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

JEFFREY R. BACON [a]*, OWEN T. BUTLER[b], WARREN R.L. CAIRNS[c], JENNIFER M. COOK[d] , CHRISTINE M. DAVIDSON [e], OLGA CAVOURA[f] and REGINA MERTZ-KRAUS[g]

[a]59 Arnhall Drive, Westhill, Aberdeenshire, AB32 6TZ, UK, e.mail: bacon-j2@sky.com
[b]Health and Safety Executive, Harpur Hill, Buxton, UK SK17 9JN
[c]CNR-IDPA, Universita Ca' Foscari, 30123 Venezia, Italy
[d]British Geological Survey, Keyworth, Nottingham, UK NG12 5GG
[e]University of Strathclyde, Cathedral Street, Glasgow, G1 1XL, UK
[f]University of West Attica, Leof Alexandras 196, 115 21 Athens, Greece
[g]Institut für Geowissenschaften, Johannes Gutenberg-Universität, Becher-Weg 21, 55099 Mainz, Germany

* review coordinator

SUMMARY OF CONTENTS

In the field of air analysis, highlights within the period covered by this review included a wearable air sampler with an inbuilt GPS sensor which enabled autonomous sampling to be performed at specific sites once the device had been preprogrammed with the requisite location coordinates. A prototype high resolution laser absorption spectroscopic instrument was developed as a potential SI-traceable alternative to ID-CV-ICP-MS for determining mercury concentrations in air and its isotopic composition. Improvements in the capabilities of single-particle aerosol mass spectrometers were noted. New measurements using tools such as LDI-MS and PTR-MS are providing new insights into the composition of carbonaceous particles.

A large amount of effort continues to be directed towards multi-element preconcentration methods for water analysis, using either liquid or solid phase extraction to boost the sensitivity of instrumentation. Species-specific preconcentration methods were developed for the determination of mercury or arsenic species and methodologies employed to isolate elements from matrices such as seawater before isotope-ratio determinations. The focus of elemental speciation has shifted towards elemental fractionation with the determination of nano-sized fractions. The advent of ICP-MS/MS instrumentation has made the analysis of non-metallic elements such as F or P possible with improved detection limits. An interesting development of the isotope dilution technique was the use of isotopically labelled cell gasses to investigate the possibility of carrying out isotope dilution analysis of monoisotopic elements such as As or Y.

Much effort has been devoted to characterising new and existing matrix-matched reference materials for calibration and quality control in the determination of the elemental and isotopic composition of geological samples. Zircon geochronology is a very active area of research and there is now considerable interest in developing U-Pb dating methods for other accessory minerals and carbonates. The application of *in situ* techniques such as LA-ICP-MS, SIMS, and LIBS to obtain geochemical information at high spatial resolution is another continuing theme.

The ongoing interest in the optimisation of methods for extraction of analytes from soil and plants included developments relating to nanoparticles, estimation of bioavailability and non-chromatographic speciation analysis. The relative maturity of the AAS, AES and AFS techniques means that there have been few reports of major advances in these fields. Many of the developments in ICP-MS have been driven by the increased availability of ICP-MS/MS instrumentation. The importance of sample preparation in LIBS has increasingly been recognised. Proximal analysis – in which chemometric approaches are applied to data obtained by atomic (and molecular) spectroscopy to infer physical or chemical properties of a sample e.g. the pH of a soil – are becoming more common, in particular in relation to field-portable techniques such as LIBS and pXRFS, with increased attention being paid to the opportunities arising from data fusion.

1. **Introduction**

This is the 35th annual review of the application of atomic spectrometry to the chemical analysis of environmental samples. This Update refers to papers published approximately between August 2018 and June 2019 and continues the series of Atomic Spectrometry Updates (ASUs) in Environmental Analysis[1] that should be read in conjunction with other related ASUs in the series, namely: clinical and biological materials, foods and beverages[2]; advances in atomic spectrometry and related techniques[3]; elemental speciation[4]; X-ray spectrometry[5]; and metals, chemicals and functional materials[6]. This review is not intended to be a comprehensive overview but selective with the aim of providing a critical insight into developments in instrumentation, methodologies and data handling that represent a significant advance in the use of atomic spectrometry in the environmental sciences.

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

2 Air analysis

2.1 Sampling techniques

Developments in *particle sampling* included a new personal sampler[7] for respirable-sized particles that was validated for use at a nominal flow rate of 9 L min^{-1} to enable more sample to be collected on filters per unit sampling time. The widely-used IOM sampler, modified with a foam disc insert to collect both respirable and inhalable aerosol fractions simultaneously, was successfully tested[8] within an In-Sn oxide manufacturing facility and so demonstrated that the concurrent sampling of both size fractions was indeed practical. However, the practical handling of foam inserts within an analytical laboratory still needs to be addressed. A new single-use, low-cost size-selective personal sampler of inhalable particles[9] was designed to address the issue of particle loss to sampler walls. Initial assessment of its performance when used in a Cu electrorefinery facility provided somewhat mixed results; measured Cu concentrations were on average 1.4 times those obtained using the reference IOM sampler. Further testing in other workplaces was therefore proposed. A new wearable iteration[10] of the compact aerosol-sampler, reviewed last year[11], enabled the daily exposure of students to $PM_{2.5}$ particles to be assessed at home, at school and in transit. An inbuilt GPS sensor together with preprogrammed location coordinates enabled autonomous sampling to be performed. It was demonstrated that small cyclonic air samplers[12] with conical contraction bodies were advantageous as they offered the same desired particle size selectivity as current cyclone designs but with reduced pressure drops. The advantage of such samplers is that smaller and lighter batteries could be used in wearable samplers. A modification[13] to a three-stage Dekati^{TM} cascade-impactor-sampler enabled 30 mm diameter quartz reflectors, suitable for TXRF analysis, to be inserted directly below the impactor's nozzle arrays. Although these reflectors required greasing to minimise particle bounce-off, the grease was readily removed by low-temperature O_2-plasma ashing. In summary, this new approach for size-selective sampling and analysis of trace metals in airborne particles required minimal sample preparation. A useful review[14] (73 references) examined the utility of various commercially available personal samplers for assessing worker exposure to NPs.

