of O_2 into the DRC to lower the ^{129}Xe background and by the use of CO_2 as reaction gas to lower the $^{129}IH_2^+$ background signal. Using both gases simultaneously resulted in a LOD of 0.73 mBq L^{-1} (0.11 ng L^{-1}) thereby making it possible to determine ^{129}I in rainwater without any chemical separation even in the presence of up to 100 mg L^{-1} ^{127}I. The use of N_2O as a reaction gas improved[78] slightly the determination of REEs in river water by boosting the yields of $^{153}Eu^{16}O^+$ and $^{172}Yb^{16}O^+$ in the reaction cell in mass shift mode. In addition, Ba-related spectral interferences on Eu were suppressed so there was no need for spectral interference corrections. The LODs improved from 0.024 (O_2 gas) to 0.01 (N_2O gas) pg mL^{-1} for Eu, and from 0.06 (O_2 gas) to 0.023 (N_2O gas) pg mL^{-1} for Lu. The method was successfully validated against the NRCC CRMs SLRS-3 and 4 (river water). In the HG-ICP-MS determination of Te, elimination of ^{128}Xe and ^{130}Xe interferences on the most abundant isotopes ^{128}Te and ^{130}Te meant[79] that an LOD of 0.07 ng L^{-1} could be achieved, thereby making the determination of Te in lake, river, bottled and seawaters possible. Results for total Te in six CRMs agreed well with certificate values.

3.4.4.1 Nanoparticle analysis. A new sampling protocol was developed[80] with the aim of *quantifying nanoparticles at real world concentrations* by ICP-MS. Seawater was filtered immediately after collection through 0.45 μm polycarbonate membrane filters to obtain a "dissolved" metal sample. The sample was then spiked with silver, TiO_2 and ZnO NPs and homogenised for 5 min before ultrafiltration of a 0.5 mL sample through a 3 kDa cut-off ultrafiltration tube conditioned for 15 min with $Cu(NO_3)_2$ to decrease ion absorption. The trapped particles were dissolved in 30% *v/v* HNO_3. The filter was washed with ultrapure water and the wash combined with the sample to give a 3-5% *v/v* HNO_3 solution for analysis by SF-ICP-MS. The LODs expressed as metal concentrations were 0.06 (Ag) to 17.5 (Zn) $\mu g\ L^{-1}$ and the recoveries ranged from 87% for Ag to 109% for Zn. Although NPs were not detected in unspiked samples in this study, in later work[81] this method was successfully used to detect NPs in seawater up to 2 km from the coast of the Black Sea.

The *pretreatment of samples for single particle ICP-MS analysis* has been investigated. Natural colloidal particles were determined[82] in lake water after filtration or centrifugation. Perhaps counter intuitively and in contrast to the method reported above in which NPs and colloids were trapped on ultrafilters, in this study samples were filtered and the filtrate analysed. Polyethersulfone membrane filters with three pore sizes were investigated to see which gave the best recovery. When samples were filtered through a conventional 0.45 μm filter, many natural colloids and particles of 100-200 nm size were removed. Increasing the pore size to 3 μm improved NP and colloid recovery in the filtrate. Surprisingly, however, a larger number of smaller particles were found when a 0.22 μm filter was used probably because the higher pressure required broke up the agglomerates. Further experiments showed that centrifugation at 2000 rpm had a similar particle selectivity as filtration through a 3 μm filter. Similar results were found[83] during the determination of silver NPs in tap and surface waters and sewage effluent. The recovery of NPs from surface water samples spiked with 60 nm diameter silver NPs increased from 60% for a 0.22 μm filter to 90% for a 0.8 μm polyethersulfone membrane filter. Transmission electron microscopy of membranes showed that heating membranes to 100 °C and then cooling them increased the mean pore size of the filters and so further improved the NP recovery. To improve the determination of microplastics in river water, samples were pretreated[84] with 10% HNO_3 for 24 h at room temperature as an alternative to filtering. This pretreatment removed DOC, carbonates and microorganisms thereby decreasing the C background in sp-ICP-MS. A particle recovery of 80% was obtained for river water spiked with polystyrene particles (2-3 μm particle size). The reduction in background signal resulted in a five-fold increase in the number of particles that could be detected.

3.4.4.2 Isotope analysis. The *determination of Hg isotope ratios* was improved[85] by the development of a purge-and-trap system that was coupled to a MC-ICP-MS instrument. The samples were treated in 40 mL vials with 0.1 mL of 20% *m/v* $SnCl_2$ to convert the Hg ions into Hg^0, which was collected on gold traps for analysis. The Hg concentration (8 ng L^{-1}) needed for accurate isotope ratio determinations was close to concentrations found in uncontaminated environments.

A procedure for the *isotopic analysis of Sb in water samples at low concentration* (< 1 μg L^{-1}) involved[86] the addition of 200 μL of a 25% *v/v* BrCl solution to a 200 mL sample to digest all the DOM in the sample. A mixture of KI, hydroxylamine hydrochloride and ascorbic acid was added to this digest to remove excess BrCl and to convert any Sb^{V} present to Sb^{III}. The Sb^{III} was then preconcentrated onto a column with a thiol resin (CleanertSH, pore size 60 Å and grain size 40 mm) and eluted for HG-MC-ICP-MS analysis. No fractionation was observed during sample preparation, and Sb isotope ratios could be determined for samples with Sb concentrations as low as 0.01 ng mL^{-1}.

In a *rapid procedure for the separation of U from environmental matrices,* the U was preconcentrated[87] from a 100 mL sea water sample by $Fe(OH)_3$ coprecipitation. The precipitate was dissolved in 3 M HNO_3 for sequential separation of the matrix from U on a TK200 resin column. The first elution step removed the main interfering elements (Au, Hg, Np, Pb, Pt, Tl), main matrix elements (Al, Ca, Fe, K, Mg, Na) and the REEs. The second elution step stripped out the Th, and the final step isolated the U. This final eluate was evaporated to dryness and then redissolved in 2% *v/v* HNO_3 for analysis by MC-SF-ICP-MS. The method was validated for seawater against the CRM IAEA-443 (Irish Sea water). The U was preconcentrated 30-fold with a 90% recovery. A batch of 20 samples could be treated within 6 h, faster than by methods requiring multiple extraction columns.

3.4.5 Laser induced breakdown spectroscopy. Research has continued into *methods for improving the sensitivity of LIBS.* In a comparison of three sampling strategies for the analysis of liquids, direct bulk liquid and liquid jet analyses gave[88] better results at higher concentrations whereas the analysis of the residue on a Teflon substrate gave the best LODs for Ca, Cd, Cr, Cu, Na, and Pb (7 ppt (Na) to 278 ppb (Cd)). After preconcentration by electrodeposition onto an Al substrate, the LODs for Cr and Pb in water[89] approached concentrations typically found in waters. The signal intensity was further improved by heating the substrate to 200 °C during analysis. In doing so the LOD for Cr decreased from 12 to 5 ng mL^{-1} and that for Pb from 17 to 12 ng mL^{-1}.

Improved sample pretreatments mean that the *LIBS detection of trace elements in water at natural concentrations* is becoming closer to being feasible. For example, by preconcentrating Pb in a 5 mL sample onto 0.1 g of a macroporous cation exchange resin with weakly acidic iminodiacetic acid groups, it was possible[90] to detect Pb at concentrations down to 88 ng L^{-1}

using LIBS-LIF interrogation of the resin. This was not quite low enough to detect Pb in canal and tap waters at natural concentrations. Recoveries from spiked samples (2 and 10 µg L^{-1} spikes) were between 91 (canal water) and 103% (tap water).

The use of LIBS has been extended to *the determination of non-metals in water*. A LOD of 0.1 mg L^{-1} for P in river water was achieved[91] by SPE of P onto FERROLOX®, an iron-hydroxide-based MOF. The solid (unreported amount) was isolated from the sample (unreported volume) before LIBS analysis. The method wasn't yet sensitive enough to determine natural P concentrations but recoveries of >96% were obtained for 0.5 mg L^{-1}spikes.

What is noticeable this year is that practitioners of LIBS seem to be blissfully unaware of the existence of RMs or the need for method validation. Now that LODs are approaching useful levels, better analytical rigour is required and should be encouraged by referees.

3.4.6 X-ray fluorescence spectrometry. It was reported[92] in Chinese that *direct TXRFS analysis of drinking water* is feasible for the determination of Al, Ca, Co, Cu, Fe, K, Mn, Ni, Sr and Zn but that recoveries were poor for Al, Ca and K due to matrix effects. The LODs were 0.001 – 0.07 mg L^{-1} and, unsurprisingly, it was concluded that improved accuracy could be obtained using preconcentration.

Significant efforts continue to be made to develop *preconcentration methods for XRFS analysis*. Some of those studies are presented in Tables 5 and 6. The freeze drying of water onto a quartz glass substrate resulted[93] in a film-like residue suitable for TXRFS analysis with LODs of 6 (Sr) to 51 (Ca) ng g^{-1}.

By combining the utility of *portable XRFS with on-site preconcentration*, it was possible[94] to determine Cu, Mn, Ni, Pb, U and Zn in spiked lake and ground waters in the field. Analytes in a 10 mL water sample were immobilised onto a nanoporous filter based on bisphosphonate-modified thermally carbonised porous silicon. The results obtained by this method were not significantly different from those obtained by ICP-MS for the concentration range 50-10000 µg L^{-1}. The LODs of 35 (Cu) to 103 (Mn) µg L^{-1} showed that this method was a viable field-screening test for the identification of contaminated waters such as mine waters.

4 Analysis of soils, plants and related materials

4.1 Review papers

Three reviews covered *techniques for elemental analysis of plants*. El Hosry *et al.*[95] (177 references) provided an accessible introduction to FAAS, ICP-AES, ICP-MS and XRFS, together with guidance on the selection of techniques for the analysis of plant-based foods. Ibourki *et al.*[96] (224 references) discussed similar topics but also featured LIBS and NAA. Aleluia *et al.*[97] (152 references) included herbal medicines and medicinal plants in their review of analytical approaches for the determination of trace element impurities in pharmaceutical products.

The spectrometric characterisation of NPs in biological and environmental samples was the topic of a critical review[98] (116 references) that discussed the determination of: NP synthesis yield; particle size and particle number concentration; elemental and isotopic composition; and surface properties.

Arsenic proved a popular topic for *element-specific reviews* with no fewer than three being published during the period covered by this ASU. With reference to soils and waters, both Patel *et al.*[99] (238 references) and Valskys *et al.*[100] (177 references) discussed As contamination, quantification, sources, mobility and health hazards. Mihucz[101] (222 references) focused on As speciation and analysis in soil, water, foods and Ayurvedic medicines. Methods for extraction, separation and detection of Se-enriched proteins and peptides in plants were included in a review by Xiong *et al.*[102] (136 references) that also covered bioavailability and bioactivity.

4.2 Reference materials and interlaboratory comparisons

Examples of *new or improved isotopic data for CRMs or RMs obtained by MC-ICP-MS* included:

- δ^{25}Mg and δ^{26}Mg values in five soils, four river sediments and five plants using Alfa-Mg, a new delta-zero reference solution for Mg isotope ratio measurement[103].
- δ^{34}S values in GBW07410 (soil), ERM-CD281 (rye grass) and NIST SRMs 2704 (river sediment) and 1515 (apple leaves) derived through an inter-laboratory study[104].
- δ^{65}Cu, δ^{56}Fe and δ^{66}Zn values in two soils and three sediments[105]
- δ^{66}Zn values in three NIST soil SRMs and nine Chinese soil CRMs[106]
- δ^{146}Nd values in three soils, one loess and eight sediments [107]

The mass fractions of 48 analytes, including the REEs and the technology-critical elements Be, Bi, Ga, Ge, Li, Nb, Sb, Ta and Tl, were determined[108] in seven plant CRMs by ICP-MS/MS to provide *benchmark values for future studies*. Krata[109] reported the first information on Hg speciation in a soil CRM, EnvCRM 03 from the National Metrology Institute of Turkey. Values determined by SSID-HPLC-ICP-MS were 316 ± 10 μg kg^{-1} for inorganic Hg and 0.54 ± 0.03 μg kg^{-1} for MeHg. The MeHg content was verified as 0.54 ± 0.03 μg kg^{-1} by off-line chromatographic separation and quantification by MeHg SSID-ICP-MS.

A German interlaboratory exercise with 28 participants compared[110] two *aqua regia* digestion methods and three analytical techniques for *the determination P in sewage sludge*. Microwave-assisted digestion according to Method EN 16174 was preferred to digestion under reflux (Method EN 13346), and ICP-AES was preferred to ICP-MS or spectrophotometric determination because this combination gave highest P recoveries and best precision.

4.3 Sample preparation

4.3.1 Sample dissolution and extraction

Reviews on digestion and extraction methods included[111] one (101 references) on rapid alkali-fusion methods for determining anthropogenic ^{236}U in soil that could provide results quickly following nuclear incidents. Automatic flow-analysis systems and potential application to multi-nuclide analysis were also addressed. Water, alkali, salt, alcohol and buffer extraction methods were reviewed[102] (136 references) for Se-enriched proteins and peptides in plants. Extraction times, efficiency and preservation of biological activity were discussed, as were separation and detection methods including HPLC-MS/MS and GC-ICP-MS. Antioxidant and neuroprotective properties of Se in specific plants were also covered.

Digestion procedures for soils and plants included that of Kochergina *et al.*[112] who combined matrix-specific acid digestion protocols and appropriate column chemistry for the determination of Nd, Pb and Sr in a broad range of environmental and archaeological materials including low-Nd silicates, carbonates, carbonatites, organic soil, plants, water, wood, alloys, bones and teeth. Analytes were determined by TIMS (Nd and Sr) or MC ICP-MS (Pb). The procedures, which are useful for laboratories handling diverse samples, were successfully verified with isotopic RMs. Dynamic versions of the SBET were successfully developed[113] for As, Cd, Cr, Cu, Fe, Mn, Pb and Zn in PM_{10}. Extractants were introduced continuously onto simulated PM_{10} samples prepared from NIST SRM 2711A (Montana II soil) and BGS 102 (Ironstone soil) loaded on TX40 filters in polycarbonate filter units. The extract eluted from the unit was either collected offline as subfractions for analysis by ICP-MS or introduced continuously into the nebuliser for online analysis. Element concentrations in residual samples were also determined. Mass balances determined by both online and offline methods agreed well with results from the analysis of separate test portions. Concentrations of 1100 ± 127 mg kg^{-1} and 1170 ± 135 mg kg^{-1} (n = 3) for bioaccessible Pb determined for NIST SRM 2711A by the offline and online methods, respectively, did not differ significantly from the certified value of 1110 ± 49 mg kg^{-1}. In addition, there was no significant difference between the bioaccessible PTE concentrations determined by the online and offline methods (Student's t-test, 95% CI, n = 3), indicating that both dynamic methods are suitable for the determination of bioaccessible PTEs in PM_{10}.

Electrothermal digestion with powdered NH_4F was proposed[114] for the determination of the halogens Br, Cl and I in soils and sediments. During the high-temperature digestion (optimised conditions: 220 °C, 2 h, 400 mg NH_4F, for 50 mg soil or 100 mg powdered rock/sediment samples), NH_3 released from the decomposition of molten NH_4F prevented loss of the sample halogens, which were leached from the resultant solid residue with 5% (*v/v*) aqueous ammonia. The SF-ICP-MS LOQs were 0.018, 2.8 and 0.003 µg g^{-1} for Br, Cl and I, respectively. Concentrations determined for Br and I in of a suite of 56 Chinese soil and sediment RMs were not significantly different from the reference values for most RMs but for Cl, positive relative measurement errors were as high as +48%. The authors suggested that this was due to the decomposition of refractory minerals by the NH_4F digestion. The mass fraction measured for I in RM GSD 13 of 0.17 ± 0.03 µg g^{-1} was lower than the certified value of 0.3 ± 0.1 µg g^{-1}, so the authors proposed a revision of the certified value.

Reaction ‘minivessels’ were constructed[115] for *the MAE of small-mass biological samples.* The internal volume of 3 mL and external diameter of 1.2 cm enabled three of the Teflon minivessels to be placed simultaneously on the platform of a standard 100 cm^3 autoclave (EasyPrep) of a MARS-5 microwave system. Digestions were performed with only 10–20 mg of sample and 1.5 mL acid per minivessel. Results from the ICP-MS analysis of CRM INCT-TL-1 (Argentine black tea leaves), CTA-OTL-1 (oriental Bulgarian tobacco leaves), CTA-VTL-2 (Virginia tobacco leaves) and IAEA-153 (milk powder) were not significantly different to certified values (n = 4-6) at 95% confidence. New data were also obtained for the concentrations of B, Bi, Ga, Nb, Tl, Y and REEs in these RMs.

In a comparison of *acid digestion methods* for the determination of Al, Cd, Mg and Mn in plant samples, Bankaji *et al.*[116] concluded that the most effective method was both element- and species-specific. Analyte concentrations in five different plant species, determined by AAS, did indeed vary significantly depending on the plant species, acid mixture and extraction conditions. Results obtained for the analysis of RMs following the same digestion procedures are troubling: for CRM BCR 62 (*olea europapea*) the measured concentrations were 1145−7730 mg kg^{-1} for Al (certified value 450 mg kg^{-1}), 175−251 mg kg^{-1} for Cd (certified value 0.1 mg kg^{-1}) and 101−1106 mg kg^{-1} for Mn (certified value 57 mg kg^{-1}). The Cd concentrations measured for BCR 279 (*ulva lactuca*) were 168−243 mg kg^{-1} (certified value 0.274 mg kg^{-1}). The authors interpreted these differences as evidence of a highly efficient digestion but the deviations from the certified values were so large that real experimental errors must be considered.

Platinum NPs from vehicle emissions can accumulate in roadside soils in urban environments and so should be monitored to assess population exposure. Ultrapure water and 0.005% FL70 (a commercial alkaline detergent) were compared[117] for the stabilisation of platinum NPs extracted from soil. The extraction involved several vortex, sonication and centrifugation steps, performed with and without addition of 0.1 M NaCl. After extraction, either ultrapure water or 0.005% FL70 were added to aid dispersion of the NPs prior to sample analysis by sp-ICP-TOF-MS. The methods were tested with LKSD-1 (lake sediment) spiked with 820 ± 150 NP mL^{-1}. Extraction with FL70 was more efficient than with ultrapure water, with particle number recoveries between 117−137% (with NaCl) and 78−102% (without NaCl).

4.3.2 Analyte separation and preconcentration

Reviews on separation and preconcentration techniques covered both multiple- and single-element determinations. Zhong *et al.*[118] reviewed (167 references) phase separation and field-assisted acceleration methods for multi-element analysis in soils, geological materials, plants and foods. Attention was drawn to the need for species-specific methods. The assessment of energy consumption and solvent toxicity in the reviewed methods was of interest. The preparation and properties of green solvents were critically reviewed[57] (150 references) with an emphasis on DESs, ILs and switchable solvents. Application to real samples was also covered . Both solid and liquid microextraction-based approaches for the determination of Hg were critically reviewed[53] (121 references) with a focus on sustainable materials and green methods for air, water, soil and biota analyses. Linear range, LOD, accuracy and precision were considered and a comparative assessment of the methods presented. Areas identified for future research included: greater application of extraction methods to solid samples; further development of cold fibre, vacuum-assisted and arrow SPME techniques (in which the tip is arrow-shaped for easier insertion into vial septa); and natural or recycled materials as sorbents.

Natural and recycled materials were employed in several separation and preconcentration methods. A novel and rapid CPE ICP-AES method[119] for the simultaneous determination of Cd and Ni utilised a DES as an environmentally friendly reagent. The DES, based on L-menthol and n-hexanoic acid, decreased the cloud point temperature of TX-114 and so enabled the rapid extraction of Cd and Ni at room temperature. Under optimised conditions, the LODs were 0.01 and 0.05 $\mu g\ L^{-1}$ for Cd and Ni, respectively. No statistical differences (Student's t-test, no CI presented) were found between the concentrations of Cd and Ni in *Salvia yunnanensis* samples, indicating that the method was a suitable low-temperature CPE alternative for extraction of Cd and Ni.