Sampling *trace gaseous species in the atmosphere* is challenging. A new sampling system[15] collected small aliquots (10 nmol) of carbonyl sulfide sufficient for reliable $^{32}S/^{34}S$. Salient features of this new portable system included: an ability to sample 500 L of air at a nominal flow rate of 5 L min^{-1}; absorption tubes for preserving carbonyl sulfide samples for up to 90 days; and a purification system that removed matrix gases such as CO_2. The determination of trace Hg concentrations in landfill gases or volcanic emissions can be problematical due to the presence of excess H_2S. In a modification[16] to existing impinger sampling trains, an alkaline trap containing $NaBH_4$ was placed in front of two $KMnO_4$ traps. This enabled H_2S to be converted to S^{2-} thereby preventing subsequent reaction with $KMnO_4$ which is required to trap Hg^0 as Hg^{2+}. An added advantage was that this reductant trap minimised pre-oxidation of Hg^0 to Hg^{2+} which could potentially be lost as an HgS_2 precipitate. A new lightweight stratrospheric air sampler weighing only *ca.* 2.5 kg was designed[17] to collect CH_4, CO and CO_2 during the ascent of a balloon.

Certain lichens species are widely used in *air pollution deposition* studies because the concentration of various elements determined in their thalli can reflect the chemical composition in air. However, it was shown[18] that different metals accumulate in different parts of the thalli so a well-defined and repeatable process in selecting the correct part of the plant was needed if consistent elemental air pollution data sets were to be generated over extended time periods. A new porous substrate[19] was synthesised by heating and casting a mixture of silica fume (a by-product of the ferrosilicon metallurgical industry), alginate and sodium bicarbonate. The new substrate had the property of sequestering particulate matter from air when placed outdoors. Coarse particles trapped on its surface were removed by the simple process of sonication in distilled water and analysed using TXRFS. Smaller particles, interstitially trapped, were recovered following an aqua-regia/HF digestion of the substrate. The authors suggested that this new substrate fashioned from a waste material could have uses as a particle-size-selective scavenger.

2.2 Reference materials and calibrants

Provision of new analytical data for existing *reference materials* is most welcome. The lack of suitable RMs with certified ^{129}I activity data has hindered environmental measurement programmes that monitor I_2 released from nuclear facilities. Work undertaken by Olson *et al.*[20] in providing new data for NIST RM 8704 (Buffalo River sediment) and SRM 2710a (Montana soil) and IAEA CRMs SL-1 (lake sediment) and 385 (Irish Sea sediment) was therefore timely. Small but subtle variations in the isotopic composition of elements such as Cu, Pb and Zn in aerosol samples offer potential for tracking the origins and fate of these elements. The publication[21] of new isotopic data for these elements in NIST SRM 2783 (air particulate on filter media) was also timely.

The preparation of suitable and stable *test aerosols* for testing the performance of new air samplers can be challenging. Use of polydisperse test aerosols[22] enabled the size-selective characteristics of new air samplers to be evaluated in a single test run. Previously, multiple challenge tests, each using a monodispersive aerosol to cover a segment of the desired particle-size range, were required. Current aerosol generation systems, such as spark discharge generators, typically produce very high particle-number concentrations, which without dilution are not representative of real-world emissions. There is therefore a need for producing low but stable airborne concentations of nanosized particles that mimic real-world emissions. Monté *et al.*[23] interfaced a piezoelectric droplet generator to a flame atomiser so enabling small but well-defined volumes of metal-containing solutions to be metered into a flame atomiser which, upon vaporisation, generated low but stable number concentrations of metal oxide NPs. The characterisation[24] of a candidate polyvinylpyrrolidone-stabilised palladium NP RM employed complementary SAXS, SEM, sp-ICP-MS and XRD techniques to provide useful size and compositional information.

New candidate *filter-based (thin layer) XRFS calibrants*, produced[25] by a desolvating nebuliser, had low elemental loadings and so mimicked real-world air filter samples. These calibrants are required because current commercially available filters have much higher and atypical elemental loadings. Their suitability as potential calibrants was confirmed in a follow-up interlaboratory study[26] involving eight international institutes that used EDXRFS and ICP-MS. The characterisation[27] of new thin-layer RMs intended for material testing purposes successfully used SR-XRFS to quantify mass depositions in the ng cm^{-2} range. In the future, such SR techniques will be most useful for characterising filter-based calibrants.

The isotopic analysis of *trace atmospheric gases* by IRMS is useful for understanding their origins and pathways and in recent years the complementary use of FTIR instruments for measuring greenhouse gases such as CH_4 and CO_2 has gained traction. Calibrant gases for IRMS are certified for data such as CO_2 amount, $\delta^{13}C$ and $\delta^{18}C$ but optical analysers determine individual amounts of isotopologues such as $^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$ and $^{16}O^{12}C^{18}O$. Griffith *et al.*[28] set out a practical guide for converting between the two equivalent descriptors and to derive isotope-specific calibrations for optical analysers. The WMO GAW sets stringent requirements for certified CO_2 gas standards. Gas cylinders constructed in aluminium were proven[29] to be suitable for storing ambient CO_2-in-dry-air mixtures provided that they were not used at low pressures (<20 bar) because losses to cylinder walls then became significant. The precision (0.001‰ for the 45/44 and 46/44 ion signal ratios) of a dual-inlet IRMS system made it possible[30] to generate data for CO_2 gas samples stored in cylinders for potential use as RMs. In an international comparison exercise[31], a new value of 7.12 ± 0.06 ppt for the ^{3}He mixing ratio in an air standard was 1-2% lower than values previously determined but remained statistically consistent.

2.3 Sample preparation

Continuous flow analysis (CFA) is used in the analysis of polar ice core samples but is less suited for core samples with higher particle loadings which can prove troublesome for microfluidic systems. This can occur with core samples collected in non-polar regions where airborne pollution concentrations are higher. In a timely review[32] (70 references), developments in CFA were discussed. Tools for preparing ice core segments were also described and suggestions for new sample handling protocols for the labelling, packing and stacking of samples presented.

The improvement of extraction, preconcentration and separation methods is a goal pursued by many researchers. A new semi-automatic apparatus[33] enabled samples for the determination of ^{14}C to be processed in <30 minutes with a CO_2-to-graphite conversion efficiency of *ca*. 75% and an instrumental blank of *ca.* 1.2 pM C. An improved method[34] for liberating ^{129}I from aerosol samples involved high temperature pyrolysis and AgI-AgCl coprecipitation. Recoveries were *ca.* 82%. The calculated LOD of 1.3×10^4 atoms m^{-3} was a 3-fold improvement over that achievable using conventional alkaline-ashing and solvent extraction. Radiocarbon studies are useful in distinguishing between fossil and non-fossil sources of airborne carbonaceous particles. Hydropyrolysis (550 °C; 15 MPa H_2) liberated[35] elemental C effectively from aerosol samples so ensuring that ^{14}C measurements were free from matrix effects. In the analysis of swab samples used in nuclear safeguarding, a procedure[36] involving Eichrom TEVA® and UTEVA® cartridges made it possible to separate fg amounts of Pu and U species for MC-ICP-MS analysis.

A simulant lung fluid, Gamble's solution, was used[37] in a *bioacessibility* assessment of PGEs in inhaled road dust. The mean PGE values in inhalable-sized dust samples as determined by INAA following preconcentration using a NiS_2 fire assay were 152, 152 and 21 µg kg^{-1} for Pd, Pt and Rh, respectively. The corresponding bioavailability fractions were 3.4, 16 and 14%, respectively. In another study[38], up to 77% of the Pb in airborne particulate matter was found to be soluble in gastric juice or lung fluid simultants suggesting that prolonged inhalation could pose a health risk. Initially, portions of air filter samples were analysed by SS-ETV-ICP-AES to determine total concentrations of As, Cd, Cr, Cu, Mn, Ni, Pb, Sr, V and Zn. Subsequently, other portions were extracted in saliva, gastric juice or lung fluid simultants to derive bioaccessibility values. A concern[39] that functional groups on the surface of quartz or PTFE filter fibres could perturb the bioaccessiblity fractions of metals in collected particles proved unfounded.

In a modification[40] of a method for the *fractionation of Ni species* in workplace air samples, commercially available disposable DigiFilters® were successfully employed to perform a four-stage sequential leach procedure (the well-established Zatka procedure).

The use of EDTA as a chelator in the *speciation* of Sb^{III} and Sb^{V} in $PM_{2.5}$ improved[41] extraction efficiencies as well as species stabilities. The method LOQs were 0.10 and 0.06 ng m^{-3} for the Sb^{III} and Sb^{V} species, respectively, when HPLC-ICP-MS was used. These two species accounted for 60% of the certified Sb content in NIST SRM 1648a (urban particulate matter). Of the total Sb extracted from urban air $PM_{2.5}$ samples, 69-87% was as Sb^{V}.

2.4 Instrumental analysis

2.4.1 Atomic absorption and emission spectrometries

A prototype *high-resolution laser-absorption spectroscopic instrument* was developed[42] as a potential absolute primary technique for measurements of Hg^0 concentrations and isotopic composition. The measurement of isotopically resolved spectra arising from absorption transitions of Hg^0 was proposed as an SI-traceable alternative to ID-CV-ICP-MS because it was rapid and accurate and had the potential for measuring Hg over wider dynamic ranges. The estimated LOQ using a 1 m single-pass absorption cell was *ca.* 0.1 µg m^{-3} but it was envisaged that, by using an instrument with a longer path length, measurements in the ng m^{-3} range would be possible. This would make the system suitable for measurements on ambient air.

A prototype *aerosol LIBS system*[43] detected every particle when challenged by 200 nm-sized $CaCl_2$ test particles at a concentration of *ca.* 4000 particles cm^{-3}. The aim was to develop a diagnostic system for the real-time monitoring of particles generated during a semiconductor manufacturing process because product quality can be compromised by airborne contaminants. The generation of electricity from renewable fuels such as biomass is growing but feedstocks containing high concentrations of alkali chlorides and sulfates can cause corrosion within power plants. There is therefore a need for new real-time diagnostic capabilities in process monitoring. The analytical performance of conventional LIBS measurements was significantly improved[44] by introducing microwave radiation to the laser-induced plasma. Linearity was enhanced and the LODs were improved up to 60-fold to 16, 19 and 10 ppb for Ca, K and Na, respectively.