Current research suggests[120] that the microbial toxicity of *amino acids-based DESs* may be lower than that of other DESs. An innovative UA matrix solid-phase dispersion method with amino acids-based DESs was developed[121] for the extraction of As from medicinal herbs. Powdered DES precursor was dispersed directly with the sample into tubes and, following

UA solid-phase-dispersion, ultrapure water was added to the mixture, which was then ultrasonicated. After phase separation on filter paper, supernatants were analysed by ICP-MS. The method LOD was 0.039 mg kg^{-1} under conditions optimised by Doehlert design (50 °C, 60 min and a sample-solvent ratio of 10:1 mg mL^{-1}). Beta-alanine-citric acid-water (1:2:17 molar ratio) was the most effective DES for As extraction. The results (n = 3) from the analysis of NIST SRM 1547 (peach leaves) and EMBRAPA E1001a (Marandu) of 0.05 ± 0.0014 and 1.71 ± 0.284 mg kg^{-1}, respectively, did not differ significantly from the certified values of 0.062 ± 0.014 and 1.69 ± 0.70, respectively. The overall 'greenness assessment' of the method, based on the Analytical Eco Scale[122], was 94 out of a possible maximum of 100 for total sustainability, clearly better than the score of 83 for MAD with HNO_3 and H_2O_2.

Recycled facemasks were used in a novel stir-bar sorptive method[123] for the extraction of Co, Ni and Pb from plant and water samples. The bar was made by inserting an iron wire into chopped up, meltblown layers of facemask and was saturated with a synthesised DES (choline chloride:3,4-dimethylphenol). The bar was then immersed into 100 mL of digested (plant) or acidified (water) sample containing 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol chelating agent and sodium acetate buffer. After stirring (6.0 min, 375 rpm), the complexed analyte ions were extracted with 4.0 mL of 1 M HNO_3 in THF under sonication for 30 s and determined by FAAS. Under optimised conditions, the linear ranges were 3−150, 2−150 and 7−500 µg L^{-1}, and the LODs were 0.91, 0.61 and 2.3 µg L^{-1} for Co, Ni, and Pb, respectively. The results of 9.8 ± 0.3, 48.6 ± 1.4 and 25.1 ± 0.6 µg L^{-1} for SPS-SW2 (surface water I - trace metals) did not differ significantly from the certified values of 10 ± 0.05, 50 ± 0.3 and 25.0 ± 0.1 µg L^{-1} for Co, Ni and Pb, respectively. Similarly, the results of 61.8 ± 1.5, 71.0 ± 1.8 and 71.2 ± 2.1 µg L^{-1} for Sigma-Aldrich RM QC-1187 (trace metals ICP sample 1) did not differ significantly from the certified values of 62.2 ± 1.1, 72.5 ± 1.3 and 72.8 ± 1.3 µg L^{-1} for Co, Ni and Pb, respectively. The method was also applied to samples of dill, coriander and spinach.

Methods for speciation analysis are particularly welcome for elements for which the oxidation state directly affects species mobility and toxicity. An HR DGT technique used with LA-ICP-MS analysis enabled[124] the selective and simultaneous 2D chemical imaging of As^{III}, Cr^{III} and Sb^{III} at the sub-mm scale for the first time. Whereas trivalent species were selectively accumulated on a mercapto-functionalised attapulgite binding gel, <2% of the higher oxidation state species were accumulated. Uptake was unaffected by pH (3.2 to 8.2) and sorption capacity was 72, 44 and 79 µg per DGT device for As^{III}, Cr^{III} and Sb^{III}, respectively. There was a linear relationship (r^2>0.99) between species uptake and LA signals, and analytical precision was adequate (RSD<10%).

Other separation and preconcentration 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 Table 8 (SPE methods).

Insert Table 8.

4.4 Instrumental analysis

4.4.1 Atomic absorption spectrometry

An ETV device with inbuilt metal ceramic heater was combined[125] with a catalytic pyrolysis furnace containing Al_2O_3 particles and a miniature spectrometer to produce an instrument for the direct *determination of Hg in soil by CVAAS*. The LOD for a 50 mg sample was 0.4 ng g^{-1} and the relative measurement errors ranged from -15 to +13% for the analysis of three Chinese CRMs. The instrument weighed only 5 kg and had a power consumption of <200 W so there was scope for field deployment as a rapid Hg screening method. In another procedure for the measurement of Hg in soil, sediment and water, Hg vapour was trapped[63] on a platinum-coated tungsten coil. This preconcentration step improved the LOD from 44.8 ng L^{-1} to 8.8 ng L^{-1}. The result obtained for RTC CRM 023 (sandy loam 7) was 79.7 ± 3.1 mg kg^{-1} (certified value 77.8 ± 5.2 mg kg^{-1}).

Analytical methods based on HR-CS-ETAAS are becoming more widely used. A simultaneous quantification of Fe and Zn in plants was based[126] on spectral lines at 307.572 nm (Fe) and 307.588 nm (Zn), both of which fell within the spectrometer bandpass. The LODs were relatively poor (0.05 mg L^{-1} for Fe and 0.02 mg L^{-1} for Zn) for an ETAAS method, due to the selection of low-intensity secondary lines, but adequate for the routine analysis of vegetable samples. Accurate results were obtained[127] for the determination of Ag in soil following preconcentration on bentonite and slurry-sample introduction. The values obtained for NIST SRMs 2709 (San Joaquin soil) and 2711 (Montana soil) were not significantly different from certified values according to a Student's t-test at 95% confidence. The LOD was 0.01 μg L^{-1} for a sample volume of 20 μL.

The Zr-based MOF UIO-66-NH_2 was synthesised[128], characterised and successfully used as *a novel matrix modifier* in the determination of Cd in soil by ETAAS. Capture of Cd within the MOF helped stabilise the analyte during the pyrolysis step of the heating programme and thereby yielded a 30% improvement in sensitivity relative to conventional $Pd(NO_3)_2$ modification.

4.4.2 Atomic emission spectrometry

A *novel ablation chamber* was designed[129] for the direct determination of Ag, Cr, Cu and Pb in soil by LA-MPT-AES. The chamber, which featured a central cylindrical channel, provided a reduced dead volume and so resulted in faster washout and more efficient and stable transport of ablated sample particles into the plasma. Following optimisation of parameters (laser energy, carrier gas flow rate, microwave power), the LODs were 0.009 – 0.093 mg kg^{-1}. Results for Cr, Cu and Pb were within 10% of certified values for three soil CRMs but results for Ag were poorer (relative error up to 26%) at the lower concentrations present.

Phytoavailable elements in soil were measured[130] with *a dielectric barrier discharge microplasma*. A 0.1 M $NaNO_3$ extract was diluted 30-fold before electrochemical accumulation of analyte cations onto an activated-carbon-electrode tip and *in situ* desorption into the plasma. The LODs for Cd, Cu, Pb and Zn were 0.8–6.0 μg kg^{-1} and results for IRMM CRM BCR 483 (sewage sludge amended soil) were not significantly different from indicative $NaNO_3$-extractable concentrations, according to a Student's t-test at 95% confidence.

A *new approach for improving sensitivity in the determination of Hg in environmental samples* involved[131] plasma-induced VG and FI gas analysis. Initially, analyte vapour was produced by a solution-anode GD unit operating without carrier gas flow (the accumulation stage). Then gas flow was restored, and the concentrated vapour swept into the ICP (the injection stage) to generate a transient signal analogous to conventional liquid sample FIA. Even though the signal increased up to an accumulation time of 120 s, a 60 s time was selected to maintain sample throughput. Recoveries of spikes from dilute HNO_3 extracts of two spiked urban soils were 102 ± 11% and 104 ± 5% (n = 3).

4.4.3 Atomic fluorescence spectrometry

A method optimised for *ultratrace determination of Cd in water and rice by CVG-AFS* involved[66] addition of Cr^{3+}/KCN to enhance the generation of Cd volatile species and a laboratory-built non-dispersive AFS instrument containing a high intensity EDL, two types of flame atomiser and a PMT. The sensitivity achieved with the flame-in-gas-shield atomiser was almost twice that obtained with the miniature diffusion-flame atomiser resulting in a LOD of 0.42 ng L^{-1}. The result obtained for analysis of NIST SRM 1568b (rice flour) following MAD in 2 M HNO_3 was 19.9 ± 1.5 μg kg^{-1} (certified value 22.4 ± 1.3 μg kg^{-1}). Concentrated acid digestion was not recommended, as introduction of a sample solution containing >0.3 M HNO_3 impaired the CVG performance and the consequent high dilution factors required affected the LOD adversely.

Progress has been made in the development of *methods for the direct analysis of soil by ETV-AFS*. A miniature nickel foam trap was positioned[132] between a modified commercial ETV unit and spectrometer for gas-phase enrichment of Cd. Analyte trapping efficiency was 100% and the LOD was 0.035 ng g^{-1} for a 20 mg sample. Subsequently, an improved system for simultaneous measurement of Cd and Hg was constructed[133] by incorporating the same type of metal ceramic heater discussed in Section 4.4.1. of this ASU together with a novel platinised nickel trap. Following stepwise vaporisation and trapping of the analytes (Hg at *ca.* 500 °C under air and Cd at *ca.* 1000 °C under Ar/H_2), the trap was heated and the analytes released. Accurate results were obtained for Chinese soil CRMs GSS-2a, GSS-16 and GSS-22

(Student's t-test, 95% confidence). Spike recoveries for real soil samples were 102–105% for Hg and 96–104% for Cd.

4.4.4 Inductively coupled plasma mass spectrometry

A review (262 references) of *applications of ICP-MS in the analysis of traditional medicines* listed[134] numerous examples featuring major or trace element analysis of whole plants or parts thereof (flowers, fruits, leaves, roots, seeds, and stems). It also covered medicines derived from animal and mineral sources and had a small section on speciation analysis by HPLC-ICP-MS.

New vapour generation methods for use with ICP-MS continue to be developed. Dong *et al.*[135] applied the procedure for the vanadium-assisted PVG of Te, noted in our previous ASU[1], to the determination of Sb. Addition of 80 mg L^{-1} V^{IV} followed by 100 s UV irradiation increased the signal three-fold (relative to when no catalyst was present) and gave a LOD of 4.7 ng L^{-1}. However, sensitivity was still only half of that achieved with cobalt-assisted PVG. Liu *et al.*[71] successfully used plasma electrochemical VG in a rapid and cost-effective approach for the determination of Cd isotopes by MC-ICP-MS. The procedure was at least 20 times faster than the usual method (a two-step anion-exchange-resin purification followed by membrane desolvation) and had improved tolerance to matrix elements. Results for δ^{114}Cd in two soil, three sediment and one basalt RM were similar to those reported by other researchers.

Although *the coupling of chromatographic separation with ICP-MS* is now routine, procedures continue to be developed, optimised and validated. Examples included: an HPLC-

ICP-MS method[136] for As speciation in soil extracts prepared by MAE in 0.5 M phosphoric acid; an HPLC-ICP-MS method[137]for As speciation in foods of plant origin that was applied to cereals, seaweed and vegetables; and a HPLC-ICP-MS method[138] for Sb speciation in soils, which was used to compare the impacts in southern Poland of a slag heap from a historical Pb/Zn mine, a modern WEEE plant and a motorway. Of particular interest to the wine enthusiasts amongst the ASU readership was an IC-ICP-MS method based on detection of the PO^+ ion that could detect[139] residues of phosphonic acid, a substance banned from use in organic viticulture in the EU since 2013. The method offered at least 20-fold lower LODs for both solid (grapes, leaves, pomace, roots, soil, stems) and liquid (wine, wine must, xylem sap) samples than the approach currently used (IC with a conductivity detector). When applied to 130 samples from across France, Germany, Italy and Spain, the mean results for phosphonic acid were 4.32 mg kg^{-1} for conventional wines and 0.32 mg kg^{-1} for organic wines.

A rapid-cooling cryogenic sample chamber facilitated[140] *the imaging of plant tissue by LA-ICP-MS*. The temperature could be lowered to -20 °C in 4 min and remained stable (±0.1 °C) for 10 h. The LODs for Cu, Fe and Zn in spiked agarose-gel calibrants improved 1.6-, 3.3- and 1.7-fold, respectively. Better spatial resolution was obtained during ablation of fresh coriander leaves as the cryo-chamber minimised heating and so tissue damage and loss of water were kept to a minimum. The same approach was applied[141] in a comparison of the distribution and effects of Ce^{3+} ions and CeO_2 NPs taken up into cucumber leaves.

The analytical capability of a *nitrogen-microwave inductively coupled atmospheric-pressure plasma* was demonstrated[142] through accurate determination of As, Cd, Co, Cr, Cu, Pb, V and Zn concentrations in seven soil RMs from BAM. Except for Ni, which was overestimated by MICAP-MS due to the presence of a nickel skimmer cone, results were comparable to those obtained by ICP-MS and similar to the reference values. The LODs of 2.11 (V) to 103 ng L^{-1} (Ni) were slightly poorer than those obtained by ICP-MS (except for Pb) but were nevertheless still fit for purpose. The lower operating costs were a major advantage of the new instrument.

An improved ICP-MS/MS method for measuring $^{135}Cs/^{137}Cs$ ratios in samples with low radiocaesium content combined[143] the authors' previously reported extraction and purification procedure with introduction of a novel gas mixture to the collision-reaction cell. The N_2O (0.55 mL min^{-1}) + He (1 mL min^{-1}) + NH_3/He (10+90 *m/m*, 4.79 mL min^{-1}) gas mixture proved effective for removal of interference from residual Ba, Sb and Sn. The ^{135}Cs and ^{137}Cs LODs were 1.66 and 0.67 fg g^{-1}, respectively. Results obtained for CRMs IAEA 330 (spinach) and IAEA 375 (soil) agreed with previously published values.

Discriminating between different types of NPs in soil remains challenging, in particular for engineered and natural NPs of similar composition. However, some advances have been made. A dual-analyte sp-ICP-MS procedure for distinguishing kaolinite and goethite NPs was based[144] on the detection of three types of events: Al unpaired events; Fe unpaired events; and paired events. Particle numbers and sizes were consistent with results obtained by single-analyte sp-ICP-MS. The ability to recognise soil NPs with different mineralogy is important because of their role in biogeochemical cycling of PTEs. The capability of sp-ICP-TOF-MS to provide multi-element information on individual particles allowed Taskula *et al.*[117] to identify naturally-occurring Pt-containing NPs in lake sediment NRCC CRM LKSD-1. This approach was based on the co-detection of Pt with Au, Bi and Ir, which are not present in engineered platinum NPs. When the CRM was spiked with engineered platinum NPs, 31–78% of the NPs formed mixed aggregates with sediment particles. Bland *et al.*[145] also used sp-ICP-TOF-MS in their study of the behaviour in soil of ^{47}Ti-enriched TiO_2 NPs, which could be distinguished from natural nanomaterials based on isotope analysis.

An analytical workflow for characterisation and quantification of engineered nanoparticles in biological tissues provided[146] useful guidance to researchers. Covering both sample preparation and analytical approaches such as single cell ICP-MS, sp-ICP-MS and synchrotron-based techniques, the protocol could be adapted for use in a variety of studies.

4.4.5 Laser-induced breakdown spectroscopy

A review (162 references) provided[147] a useful overview of recent progress and challenges in the application of LIBS to geotechnical samples. It included: information on the fundamental principles of LIBS; physical and chemical matrix effects; spectral pre-processing methods; quantitative analysis (both with calibration and calibration-free); and chemometric approaches for information extraction. In addition, examples of applications to the analysis of minerals, rocks, soils, concrete and fluids were presented. Another review (174 references) focused[148] specifically on machine learning and how it might enhance the capabilities of LIBS for both elemental analysis and soil classification.

Research continues into *means for enhancing signal intensity in LIBS analysis*. Zhou *et al.*[149] investigated NP-enhanced LIBS for the determination of Cu, Fe, Mn and Zn in soil. Silver NPs were either deposited on top of a pressed soil pellet or dried onto a glass slide and overlain with a 2 M HCl soil extract that was dried prior to ablation. The second approach gave better performance. Calibration curves prepared using a series of Chinese GBW soil CRMs had r^2 >0.98 for all four elements. Sensitivity for the determination of Hg in dried tangerine peel was improved[150] six-fold by coating the sample pellet with gold NPs and purging the sample stage with 15 L min^{-1} of Ar to reduce quenching of analyte emission lines by oxygen. A comparison of different sizes and shapes of NPs led to the selection of 40 nm Au nanocages at a surface concentration of 1.77×10^{-3} mg cm^{-2} as being optimal. By studying the effect of KCl addition and sample temperature, Li *et al.*[151] found that signal intensities for Al and Cd in lake sediment were enhanced (1.6- and 2-fold, respectively) in the presence of 15% KCl at 180 °C compared with analysis at room temperature without the additive. Meng *et al.*[152] achieved similar improvements (2.5 to 2.8-fold increase in signal for Al, Cd, Fe and Pb in soil) at 180 °C with planar mirror confinement (an approach in which the sample is ablated between two parallel mirrors to compress the plasma plume into a smaller volume) rather than by chemical addition. Amador-Mejia[153] also recommended sample heating but to a higher temperature (400 ± 20 °C), together with re-excitation of the laser plasma using a high-voltage discharge. This gave an up to seven-fold increase in signal intensity for As, Be, Cd, Cr, Ni, Pb, V and Zn in loam soil. Two remarkably similar articles by Rahim *et al.*[154, 155] explored the impact of magnetic field confinement and laser fluence on the emission lines of As, Ba, Co, Cr, Mn and Ti in river sediment samples. They claimed up to six-fold enhancement under optimised conditions. The novel APGD cylindrical-confinement approach discussed in last year's ASU[1] was applied[156] to improve LODs in the determination of selected REEs in soil.

Although something of a contradiction in terms of nomenclature, a *calibration-free LIBS method with one-point calibration* decreased[157] matrix effects in the determination of Ca, Fe and Mg in soybean leaf samples. Results were first normalised to a TiO_2 IS added to the sample pellets at a concentration of 0.5 wt% and then empirical corrections, based on the results for one sample, were applied to the emission line intensities in the other samples. An

RMSE of <10% relative to AAS data was achieved. The same approach was later applied[158] to measure Hg in soil and the residues from dried landfill leachates. Samples were first analysed under optimised conditions by DP-LIBS and then corrections based on one sample type (the soil) were applied throughout. The mean relative absolute error in the concentration predicted for analysis of two sandy loam CRMs was improved from 89 to 6.9%.

An alternative approach for reducing matrix interference is LA-LIBS in which a sample aerosol is generated by an ablation laser and then transported in a carrier gas to a different location for plasma formation by a second laser. However, the instrument system is more complex than conventional LIBS, and LODs are poorer. Han *et al.*[159] overcame these limitations by incorporating the two lasers in a single chamber. The output of a high-energy plasma-generation laser (200 mJ per pulse) was focused onto the aerosol plume produced by a low-energy ablation-laser (3 mJ per pulse). Improved signal stability was achieved together with an LOD of 7.8 μg g^{-1} for the determination of K in soil, an improvement over the 9.8 μg g^{-1} for the traditional combined sample-ablation and plasma formation. Results for three real samples were similar to those obtained by AAS.

Other *notable advances in the LIBS analysis of soils* included: a mathematical procedure[160] to correct for spectral line self-absorption; a method[161] based on key parameter monitoring and a back-propagation neural network that improved precision; and a theoretical model[162] of ablation-crater morphology that allowed analysis to be optimised in such a way as to reduce confinement effects.

Also published were numerous *methods for the determination of specific elements in soil*. A procedure for C in Brazilian soils overcame[163] interferences from Al and Fe, both of which are typically present at high concentrations in such samples. Two methods were reported for the determination of Cd. The first involved[164] polarisation-resolved LIBS and a support-vector regression algorithm. The second featured[165] co-linear DP-LIBS and a particle-swarm-optimised least-squares support vector machine. The performance of a linear-weighted network was improved[166] for the determination of Cr by addition of adaptive weighted normalisation. The application of a novel ion-enrichment chip containing an anion exchange resin (for Cr^{VI}) and an active carbon fibre (for total Cr) made[167] speciation analysis possible. Although potentially useful for solution analysis, the assertion that the method was suitable for the determination of total Cr in soil is highly questionable. Soils with naturally low concentrations of Cr were spiked with standard solutions to give Cr concentrations of 100 - 1000 mg kg^{-1}. The Cr was extracted with deionised water (1:3 *m/v*) and the extract passed through the ion-enrichment chip for preconcentration and LIBS analysis. Hence, only the water-soluble Cr fraction and not Cr associated with solid soil minerals could be measured.