2.4.2 Mass spectrometry

2.4.2.1 Inductively coupled plasma mass spectrometry. *Novel ICP-MS systems* included a RDD-SMPS-ICP-MS system[45, 46] for the simultaneous on-line sizing and elemental analysis of combustion-generated nanomaterials. In the first paper, a calibration strategy involving TGA for generating calibrant $ZnCl_2$ NPs was presented. The measured loss in weight correlated linearly ($R^2 = 0.9985$) with averaged Zn intensities measured by ICP-MS. The system LOD was *ca*. 32 ng cm^{-3}. In the second paper, this new system was further evaluated using simulant metal oxide aerosols (CdO, CuO, PbO and ZnO) and used to explore the kinetics of ZnO NPs released from the burning of Zn-impregnated wood samples. A fast quantitative method[47] for ascertaining the dimensions of metal nanorods was realised by coupling a differential mobility analyser to a sp-ICP-MS system. Several gold nanorod RMs with different dimensions (11.8-38.2 nm, aspect ratios 1.8-6.9) were used for method validation. Performance was comparable to that obtained by TEM. A system employing a particle-into-liquid sampler collected[48] airborne particles in a flowing water rinse that was introduced on-line into the plasma of an ICP-MS instrument. Highly time-resolved measurements (*ca.* 10 minutes) could be performed and transient pollution episodes monitored.

There is ongoing interest in the potential of *sp-ICP-MS.* A wide-ranging tutorial review[49] (231 references) on the use of ICP-MS for analysis at the nanoscale presented the relative merits of this technique and others such as LA-ICP-MS and FFF-ICP-MS. Three sample introduction systems evaluated[50] for sp-ICP-MS applications were a HEN, a total consumption nebuliser and a more conventional concentric-cyclonic spray chamber combination. The HEN was preferred because smaller particles at lower particle number-concentrations could be detected.

A revised *LA-ICP-MS* protocol[51] for the elemental analysis of size-segregated particles employed a glycerol coating to fix particles once they had impacted on a sample collection plate. This minimised any subsequent loss during the ablation process. Quantification was achieved by ablating dried-spot calibrants prepared from aqueous standard solutions. The LODs were 0.01-0.1 ng m^{-3}. The potential of a TOF system to acquire data from short duration events such as LA was demonstrated[52] in the isotopic analysis of μm-sized U RM particles deposited on carbon discs. Precisions (<0.4%) for measurements of the $^{235}U/^{238}U$ ratio better than those achievable by

LA-MC-ICP-MS could be obtained when due care was taken in correcting for peak tailing of ^{238}U and by working within the linear ranges of the detector.

2.4.2.2 Other mass spectrometry techniques. A study[53] to ascertain whether use of fs lasers rather than the currently used ns lasers could be of benefit in *single-particle aerosol mass spectrometry* produced mixed results. It was thought that the use of fs lasers with their higher power-density would result in a more complete ionisation of particles and so improve compositional analysis. An increase in ion intensities was indeed noted but the spectral complexity also increased due to formation of new ion fragments and clusters. This hindered data interpretation and, with an inability to ionise completely the more refractory particles that remained, the authors suggested that further work was needed. A combination of spectra obtained by fuzzy classification, laboratory-generated reference spectra, marker peaks and peak ratios improved[54] the identification by SPAMS of single particles sampled at a rural location. Quantification was then attempted using particle DE factors, generated from the laboratory analysis of known test aerosols, to determine a total particle mass. Although there were uncertainties with this quantification approach, such as the reliability of derived DE factors and the underlying assumptions made about particle shape and density, the total particle mass determined was in good agreement with the total mass determinations made by aerosol MS. The feasibility of using a machine-learning approach to classify aerosol types from data generated by SPAMS was explored[55]. The classification accuracy was *ca.* 87% when this approach was applied to data representative of species such as SOA, minerals, soil dusts and biological aerosols.

Organosulfur compounds are important components of SOAs but there have been difficulties in interpreting their mass spectra when analysed by *aerosol mass spectrometry.* Close examination of the mass fragmentation patterns of organosulfur compounds and inorganic sulfates made it possible[56] to deconvolute the total sulfate signal into inorganic and organic components. It was demonstrated that 4% of measured sulfate in aerosols from Southeastern USA was organosulfur. This was considered not to be a negligible proportion. The authors suggested that other aerosol MS datasets should be examined using this approach so that a better global estimation could be derived. A collection efficiency factor is required in aerosol MS studies to account for loss of particles due to bounce within the inlet and vapourisation units. A new sample introduction system, designed to minimise such losses, shifted[57] fragmentation patterns to smaller molecular ion masses compared to those obtained using the original sample inlet. These shifts were attributed to increased thermal decomposition effects arising from an increase in the residence time of particles within the new inlet and hence more collisions with hot surfaces. To aid others in the aerosol MS community contemplating using this new system, the authors usefully made available a web-based database of mass spectral data generated with the new inlet. Whereas the elemental analysis of extracts of organic aerosols typically requires mg quantities of sample, a new approach[58] required only µg quantities. An USN enabled µL quantities of extracts from air filter samples to be aerosolised as droplets in the 100-300 nm size range. This provided sufficient sample mass for reliable measurements by aerosol MS, even with a transport efficiency as low as 0.1%.

The doubly substituted isotopologues of atmospheric O_2 are potentially useful as tracers for studying O_3 chemistry. The use of a new *isotope ratio* method[59] at medium mass resolution ($M/\Delta M = 10000$) enabled isotopic measurements free from interferences to be made. Complementary techniques were used in tandem to provide a better understanding of carbonaceous aerosols. In an interesting study[60], the OM in size-segregated particles was thermally desorbed at temperatures between 100 and 350 °C. The OM desorbed at <200 °C was classified as less-refractory C and that desorbed at >200 °C as more-refractory C. Liberated volatile compounds were analysed by IRMS and by PTR-MS. Fossil-fuel burning was the dominant source of less-refractory OM in the smallest particles examined (D_{50} <0.18 µm) whereas biomass burning was the dominant source of the more-refractory OM in the larger particle size ranges ($0.32 < D_{50} < 1$ µm).

Other mass spectrometry developments included refinements to an airborne HR-TOF-CIMS system[61] which enabled a better discrimination of nocturnal but reactive nitrogen oxide species to be made. A new method[62] for the size-resolved chemical analysis of nanoaerosol particles used a TD-differential mobility analyser in conjunction with CIMS. An IR TD DART approach was used[63] to determine both non-volatile inorganic and organic components of particulate residues of explosives collected as surface swab samples. A revised procedure[64] for the simultaneous measurement of Pu and U isotopes in individual radioactive particles used SEM in conjunction with a new large-geometry SIMS-based scanning ion-imaging method.

2.4.3 X-ray spectrometry

In an assessment of the effect of biomass burning activities on air quality in Beijing, an Xact 625® *in-situ XRFS* system was deployed[65] to determine K and other metals in aerosol samples at high time resolution. A co-located IC system was used to determine water soluble ionic K^+, a useful elemental marker for emissions from burning. Using the K/Ca ratio as a marker of particle emissions derived from the resuspension of crustal dust, the K/Pb ratio to represent aerosols derived from coal combustion and the K/K^+ ratio derived from measurements from the two instruments, it was calculated that *ca.* 50% of autumnal $PM_{2.5}$ pollution was indeed derived from biomass burning. The contribution from biomass burning would have been overestimated if K alone were used as marker because coal burning was also a major source of this element.

A short overview article illustrated[66] how *TXRFS* could be used for the analysis of small airborne particles. It also described an application for assessing the release of silver NPs from fabrics. In a new sampling method[67], Hg^0 was sampled passively from workplace air directly onto silver-NP-coated TXRFS quartz reflectors. The use of quartz reflectors as impaction plates to collect size-segregated particles directly has been proposed[13] and further details can be found in section 2.1.

The use of *synchrotron-based* X-ray techniques for the analysis of radioactive particles released from the Fukushima Daiichi nuclear power plant incident was comprehensively reviewed[68] (66 references). The XAS data[69] from the analysis of $PM_{2.5}$ emitted from the combustion of residual oil identified a dominant $ZnSO_4.7H_2O$ species. The authors suggested that this speciation detail was valuable for source apportionment and health effect studies and for establishing a connection between the two. Hair samples are often used to assess exposure to certain metals. Both μSR-XRFS and XANES were used[70] to map the Pb distribution across and along strands of hair and to identify possible Pb species. Results suggested that Pb binds with cysteine from keratin in the cortex. The dominant Pb species identified were $Pb_3(PO_4)_2$ and Pb bound to cysteine.

2.4.4 Other instrumental techniques

New measurements are providing insights into the highly variable and poorly understood light-absorption properties of *brown carbon* particles. Different types of aerosols containing brown carbon were generated[71] in controlled laboratory combustion-experiments using benzene and toluene as fuels. Volatile species were stripped away from the fume by passing the sample through a thermal denuder and the remaining solid particles were then analysed by LDI-MS. Black carbon components along the brown-black continuum were produced by systematically varying the combustion conditions. The brown carbon progression from light to dark was associated with an increase in molecular size and a decrease in volatility. The molecular composition of brown carbon particles produced by burning of a sage brush material was investigated[72] using solvent extraction and a HPLC system equipped with both PDA and HR MS detectors. Greater than 40% of the solvent-extractable and light-absorbing brown carbon material was composed of compounds such as the PAHs and their derivatives that are semipolar (non-water soluble) in nature. The polar and water-soluble brown carbon compounds accounted for <30% of the light absorption.

Determining *elemental carbon* in emissions from marine diesel engines is challenging as the chemical composition and physical properties of particles can vary and depend on the type of engine, the composition of the fuel and the type of emission controls deployed. For such samples, the EUSAAR2 combustion protocol performed[73] better than the alternative NIOSH 5040 protocol in distinguishing elemental carbon from other carbon forms present in filter samples. In a confirmatory interlaboratory trial, filter samples were sent to three participants, all using the EUSAAR protocol. The between-laboratory RSD was 2-28% with an average of 10%.

Correlations between *black carbon* measurements and elemental C measurements were established[74] by optically scanning air filter samples collected from different locations and then applying the EUSAAR2 combustion protocol. This protocol is mandated in the EN 16909 standard that underpins the EU regulatory measurements of elemental C in ambient air. The rationale behind this work was to ascertain whether a fast and non-destructive optical method for measuring black carbon could be used as an alternative to the slow and destructive reference combustion method. The study confirmed that this was indeed possible but with the caveat that site-specific correlations between the two methods need to be initially established because the chemical composition and physical properties of soot particles (combustion and optical properties) can vary from location to location. In an inter-comparison exercise[75], six different instruments for measuring black carbon were exposed to smoke from the burning of biomass. The deviations between instruments became more substantial with increasing organic content of the emitted particles.