In the *LIBS analysis of plants*, a back-propagation neural network that had been optimised using a sparrow search algorithm was used[168] successfully to predict concentrations of Cd, Cu and Pb in *Fritillaria thunbergia*. Fang *et al.*[169] explored the possibility of analysing Cd- and Pb-spiked laurel leaves without the need for grinding and pelleting. For calibration, small (10 mm diameter) wafers were cut from leaves that had been soaked in solutions with different analyte concentrations for two days, rinsed with deionised water and dried before the laser interrogation. Unsurprisingly, the spatial variability was high (RSDs of 13–160%, n = 12). However, an r^2 value of 0.8272 was obtained when the LIBS signal intensity for Pb at 405.78 nm was plotted against results obtained for the same samples following MAE and ICP-MS. This is an encouraging result.

The effect of laser-spot size on the LIBS analysis of heterogeneous agricultural samples such as plants was studied[170] at constant fluence using soybean grist as a test substrate. Laser characteristics of three types of LIBS instrument were simulated: a hand-held instrument with low pulse energy and small laser beam diameter (0.12 mm); a typical laboratory-based instrument with moderate pulse energy and beam diameter (0.53 mm); and an industrial system, found typically on a production line, with high pulse energy and large beam diameter (1.1 mm). As might be expected, the larger beam profile gave better linearity and accuracy for the determination of Zn.

4.4.6 X-ray fluorescence spectrometry

Research continues on *improvement of the performance of XRF spectrometry methods.* A new prediction framework for reducing spectral background included[171] pre-processing, signal extraction, feature selection and decision-making. The framework was based on an ‘iterative adaptive window empirical wavelet transform’ method for signal analysis in time and frequency domains. Following application of the background subtraction algorithm, the peak intensities had a stronger correlation with element concentration than the original spectra resulting in improved r^2 for all elements. There was a marked improvement for Pb, for which r^2 increased from 0.664 to 0.881 and for V for which R^2 increased from 0.748 to 0.912.

Monochromatic EDXRFS with a silicon drift detector was used[172] together with a fundamental parameters algorithm for the determination of 20 elements in soils and sediments. The LODs for all elements except Cr and V were lower than those obtained by WDXRFS. The LOD for Cd (0.04 mg kg^{-1}) was particularly low. Concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn obtained for 17 soil and sediment CRMs correlated (r^2 >0.98) with certified values for all elements. Monochromatic-excitation EDXRFS coupled with a fundamental parameters approach was applied[173] for the first time to the determination of As, Cd and Pb in herbal medicines. Analysis time was only 10 to 30 min and the cost of analysis was a tenth of that by ICP-MS. The LODs were 0.093, 0.144 and 0.232 mg kg^{-1} for As, Cd and Pb, respectively. Linear regression between 99 pairs of ICP-MS and XRFS results yielded r^2 values of 0.91 for As and of 0.96 for Cd and Pb.

The XRFS analysis of organic samples in which the low-*Z* elements C, H, N and O predominate generally requires an increased sample mass per unit area (sample thickness) in the sample cup than the analysis of soil and rock samples. Zhou *et al.*[174] developed a mass-correction model for quantification of As, Cu, Fe and Zn in thicker samples of organic materials. When 39 organic materials including animal tissue, fungi and plants were analysed, the measured concentrations decreased with increasing sample thickness in a power-law relationship. The model corrected for this concentration decrease and allowed predictions of concentrations in infinitely thick samples to be made. For samples of intermediate thickness, the concentrations of As, Cu, Fe and Zn were predicted by applying a simple linear regression previously derived by cross calibration with ICP-MS data. The relative measurement errors of results when compared to ICP-MS data of <18% (As) to <34% (Fe) indicated that with further development pXRFS had potential for the analysis of organic matrices.

Two papers described the *integration of XRFS technology into new hardware and software applications* with the aim of accumulating data over large areas with rapid real-time data sharing. Huang *et al.*[175] presented the concept for an ‘integrated unmanned aerial vehicle-based soil heavy metal pollution rapid detection system’ yet to be built. The drone-like multi-rotor vehicle would fly to a specific investigation site where data would be collected at a height of 5 cm above the ground by an onboard pXRF spectrometer. Kim *et al.*[176] developed a smart-glasses-based app that enabled the wearer to move to predetermined sampling points by navigating a satellite image, to analyse samples by pXRFS and to enter the results into the app *via* a wearable keyboard. The app calculated pollution indices and identified potentially contaminated locations. Data could be uploaded to the cloud server and shared in real time with other users on- and off-site. Both developments highlight the tremendous potential of XRFS for remote and real-time monitoring.

4.4.7 Accelerator Mass Spectrometry

Advances in *the determination of radionuclides by AMS* included[177] a method for the determination of ^{90}Sr in soil. Isobaric interference from ^{90}Zr, largely removed by chemical separation, was further suppressed using the recently-developed AMS "add-in" ion-laser interaction MS in which a collision-reaction cell filled with He/O_2 gas and co-linear (with the ion beam) laser was positioned between the ion source and tandem accelerator injection-magnet. A LOD of <0.1 mBq was achieved. A method for the ultrasensitive determination of ^{244}Pu in sediments gave[178] results similar to published data for CRMs IAEA-410 (Bikini Atoll sediment) and IAEA-412 (Pacific Ocean sediment) and had an inferred LOD of around 4 ag. A new and free online database released[179] by NERC contained AMS results obtained by the UK Radiocarbon Laboratory (available at: https://www.environmental14c.co.uk/form_ams.php). This complemented the existing database of radiometric data and should prove to be a valuable resource for the radiocarbon community.

5 Analysis of geological materials

5.1 Reference materials and data quality

The production of *new RMs for trace element determinations* has been mainly directed to addressing the need for more matrix-matched RMs for microanalysis. A useful addition to the range of available glass RMs was three natural glasses, andesitic glass OJY-1 and rhyolitic obsidians OH-1 and OA-1, which were characterised**[180]** for 54 major and trace elements and for Pb isotope ratios by a variety of analytical techniques. Microanalyses (10-120 µm) demonstrated that all three glasses were homogeneous with respect to these determinands except for Ni in OJY-1 and Ce, Cu and Zr in OH-1. Four carbonate powders, developed by Sun *et al.***[181]** from natural raw materials by a coprecipitation method, were assigned certified values for more than 35 element mass fractions determined by solution techniques. Pressed pellets prepared from these powders were checked for homogeneity and stability by LA-ICP-MS; although the repeatability for many elements was comparable to those obtained from homogeneous glasses, values for some elements, such as Cd, Co, Ga, Ge, Mo, Ni, Se and U, fell outside acceptable limits. After characterisation of their major and trace compositions by EPMA and LA-ICP-MS, two clinopyroxene megacrysts (DMP-2 and DMP-3) were considered[182] to be sufficiently homogenous for *in situ* microanalysis. Recommended and information values for 32 elements were reported together with their uncertainties (2SD). Of the 12 apatite samples tested by Kennedy *et al.***[183]** as potential RMs for SIMS analysis, three (SLAP, NUAN and GR40) were internally homogeneous. Most of the trace element mass fractions determined by LA-ICP-MS had precisions of ≤2.0%. On the other hand, AFG2 and BR5 were considered the best for U-Pb dating as these had relatively high Th and U contents and $^{206}Pb/^{204}Pb$ ratio and were more homogeneous than many naturally occurring apatites.

However, because of the variable amounts of common Pb, none of the apatites studied could be used as a single-chip ID-TIMS U-Pb RM. Four natural chromite samples from the Luobusa ophiolite (China) and Stillwater Complex (USA) were evaluated**[184]** as potential RMs for *in situ* microanalysis by LA-ICP-MS. Recommended values for major oxides (Al_2O_3, Cr_2O_3, FeO and MgO) and trace elements (Co, Ga, Mn, Ni, Sc, Ti, V and Zn) were derived from solution ICP-MS data and the homogeneities of the major and trace elements were checked by EPMA and LA-ICP-MS, respectively. Prasad *et al.***[185]** described the production of a bauxite CRM (BARC-B1201) and its certification for 8 major and minor elements and LOI following an inter-laboratory comparison exercise involving 17 laboratories in India.

A bibliographic review (28 references) of selected papers published in 2021 containing *analytical data for geological and environmental RMs* highlighted**[186]** the large proportion of papers reporting values for isotopic systems and the characterisation of new RMs for isotope analysis. This trend is reflected in Table 9, which lists new geological RMs for isotope measurements published within the period covered by this ASU. Another trend observed in the review by Weis *et al.***[186]** was the analysis of established RMs by new and improved methods and techniques thereby providing reference values for a wider range of trace elements and isotope systems than the original certificate. This continues to be the case and new data for existing geological RMs concerned with isotope systematics and dating protocols are listed in Table 10.

Insert Tables 9 and 10

Potts and Webb**[187]** proposed a simple test for assessing the *fitness-for-purpose of values for a RM*. Their approach involved comparing individual reference value uncertainties with a target uncertainty calculated using a modified form of the Horwitz function that models the variation of precision with mass fraction over a range of six orders of magnitude. They provided worked examples for various geological CRMs to demonstrate that a Quality Factor, calculated as the ratio of the reference value uncertainty to one third of the target uncertainty derived from the Horwitz function, provided an overall indication of the quality of a RM and whether the material was appropriate for its intended use.

5.2 Sample preparation, dissolution and chemical separation

Logue *et al.*[188] presented a novel *laser ablation microsampling technique* as a non-mechanical alternative to micro-milling for sampling single crystals and interstitial phases. Target phases delineated by LA were extracted using a binocular microscope and common mineral-separation tools and digested for the determination of Nd and Sr isotope ratios by ID-TIMS. However, this technique had limited usefulness for thicker samples because the efficiency of LA instruments decreases rapidly beyond 200 µm depth.

Vlastelic and Piro[189] investigated the *volatilisation of trace elements* during the evaporation-to-dryness of basaltic samples dissolved in HF under both open- and closed-vessel systems. With the exception of B, sublimation at 80 °C in open systems was low (≤ 3%). However, the closed-vessel system included a PTFE elbow and volatilisation losses of >3% were recorded for a significant number of trace elements, including refractory elements such as Hf, Nb, U and Yb. It was concluded that the higher vapour pressure of HF in the closed system gave rise to highly fluorinated species with low sublimation temperatures, or to unstable species such as the REE tetrafluorides. These findings indicated that closed-system evaporation must be used with caution for quantitative analyses.

A method based on *sequential leaching* to obtain reliable SiO_2 concentrations in sediments was devised**[190]** to overcome the problem of the release of volatile SiF_4 during conventional HF-HNO_3 digestions. Five powdered RMs were processed using a two-step leaching procedure utilising HCl to digest authigenic minerals such as carbonates, ignition in a muffle furnace to remove any remaining OM and digestion with concentrated HF-HNO_3 at high pressure and temperature to attack detrital silicate phases. Measured values were within ±2% (1 RSD) of the reference values and the precisions were better than 0.46%. Advantages over other methods were low sample consumption and high efficiency.

Rapid and simple digestion procedures that achieve total dissolution remain a priority. Liu *et al.***[191]** evaluated the ability of ammonium bifluoride (NH_4HF_2) to digest Ti-rich minerals such as rutile, ilmenite, titanite and perovskite for the determination of major and trace elements by ICP-MS. Complete digestion of 50 mg samples was achieved in 4 h using 300 mg of NH_4HF_2 at 230 °C. This was claimed to be 18-42 times faster than a closed-vessel acid digestion procedure. The analysis of Ti-rich materials using the two digestion methods gave ICP-MS datasets for 36 trace elements that were within ±10% for most elements. The one exception was rutile, for which the closed-vessel method suffered from the formation of an insoluble precipitate that caused low recoveries of Nb, Ta, Ti and V. He *et al.***[114]** employed NH_4F digestions in the determination of Br, Cl and I in geological materials by SF-ICP-MS. Ammonia released from the decomposition of molten NH_4F at 200-240 °C in a screw-top PFA vial was effective in preventing the loss of halogens released from geological samples. Analysis of a range of RMs confirmed that the method was capable of extracting Br, Cl and I quantitatively from rocks, sediments and soils, with LOQs of 0.018, 2.8 and 0.003 $\mu g\ g^{-1}$, respectively.

A rapid method for the *separation of REEs from barium* when analysing Ba-rich samples containing barite or witherite was developed[192] to eliminate the Ba interference for accurate determination of REE content by ICP-MS. This method relied on barium nitrate being almost insoluble in concentrated HNO_3 whereas the REEs were not. The whole separation procedure took <2 h and only consumed 1.5 mL 15 M HNO_3. Analysis of four barite RMs with $BaSO_4$ contents of 19 - 42 wt% gave results within ±4% of the reference values.

5.3 Instrumental analysis

5.3.1 Laser-induced breakdown spectroscopy

A *review* (163 references) of applications of LIBS in geotechnical engineering covered[147] recent developments, perspectives and challenges. Various applications in mineralogy, soil studies, rock investigations and fluid analysis were discussed, as well as calibration-free LIBS methods such as chemometrics, ANNs and support vector machines for quantification. An overview (244 references) of LIBS-based sample classification provided[193] guidance on good practices necessary to achieve reliable, robust and reproducible results. Advantages and limitations of the most common machine learning algorithms were discussed and a summary of relevant literature provided.

Yang *et al.*[194] explored the *effect of sample surface morphology* on LIBS spectra. Images of the plasma were recorded with an intensified CCD camera during LIBS analysis of samples with various surface reliefs and roughness. Functional relationships between the surface morphology and characteristic parameters of LIBS spectra were examined. Although this study provided a basis to account for some of the unpredictability of LIBS spectral anomalies, it had limited value for field-based *in situ* measurements for which the surface morphology of the sample was unknown.

As in previous years, various contributions in the field of LIBS focused on topics related to *exploration and mining*. In their quest to develop a downhole geochemical assay tool, Fontana *et al.*[195] investigated the optimal number of LIBS analyses required to provide data of a similar quality to whole rock geochemical data for major elements (Al, Ca, Fe, K, Mg, Na, Si, and Ti). Rocks with diverse chemical, textural and mineralogical properties were tested by averaging LIBS spot analyses performed along a drill core and comparing the results to whole-rock geochemical data obtained in the laboratory for the corresponding core interval. The greatest influence on the number of LIBS analysis required was the concentration range of each element; a wider range of major element contents required more LIBS analyses to estimate whole rock geochemistry. Lesser factors were the number of minerals that hosted an element and grain size. It was concluded that between 30 and 560 spot analyses per meter were necessary to achieve whole rock geochemistry by LIBS. A laser-fusion pre-treatment method was proposed[196] for the quantitative determination of element concentrations in sandstone. A quasi-continuous-pulse high-frequency (50 kHz) laser was directed at the sandstone powder for 20 s to produce glass beads which were then analysed by LIBS. Comparison of results for CRMs prepared in this manner with those from LIBS analysis of a traditional powder pellet showed that the LODs for the laser-fused glasses were better and the spectral signals more stable than those from the pellets.

The versatile nature of *LIBS for in situ analysis of a wide range of potential ores* has been demonstrated in several papers. Identification in the field of different types of bauxite was based[197] on a convolutional neural network approach and PCA. Fast and detailed analysis of mineral species in copper ores was achieved[198] by preliminary screening using hyperspectral imaging to discriminate between Cu-sulfides and barren minerals, followed by detailed elemental and mineralogical analysis by μLIBS. In a follow-up paper, multivariate calibration techniques such as PLS, ANN and MCR-ALS were compared[199] as quantification approaches for improved mineralogical analysis of copper ores. A new method was proposed[200] to overcome matrix interferences in the quantitative determination of total Fe in iron ores using variable-importance back-propagation ANN (VI-BP-ANN). Compared with other models, the VI-BP-ANN model reduced overfitting and obtained the highest r^2 and lowest RMSE for calibration and prediction. Complex ferromanganese nodules were analysed[201] rapidly on-board ship with a prototype mobile LIBS setup that incorporated a portable diode-pumped solid-state laser with a high repetition rate. Similar results were obtained by LIBS with an intensified CCD camera and by EDXRFS demonstrating that minimal sample treatment (milling and pelletisation) was sufficient for the semiquantitative determination of major and minor elements with this instrumentation.

Other *critical-metal ores* analysed by LIBS included[202] the determination of La in REE ores, in which LIBS was combined with LIF and the standard addition method to decrease the influence of matrix effects and self-absorption. The LOD for La was 7.2 ppm. A specially designed set of calibration standards was employed[203] for the direct LIBS determination of lanthanides in REE-rich niobium and uranium ores. The content of each REE in the calibration set covered two orders of magnitude and analytical lines were selected through thermodynamic modelling of the LIBS spectra. Under these experimental conditions, PLS regression provided better analytical performance for La, Nd and Sm quantification in ores than univariate regression. An assessment of hand-held LIBS for its potential in the exploration of pegmatite- or granite-related mineralisation was based[204] on a univariate calibration curve. Simultaneous quantification of Li contents and major element ratios, such as Si/Al, allowed rapid discrimination between different Li-bearing silicates that can be difficult to identify in the field on the basis of macroscopic criteria. Ferreira *et al.*[205] used both a commercially available handheld device and a laboratory prototype in their extensive comparison of the performances of different algorithms for quantifying Li by LIBS when prospecting for Li ores. They concluded that, when covering a wide range of concentrations typical of a mining environment, non-linear methodologies offered better performances than linear methods which were more affected by saturation and matrix effects. A study of the capability of LIBS to determine Pd in a one-meter-long core ore sample identified[206] three main mineralogical phases by PCA. The instrument was calibrated using three sets of CRMs in the form of compressed powders with concentrations ranging from 1 to 500 ppm Pd. The LIBS analysis highlighted significant heterogeneity of the Pd distribution on the core surface and revealed sulfide-rich zones also particularly rich in Pd. Elhamdaoui *et al.*[207] used pressed powder pellets of RMs doped with Pd solution to establish calibration curves for the measurement of trace amounts of Pd by LIBS and LIBS-LIF. The LIBS-LIF LODs of 160 ppb for a single laser shot or 16 ppb for 100 shots were greatly superior to the LODs obtained by LIBS. Unlike LIBS, LIBS-LIF could resolve spectral interferences on the Pd spectral lines in iron-rich mineral matrices thereby making it a good candidate for *in situ* analysis of ore samples.

Other examples of the use of *LIBS in combination with other techniques* included[208] application of µLIBS, µXRFS and EMPA to a rock thin-section for rapid mineral-classification and multi-elemental quantitative imaging of major to trace elements down to the ppm level. Crystallographic information was acquired by Raman spectroscopy. Results from μLIBS micro-mapping were compared[209] with those from EDXRFS macro-mapping to illustrate the advantages of LIBS, such as speed, lateral and in-depth resolutions and the capability to determine light elements. However, it was recognised that a combination of the two techniques was preferable to provide a rapid classification of geological materials with different compositions. In an interesting development, Zhao *et al.*[210] proposed a confocal-microscopy-controlled Raman-LIBS hybrid method with high spatial resolution and anti-drift properties. The axial-focusing resolution and lateral resolution for morphological imaging were *ca.* 15 and 66 nm, respectively. The authors claimed to be the first to combine Rayleigh/reflected light, LIBS and Raman spectra to acquire simultaneously geometrical topography and information on elemental composition and molecular structure. A LIBS-XRF analyser that combined PCA and PLS regression methods was developed[211] for rapid assessment of coal quality. The experimental results for calorific value, ash content, volatile matter and S content demonstrated good accuracy and stability, with the measurement repeatabilities meeting national standards. Further development of the online system was required in order to monitor the coal quality on a conveyor belt in real time.