Analysis of air filter samples by *FTIR* can be rapid. Results for NH_4^+ and NO_3^- concentrations in $PM_{2.5}$ measured by ATR-FTIR correlated well[76] with those obtained by a more conventional IC assay that involved a water extraction step. This new assay was considered to be most useful for monitoring transient air pollution episodes given that filter screening took only *ca.* 7 minutes and method sensitivity was not of prime importance. Silicosis is a particularly unpleasant lung disease caused by inhaling crystalline silica dust. A field-portable FTIR method[77] was proposed by NIOSH for the analysis of crystalline silica in dust collected on air filters from mine workers' personal samplers. Since mineralogy varied from mine to mine, interferences from other phases in the measured FTIR spectrum of silica could lead to significantly biased results if left uncorrected. Such corrections involved the detailed XRD examination of these other mineral phases in representative settled dust samples to interpret collected FTIR spectral data better, the use of spectral deconvolution software and the establishment of a location-specific cross-calibration between FTIR measurements and laboratory-based XRD silica measurements (NIOSH method 7500). In this way it was possible to restrict the difference between FTIR measurements and reference laboratory XRD measurements to 2.8%. Although considerable effort may be required to set up this new method at a worksite, on-site FTIR measurements can be rapid so allowing the timely monitoring of miners' exposure. An *in-situ*, real-time compact FTIR system[78] with a hollow waveguide as a miniaturised gas cell was used to measure NO, NO_2 and N_2O concentrations simultaneously. The LODs were 10, 1 and 0.5 ppm for NO, NO_2 and N_2O, respectively. Possible future refinements included the use of preconcentration techniques and/or tunable cascade lasers to increase sensitivity.

3 Water analysis

3.1 Reviews

A short *overview of methods* (59 references) for the analysis of waste waters[79] by atomic spectrometry put the importance of water analysis into context. The authors estimated that half of the global consumption of water (3900 billion m^3 per year) becomes waste water. The Russian Federation alone discharges 52 km^3 of waste water per year into its water bodies and the need to modify Federal standard methods for the analysis of waters is recognised. Suitable sample pre-treatments for most common kinds of atomic spectrometry instrumentation were summarised. In an article on the determination of Se in waters, Kumkrong *et al.*[80] compared the current regulatory levels for drinking water and aquatic environments with the capabilities of standard analytical procedures. They concluded that although there are many ways of achieving improved sensitivity, any method modification had to meet the performance criteria of the standard method by having adequate LOD, LOQ, accuracy and precision. A companion paper[81] by the same research group concentrated on methods to determine Se speciation which is important for assessing the bioavailability of this essential element.

Two papers demonstrated *current analytical performance* for the determination of Hg in drinking waters. A LOD of 0.03 ng L^{-1} could be achieved[82] routinely using a commercially available AFS instrument with a dual amalgamation system. Good comparability between results obtained in three laboratories for Ag, silver NPs and trace elements in a Dutch water channel demonstrated[83] the high accuracy and reproducibility of analytical methods currently in use.

3.2 Certification of reference materials

The *interlaboratory certification* of the new NRCC CRMs NASS-7 (seawater) and CASS-6 (near shore seawater) has been described[84]. At the NRCC itself, column separation was used before determination of Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, U, V and Zn, whereas As and B were determined directly following dilution. All analytes were determined by HR-ICP-MS using double IDA for B, Cd, Cr, Cu, Fe, Mo, Ni, Pb, U and Zn and standard-addition calibration for mono-isotopic As, Co, Mn and V. In addition, all analytes were measured using a standard-addition calibration with ICP-MS/MS to provide a second dataset. Expert laboratories worldwide were asked to provide results using different analytical approaches. As a result, certified reference values and associated uncertainties were assigned to 14 elements. One of the laboratories involved published[85] separately their results obtained using a commercially available automated sample-preparation-system with off-line HR-ICP-MS detection. The results agreed with the consensus values thereby validating the method that was then used to provide values for the IRMM candidate CRM ERM CA-403 (seawater).

A double ID-HR-ICP-MS method[86] was used to determine reference values for Ca, K, Mg and Na in the *candidate drinking water* NRCC CRM AQUA-1. The method was validated by the analysis of the NRCC CRMs SLRS-5 and SLRS-6 (river waters) and the NIST SRM 1640a (natural water).

3.3 Sample preconcentration

The most significant advances in analyte preconcentration for water analysis are summarised in Tables 1 (solid phase extraction) and Table 2 (liquid phase extraction).

[Tables 1 and 2]

3.4 Speciation and nanomaterial analysis.

The *species-specific microextraction* of $AgCl_n^{(n-1)-}$ complexes in seawater[87] was carried out using micro stirbars constructed from polypropylene hollow microfibres filled with a 2.5% *v/v* solution of the ionic liquid trihexyltetradecylphosphonium chloride dissolved in a 1+9 solution of dodecan-1-ol in kerosene. These filled fibres extracted Ag complexes selectively from seawater, even in the presence of DOC concentrations of up to 10 mg L^{-1}, without disturbing the dissolved Ag equilibria in solution. This microextraction technique required only 16 mL of sample instead of the 100 mL required in the past and achieved an LOD of 0.4 ng L^{-1} with ETAAS detection. Both organic and inorganic As species were extracted[88] from lake water using DLLME with methyltrioctylammonium chloride as the complexing agent. By replacing the commonly used chlorinated solvents with octanol as the receiving solvent and methanol as the dispersal solvent, the extract was more compatible with reversed phase HPLC-ICP-MS when using sodium butanesulfonate and malonic acid as ion-pairing agents. Under optimised conditions with ICP-MS detection, the LODs ranged from 1.0 ng L^{-1} for 3-nitro-4-hydroxyphenylarsonic acid after a 40-fold enrichment to 39 ng L^{-1} for 4-aminophenylarsonic acid after a 6-fold enrichment.

A SPE-ICP-MS method for studying the *fractionation of Cu* in riverine, estuarine and seawaters[89] relied on the specific extraction of the target analytes (hydrophobic Cu, Cu^I and Cu^{II}) in the field onto a C_{18} SPE cartridge. Hydrophobic Cu was absorbed on the cartridge unmodified whereas Cu^I was retained as a complex with bathocuproin disulfonate. Partial reduction of Cu^{II} was prevented by addition of the complexing agent EDTA. Finally, the Cu^{II} was retained together with Cu^I after reduction with ascorbic acid. The quoted ICP-MS LOD for Cu of 0.0008 µg kg^{-1} was sufficient for the characterisation of waters from the Tokushima prefecture in Japan.

An existing IC method for *Cr speciation* with colorimetric detection was adapted[90] for use with ICP-MS detection to make it more robust when applied to waste waters containing high levels of other transition metals. The Cr^{III} species were chelated with 2,6-pyridinedicarboxylic acid to prevent redox interconversion and so obtain only one peak for all the Cr^{III} species. In order to reduce the amount of salts entering the plasma, NH_4OH instead of NaOH was used to adjust the pH of the mobile phase. The column length was shortened from 250 to 50 mm so a lower flow rate could be used through the column. The LODs of 0.092 and 0.077 µg L^{-1} for Cr^{III} and Cr^{VI}, respectively, obtained using the ICP-MS in collision mode and monitoring at *m/z* 52, were two orders of magnitude better than those of the colorimetric methods using 1,5-diphenylcarbazide proposed in ISO 11083 and the Japanese JIS K0102 standard methods.

The wider availability of ICP-MS/MS instrumentation means that some *non-metallic elements and their compounds* can now be determined in water samples. In the determination[91] of PFASs, a class of widely used fluorinated compounds, the target compounds were separated by a previously developed RP HPLC procedure. Fluorine was detected as the polyatomic ion

$[^{138}Ba^{19}F]^+$ after post-column addition of Ba to the eluent. To reduce interferences, both quadrupoles were set to *m/z* 157 and O_2 introduced as a reaction gas. The use of ICP-MS as an element-specific detector enabled the detection of some PFASs that are difficult to ionise using an ESI or APCI source and so made it possible to screen waters for unknown or uncharacterised PFASs. The instrumental LOD was 0.5 mg F L^{-1} using perfluorooctanoic acid as the calibrant. By preconcentrating a litre of river water, µg L^{-1} LODs were achievable. A direct HPLC-ICP-MS/MS method[92] was developed for the determination of glyphosate, its breakdown product aminomethylphosphonic acid and other organophosphorus herbicides. All ions with a *m/z* of 31 were reacted with O_2 to shift the P peak to *m/z* 47. The LOD for P of 0.1 µg L^{-1} was 20-fold better than that achievable using single quadrupole ICP-MS with CCT. No derivatisation was needed when the analytes were separated using a Hamilton PRP X-100 anion-exchange column. The higher sensitivity of ICP-MS/MS meant that no preconcentration step was required, making this method faster and more robust than HPLC-ESI-MS/MS methods.

Deficiencies of the US EPA method 1630 (2001) for *methyl mercury in water* by distillation, aqueous ethylation, purge and trap and CV-AFS detection were addressed[93] in an improved distillation method. Use of sodium tetra (n-propyl)borate as derivatising agent meant that EtHg could be determined. As previous studies had shown that addition of $CuSO_4$ can break the CH_3Hg–S bond, thereby releasing organomercury compounds from samples with high sulfide levels, 100 µL of 1% *m/v* $CuSO_4$ was added to the sample to improve the recovery of EtHg in river water from 38 to 86%. Using GC-CV-AFS detection of Hg, recoveries were 85-113% and 80-88% for MeHg and EtHg, respectively. The corresponding MDLs were 0.007 and 0.004 ng L^{-1}. Further work was needed to prevent the methylation of Hg^{2+} in samples with high concentrations of Hg.

The *speciation of Se in water* remains of interest. A rapid (5 minutes) IC-ICP-MS procedure[94] for separating Se^{IV}, Se^{VI}, seleno-DL-methionine and Se-(methyl)selenocysteine hydrochloride involved use of a Dionex AS7 anion-exchange column with dilute HNO_3 as the mobile phase (step gradient from 50 to 400 mM at 2 minutes). Using an ICP-MS instrument with H_2 as the reaction gas, Se was quantified at *m/z* 80 with LODs of 4 and 9 ng L^{-1} for the inorganic species and seleno-DL-methionine, respectively. The method was validated by spike recovery from river water samples and analysis of NIST SRM 1640a (trace elements in natural water) certified for total Se. This study demonstrated that it is possible to obtain acceptable LODs without the need for preconcentration or other sample pretreatment.