Data processing is a crucial aspect of LIBS analysis. To enable the sharing of prediction models between LIBS instruments, a transfer-learning method based on dynamic time warping (DTW) algorithms was proposed by Rao *et al.*[212] Even though the method based on DTW was superior to a piecewise direct standardisation algorithm for prediction of both lithology and quantitative elemental composition on another instrument, the Pearson coefficient was introduced to improve the performance of the prediction further. Multivariate regression models based[213] on machine and transfer learning were developed to correct for chemical and physical matrix effects. A set of 27 fully characterised rocks were prepared as pressed powder pellets, and LIBS spectra of both the pellets and the parent rocks recorded.

Spectra from the pellets were used to train multivariate regression models based on a machine-learning approach that combined feature selection and a back-propagation neural network. Tests with rocks revealed the influence of the physical matrix on the prediction performance of the models, which could be improved significantly by introducing transfer learning to the model. The polynomial interactive reconstruction method was proposed**[214]** to improve the accuracy of classifying gem minerals by portable LIBS. In a classification experiment involving 24 types of gemstone minerals, an accuracy of 94% was achieved compared to 83% and 82% for the conventional spectral-intensity and whole-spectrum methods, respectively.

5.3.2 Dating techniques

In-situ Rb-Sr dating by LA-ICP-MS/MS continues to offer exciting prospects for researchers working in the field of igneous and metamorphic petrology. Wang *et al.***[215]** described advances in this technique using N_2O as the reaction gas and H_2 as a trace molecular gas to improve the accuracy of the measurements by reducing the mass bias. They confirmed that NIST SRM 610 (trace elements in glass) was generally unsuitable for ^{87}Rb/^{87}Sr corrections and recommended the CRPG RM Mica-Mg for calibrating ^{87}Rb/^{86}Sr ratios in phases with high Rb/Sr contents. The applicability of this method to rocks of widely different ages (late Archean to 20 Ma) was demonstrated. The model ages of biotites calculated from single-spot analysis by LA-ICP-MS/MS were compared**[216]** with those derived by the classic isochron approach for samples from a range of geological contexts that yielded isochronous and dispersed Rb–Sr datasets. By applying textural analysis of thin sections, the preferred orientation of biotite fabrics was quantified, revealing a correlation between diversity of grain orientation and biotite age complexity.

A new technique for *in situ U-Th disequilibrium dating by LA-ICP-MS* was developed**[217]** for the analysis of inclusion-bearing ilmenite in order to date young volcanic deposits. Such rocks often do not contain minerals such as zircon or K-bearing phases, thus limiting the application of more conventional dating techniques. Isochrons were generated by combining LA-SF-ICP-MS measurements of the host ilmenite (low in U and Th mass fractions) with those of numerous inclusions (higher U and Th mass fractions) with a large spread of ^{238}U/^{232}Th ratios. Estimates of age overlapped within the uncertainty of published ages. The main caveat was that large ablation spots (*ca.* 250 µm diameter) were required because of the low U mass fractions and this could result in a mixed signal of ilmenite host and various inclusions. Although bastnaesite is an important geochronometer for recording the time of REE mineralisation in such deposits, there is a very limited supply of bastnaesite K-9, the only reliable primary RM for *in situ* U-Th-Pb dating of bastnaesite. For this reason, Tang *et al.***[218]** assessed xenotime XN01 as an alternative RM and found that the ^{206}Pb/^{238}U and ^{208}Pb/^{232}Th ratios of xenotime XN01 were more uniform than in bastnaesite K-9 and that any difference in isotopic fractionation in Th/Pb and U/Pb ratios between the two materials was almost negligible. The addition of nitrogen in the ablation cell played an important role in minimising these fractionation effects. It was concluded that xenotime XN01 was a better primary RM than bastnaesite K-9 for *in situ* U-Pb dating of bastnaesite. Niki *et al.***[219]**developed an *in situ* ^{238}U-^{230}Th dating method using multiple spot measurements by a fs LA-ICP-MS system equipped with collision/reaction cell technology. This system was evaluated by analysing four Quaternary zircon samples with ages between 110 ka and 16 ka and three reference zircons (GJ-1, OD-3 and Plešovice). The resulting ages for the Quaternary zircons were consistent with chronological constraints including fission track ages. Whereas the measured ^{230}Th/^{238}U values for GJ-1 and Plešovice agreed with ^{230}Th/^{238}U in secular equilibrium, the ^{230}Th/^{238}U values for OD-3 were significantly higher than the secular equilibrium value, an observation that had been reported previously.

Several contributions focused on issues related to *in-situ U-Pb geochronology*. In a study to assess the long-term reproducibility of U-Pb ages of zircon RMs by LA-ICP-MS, characteristic excess variances for ^{206}Pb/^{238}U and ^{207}Pb/^{206}Pb ages were calculated[220] from results obtained from more than 100 measurement sessions over six years for each of seven zircon RMs. This exercise provided an example of how to compile large datasets and to assess the intermediate measurement precision of long-term zircon age data. Jenkins *et al.*[221] investigated the ablation behaviour of garnet and rutile and the implication for U-Pb geochronology measurements. The influence of analytical parameters such as fluence and laser beam size on crater morphology, ablation rates, downhole fractionation and U-Pb ages was very different for the two minerals. Some recommended LA sampling strategies for these minerals were provided on the basis of these findings.

The *^{40}Ar/^{39}Ar geochronometer* relies on the co-irradiation of samples with neutron-fluence (or flux) monitors of known age. Biotite is often used as a primary monitor because it is difficult to fully degas argon from the otherwise preferable sanidine melts. The potential of a first-principles method to calibrate ^{40}Ar/^{39}Ar neutron-fluence mineral monitors was illustrated[222] by measuring ^{40}Ar abundances using an Absolute Quantities of Argon pipette system and combining these with existing ^{40}K abundance data. Ages for HD-B1 and MD2 biotite fluence monitors were calculated and combined with intercalibration data for HD-B1 and Fish Canyon sanidine to determine the ^{40}Ar/^{39}Ar age of Fish Canyon sanidine. The SK01 sanidine RM was analysed[223] at three different laboratories to test its homogeneity and ^{40}Ar/^{39}Ar age consistency. Incremental heating of 5 mg aliquots gave a weighted mean age of 27.58 ± 0.06

Ma (95% confidence level). Total fusion analysis of 23 single crystals gave ages between 27.070 ± 0.108 and 27.736 ± 0.062 Ma; the older ages were interpreted to reflect an inherited or excess argon component in some crystals. It was concluded that further work was required to evaluate the age dispersion more fully before SK01 sanidine could be utilised as a ^{40}Ar/^{39}Ar RM. A sanidine sample separated from Yunshan obsidian and selected as a potential neutron-flux monitor had**[224]** homogenous Ca and K contents and no significant intragrain differences in its major element composition. Results from step heating and single-grain laser-fusion yielded a weighted mean age of 93.45 ± 0.21 Ma (2SD). Although this sanidine was not considered to be an ideal RM for monitoring the neutron flux in high-precision analysis because of its relatively high atmospheric argon content, it was acceptable as a secondary RM for monitoring analytical procedures.

5.3.3 Inductively coupled plasma mass spectrometry

Several papers focused on improvements in *trace element determinations by LA-ICP-MS*. In this technique, normalisation by summing the element oxides to 100 wt% can be a viable alternative to internal standardisation when calculating the ablation-yield correction-factor for the accurate determination of major and trace elements. This strategy was modified for the analysis of minerals such as fluorapatite**[225]** and mica**[226]** to take account of volatile components and elements with low IPs. By normalising the bulk element oxides to a certain value (not 100 wt%) based on the mineral formula, the results were within ±1% and ±5% of those obtained by the IS method for fluorapatite and mica, respectively. Michaliszyn *et al.***[227]** introduced simultaneously (*via* a Y-piece) both SI-traceable solutions with various isotope ratios and ablated material from the sample into the plasma of an LA-ICP-MS instrument. This approach, combining ID and standard addition, was demonstrated by the determination of B in NIST SRM 612 (trace elements in glass) (certificate information value 32 µg g^{-1}) for which a value of 33.3 ± 3.7 µg g^{-1} was obtained. This measurement uncertainty was lower than those for previously published LA-ICP-MS measurements. A protocol developed by Belgrano *et al.*[**228**] to determine ultra-trace Ag, As, Au, Pt and Re mass fractions in volcanic glasses and rock-powder nano-pellets by LA-ICP-MS was based on previous studies. A key finding was that the amount of material remobilised from the sample chamber or tubing during ablation must be quantified and a correction applied for accurate ng g^{-1}-level Au determinations. This approach resulted in a LOQ for Au of 0.38 ng g^{-1}. A novel LA-ICP-MS/MS method, more sensitive than other LA-ICP-MS methods, employed[**229**] N_2O as a reaction gas to assess the content and distribution of Ge in rock-forming minerals. Multiple polyatomic and isobaric interferences were avoided by measuring Ge as GeO^+. Whereas ^{74}Ge, the most abundant Ge isotope, was the best isotope for Ge measurements in silicates, the oxide-shift method permitted the measurement of ^{70}Ge, ^{72}Ge and ^{73}Ge free of interferences and so provided flexibility on the choice of the best isotope for other matrices (*e.g.* ^{70}Ge for sulfides).

The considerable research effort focused on *isotope ratio determinations by MC-ICP-MS* and other techniques is reflected in Table 11. Because the range of elemental isotope ratios now being measured in geological materials is so extensive, 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 advances as many of the studies provided modest improvements to existing separation procedures or analytical protocols.

Insert Table 11

The availability of commercial *ICP-TOF-MS instruments* has expanded the range of spatially resolved element information that can be obtained by LA-ICP-MS. Maeda *et al.*[230] assessed the potential of state-of-the-art LA-ICP-TOF-MS instrumentation for quantitative elemental mapping of chondritic meteorites at a spatial resolution of 5 x 5 µm square pixels by comparing it with conventional approaches such as EPMA and LA-SF-ICP-MS in spot-mode. Although the ICP-TOF-MS technique had lower sensitivity and narrower linear dynamic range than SF-ICP-MS, the main host mineral phase(s) of an element could be readily identified and the major and trace element abundances in the phase(s) could be quantified with an accuracy approaching that of the spot analysis. Savard *et al.*[231] described a new protocol for producing elemental distribution maps (Na to U) across a variety of minerals. They used a LA-ICP-TOF-MS instrument incorporating a fast-funnel device to increase the aerosol transport speed. Geological thin sections were mapped at a rate of *ca.* 12 mm^2 h^{-1} and a resolution of 12 x 12 µm per pixel. The LODs for mid- and heavy masses were 0.1 - 10 µg g^{-1}. The analytical protocol employed multiple RMs with various matrices (sulfide, mafic-glasses, felsic-glasses, natural apatite) to produce calibration blocks, and quantification was performed using a recently developed data reduction scheme in IOLITE v4. After the software had identified the mineral phases present, a normalisation approach was applied to each of the phases individually, thereby avoiding the need for separate measurements of major elements to act as ISs. A new methodology was developed[232] for the thin-layer sampling of zircons to determine REE mass fractions and U-Pb ages simultaneously from depth profiles by ICP-TOF-MS**.** Element sensitivities were enhanced with an alternative sampler cone and the S/Ns were improved using a multiple-spot LA protocol to construct a ‘moat’ around the analytical area to minimise mixing of particles released from different layers. Mass spectra were acquired every 30 µs and a single analysis sequence corresponded to a sampling depth of about 0.6 µm. Sets of blank and thin-layer measurements were repeated 21 to 31 times to obtain depth profiles for each zircon. Four Quaternary zircon samples with ages between 16 and 110 ka and three zircon RMs (91500, Plešovice and OD-3) were analysed down to sampling depths of 0.59 – 0.66 µm. The resulting U-Pb ages and REE abundances agreed within analytical uncertainty with previously published values. Application of the technique to zircon samples from the Himalayas revealed multiple thermal events during formation of the zircons.

5.3.4 Secondary ion mass spectrometry

The generation of large sets of *in-situ oxygen isotope data* and their application in the Earth sciences has been facilitated by advances in techniques such as SIMS. A review (130 references) of approaches for the measurement, assessment and reporting of zircon O isotope data by SIMS provided[233] an analytical framework for geologically meaningful interpretation of such data. Zhang *et al.*[**234**] investigated the instrumental bias during O isotope analysis of olivines by SIMS using 16 olivine, 9 orthopyroxene and 3 clinopyroxene RMs. A new suite of olivine and pyroxene RMs with an expanded range of compositions was developed to provide better analytical precision and instrumental bias correction in the analysis of olivine and low-Ca pyroxene in primitive chondrule minerals. A novel method for the determination of $\delta^{18}O$ and molar ratio Fe/(Mg + Fe) (known as Fe#) in dolomite by SIMS involved[**235**] the concurrent measurement of $^{18}O^{16}O$, $^{56}Fe^{16}O$ and $^{24}Mg^{16}O$, thereby avoiding the need for additional EPMA compositional information. Five newly developed dolomite RMs with a Fe# range of 0.01 to 0.35 were employed for calibration. A logistic equation based on $^{56}Fe^{16}O$ / $^{24}Mg^{16}O$ ratios was proposed as the best-fit curve to represent the matrix effect on $\delta^{18}O$. For a carbonatitic dolomite with variable Fe# but homogeneous O isotopes, this online method gave a homogeneous $\delta^{18}O$ value of 7.94 ± 0.34‰ (2SD, n = 40), comparable with that (7.94 ±

0.20‰, 2SD) obtained from bulk analysis. In an application of NanoSIMS to the measurement of H and O isotopes in clay minerals in palaeosols, preparation of the samples as thin sections was preferable**[236]** because their resin contents were lower than those of thick polished sections. The high spatial resolution of NanoSIMS enabled the isotopic ratios to be measured in selected positions within the samples so that only the clay minerals of interest could be targeted.

Because marcasite RMs are scarce, Li *et al.***[237]** evaluated the accuracy of using a pyrite (FeS_2, isometric) as the RM to calibrate *the SIMS measurement* of *sulfur isotope ratios* in marcasite (FeS_2, orthorhombic). The $\delta^{34}S$ SIMS value for a natural marcasite sample (NJUMc-1) calibrated against a pyrite RM (UWPy-1) agreed within analytical uncertainties with the values obtained by IRMS, thus confirming the reliability of this procedure. A method to determine the S isotope composition of framboidal pyrite by NanoSIMS combined**[238]** high lateral resolution (*ca.* 1 x 1 μm^2) with a reproducibility of better than 0.5‰ (1 SD) for $\delta^{34}S$. This was achieved by improving the transmission and reducing the intensity of the primary beam. Recommendations were provided to minimise the effects on the accuracy of electron multiplier aging and of the distance between the immersion lens and the sample surface.

Trace element zoning in four widely used zircon RMs (91500, Mud Tank, Temora and Plešovice) was investigated**[239]** at sub-μm resolution using focused ion beam SEM coupled to TOF-SIMS. This technique rapidly resolved variations in trace element concentrations at the $\mu g\ g^{-1}$ level with a spatial resolution of 195 nm and revealed that zircon 91500 was the least zoned of the four zircon RMs examined.

5.3.5 X-ray fluorescence spectrometry and related techniques

Hand-held and portable XRFS instrumentation is widely used in a broad range of geological applications, especially *in situ* to provide rapid feedback in, for example, mineral exploration. A tutorial review (73 references) by Potts and Sargent**[240]** provided an overview of the development of hand-held XRFS and discussed some important issues that can affect the interpretation of the data produced by these instruments. This excellent review paper was intended to offer guidance to operators without extensive training in XRFS methodology, but more experienced users would also benefit from the guiding principles for the correct interpretation of hand-held-XRFS measurements. Da Silva *et al.***[241]** also highlighted the danger of using manufacturers' built-in calibrations and of interpreting elemental concentrations without checking the LOQs of the portable XRF spectrometer and its calibration model. They presented a general workflow and guidelines for building an empirical calibration model for pXRFS measurements of geological samples. These guidelines included the choice of RMs, validation of the calibration's efficiency and calculation of the LOQs. A prototype XRFS instrument with a ^{57}Co excitation source was developed**[242]** for the underwater determination of Hg in sediments. It proved possible to detect Hg by K-shell emission thus enabling environmental screening of marine sediments for the quick identification of heavily polluted sites. The Hg LOD was 2880 ppm.

A review (49 references) of the elemental analysis of polymetallic deposits by *total reflection XRF spectrometry* emphasised**[243]** the importance of an appropriate sample-pretreatment strategy to obtain accurate results. Two pretreatment methods, slurry sampling and acid digestion, were described in detail and their relative merits assessed. Pashkova *et al.***[244]** described an improved sample preparation procedure for the analysis of ores by TXRFS. Wet grinding of 100 mg of powdered copper-nickel sulfide ores in 4 mL of ultra-pure water with 20 g of grinding balls (1 mm in diameter) produced a homogeneous suspension of ultra-fine particles with a monomodal particle-size-distribution with 90% of the particles <6 µm in size. Relative analytical precisions calculated from duplicate pairs of suspensions were 10, 9, 15 and 16% for Cu, Fe, Ni and S, respectively.

The quantification of low-*Z* elements (Z<14) by *energy dispersive XRF spectrometry* is challenging partly because of scattering from the sample dark matrix. Shao *et al.*[245] developed a chemometric model for Al, Mg, Na and O in geological samples by training the back propagation neural network (BPNN) using the Compton scatter data combined with concentrations of measurable elements. The coefficient of determination between the true and predicted values was >0.95 for these elements, indicating that the BPNN model largely overcame the matrix effects. A new fundamental parameters approach to quantify elements using EDXRFS spectra also focused[246] on the accurate measurement of low-*Z* elements. In this approach, quantitative absorption data for the residual matrix (*e.g.* contributions from C, N and O) were recorded and used to enhance the resolution of elemental spectra. The method was validated by analysing NIST SRMs 2710 (Montana soil) and 2704 (river sediment); values within 2 to 8% of the reference values were obtained. Yuan *et al.*[247] developed a workflow for the fast recognition of Nb minerals by multi-stage filtration and accurate quantitative analysis and classification by SEM-EDS. The Nb particles were initially identified using a grey threshold value based on pyrite as the grey standard. Subsequently, the chemical composition of the Nb minerals was determined using a combination of two image scans and two EDS acquisitions. The proposed method effectively avoided spending time analysing irrelevant minerals and had potential for the rapid identification of fine mineral particles in large areas, such as in the search for REE minerals in REE deposits.

In a method to estimate the As content of geological samples by *wavelength dispersive XRF spectrometry*, a novel concept of concentration equivalence factor was developed**[248]** to address the serious problem of line overlap of the As K$\alpha_{1,2}$ lines (the most intense As lines) by Pb L$\alpha_{1,2}$ lines of similar intensity. A LOD of <10 mg kg^{-1} was achieved by employing an arsenic-lead concentration-equivalence-factor for the combined As K$\alpha_{1,2}$ and Pb L$\alpha_{1,2}$ lines peak. This factor was constant for a variety of geological matrices regardless of their Pb content. The analysis of 22 CRMs demonstrated that it was possible to determine As concentrations below 5 mg kg^{-1} in the presence of lead at concentrations of up to 1000 mg kg^{-1}.

5.3.6 Other techniques

Improved methods for the EMPA determination of element compositions in a variety of geological materials included**[249]** the elemental analysis of ilmenite for which there is a lack of RMs. Having characterised a natural ilmenite (PZH12-09) as a potential RM, a high-precision EMPA method for the determination of trace elements at the <100 mg g^{-1} level was developed. This involved the use of a high accelerating voltage (20 kV) and a beam current of 200 nA in combination with approaches involving large Bragg crystals, long count integration times, aggregate intensity counting function, enhancement of peak/background ratios, suppression of peak spectral interferences and secondary RM corrections. Low LODs of 11 - 27 µg g^{-1} at a spatial resolution of 1-2 µm were reported and the measurement precisions were within ±15% RSD at various concentrations of trace elements (except for Nb and Ni). Wu *et al.***[250]** explored the optimum analytical conditions for the *in situ* EPMA determination of Be in different Be-bearing minerals including oxides, silicates, borates and phosphates. The beam current was adjusted from 50-100 nA for hydrous Be minerals to >100 nA for anhydrous Be minerals. The chosen RMs had to have the same structural environment of Be atoms as the samples. Eleven types of Be minerals analysed by the optimised method provided Be results within the range of uncertainty or close to a theoretical value based on the crystal structure as determined by X-ray single crystal diffraction. A series of seven F-free references glasses with a range of FeO_T mass fractions ranging from 1 to 20 wt% was synthesised[251] to improve the correction of interfering Fe lines on F peaks in the EPMA measurement of Cl, F, Nb and P in Fe-rich melt inclusions. Applying this method to USGS reference glasses revealed that USGS BHVO-2G (basalt) had the highest degree of homogeneity for both Cl and F in geological samples. Ghosh *et al.*[252] reported an EMPA method to determine Ti concentrations in zircon and quartz to retrieve thermal conditions of metamorphism and magmatism by Ti-in-zircon and Ti-in-quartz thermometry. To meet the challenges posed by X-ray intensities being only slightly above Bremsstrahlung background when measuring trace elements, this method combined long counting times at peak and background positions, simultaneous acquisition of Ti in three spectrometers and processing of data using the sub-counting method in which the total analytical time was split into smaller cycles to reduce any effects from surface damage on the final counts. The improved Ti-in-zircon and Ti-in-quartz methods yielded analytical precisions that were well within the accepted error limit (*ca.* 10%) of trace element analysis with LODs of 5 and 7 µg g^{-1}, respectively.

Quantification of the water content in silicate glasses is important in understanding magma evolution and metamorphic reactions. Tu *et al.*[253] described a confocal Raman spectrometry method to measure the content and speciation of water in silicate melts. Synthetic rhyolitic glasses prepared with water contents of 0.33 to 9.05 wt% were shown by synchrotron-FTIR mapping to be relatively homogeneous. Deconvolution of the total-water Raman bands into four Gaussian components enabled the quantification of speciation data for OH groups and $(H_2O)_m$ molecular clusters; these showed a similar trend to water speciation data derived from FTIR analysis. Papers presenting new data for the water content of amphibole, clinopyroxene and orthopyroxene RMs are included in Table 10.

5.4 Software and databases

Several research groups have developed *software for facilitating the processing and reduction of isotopic data*. IsoCor was designed[254] for the automated calculation of isotope ratios from transient signals generated by coupling chromatography or electrokinetic separation techniques (*e.g*. CE, GC and LC) to MC-ICP-MS instruments. This stand-alone, open-source application included baseline subtraction, peak detection, mass bias correction, isotope ratio calculation and delta calculation. The user-friendly interface allowed modification of the main parameters to enable a detailed investigation of the raw data. A software package called Parmanu-Gunak was proposed[255] as a straightforward data reduction scheme for IDA that could be applied to any isotope system. This software had the advantages over other published spiked-isotope data-reduction programs of being freely available, being cross-platform-based and not requiring knowledge of any programming language to use it. The robustness of the program was demonstrated through the processing of Mo and Nd isotope data.

Other freeware packages (written in Python) have become available for the *reduction of U-Pb data obtained by LA-ICP-MS*. One, U-Pb Saturn, offered[256] dynamic graphic interfaces to view, evaluate and plot U-Pb and Pb-Pb isotope data. Online operation gave the operator freedom to change parameters and reprocess data at any stage of data acquisition. The main interface allowed the user to choose the best statistics for drift correction, to include or exclude offset factors and to apply (or not) corrections for common Pb in different modes. Spot analyses could be visualised on Concordia diagrams and all graphic windows were interactive so that any modification to the data treatment was immediately reflected in the data tables. Lui *et al.*[257] wrote an alternative program designated Brama (Bayesian regression and age mapping application) for producing HR spatial maps of trace element and isotope ratios as well as age data from line scans. It was capable of importing data from different quadrupole mass spectrometers and linking them to laser data. Examples of U-Pb dating of calcite and apatite by LA-ICP-MS were provided to demonstrate the key advantages of Brama.

An R package called LABLASTER was designed[258] primarily to quantify the *elemental composition of carbonate shells and skeletons*. Data from a single time-resolved LA-ICP-MS analysis were imported into the software package which automatically identified when the laser penetrated the sample or ablated across a mineral boundary. A smoothing function to de-spike and flatten elevated signals reduced the likelihood of a false-positive detection of a change in the composition of ablated material. By this means, the program was able to identify quickly the analytical signal corresponding to a particular phase for further data processing. This capability increased the transparency and repeatability of such workflows, which would otherwise be time-consuming, laborious and prone to subjective differences between operators if undertaken manually.

A welcome development is the Uranium Isotope Database that contained[259] over 14,000 entries of U isotope data from more than 320 publications. The data were normalised to the values for US Department of Energy CRM-145 (uranyl nitrate). Metadata provided in the original publications, *e.g.,* sample type, concentrations and measurement technique, were included in the database together with recommended δ^{238}U values for U CRMs and geological RMs. This database will be updated regularly.

6 Glossary of abbreviations

2D	two dimensional
AAS	atomic absorption spectrometry
ADMM	alternating direction method of multipliers
AEC	anion exchange chromatography
AES	atomic emission spectrometry
AFS	atomic fluorescence spectrometry
ALF	alveolar lysosomal fluid
ALS	alternating least squares
AMS	accelerator mass spectrometry
ANN	artificial neural network
APDC	ammonium pyrrolidine dithiocarbamate
APGD	atmospheric pressure glow discharge
APM	atmospheric particulate matter
ASU	Atomic Spectrometry Update
ATR	attenuated total reflectance
BAM	Bundesanstalt für Materialforschung und -prüfung
bam	beta attenuation monitor
BCR	Community Bureau of Reference (of the Commission of the European Communities)
BET	Brunauer-Emmett-Teller
BGS	British Geological Survey
BPHA	N-Benzoyl-N-phenylhydroxylamine
BPNN	backpropagation neural network

C_{18}	octadecyl bonded silica
CA	chemical abrasion
CC	collision cell
CCD	charged coupled device
CCT	collision cell technology
CE	capillary electrophoresis
CF	continuous flow
CFD	computational fluid dynamics
CI	confidence interval
CNT	carbon nanotube
COV	coefficient of variation
CPE	cloud point extraction
CPMA	centrifugal particle mass analyser
cps	counts per second
CRM	certified reference material
CRPG	Centre de Recherches Petrographiques et Geochimiques
CS	continuum source
CV	cold vapour
CVAAS	cold vapour atomic absorption spectrometry
CVG	chemical vapour generation
DDTC	diethyldithiocarbamate
DES	deep eutectic solvent
DGA	diglycolamide
DGT	diffusive gradient in thin films
DLLME	dispersive liquid liquid microextraction
DMDSe	dimethyl diselenide
DMS	dimethyl sulfide
DOC	dissolved organic carbon
DOM	dissolved organic matter

DP	double pulse
DRC	dynamic reaction cell
DTW	dynamic time warping
EC	elemental carbon
ECCC	Environment and Climate Change Canada
EDL	electrodeless discharge lamp
EDS	energy dispersive (X-ray) spectrometry
EDTA	ethylenediaminetetraacetic acid
EDXRFS	energy dispersive X-ray fluorescence spectrometry
EMBRAPA	Brazilian Agricultural Research Corporation
EN	European Committee for Standardisation
EPMA	electron probe microanalysis
ERM	European reference material
ESI	electrospray ionisation
ETAAS	electrothermal atomic absorption spectrometry
ETH	Eidgenössische Technische Hochschule, Zürich
ETV	electrothermal vapourisation
EU	European Union
FAAS	flame atomic absorption spectrometry
FESEM	field emission scanning electron microscopy
FGD	flue gas desulfurisation
FI	flow injection
FIA	flow injection analysis
FTIR	Fourier transform infrared
GC	gas chromatography
GD	glow discharge
GEM	gaseous elemental mercury
GMD	geometric mean diameter
GOM	gaseous oxidised mercury

GSJ	Geological Society of Japan
HEN	high efficiency nebuliser
HG	hydride generation
HILIC	hydrophilic interaction chromatography
HPLC	high performance liquid chromatography
HR	high resolution
IAEA	International Atomic Energy Authority
IC	ion chromatography
ICP	inductively coupled plasma
ID	isotope dilution
IDA	isotope dilution analysis
IL	ionic liquid
IMPROVE	Interagency Monitoring of Protected Visual Environments
INCT	Institute of Nuclear Chemistry and Technology (Poland)
IP	ionisation potential
IPGP	Institut de Physique du Globe de Paris
IRMM	Institute for Reference Materials and Measurements
IRMS	isotope ratio mass spectrometry
IS	internal standard
KED	kinetic energy discrimination
KNN	k-nearest neighbour
LA	laser ablation
LC	liquid chromatography
LEQ	linear electrodynamic quadrupole
LIBS	laser-induced breakdown spectroscopy
LIF	laser induced fluorescence
LII	laser induced incandescence
LLE	liquid liquid extraction
LLME	liquid liquid microextraction
LOD	limit of detection

LOQ	limit of quantification
LPE	liquid phase extraction
LPME	liquid phase microextraction
LREE	light rare earth element
μLIBS	micro laser-induced breakdown spectroscopy
μSPE	micro solid phase extraction
μXRFS	micro X-ray fluorescence spectrometry
MAC	mass absorption cross section
MAD	microwave-assisted digestion
MAE	microwave-assisted extraction
MC	multicollector
MCE	mixed cellulose ester
MCG	magnetic colloidal gel
MCR	multivariate curve resolution
MDL	method detection limit
MeHg	methyl mercury
MFC	mass flow controller
MICAP	microwave inductively coupled atmospheric-pressure plasma
MIP	microwave induced plasma
MOF	metal organic framework
MP	microwave plasma
MPT	microwave plasma torch
MRI	magnetic resonance imaging
MS	mass spectrometry
MS/MS	tandem mass spectrometry
MWCNT	multi-walled carbon nanotube
MWCO	molecular weight cut-off
m/z	mass to charge ratio
NAA	neutron activation analysis
NBL	New Brunswick Laboratory

NCRM	National Research Centre for Certified Reference Materials, China
NCS	NERC Natural Environment Research Council (UK)
NIST	National Institute of Standards and Technology
NMR	nuclear magnetic resonance
NP	nanoparticle
NRCC	National Research Council of Canada
NRCSM	National Research Center for Standard Materials, China
NSMCC	National Standard Material Centre of China
NWRI	National Water Research Institute
OC	organic carbon
OM	organic matter
OPC	optical particle counter
P	pressure
PAN	1-(2-pyridylazo)-2-naphthol
PAS	passive air sampler
PCA	principal component analysis
PD	point discharge
PFA	perfluoroalkyl
PILS	particle into liquid sampler
PIXE	proton induced x-ray emission
PLS	partial least squares
PM	particulate matter
$PM_{2.5}$	particulate matter (with an aerodynamic diameter of up to 2.5 µm)
$PM_{2.5-10}$	particulate matter (with an aerodynamic diameter of between 2.5 – 10 µm)
PM_{10}	particulate matter (with an aerodynamic diameter of up to 10 µm)
PMT	photomultiplier tube

ppb	part per billion
ppm	part per million
ppqv	part per quadrillion per volume
ppt	part per trillion
PSL	polystyrene latex
PTE	potentially toxic element
PTFE	polytetrafluoroethylene
PVG	photochemical vapour generation
pXRFS	portable X-ray fluorescence spectrometry
QC	quality control
QF	quartz fibre
REE	rare earth element
RH	relative humidity
RM	reference material
RMSE	root mean square error
rpm	revolutions per minute
RSD	relative standard deviation
SAA	surface area analysis
SAX	strong anion exchange
SBET	simplified bioaccessibility extraction test
SBF	simulated body fluid
SCR	selective catalytic reduction
SCX	strong cation exchange
SD	standard deviation
SDD	silicon drift detector
SDEP	semi dry electrostatic precipitator
SEM	scanning electron microscopy

SF	sector field
SFOD	solidified organic floating drop
SHRIMP	sensitive high resolution ion microprobe
SI	système international d'unités
SIMS	secondary ion mass spectrometry
S/N	signal-to-noise ratio
sp	single particle
SPE	solid phase extraction
SPME	solid-phase microextraction
SPS	Spectrapure standards
SQT	slotted quartz tube
SRM	standard reference material
SSB	sample standard bracketing
SSID	species specific isotope dilution
T	temperature
TBP	tributyl phosphate
TC	total carbon
TD	thermal desorption
TEM	transmission electron microscopy
THF	tetrahydrofuran
TIMS	thermal ionisation mass spectrometry
TOA	thermal optical analysis
TODGA	N,N,N′,N′-tetraoctyl diglycolamide
TOF	time-of-flight
TOR	thermal optical reflectance
TOT	thermal optical transmission
TSP	total suspended particle

TWA	time weighted average
TXRFS	total reflection X-ray fluorescence spectrometry
UA	ultrasound-assisted
UAE	ultrasound-assisted extraction
UAV	unmanned aerial vehicle
USGS	United States Geological Survey
UV	ultraviolet
VCDT	Vienna-Cañon Diablo Troilite
VG	vapour generation
VOC	volatile organic carbon
VPDB	Vienna Peedee Belemnite
VSM	vibrating sample magnetrometry
VSMOW	Vienna Standard Mean Ocean Water
WDXRFS	wavelength-dispersive X-ray fluorescence spectrometry
WEEE	waste electrical and electronic equipment
WSOC	water soluble organic carbon
XAFS	X-ray absorption fine structure
XAS	X-ray absorption spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
XRFS	X-ray fluorescence spectrometry
Z	atomic number

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Table 1. Applications of LIBS for air sample measurements

Analyte	Sample matrix	Study rationale	Technique	Findings	Reference
C	Air	Evaluation of a technique for the rapid detection of total gaseous C.	LIBS	Use of a total nitrogen IS method enabled a LOD of 14 ppm to be achieved, which was improved to 5 ppm when a multivariate calibration model with an ADMM algorithm used for optimisation purposes.	260
Cs	Surrogate nuclear fallout particles containing Cs, Cu and Na	Ascertaining potential for real-time and stand-off measuring capability – assessment of elemental fractionation effects.	LIBS	In presence of Cu, Na resonance emission enhanced but Cs resonance emission reduced. Use of fs LA found to reduce such fractionation effects by 50%. Such effects arise because the particle matrix can induce changes to local plasma temperature, population of atomic states and emissions.	261
Indoor air aerosols	Indoor air simulation studies	Evaluation of a potential tool for the rapid interrogation of changes in indoor air quality.	LIBS	Four common indoor air quality perturbations were simulated, including burning C, burning incense, spraying perfume and running a hot shower. The elemental spectra determined from these different scenarios were examined by PCA analysis. The air environment was classified by KNN algorithm with an accuracy of 99.2%, demonstrating that the use of LIBS with machine learning tools to detect changes in air quality and predict air composition concentrations was possible.	262
Inhalable particles	Four different test aerosols mimicking those found in the workplac	Evaluation of a potential in-situ measuring tool for determining the elemental composition of inhalable particles present in the workplace.	LIBS	Prototype sensor used a passive sampling inlet and an optical triggering system for initiating a particle ablation process. Particle composition was quantified by interrogation of emission spectra using a real-time material classification algorithm. Validation performed on 1480 spectra arising from measurement of four test aerosols. Potential for combining with a previously developed direct-reading particle sizer thereby producing a portable system for counting, elemental determination and sizing of large inhalable particles.	263
Single ambient aerosol particles	NaCl test particles	Evaluation of a novel method for the analysis of the elemental composition of single aerosol particles	LIBS	Proof-of-concept with 300 nm NaCl particles yielded a LIBS hit ratio of >90% for particle concentrations of <1 particle/cm^3. Exceptional potential for a portable analysis platform for various applications in the field of aerosol research ranging	264

		sampled directly from the aerosol phase using size amplification-aided aerosol charging, linear electrodynamic quadrupole as an alternative to the commonly used aerosol MS.		from atmospheric ice nucleation studies to human respiratory particle studies.	
Smoke	Smoke arising from burning of plastics	Evaluation of a potential tool for identifying the smoke signature arising from burning of plastics	LIBS	The accuracy in identifying the plastic origins of a waste burn by monitoring the characteristic C, H, N and O elemental emissions in smoke in conjunction with the use of PCA and error back propagation ANN techniques reached 77%.	265
UF_6	UF_6 test gases with reported ^{235}U:^{238}U ratios (enrichment values) determined by gas source MS	Evaluation of the potential for developing a continuous on-line tool to monitor the enrichment process within a nuclear centrifugal enrichment facility.	LIBS	By optimising fs-LIBS measurement conditions for prominent 424.437 and 424.412 nm isotope pair emissions associated with ^{238}U and ^{235}U undertaken, mean absolute errors as low as 0.3% in reported enrichment values obtained that demonstrated the potential effectiveness and applicability of this approach.	266
Volcanic plume ash	Surrogate ash suspended in air using a laser-induced shockwave in a test chamber to simulate a plume	Evaluation of a calibration-free quantification method.	LIBS	Calibration-free LIBS-derived elemental data (tabulated as oxides) in good agreement with data derived from measurements by XRFS, typically <10% difference for majors (Al and Si) and 10-50% difference for minor elements (Ca, Fe, K, Na and Ti). Future endeavours to include making concurrent particle size measurements and making instrumentation portable for field use.	267

Table 2. Application of ICP-MS for air sample measurements

Analyte	Sample matrix	Sample preparation/introduction	Technique	Findings	Reference
Ag	NPs released from textile products	Extraction from textiles by centrifugation using H_2O. Suspension nebulisation.	sp-ICP-MS	LOD of 4.59 X 10^4 NPs per gram of textile achieved. NP size LOD was 12 nm. Recoveries of silver NP spikes (20, 40 and 60 nm sizes) added to textiles were 102-113%.	268
^{129}I	Deposition rainwater samples	0.1% NH_4OH, 10 g L^{-1} ascorbic acid and 3% Tween® diluent used to minimise memory effects. Solution nebulisation.	ICP-MS-MS	^{129}Xe isobaric interferent decreased using O_2-mediated mass-shift cell chemistry. Improved LOD of 11 mBq L^{-1} achieved.	269
^{129}I	Deposition rainwater samples	None. Solution nebulisation using a HEN.	ICP-MS-MS	^{127}I hydride and ^{129}Xe isobaric interferences decreased with O_2-CO_2 cell reaction chemistry.	77
^{129}I, ^{63}Ni, ^{237}Np, ^{239}Pu, ^{90}Sr, ^{99}Tc, ^{93}Zr	Air Samples (and other environmental matrices)	Microwave-assisted digestion as per EN 14902. Solution nebulisation.	ICP-MS-MS	H_2 and He collision gas KED; O_{2gas} and $NH_{3\ gas}$ mediated mass shift cell chemistries optimised for improved multiple radionuclide measurements in a variety of environmental matrices.	270
^{204}Pb ratios	PM_{10}	MAE using HNO_3/H_2O_2. Solution nebulisation.	Quadrupole ICP-MS	Repeat measurements of digested BCR CRM 482 (Lichen – trace metals) at 1 µg L^{-1} demonstrated an external precision <0.34% and differences from reference values of <2‰ suggesting that isobaric interference of ^{204}Hg on ^{204}Pb had been corrected.	271
Pt	Road dust NPs	Pt NPs - UAE using H_2O, centrifugation, and dilution. Suspension nebulisation. Total Pt – MAE using	sp-ICP-MS	Size, mass- and particle-based concentrations determined in <11 min *ca.* 12 % of Pt in BCR CRM 723 (road dust Pd Pt Rh) measured as NPs. Platinum NPs in measured road dust samples were 15-75 nm at concentrations of 6-20 ng g^{-1} and represented 11-27% of total measured Pt content.	272

		HNO_3/HCl. Solution nebulisation.			
PTFE microparticles	Particles	n/a Suspension nebulisation.	sp-ICP-MS	Detection of a F elemental marker through use of a BaF_2 proxy measurement and elimination of polyatomic isobaric interferences at *m/z* 157 using O_2-mediated chemistry in the DRC.	273
Rh	Road dust NPs	Rh NPs – ultrasonic assisted extraction using rainwater. Suspension nebulisation. Total Rh – MAE using HNO_3/HCl. Solution nebulisation.	sp-ICP-MS	A CPE preparatory step required to remove dissolved ionic Rh signal for successful NP determination. Size LOD of 9 nm achieved even in the presence of high levels (x1000) of dissolved Rh.	274
Si (dissolved)	Rainwater	n/a. Solution nebulisation.	ICP-DRC-MS	Successful removal of isobaric interferents at *m/z* 28 and signal enhancement using CO_2 in the DRC and by adding CH_4 modifier to the plasma.	75
U	Particles	n/a.	LA-ICP-MS	Results comparable with those obtained by large geometry SIMS indicating that LA can offer a rapid U isotopic analysis capability without undue loss in analytical performance.	275
Zn	Size fractionated PM	HNO_3/HF digestion , Zn separated from matrix elements by AEC. Solution nebulisation. Direct analysis.	MC-ICP-MS XAFS.	Zn in particles of 0.65 – 4.7 µm contained remarkably light δ^{66}Zn. ZnO and ZnS species originated from brake/road/tire dust, $ZnCl_2$ and $ZnSO_4$ from industrial emissions and Zn oxalate from vehicular exhaust. Simultaneous application of speciation/isotopic assays on size segregated APM a powerful tool to estimate origin and formation of Zn species in aerosols.	10
Various	$PM_{2.5}$ particles	Sonication.	sp-ICP-MS	Metals in individual particles measured and a machine learning protocol applied for source apportionment	276

		Suspension nebulisation.		studies which demonstrated a 73% accuracy on a physically mixed model test sample.	
Various	Gun-shot residues.	Tape sampling followed by extraction. Suspension nebulisation.	sp-ICP-TOF-MS	Ability to analysis large number of particles rapidly and to determine minor elements other than Ba, Pb and Sb to aid particle classification.	277

Table 3. Application of mass spectrometry for air sample measurements

Analyte	Sample matrix	Study rationale	Technique	Analytical Findings	Reference
APM	Particles collected on small air filter/impactor samplers deployed on a UAV	Evaluation of a micro-nebuliser system to efficiently introduce those small (ng) quantities of aerosol samples that are typically collected.	Aerosol MS	Micro-nebuliser enabled sample volumes as low as 10 µl to be processed. Instrumental LOD of 0.75 and 0.19 ng determined using test SO_4^{2-} and NO_3^- solutions. Results obtained for these ions on PM extracts in agreement with IC determinations.	278
APM	Standard-sized particles (PSL and SiO_2) as calibrants. Standard elemental solution droplets and suspension particles as test samples	Evaluation of a new spectrometer for accurate sizing and isotopic analysis of individual particles.	sp aerosol MS	Instrument optimised and a universal formula proposed for size calibration. The measured isotopic ratio for most elements investigated were accurate to 5%.	279
C	Propane gas	To evaluate the accuracy of this versatile technique that only requires a small gas volume for analysis in the determination of position-specific $\delta^{13}C$ values which is useful for understanding the evolutionary history of natural gases.	GC-pyrolysis-GC-IRMS	Comparative testing against accurate ^{13}C NMR measurements (but which requires a large gas volume size and is slow) on nine natural gas samples undertaken. Results showed that large isotope fractionation effects occurred during pyrolysis step but the extent can vary from instrument to instrument necessitating individual instrument calibration with isotopic gas reference standards. Study also highlighted the need for new position-specific isotope standards for propane and other gases such as CH_4.	280
O	Oxygen	Evaluation of extent of Ar interferences on $^{18}O/^{16}O$ ratio measurements and improving ways of obtaining more accurate $\delta^{18}O$ values.	CF-IRMS	$^{18}O/^{16}O$ ratio measurements byCF-IRMS (GC-IRMS and GasBench^{TM} IRMS) were subject to Ar interferences that led to increases of δ^{18} O values by up to 6‰. These interferences were minimised by improving the chromatographic separation of Ar and O_2 signals and by applying a post measurement correction protocol.	281
S	Gases	Improving $\delta^{36}S$ measurements.	IRMS	Contamination in He GC carrier gas supply	282

				discovered. New SF_6 fluorination and purification system built. Without purification, measured $\delta^{36}S$ values were >10 ‰ higher than expected. With purification measured $\delta^{36}S$ values before and after passing through GC were < instrumental error of 0.2‰.	
U	Particles	Investigation into the use of negative-ion molecular-oxygen primary-beams for particle analysis.	SIMS	Use of O_3^- primary ions provided higher U^+ yields, lower mass fractionation and more consistent results across substrates compared to using other O beam species.	283
VOC	Gases	Evaluate instrumental approach for measuring $\delta^{13}C$ values as a potential tool for source identification.	SPME-GC-combustion-IRMS	Collection and equilibrium time to collect VOC on SPME fibre was 700-800 min but compensated by fast extraction and analysis times. $\delta^{13}C$ values for benzene from vehicular exhausts and from air in the vicinity of a petrol station were -25.3 ± 1.0‰ and -26.2 ± 0.7‰ suggesting utility for this approach.	284

Table 4. Application of techniques for carbonaceous particle measurements

Analyte	Sample matrix	Study rationale	Technique	Analytical Findings	Reference
C	Carbonaceous particles collected on filter tapes from bam samplers (an air sampler design widely deployed for the real-time determination of particle mass)	Evaluation of a low-cost method for determining black carbon using an off-line image reflectance-based method.	Optical spectroscopy	Mobile-phone camera images used to determine black carbon in spot samples collected on filter tapes. LOD of 0.15 µg achieved for an hourly sample collected at 1 m^3 h^{-1}. Post-analysis of filter tape samples could be a valuable source of new APM compositional data.	285
C	Diesel fume emissions in railway stations.	Study aims: measure worker exposure to diesel fume as using wearable aethalometers and to investigate variables that influence emissions.	Optical spectroscopy	Real-time personal measurements demonstrated that the extent and frequency of exposures, especially peak exposures, was indeed as suspected intrinsically linked to job role and location within station and the frequency at which diesel-powered trains entered and left stations, but powerfully demonstrated for the first time using wearable fast-response real-time sensors.	286
C	CNT in workplace air	One study aim was to ascertain potential for measuring worker exposure to CNT in real-time using wearable aethalometers (black carbon sensors) as a complementary tool to measuring exposure using TWA filter sampling and off-line EC determinations in the laboratory.	Optical spectroscopy	Transport losses of coarser CNT-containing particles emitted from work processes, within the sampling tube (1 m in length) and internal losses in the aethalometer suggested as a reason why no significant correlation between EC and black carbon measurements was noted. Authors advocated that further studies on potential sampling losses of larger particles required.	287
C	Carbonaceous aerosols	Determination of EC in aerosols collected in the Tibetan Plateau.	TOR analysis	High OC content in sampled aerosols resulted in a positive bias of 25-40% in EC determinations (conversion of some OC to pyrolytic carbon during the assay and hence misclassification as EC). Authors suggested that this overestimation	288

				and its impact on radiative forcing should be considered when comparing observations with model simulations.	
C	Carbonaceous particles	Evaluation of predictive models to estimate MAC values where direct calculations based upon aerosol light absorption and black carbon mass determinations not possible.	Optical spectroscopy	Five models (3 models based upon light scattering theories, one empirical model based upon particle mass concentrations determination and a machine learning model) evaluated. Machine learning model worked well for samples studied but model performance degraded when applied to aged black carbon particles (i.e., coated particles). Generally, the empirical model tended to over-predict MAC whilst models based upon Mie light scattering concept tended to under-predict MAC.	289
C	Carbonaceous particles	The microphysical properties of fresh black carbon emitted from traffic (petrol and diesel fuels) and aged black carbon emitted from solid fuel burning sources (coal, cotton stem, rice stem and mulberry) studied.	Single particle soot photometer, differential mobility analyser, CPMA	Core size, number size and coating thicknesses determined that emphasised the large property differences in black carbon particles derived from fresh traffic emissions compared to those derived from aged solid-fuel-burning emissions that have over time mixed with other atmospheric species. Such differences need to be considered in climatic models.	290

Table 5. Preconcentration methods using solid-phase extraction for the analysis of water.

Analytes	Matrix	Technique	Substrate	Coating or modifier	LOD in µg L^{-1} (unless stated otherwise)	Validation	Reference
Ag	Soil and water	HR-CS-ETAAS	Bentonite		0.01	NIST SRM 2709 (San Joaquin soil), NIST SRM 2711 (Montana soil) and NIST SRM 1643e (trace elements in water)	127
Ag, Au NPs	Water	ETAAS	Ferrite particles	Ammonium diethyl dithiophosphate	4 (Ag) 12 (Au) ng L^{-1}	NIST SRM 1640a (spring water) and ECCC CRMs TM-23.4 (trace element fortified water), TM-25.4 (low level fortified water sample), and TMDA-62.2 (Lake Ontario fortified water)	291
As^{III}, As^{V}	Water	ICP-MS	SAX and SCX columns		0.03	NRCC CRMs	292

						CASS 5 (near shore seawater) and SLRS-2 (river water)	
As^{V}	Water	EDXRFS	Poly(vinylidene)fluoride membrane	MIL-101 (Fe) (an Fe-based MOF)	0.094	Spike recovery	293
Cd	Pure and tap water	ETAAS	Fe_3O_4 NPs	Amine-functionalised shell, ion imprinted with Cd^{2+}	0.64 ng L^{-1}	Spike recovery and comparison with ICP-MS results	294
Cd, Co, Cr, Cu, Fe, Mn, Ni	Water and plant samples	FI-FAAS	$Bi(OH)_3$ coprecipitation		1 (Cd)-27 (Ni)	IRMM BCR-715 (industrial effluent waste water)	295
Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, Ti, V, Zn	Water and waste water	FI-ICP-AES	Carboxymethylated polyethyleneimine 600 resin		0.0012 (Cd)-0.11(V)	SCP science RMs EnviroMAT ES-L-1 (ground water) and EU-L (waste water)	296
Cd, Cr, Cu, Ni, Pb	Water	ICP-MS	Silica gel	C18-alkylimidazolium ionic liquid, metal ions complexed with 1-(2-pyridylazo)-2-naphthol (PAN)	0.11 (Cd)-11.3 (Ni)	Spike recovery	297
Cd, Cu, Fe, Ni, Pb	Seawater	FAAS	3-phenyl-1-(2-pyridyl)thiourea resin		0.13 (Cu)-2.63 (Ni)	Spike recovery	298
Cd, Cu, Pb, Zn	Seawater	AAS	Polystyrene resin microspheres	EDTA-type amino polycarboxylic groups	0.01 (Cd)-3.1 (Zn)	Spike recovery and analysis of a seawater RM from Beijing	299

						Putian Tongchuang BioTech Co., Ltd	
Cd, Pb	Tap and river waters, agricultural products	ETAAS	KCC1 fibrous Si nanospheres	Amine functional groups	0.02 (Cd) and 0.18 (Pb)	Spike recovery	300
Co, Ni	Water and plants	FAAS	Multiwalled carbon nanotubes	3-(2,4-dihydroxyphen-1-ylazo)-1,2,4-triazole	0.3 (Co) and 0.6 (Ni)	ECCC RM TMDA-52.3 (fortified Lake Ontario water) and NIST SRM 1570A (spinach leaves)	301
Cr^{VI}, total Cr	Sea, well and tap waters	ICP-AES	Magnetic graphene oxide	4-aminobenzenesulfonic acid	0.1 (Cr^{VI}) and 0.08 (total Cr)	ECCC CRM TMDA 54.4 (fortified lake waters) and SPS RM SW2 (surface water)	302
Cu	Tap, river and seawaters	FAAS	Silica gel	N-{3-[(3-aminopropyl)amino]propyl}-2-hydroxy-benzaldimine	0.45	ECCC TMDA 54.4 (fortified lake waters) and NWRI ECCC RM NWTM-15.2 (fortified water)	303
Ga	Seawater	IDA-ICP-	Nobias chelatePA 1 resin		0.10 pmol	Spike recovery	304

		MS			L^{-1}	and comparison with standard coprecipitation method	
Ga, In	Waters, soils, electronics	ETAAS	Fe_3O_4 NPs		0.01 (In)-0.02 (Ga)	ECCC RMs TM-25.4 (low level fortified lake water) and TMDA-62.2 (Lake Ontario fortified water)	305
Ni	Water, tomato leaves	HR-CS-FAAS	Fe_3O_4 NPs	2-(5-bromo-2-pyridilazo)-5-(diethylamino)phenol	15	NWRI ECCC CRM TMDA-64.3 (Lake Ontario water) and NIST SRM 1573a (tomato leaves)	306
Pd	Tap, river and seawaters	HR-CS-FAAS	Graphene oxide NPs	titanium aluminum carbide	0.3	Spike recovery	307
Pu	Water, seawater	ICP-MS/MS	TK 200 resin		0.32 µBq L^{-1} (0.14 fg L^{-1})	CRM IAEA-443 (Irish Sea water)	308
REEs	Seawater	SF-ICP-MS	seaFAST-3™ mixed functional group proprietary resin		0.01-0.03 ng L^{-1}	NRCC CRM SLEW-3 (estuarine water)	309
U	Mineral, river, lake and sea	TXRFS	Graphene oxide	β-cyclodextrin	0.014	NIST SRM 1640a (trace elements in	310

	waters					natural water) and spike recovery	

Table 6. Preconcentration methods using liquid-phase extraction for the analysis of water

Analytes	Matrix	Technique	Method	Reagents	LOD in µg L^{-1} (unless stated otherwise)	Validation	Reference
Cd	Oil production waters	ETAAS	DLLME	Diethyldithiocarbamate and chloroform	5 ng L^{-1}	NRCC CRM CASS 5 (near shore seawater) and NRCC CRM SLEW-3 (estuarine water)	311
Co, Ni	Water, fruit juice	FAAS	DLLME	Choline chloride, butyric acid and phenylacetic	0.1 (Co) and 0.17 (Ni)	SPS RM WW2 (wastewater)	312
Co, Pb, Pd	River water, wastewater	FAAS	DLLME-SFOD	folic acid, 1-undecanol and acetone	0.022 (Pb) to 0.055 (Pd)	Spike recovery and NIST SRM 1643f (trace elements in water)	313
Cr^{III}, Cr^{VI}	Water	ETAAS	Dual drop LPME	DDTC, 1-phenyl-3-methyl-4-benzoylpyrazol-5-one and 1-decanol	1.1 (Cr^{III}) and 1.4 (Cr^{VI}) ng L^{-1}	Chinese CRMs GSBZ50027-94 and GBW(E)080039 (waters)	314
Cu	Water	ETAAS	DLLME	2-(5-bromo-2-pyridylazo)-5-dimethylaminoaniline, ammonium acetate, chlorobenzene and acetonitrile	0.01	Spike recovery	315
Cu, Pb	Water, fruit juice	FAAS	DLLME	DDTC, chloroform and folic acid	0.07 (Pb) and 0.08 (Cu)	SPS RM WW2 (wastewater)	316

Hg	Tap and lake waters	AFS	CPE	Triton X-114 and Thio-Michler's Ketone	0.003	Spike recovery	317
I	Brine	EDXRFS	LPE	Trihexyltetradecylphosphonium chloride and trioctyl ammonium chloride	Not reported	Spike recovery	318
Ni	Seawater	ETAAS	Electro-membrane assisted micro LPE	di-2-ethylhexyl phosphoric acid in kerosene.	23 ng L^{-1}	IRMM CRM BCR-403 (seawater)	319
Se^{IV}	Ground water	ETAAS	LPE	$ZnCl_2$: CH_3CONH_2 and APDC	25 ng L^{-1}	Spike recovery	320
Sm	Wastewater	ICP-AES	Air assisted CPE	ammonium salt of aurintricarboxylic acid and Triton X-114	0.06	Spike recovery and NIST SRM 2780a (hard rock mine waste)	321
Te^{IV}	Water, beverages	ETAAS	DLLME	APDC, choline chloride and phenol	3.5 ng L^{-1}	Spike recovery	322
V^{IV}, V^{V}	Water	ETAAS	Dual drop LPME	1-(2-Pyridylazo)-2-naphthol, 1 undecanol and chloroform	1.5 (V^{V}) and 2.4 (V^{IV}) ng L^{-1}	Chinese CRM GSBZ 50029–94 (water)	323

Table 7. Methods for photochemical vapour generation in the analysis of water

Analyte	Matrix	Technique	Vapour generation reagents	LOD in µg L^{-1} (unless stated otherwise)	Validation	Reference
Hg, Ni, Se	Water, river water, fish	AFS and micro PD-AES	Formic acid and HNO_3	0.002 (Hg) to 0.01 (Se)	NSMCC CRMs GBW08603, GBW08607, GBW(E)080395 (water) and NRCC CRMs DORM-4 (fish protein) and DOLT-5 (dog fish liver)	324
Ir	Spring, river, lake and sea waters	ICP-MS	Formic acid with Cd and Co as sensitisers	3 pg L^{-1}	Spike recovery and NIST SRM 2556 (used auto catalyst)	325
Sb	Water, sediments	ICP-MS	Formic acid, acetic acid and V^{IV} sensitiser	4.7 ng L^{-1}	NRCSM CRMs GBW07303a, GBW07305a (sediment) and spike recovery	135
Te^{IV}	Water	AFS	Formic acid and acetic acid, with release of Co from, and preconcentration of Te on Co-MOF-74	0.08	Spike recovery	326

Table 8. Preconcentration methods involving solid-phase (micro)extraction used in the analysis of soils, plants and related materials

Analyte(s)	Matrix	Technique	Extraction mode/ Reagent(s)	Findings/ Comments	Validation	Reference
Ag	Soil, water	HR-CS-ETAAS	UA dispersive µSPE with bentonite sorbent	pH, sorbent mass, ultrasound time and HR-CS-ETAAS parameters optimised, Preconcentration factor = 34, RSD 5%.	NIST SRM 2709 (San Joaquin soil), NIST SRM 2711 (Montana soil), NIST SRM 1643e (trace elements in soil)	127
Cd	Lake and mineral waters, tomato leaves	Flame-Furnace AAS	Vortex-assisted dispersive magnetic SPE with Fe_3O_4@C	Nanocomposite characterised by ATR-FTIR, SEM, VSM, XRD. Optimised conditions: 10 mL sample, 2 mg sorbent, pH = 8. Magnetic particles collected by stainless steel rod. Linearity 15-750 ng L^{-1}, RSD 1-4% (n = 10).	NIST SRM 1643e (water), SRM-1573a (tomato leaves)	327
Co, Ni	Food, juice, and water samples	FAAS	UA dispersive µSPE with multiwalled CNT and 3-(2,4-dihydroxyphen-1-ylazo)-1,2,4-triazole chelating agent	Effective at pH = 8. Linear range 1.0-200 µg L^{-1} for Co and 2.0-300 µg L^{-1} for Ni.	NIST SRM 1570A (spinach leaves), TMDA-52.3 (enriched water)	301
Cu	Artichoke leaves	SQT FAAS	Dispersive SPE with CdS- NPs	CdS precursor synthesised from microwave-assisted reaction. Sorbent characterised by FTIR, SEM and XRD. Optimum conditions: 40 mL sample volume; 0.1 mL buffer (pH 4);	Spike recovery (artichoke leaf extracts)	328

				7.5 mg CdS NPs; 30 s sonication; 100 µL HNO_3. Linear range 2.5-30 µg L^{-1}.		
Ga, In	Electronic devices (mobile phones, non-touch laptop screens, diodes of LED bulbs), soil, water	ETAAS	Dispersive SPME with Fe_3O_4	Ga desorbed with 2 M NaOH (50 µL), In desorbed with 4 + 1 mixture of 0.1 M EDTA and 2 M HNO_3 (50 µL). Linear range 0.1-15 µg L^{-1} for Ga, 0.05-1 µg L^{-1} for In.	NIST SRM 2711 (Montana soil); NCS DC 73319a (soil); ECCC TM-25.4 (water) and TMDA-62.2 (water). spike recoveries	305
Ni	Cornflakes sage, green tea, yogurt	HR CS FAAS	Magnetic SPE with Fe_3O_4@ Diaion HP-2MG resin, 2-(5-bromo-2-pyridilazo)-5-(diethylamino)phenol chelating agent	0.15 mg sample, 15 mg sorbent, pH = 8, 3 M HNO_3 eluent (0.4 mL), 60 s vortex. Resin reused 15 times without performance degradation. pH, sorbent mass and sample volume optimised.	NIST SRM 1573a (tomato leaves) ECCC TMDA-64.3 (fortified water)	306
Pb	Food, water	FAAS	Dispersive magnetic SPE with MWCNTs@$MgAl_2O_4$@TiO_2 nanocomposite	Nanocomposite synthesised using sol-gel method and characterised by FTIR, SEM and XRD. pH, sorbent mass and sample volume optimised.	ECCC TMDA 64.3 (fortified lake water, NCS DC 73349 (bush, branches and leaves)	329
Pb	Biscuit, chili oat flour, chili pepper (dried), garlic, infant formula, pepper, sumac tobacco, water	FAAS	Dispersive µSPE with Ag modified ZnO nanoflowers	Nanoflowers synthesised by hydrothermal method and characterised by BET, EDX, FESEM, FTIR, XRD. Optimised conditions: 500 mg sample, pH = 4, 6 mg sorbent, 0.25 M HNO_3 eluent (0.4 mL).	Chinese RMs GBW07424 (soil) and GBW07425 (soil)	330
Pd	Medical devices,	HR-CS-FAAS	SPME with Ti_3AlC_2	Nanocomposite characterised	Spike recovery	307

	soil, water		max phase graphene oxide nanocomposite	by EDXRFS, FTIR, SAA, XRD. pH, sorbent mass, sample volume, vortex time, desorption conditions were optimised.	(medical devices, soil and water)	
Rh	Soil	SQT-FAAS	Dispersive SPE with magnetic colloidal gel (MCG)	MCG produced by mixing Fe_3O_4 based magnetic NPs and DES (choline chloride and phenol 1:3). Optimised conditions: 5 g dried soil, pH=7, 125 µL DES-MCG, 14.7 M HNO_3 eluent (75 µL).	Spike recovery (soil extract)	331
Rh	Soil	FAAS	Dispersive SPE with $MnFe_2O_4$ NPs	pH, buffer volume, sorbent mass, sample volume, eluent concentration and volume were optimised.	Spike recover (soil extracts)	332

Table 9. New geological reference materials for isotope measurements

Determinands	Matrix	Technique	RM name	Comments	Reference
Cu isotopes	Chalcopyrite	fs-LA-MC-ICP-MS	14ZJ12-1, JGZ-29, JGZ-78	3 natural chalcophyrites. Homogeneity demonstrated by intermediate precision of 0.07 - 0.08‰ (2SD) for δ^{65}Cu. Recommended values for RMs relative to NIST SRM 976 (copper) obtained by solution MC-ICP-MS.	333
Fe isotopes	Pyrite	LA-MC-ICP-MS	Tianyu-Py	Recommended values of 0.49 ± 0.03‰ (2SD, n = 4) for δ^{56}Fe and 0.73 ± 0.04‰ (2SD, n = 4) for δ^{57}Fe based on solution analysis. Homogeneity of Fe isotopes verified by LA-MC-ICP-MS.	334
Fe isotopes	Chalcopyrite	fs- and ns-LA-MC-ICP-MS	Tianyu-Ccp	Recommended values of 0.39 ± 0.07‰ (2SD, n = 4) for δ^{56}Fe and 0.57 ± 0.06‰ (2SD, n = 4) for δ^{57}Fe based on solution analysis. Homogeneity of Fe isotopes verified by LA-MC-ICP-MS; precision 0.19‰ (2SD, n = 86) for δ^{56}Fe for spot size of 16 µm.	335
Fe isotopes	Fe metal	fs-LA-MC-ICP-MS	IRMM-524A	IRMM-524A (Fe metal) characterised relative to IRMM-014, which is commercially unavailable. Results identical to published values by solution MC-ICP-MS within analytical uncertainty.	336
Hf isotopes	Zircon	LA-MC-ICP-MS	Ban-1	Recommended value for ^{176}Hf/^{177}Hf of 0.282983 ± 0.000009 (2SD, n = 130) obtained by solution MC-ICP-MS. Considered sufficiently homogeneous for *in situ* isotope determinations of Hf and Zr (see later entry).	337
Li isotopes	Clinopyroxene	LA-MC-ICP-MS	CPXA01, CPXB01-05	Six synthetic clinopyroxene RMs prepared by mixing metallic oxides with either USGS RM GSP-2 (granodiorite) or IAEA CRM L-SVEC (Li carbonate)	338

				and fusing to make glasses. Homogeneity testing gave 2s of <1‰, the long-term precision for δ^{7}Li by LA-ICP-MS.	
Mg isotopes	Mg solution	MC-ICP-MS	Alfa-Mg	New delta-zero Mg solution with certified $\delta^{26/24}$Mg of -1.40‰ relative to DSM3 with uncertainty of 0.05‰ (k = 2). $\delta^{26/24}$Mg values reported for 14 environmental RMs.	103
O isotopes	Lawsonite	SIMS	LM-19	Recommended δ^{18}O value of 8.98 ± 0.10‰ (1SD). Main limitation was chemical variability in Fe and Ti that may cause a minor matrix effect resulting in an δ^{18}O bias of -0.90‰.	339
O isotopes	Monazite	SIMS	COM-1, Hongcheon-1, Hongcheon-2	Recommended $\delta^{18}O_{VSMOW}$ values of 6.67 ± 0.08‰, 6.60 ± 0.02‰ and 6.08 ± 0.07‰ for the three RMs, respectively.	340
Pb isotopes	K-feldspar	LA-MC-ICP-MS	Albany K-feldspar	Double-spike TIMS used in conjunction with LA-MC-ICP-MS to characterise Pb isotope composition. No Pb isotopic heterogeneity detected in Albany K-feldspar but Shap K-feldspar heterogeneous at precisions of <0.15%; leaching to remove secondary radiogenic Pb recommended.	341
S isotopes	Sulfides	LA-MC-ICP-MS	SPH-1 (sphalerite), GC-1 (chalcopyrite), NWU-GN (galena), RPPY pyrite powder)	δ^{34}S values determined by GS-IRMS and solution MC-ICP-MS relative to V-CDT. LA-MC-ICP-MS data consistent with preferred values within analytical uncertainty.	342
S isotopes	Sphalerite	LA-MC-ICP-MS	GBW07270	Natural powders prepared as a sintered material. Recommended $\delta^{34}S_{V\text{-}CDT}$ of -5.44 ± 0.18‰ (2SD) agreed with IRMS value within analytical uncertainty.	343
Sn isotopes	Cassiterite	LA-MC-ICP-MS	Synthetic cassiterite	Sintered material prepared from ultrafine cassiterite powder. Homogeneity (2SD) as assessed	344

				by LA-MC-ICP-MS was improved from 0.64‰ in the original cassiterite to 0.10‰ by sintering. Recommended $\delta^{124}Sn/^{120}Sn$ of 0.60 ± 0.03‰ (2SD, n = 5) by solution MC-ICP-MS.	
Sr isotopes	Plagioclase	LA-MC-ICP-MS	AMNH-107160 (Labradorite), G29958 (Anorthite), Hrappsey 14-2 (Bytownite)	RMs developed as part of wider recommended procedures and data reduction strategies for Sr isotope measurements in geological materials by LA-MC-ICP-MS.	345
Sr isotopes	Calcite	LA-MC-ICP-MS	MNP	MNP has a low Rb/Sr ratio, low amounts of heavy REEs and high Sr content. Recommended $^{87}Sr/^{86}Sr$ value of 0.70617 ± 0.00005 (2SD, n = 18) determined by TIMS and solution MC-ICP-MS. An average $^{87}Sr/^{86}Sr$ ratio from LA-MC-ICP-MS analyses on random calcite crystals was identical to that of the solution-based data.	346
U-Pb dating	Columbite	LA-ICP-MS	SN3	ID-TIMS age of 404.0 ± 1.3 Ma (2SD), with low common Pb content; 96% of LA-ICP-MS data within the ID-TIMS $^{206}Pb/^{238}U$ age.	347
U-Pb dating	Garnet	TIMS, LA-ICP-MS	IUC-1	Gem quality andradite-rich garnet with assigned age of 20.4 ± 0.5 Ma (2SD) proposed as secondary garnet RM for *in situ* dating.	348
U-Pb dating, Nd-Sm isotopes	Titanite	LA-ICP-MS	Khan River, Bear Lake	U-Pb data were acquired by a variety of microbeam techniques including ID-TIMS and bulk measurements. Khan River was considered suitable as a secondary RM for U-Pb geochronology and Nd isotope ratios, whereas Bear Lake could be used for *in situ* trace element microanalysis and Nd-Sm isotope analysis, as well as U-Pb dating.	349
U-Pb dating and Nd isotopes	Apatite	LA-ICP-MS	MAP-3	Shown to be free of mineral inclusions with a $^{206}Pb/^{238}U$ age of 800.5 ± 0.9 Ma (2SD, n = 11)	350

				determined by ID-TIMS. High degree of chemical and isotopic homogeneity demonstrated, making it suitable as a primary RM for *in situ* U-Pb and Nd isotope measurements.	
U-Pb ages and Hf-O-Zr isotopes	Zircon	LA-ICP-MS, TIMS, SIMS, SHRIMP	SLZA, SLZB and SLZC	U-Pb ages determined by CA-ID-TIMS; Hf isotopes by solution MC-ICP-MS; O isotopes by laser fluorination method and SIMS, and Zr isotopes by double spike TIMS. SLZA exhibited slight heterogeneity for U-Pb, Hf and Zr isotopic compositions, whereas SLZB and SLZC considered to be homogeneous.	351
(U-Th)/He and U-Pb dating	Zircon	LA-ICP-MS	SA01	*In situ* laser microbeam (U-Th)/He and U-Pb double dating method applied and compared with traditional solution (U-Th)/He method. Concordia age of 535.2±71 Ma (n = 32) indistinguishable from published ages.	352
Zr isotopes	Zircon	LA-MC-ICP-MS	Ban-1	Recommended values of $\delta^{94}Zr/^{90}Zr_{IPGP\text{-}Zr}$ of -0.09 ± 0.006‰ (2s, n = 5) by double spike TIMS. Considered sufficiently homogeneous for *in situ* isotope determinations of Zr and Hf (see earlier entry).	337

Table 10. New data for existing geological reference materials

Determinand	Matrix	Technique	Comments	Reference
He dating	Apatite and zircon	Fission-track dating	Zircon FC1 from the Precambrian Duluth Complex, Minnesota, recommended as a RM for zircon (U-Th)/He dating, in addition to U-Pb geochronology. Apatite FC1 from the same location not suitable as RM because of wide dispersion of ages obtained. Air abrasion recommended to control α-ejection in (U-Th)/He dating.	353
Hf isotopes	Mafic rocks	MC-ICP-MS	^{176}Hf/^{177}Hf ratios plus Lu and Hf mass fractions measured in 10 mafic and ultramafic rock RMs. ^{176}Hf/^{177}Hf precision of <60 ppm (2SD) achieved on test portions of 0.06 to 0.3 g for 7 recommended RMs.	354
Nd isotopes	Geological RMs	MC-ICP-MS	Nd isotopic compositions of 27 RMs, including silicates, sediments, soils and carbonate, 13 of them for the first time. δ^{146}Nd/^{144}Nd long-term measurement precision <0.030‰ (2SD) relative to RM JNdi-1.	107
Rb isotopes	Geological RMs	MC-ICP-MS	$\delta\,^{87}$Rb reported for 21 RMs including igneous, sedimentary and metamorphic rocks as well as a seawater RM relative to NIST SRM 984 (RbCl). Long-term measurement reproducibility <0.06‰ (2SD).	355
Rb-Sr dating	K-feldspars, mica	LA-ICP-MS/MS	4 RMs, GL-O (glauconite), Mica-Mg (phlogopite), Mica-Fe (biotite) and FK-N (K-feldspar) prepared as nano-powder pellets and tested for *in situ* Rb-Sr dating, complemented by ID-MC-ICP-MS data. Only nano-pellets of Mica-Mg and GL-O proved suitable for this application.	356
Rb-Sr dating	K-feldspars, mica	LA-ICP-MS/MS	Grains of 4 RMs (Mica-Mg, Mica-Fe, GL-O and FK-N) found to have variable degrees of heterogeneity by SEM-EDS and EPMA imaging. Powdered material analysed by ID-TIMS and ID-MC-ICP-MS provided proposed working values for ^{87}Sr/^{86}Sr and ^{87}Rb/^{86}Sr and associated uncertainties when using these RMs for *in situ* dating.	357
S	Geological RMs	SF-ICP-MS	Rapid method developed for quantification of S mass fractions based on *aqua regia* digestion at 90°C in open vessels applied to 60 geological and environmental RMs. The use of a heating-condensing sample introduction into the ICP provided an LOQ of <1.0 µg g^{-1} in the solid.	358

S	Rock RMs	XRFS, elemental analyser, iodo-titration	Compilation of >1700 measurements of S mass fractions for 37 geological RMs obtained by several analytical techniques over 25 years.	359
Sn isotopes	Rock RMs	MC-ICP-MS	δ^{120}Sn/^{118}Sn data relative to NIST SRM 3161a (Sn isotope solution) reported on 10 geological RMs, seven for the first time. Overall method precision estimated as ±0.07‰ (2SD, n = 6) for USGS RM BHVO-2 (basalt).	360
Trace elements	Uraninite	EPMA, LA-ICP-MS	Additional information on matrix effects and trace element homogeneity for the Happy Jack Uraninite RM. REE discrepancy between LA and bulk solution ICP-MS measurements likely to be the result of digestion of mineral inclusions.	361
U isotopes	Geological RMs	MC-ICP-MS	^{233}U-^{236}U double spike technique used to determine U isotopes in 29 Chinese rock RMs with U mass fractions ranging from 0.11 to 18.7 µg g^{-1}.	362
U-Pb dating	Cassiterite	LA-ICP-MS	Confirmed ages and better estimates of uncertainties for SPG, Yankee, AY-4 and Jian-1 cassiterite RMs previously analysed by ID-TIMS.	363
U-Th-Pb dating	Titanite and apatite	LA-ICP-MS	New U-Th-Pb isotope and trace element mass fraction data for 10 titanite and 5 apatite RMs based on integrated EPMA, LA-ICP-MS and ID-MC-ICP-MS characterisation.	364
Water and trace elements	Amphiboles	Karl-Fischer titration, LA-ICP-MS	New data on water content and trace element mass fractions reported for two amphibole microanalytical RMs from the Smithsonian.	365
Water content	Clinopyroxene, Orthopyroxene	SIMS and FTIR spectroscopy	4 clinopyroxenes and 5 orthopyroxene potential RMs analysed and found to be homogeneous in terms of water content as indicated by a low standard deviation of <18.6% (2SD) for both inter- and intra-fragments.	366
Zn isotopes	Geological RMs	MC-ICP-MS	Demonstration that δ^{66}Zn can be precisely and accurately measured within ±0.03‰ (2SD) by MC-ICP-MS. Zn isotope data reported for 21 geological RMs, some for the first time.	367
Zr isotopes	Zircon	LA-MC-ICP-MS	Long-term stability of 0.08‰ for δ^{94}Zr/^{90}Zr achieved in study of Zr	368

			isotope variations in a range of zircon RMs.	

Table 11 Methods developed for the determination of isotope ratios in geological material

Element	Matrix	Sample preparation	Technique	Comments	Reference
B	Silicate and carbonate RMs, corals	*In situ* analysis of RMs as glasses or pressed powder pellets; corals cleaned and embedded in epoxy resin.	UV-fs-LA-MC-ICP-MS	Calibration against NIST SRM 610 (glass). External reproducibility of ±0.9‰ (2SD). No laser-induced or ICP-related matrix effects observed within stated precision.	369
Ba	Barite	Barite RMs sintered under high pressure to stabilise them for *in situ* analysis.	LA-MC-ICP-MS	Long-term precision for $\delta^{137}Ba/^{134}Ba$ ±0.09‰ (2SD). Good agreement with values obtained by solution double-spike method within analytical uncertainty.	370
Ba	Geological RMs	A simplified two-column method using AG50-X8 and Eichrom Sr resins enabled efficient and simultaneous Ba separation in multiple samples.	MC-ICP-MS	SSB and double-spike (^{135}Ba-^{136}Ba) methods compared; SSB providing the better precision. Long-term reproducibility was ≤±0.07‰ (2SD) for $\delta^{138}Ba/^{134}Ba$. Ba isotope data for 9 geological RMs confirmed accuracy of method.	371
C, N	Natural diamonds	Both isotope ratios obtained from a single *ca.* 10 µm diameter pit.	SIMS	Spot-to-spot reproducibility of $\delta^{13}C$ and $\delta^{15}N$ for UWD-1 RM, a natural N-rich diamond from Kelsey Lake, USA, were 0.3‰ and 1.6‰, respectively (2SD). UWD-1 confirmed to be isotopically homogeneous.	372
Ca	Geological RMs	After dissolution, ^{42}Ca-^{43}Ca double spike added and published separation chemistries employed depending on sample matrix.	MC-ICP-MS/MS	CCT with double spike gave long-term precision for $\delta^{44}Ca/^{40}Ca$ of ±0.035‰ (2SD), an improvement on previous TIMS or MC-ICP-MS studies. Capable of determining both radiogenic and stable Ca isotope ratios on small amounts of Ca.	373
Ca	Geological RMs	Mixed acid attack dissolution and separation of Ca on AG50W-X12 resin.	CC-MC-ICP-MS	SSB method required matching of Ca intensities within 3% between sample and standard. Long-term precision of <±0.07‰ (2SD for $\delta^{44}Ca/^{40}Ca$). Capable of determining both radiogenic and stable Ca isotope ratios on small amounts of Ca.	374

Ca, Fe, Mg	Lunar samples	3-step purification scheme to separate Ca, Fe and Mg from a single aliquot of sample digest with amounts of these elements down to 15, 20 and 10 µg, respectively, via a combination of columns filled with AG1X-8, DGA and AG50W-X8 resins.	MC-ICP-MS, TIMS	Ca isotopes measured by TIMS, Fe and Mg by MC-ICP-MS. Long-term precisions of ±0.03‰, ±0.02‰ and ±0.03‰ for $\delta^{44}Ca/^{42}Ca$, $\delta^{56}Fe$ and $\delta^{26}Mg$, respectively, obtained on three USGS basalt RMs.	375
Cd	Geological samples	^{111}Cd-^{113}Cd double spike added to samples before digestion. Modified two-step column separation procedure employing AG1-X8 and TRU Spec resins, designed to avoid use of HBr to separate Zn from Cd.	MC-ICP-MS	Cd and Zn eluted together but did not affect measured Cd isotope data when Zn/Cd <10^3. Long-term precision of ±0.05‰ for $\delta^{114}Cd/^{110}Cd$ based on measurements of pure Cd solutions.	376
Cd	Geological samples	^{111}Cd-^{113}Cd double spike added to samples before digestion. Two-step column separation method employing AG MP-1M anion-exchange and BPHA extraction resins.	MC-ICP-MS	Sample P/Cd ratios ≥100 shown to result in positive Cd isotope shifts, which may be attributed to organic P compounds co-eluted with Cd from TRU Spec resin; hence use of BPHA instead. $\delta^{144}Cd/^{110}Cd$ for USGS rock RMs agreed with published values within analytical uncertainties.	377
Cd	Geological and biological RMs	Evaluation of double spike standard addition method for ultra-trace Cd samples. After sample digestion, ^{111}Cd-^{113}Cd spike added and Cd purified using AG MP-1M resin.	MC-ICP-MS	$\delta^{114}Cd/^{110}Cd$ values measured in samples with as low as 2.09 ng Cd consistent with recommended values within uncertainty. No significant difference between single and multiple standard additions of Cd spike. Overall precision 0.041 ± 0.022‰ (2SD, n = 46).	378
Cd, Cu, Fe, Zn	Rock, soil and sediment RMs	One-step method to separate Cd, Cu, Fe and Zn using AG MP-1M anion-exchange resin. Recoveries were 99±1, 100.1 ± 0.8, 99.8 ± 0.7 and 100 ± 0.8% (2SD, n = 3).	MC-ICP-MS	Method validated by measurements of $\delta^{110}Cd/^{114}Cd$, $\delta^{65}Cu$, $\delta^{56}Fe$ and $\delta^{66}Zn$ in a range of geological RMs; results for 10 geological RMs agreed with published values within analytical uncertainties.	105
Ce, Nd	Geological RMs	Two-step procedure employed AG50W-	MC-ICP-MS	SSB combined with Sm and Eu employed as	379

		X12 column to preconcentrate Ba and REEs before a second column of TODGA cation-exchange resin was used to collect separate Ce and Nd fractions. Yields of Ce and Nd were >99.3%.		ISs for Ce and Nd respectively, gave long-term reproducibilities of <0.04‰ (2SD) for $\delta^{142}Ce/^{140}Ce$ and <0.03‰ (2SD) for $\delta^{146}Nd/^{144}Nd$. Results for 6 rock RMs agreed with published values within analytical uncertainties.	
Cl	Planetary materials	Cl-bearing solutions were precipitated as AgCl and mixed with Nb powder, before being loaded into stainless steel cathodes prior to insertion in the ion source.	AMS	Bulk $\delta^{37}Cl$ measurements made with values from 0 to +45‰ with an accuracy of ±1‰ in samples with Cl masses as low as 1 µg; typical precision was 1-3‰. Method designed to complement SIMS and IRMS data.	380
Cr	Terrestrial and cosmochemical materials	A complex 4-step chemical purification method developed for a range of very diverse matrices including U ores, Cr ore residues and contaminated soils. The Cr yield always >87% with a mean value of 95%.	TIMS	A full multi-dynamic data reduction scheme developed. Reproducibilities of 5 and 13 ppm (2SD) for $^{53}Cr/^{52}Cr$ and $^{54}Cr/^{52}Cr$ respectively. Accuracy for terrestrial materials confirmed by measuring 4 USGS rock RMs as well as extra-terrestrial samples.	381
Cr	Terrestrial and cosmochemical materials	Powdered meteorites digested in HF-HNO_3 and Cr separated in four-step column separation procedure. Total Cr yield >90%.	TIMS	Correlated variation between $\mu^{53}Cr$ and $\mu^{54}Cr$ in repeated TIMS measurements of isotope RMs thought to be caused by evaporation of Cr-oxide species during thermal ionisation. Problem alleviated by use of W filaments instead of Re filaments.	382
Cu	Geological RMs	Powdered rock RMs digested in HF-HNO_3 and Cu purified in two-stage chromatography procedure with AG MP-1M resin.	MC-ICP-MS	SSB technique in low resolution mode. Intermediate precision of ±0.030‰ (2SD) for $\delta^{65}Cu$. Data for 11 geological RMs consistent with published values within analytical uncertainties.	383
Fe	Geological RMs	Powdered rock RMs dissolved in mixed acid digestion, and Fe purified in a two-step procedure involving AG MP-1M	CC-MC-ICP-MS	SSB technique in low resolution mode with He and H_2 added to the collision cell to minimise ArO^+, ArN^+ and $ArOH^+$ ion	384

		and AG-1-X8 resins.		formation. Major advantage was high Fe sensitivity, with δ^{56}Fe precisions typically <0.03‰ (2SD) for Fe contents *ca.* 30 ng mL^{-1}, opening up new applications for small or Fe-depleted samples	
Fe	Geological RMs	Samples dissolved in mixed acid digestion and Fe purified by one-step column anion-exchange separation on AG MP-1M resin.	MC-ICP-MS	Large-geometry, high-resolution (3000, 10% valley) instrument able to resolve completely Ar-related interferences. Long-term precisions of <±0.03‰ (2SD) for δ^{56}Fe and <±0.06‰ (2SD) for δ^{57}Fe. Values for 5 geological RMs agreed with published data with uncertainties.	385
Hf	Zr-bearing minerals	*In situ* analysis of RMs	LA-MC-ICP-MS	Hf isotopes and ^{177}Hf^{16}O signals measured concurrently to monitor influence of rate of REE oxide formation on ^{177}Hf/^{176}Hf ratios. SA02 zircon recommended as primary RM for testing accuracy of method as it has a high REE/Hf compared to other zircon RMs.	386
Hf	Cassiterite	*In situ* analysis of RMs	LA-MC-ICP-MS	Corrections for Lu and Yb interferences required for ^{177}Hf/^{176}Hf determinations in spite of low Yb/Hf and Lu/Hf ratios in cassiterite. Several possibilities for matrix-matched RMs for *in situ* analysis suggested.	387
K	Carbonates	Dual-column K purification method developed using AG50W-X8 resin to separate K from the carbonate matrix before purification on AG50W-X8 resin. Yield *ca.* 100% for 100-150 mg sample size.	MC-ICP-MS	NIST SRM 1d (limestone) and USGS RM BHVO-2 (basalt) used to confirm accuracy of method. Low and varied δ^{41}K values for RM JCp-1 (coral aragonite) were ascribed to RM heterogeneity.	388
K	Lunar samples	Samples digested in HF-HNO$_3$ mixture, and K separated from other matrix elements in two-stage column	CC-MC-ICP-MS	Influence of Ca on K isotope measurements dramatically reduced if D$_2$ rather than H$_2$ employed as reaction gas. Long-term	389

		procedure with K yield >99%.		precision for QC solution ±0.06‰ (2SD). δ^{41}K values in 6 geological RMs and a seawater RM agreed with literature values within uncertainty.	
K	Planetary materials	Samples digested in $HF-HNO_3-HCl$ mixture and K separated and purified in a two-step ion-exchange column procedure employing AG1-X8 and AG50W-X12 resins. Recoveries >95%.	TIMS	Instrument equipped with 10^{13} Ω amplifier to collect ^{40}K signal; new method for gain and baseline calibrations developed. Long-term producibility 0.40 for ε^{40}K (2SD) with sample size of ca. 50 ng. ε^{40}K values for 7 USGS rock RMs agreed with literature values within uncertainty.	390
K	Geological RMs	Test solutions prepared from a commercial K standard solution (1000 µg g^{-1}) and purified digest of USGS RM AGV-2 (andesite).	CC-MC-ICP-MS	Improved tolerance to differences in K concentrations between standard and sample in SSB method in the measurement of K ratios was achieved by optimising RF voltage applied to the hexapole rods and the He and H_2 cell gas flow rates.	391
Li	Geological materials	Samples digested in $HF-HNO_3$ and then *aqua regia*. Chemical purification was achieved using a single column containing AG50W-X12 resin.	CC-MC-ICP-MS	Precision of <±0.20‰ (2SD) for δ^7Li in geological RMs over eight months. Values for 11 rock RMs consistent with published data within uncertainty limits.	392
Li, Mg	Geological materials	Digestion in $HF-HClO_4$ acids followed by modified method for chemical purification on a single column containing AG MP-50 resin to reduce separation time, reagent volumes and procedural blanks. Yields of Li and Mg *ca.* 100%.	MC-ICP-MS	Long-term precision of <±0.6‰ for δ^7Li and <±0.08‰ for δ^{26}Mg (2SD). Values of Li and Mg ratios in a range of geological RMs agreed well with published data within uncertainty limits.	393
Lu, Hf	Xenotime, apatite, garnet	*In situ* analysis. A small amount of N_2 was added to the carrier gas after the ablation cell to enhance sensitivity.	LA-ICP-MS/MS	High purity NH_3 was more effective as reaction gas than the 1 + 9 NH_3-He mixture often used. A reaction product of ^{176}Hf was measured at mass 258 to separate it from ^{176}Lu and ^{176}Yb. Matrix-matched RMs were	394

				required to correct for a matrix-induced bias on $^{176}Lu/^{177}Hf$ ratios. Accuracy of single-spot ages in xenotime generally <±1.5%, comparable to that obtained by *in situ* U-Pb analysis.	
Mg	Carbonates	4 magnesite, 5 dolomite and 4 siderite samples analysed. Addition of water vapour before the ablation cell significantly suppressed isobaric interference of $^{48}Ca^{2+}$ on $^{24}Mg^{+}$ and downhole fractionation.	LA-MC-ICP-MS	MGS-3 magnesite, DOL-8 and DOL-9 dolerites, and SD-5 siderite were found to be suitable as calibration standards with Intermediate precisions <±0.14‰ (2SD) for $\delta^{26}Mg$ and <±0.15‰ (2SD) for $\delta^{25}Mg$.	395
Nd, Sm	Geological samples	Glass RMs with low Nd contents analysed *in situ*. Small amount of water vapour added to carrier gas prior to LA.	LA-MC-ICP-MS	Nd signal intensity improved by factor of 1.9 - 3.6 with addition of water vapour and different cones in the ICP interface. Sm-Nd isotope data for 8 reference glasses were consistent with recommended values within analytical uncertainty.	396
Nd, Sr	Geological samples	Rock powders digested in HF-HNO_3-HCl acids before separation of LREE and Sr from matrix elements on AG50W-X8 resin and purification of the Sr and Nd using Sr-Spec and Ln-Spec resins.	TIMS	Demonstration of the capabilities of the latest generation of TIMS instrumentation. External precisions of 5-6 ppm (2SD) for $^{87}Sr/^{86}Sr$ and 4-5 ppm (2SD) for $^{143}Nd/^{144}Nd$ reported.	397
Nd, Pb, Sr	Silicate rocks	Sequential separation of Pb, Sr and LREEs from a single aliquot of digested silicate sample. AG50W-X8, Sr-Spec and Ln-Spec resin columns employed to achieve 80-90% recovery of each element with high purity. The LREE fraction was oxidised with >5 mM $NaBrO_3$ prior to loading on the Ln resin.	TIMS	Measured Nd-Pb-Sr isotope ratios in 9 rock and sediment RMs from GSJ and USGS were consistent with recommended values within analytical uncertainty.	398
Pb	Geological and cosmochemical samples	Samples digested in HF-HNO_3-$HClO_4$ mixture and enriched spike of ^{207}Pb added. No separation procedure. Bi and	Quadrupole ICP-MS	SSB combined with matrix matching to correct for mass bias. Good agreement with published Pb isotope ratios for	399

		Pb contents also determined.		Allende meteorite (Smithsonian Institution) and GSJ RMs JA-2 (andesite), JB-2 (basalt), JB-3 (basalt) and JR-1 (rhyolite) within uncertainty.	
Pb	Melt inclusions	Mineral grains mounted in epoxy resin and polished until the inclusions were exposed at the surface. 24-90 µm diameter laser spots, low energy fluences (3-4 J cm^{-2}) and low repetition rates (3-4 Hz) with a 193 nm ArF excimer LA system.	LA-MC-ICP-MS	A device to remove Hg from the He and sample gas lines reduced the ^{202}Hg background by >80%. Reference glasses KL2-G (2.07 mm Pb) and BCR-2G (11 ppm Pb) used for mass bias correction of samples with low and high Pb contents respectively. Analytical precisions for Pb isotope ratios ^{20x}Pb/^{204}Pb in seven geological glass RMs were <1% (2RSD) when ^{208}Pb signals >10^5 cps.	400
Pb	Geological materials	Sample powders digested in HF-HNO_3 and Pb purified on columns of AG1-X8 anion resin. Yields were 82 ± 10%.	TIMS	A novel silicon nitride emitter on a Ta filament was developed as a low-cost alternative to silica gel on a Re filament. Good external precision of 0.10 - 0.18% (2SD, n = 6) was obtained for ^{20x}Pb/^{204}Pb ratios in USGS RM BCR-2 (basalt) and Chinese RM GBW08401 (coal fly ash).	401
Pb, Th, U	Geological materials	Capabilities of a new technology, incorporating an extreme UV LA system operating at 46.9 nm (26.4 eV photon energy) was evaluated for Pb-Th-U isotope measurements. Sample area ablated 8 x 8 µm with depths ≤500 nm, comparable to a single spot analysis by traditional laser-based methods.	Extreme UV, TOFMS	^{232}Th/^{238}U ratios measured directly in geological glasses, FeMn oxide, zircons and monazite were within ±2SD of expected value without external calibration, whereas ^{206}Pb/^{238}U ratios were systematically low and were corrected using NIST SRM 610 (glass) as a non-matrix-matched external calibration standard.	402
Ra, Th	Sediments and porewaters	Dried sediment was spiked with ^{228}Ra before digestion in HF-HNO_3-$HClO_4$ acids. After separation from matrix elements on AG resin, Ra and Ba were	SC-SF-ICP-MS	^{226}Ra in 20-50 ml of porewater or 100 mg sediment measured with an internal precision of *ca.* 1.0%, much better than *ca.* 3% using conventional radiometric	403

		preconcentrated by MnO_2 precipitation before further purification on AG.		methods. ^{230}Th also determined by ID in separate aliquot for estimation of ^{226}Ra flux from sediment core.	
Rb, Sr	Terrestrial and cosmochemical materials	*In situ* method applied to the analysis of small and precious samples.	LA-MC-ICP-MS/MS	Instrument fitted with double Wien mass filter. Collision cell filled with SF_6; Sr isotopes measured as SrF^+ and Rb as Rb^+. Accurate measurements of $^{87}Sr/^{86}Sr$ ratios in the presence of elevated $^{87}Rb/^{87}Sr$ demonstrated.	404
S	Geological and biological RMs	Comparison of various preparation protocols concluded that for sulfide mineral RMs, addition of H_2O_2 to main digestion acid mixture significantly increased S recovery. For other silicate RMs, similar $\delta^{34}S$ results obtained whether *aqua regia* or mixed acids with HF were employed.	MC-ICP-MS	Good agreement for $\delta^{34}S$ and $\delta^{33}S$ between results from wet and dry plasma conditions, better precision for dry conditions. Si internal correction significantly improved accuracy and precision. Values obtained for $\delta^{34}S$ and $\delta^{33}S$ for a range of RMs agreed with published values within analytical uncertainty.	104
Sb	Geological samples	Method developed for rocks with low Sb content (<1 μg g^{-1}). Mixed HF-HNO_3 digestion followed by addition of H_2O_2 and HNO_3. A single column containing AG50W-X8 was used to separate the Sb fraction. An aliquot solution containing 5 ng Sb was mixed with 45 g Sb of high purity Sb standard solution for isotope measurements.	MC-ICP-MS	SSB combined with Sn internal normalisation technique. Long-term reproducibility for $\delta^{123}Sb$ <±0.03‰ (2SD). $\delta^{123}Sb$ values for two Chinese RMs, GSD-11 (stream sediment) and GSS-5 (soil) were consistent with other reported values within analytical uncertainties.	405
Sm	Geological samples	New 2-column procedure (AG50W-X12 and TODGA) to extract Sm quantitatively (99.4 ± 0.3%).	MC-ICP-MS	SSB and Eu internal normalisation to correct instrument mass bias. Long-term precision of <±0.04‰ (2SD) for $\delta^{152}Sm/^{149}Sm$ significantly better than those of existing MC-ICP-MS and double spike-TIMS methods. Values for GSJ RMs JB-2 (basalt) and JG-2 (granite) agreed	406

				within analytical uncertainties with published data.	
Sn	Geological materials	Sample equilibrated with ^{117}Sn-^{122}Sn during dissolution, and then Sn was purified from the rock matrix using TRU spec resin.	MC-ICP-MS	For accurate results, Sn concentration match between sample and bracketing standard should be better than ±20% and Cd/Sn <0.01. Long-term precision for $\delta^{122}Sn/^{118}Sn$ <±0.069‰ (2SD) for a spiked solution of 100 $\mu g\ g^{-1}$ Sn. Values for nine rock RMs agreed with published data within analytical uncertainties.	407
Sn	Cassiterite	*In situ* analysis of cassiterite embedded in epoxy resin. Natural cassiterite (#cas17) crystal used as matrix-matched RM. New digestion method developed for solution MC-ICP-MS; $\delta^{122}Sn/^{118}Sn$ reported as 0.36 ± 0.02‰ for #cas17.	ns LA-MC-ICP-MS	SSB with elemental Sb introduced by solution nebulisation. Precision for $\delta^{122}Sn/^{118}Sn$ <±0.12‰ (2SD).	408
Sn	Terrestrial rocks and chondrites	Novel two-step protocol for chemical separation of Sn using a resin based on tributyl phosphate (TBP), which had a strong affinity for Sn. Sample with ≤200 mg Sn gave an average yield of *ca.* 80%. Performance of TBP and TRU-Spec resins was compared.	MC-ICP-MS	Instrumental mass discrimination was corrected using the exponential law and internal normalisation of $^{116}Sn/^{120}Sn$ = 0.4460 and corrections for Te and Cd isobaric interferences applied.	409
Sr	Geological materials	After dissolution, Sr was purified on columns containing Sr-Spec resin.	MC-ICP-MS	Zr-doped SSB method for simultaneous determinations of $^{87}Sr/^{86}Sr$ and $^{88}Sr/^{86}Sr$ resulted in better sample throughput compared to double-spike TIMS. Long-term reproducibilities of ±0.000015‰ (2SD) for $^{87}Sr/^{86}Sr$ and ±0.03‰ (2SD) for $^{88}Sr/^{86}Sr$ were comparable to double-spike TIMS precisions.	410
Tc	Environmental samples	Alkali fusion instead of acid digestion prevented loss of Tc and simple Tc	ICP-MS/MS	O_2 employed as reaction gas to remove Mo isobaric interference. Spiked recoveries of	411

		separation method established based on TRU Spec resin in alkaline solution.		Tc were >85% for 1 g solid samples. LOD of ^{99}Tc 0.04 pg g^{-1} for a 1 g solid sample, suitable for rapid monitoring of ^{99}Tc in the environment.	
Te	Terrestrial rocks and meteorites	New 3-step purification procedure developed based on AG1-X8 and TRU Spec resins. Samples with Te content <50 ng g^{-1} were processed through an additional step to remove residual matrix elements. Full procedural yields ranged from 85 to 95%.	MC-ICP-MS	Double spike technique with ^{125}Te-^{128}Te. Between-run reproducibility of ±0.07‰ (2SD) for δ^{130}Te obtained on solutions containing 6 ng Te. Values for Alexo komatiite RM KAL-1 and 3 USGS RMs agreed within analytical uncertainties with published data.	412
Ti	Rutile and ilmenite	*In situ* analysis of 5 rutile and 4 ilmenite samples in single fixed position spot mode (30 µm diameter) to increase spatial resolution.	fs-LA-MC-ICP-MS	Potential matrix effects identified, making the use of matrix-matched RMs a necessity for accurate ^{49}Ti/^{47}Ti data. KNW rutile (2SD = 0.08‰) and PZH12-15 ilmenite (2SD = 0.09‰) were homogeneous at the 30 µm scale and recommended as bracketing standards.	413
Ti	Rutile	*In situ* analysis; single spot analytical mode with spot sizes of 10 - 20 µm.	fs-LA-MC-ICP-MS	High sensitivity cones and signal smoothing device employed. Long-term precision of ±0.11‰ (2SD) obtained for δ^{49}Ti in a rutile. Accuracy confirmed by solution MC-ICP-MS. Four rutile crystals homogeneous for δ^{49}Ti within an uncertainty of <0.13‰, making them suitable as RMs for *in situ* analysis.	414
Tl	Geological samples	After HF-HNO$_3$ digestion, samples refluxed with 15% *aqua regia* – 13% v/v Br$_2$ solution to ensure complete oxidation of Tl to Tl^{3+}. Two-step column method with tributyl phosphate extraction resin and AG50W-X12 cation ion-exchange resin. Recoveries >98%.	MC-ICP-MS	External normalisation to NIST SRM 981 (Pb isotopes) with SSB using NIST SRM 997 (Th isotopes) to correct for instrumental mass bias. Overall precision for ε^{205}Tl was ±0.8 (2SD) for USGS RM NOD-A-1 (Atlantic Ocean Mn nodule) expressed as per 10^4 deviation of ^{205}Tl/^{203}Tl from NIST SRM 997.	415

W	Geological RMs	^{180}W-^{183}W double spike added to samples after digestion and W separated on columns of AG50-X8 and AG1-X8 resins. W yields were typically 75-90%.	MC-ICP-MS	Measurement precision for $\delta^{186}W/^{184}W$ when analysing USGS RM NOD-A-1 (Atlantic Ocean Mn nodule) was <±0.024‰ (2SD). Data for eight USGS geological RMs agreed with published data within analytical uncertainties.	416