Although the determination of *nanoparticles in water* becomes more commonly reported in the literature, much of the research has involved addition of NPs to water samples and then analysis. Emphasis is, however, switching to developing simpler fractionation methods for determining NPs in real samples. In a simplified method for the fractionation of dissolved or nanoparticulate Au in water[95], the Au^{III} ions and gold NPs were selectively extracted onto the surface of Fe_3O_4 magnetic NPs in the presence of different reducing agents. The addition of 1 M $Na_2S_2O_3$ to the sample reduced the dissolved Au^{III} present to the $[Au(S_2O_3)_2]^{3-}$ complex that had no affinity for the magnetic NPs. This resulted in a selective extraction of gold NPs from the sample. For the determination of total Au, 1 M ascorbic acid was added to a second aliquot to slowly reduce the Au^{III} to Au^0, which was also adsorbed onto the surface of the Fe_3O_4 magnetic NPs. The Au-rich Fe_3O_4 NPs were separated from the samples by application of a magnetic field. After removal of the supernatant, the NPs were injected into an ETAAS system for determination of Au. The MDL of 20 ng L^{-1} was independent of the Au form for a 200-fold sample enrichment factor. This method was rapid and did not require elaborate back extraction procedures but unfortunately it did not allow particle sizing to be performed. The release of toxic NPs into aquifers from underground ore sources in Inner Mongolia was studied[96]. The naturally occurring NPs were collected in polyethylene bottles and deposited onto carbon-coated nickel TEM grids before visualisation by high-resolution TEM and analysis by EDXRFS. The most abundant NPs contained Cu, Fe, Pb and Zn. Some samples contained NPs rich in As, Bi, Cr, Mn, Sb and Sn. The As, Pb and Sb concentrations determined by ICP-MS exceeded Chinese drinking water limits, whereas those for Co, Cr, Cu, Mo, Ni and Zn did not. This suggests that ICP-MS screening for the assessment of groundwater quality does not taken into account the hazards posed by the presence of NPs. The authors concluded that NP analysis should also be carried out occasionally during groundwater safety assessments, especially when the presence of ore bodies is suspected.

3.5 Instrumental analysis

3.5.1 Atomic absorption spectrometry

Although *the use of slotted quartz tubes for enhancing AAS detection limits* has been practised since the 1980s, their use is undergoing a renaissance with the invention of H_2-gas-activated release of elements trapped on a quartz surface. In one such method[97], water samples containing Cd were nebulised into an extremely fuel-lean AAS flame for 5 minutes and the Cd atoms trapped in a slotted quartz tube. Release of Cd after the addition of a H_2 gas flow resulted in an enhanced transient signal. The LOD of 0.1 µg L^{-1} was substantially better than that (12 µ L^{-1}) achievable using an AAS instrument fitted with a traditional slotted tube. The same research group demonstrated[98] similar enhancements for the determination of Sb in water samples. Using the quartz tube as an atom trap, an LOD of 0.75 µg L^{-1} was possible with quantitative recoveries of Sb from spiked tap and mineral waters. However, the introduction of hydrogen into a lean air-acetylene flame is a potentially unsafe procedure.

Surface waters from a Brazilian mining area were analysed[99] for *rare earth elements by CS-HR-AAS*. With the instrument in fast sequential mode to maintain sensitivity, a segmented-flow FI sampling system to reduce sample uptake, a nitrous oxide-acetylene flame and KCl as an ionisation buffer in undiluted samples, LODs of 0.004 (Eu) to 0.5 (Tb) µg mL^{-1} could be achieved when 10 REEs were measured in triplicate in 15 mL samples. The results were comparable to those obtained with an ICP-MS instrument.

3.5.2 Vapour generation

Although HG is a well-established technique, it suffers from some well-known drawbacks such as the short shelf life of reagents and the need for disposal of the chemical wastes generated. *Electrochemical hydride generation* has potential for minimising reagent consumption but it suffers from interference effects during electrodeposition of As^{III}. To overcome some of these problems, a gold electrode coated with polyaniline film was proposed[100] to improve electrode mechanical stability, resistance to passivation and efficiency. When AAS was used for As detection, optimum absorbance was obtained with 0.5 M HCl as the supporting electrolyte and a 0.5-0.8 A electrolytic current. Above 0.8 A, excessive H_2 generation at the cathode produced a very noisy signal. Under optimum conditions, the LOD was 2.5 µg L^{-1} for As in water. The method was validated by analysis of the NIST SRM 1643d (trace elements in water) and spiked well water samples and by comparison of the results with those obtained by HG-AAS analysis of the same samples.

The improvement *of photochemical vapour generation* continues, with the vogue seeming to be the addition of metal ions to improve VG efficiency. Zhou *et al.*[101] found that whereas Fe^{3+} in formic acid produced an enhancement for only As^{III}, the use of 30% *v/v* acetic acid spiked with Cd at a final concentration of 20 mg L^{-1} resulted in a 10-fold signal improvement for both As^{III} and As^{V}. With AFS detection, the LOD was 0.05 µg L^{-1}. The method was validated by spike recovery from river waters and comparison of the results with those obtained by ICP-MS analysis of the same waters. The addition of 60 µg mL^{-1} Fe^{3+} to the acetic -formic acid mixture increased[102] greatly the reaction kinetics and efficiency of VG of $(CH_3)_3Bi$ from Bi^{3+} present in solution. With ICP-MS detection, the sensitivity was improved 30 times compared to that for solution nebulisation and resulted in a LOD of 0.3 ng L^{-1}. Accuracy was demonstrated by quantitative spike recoveries from tap, lake and river waters. Molybdenum VG was improved[103] up to 15 times by the addition of Co^{2+} and Cu^{2+} ions to a 20% *v/v* formic acid solution and resulted in an ICP-MS LOD of 6 ng L^{-1}. Soukal *et al.*[104] found that the addition of mg L^{-1} concentrations of Fe^{3+} improved the VG of Mo from a 30-50% (*w/v*) formic acid reaction medium; the ICP-MS LOD was 1.2 ng L^{-1}.

The *use of vapour generation for improving the detection limits* of lower cost detectors is common. When HG was employed[105] with LIFS in the determination Ge in water, use of 2 M H_3PO_4 instead of HCl as the acid carrier made the method more sensitive and less dependent on the acid concentration. With 0.5% m/v $NaBH_4$ as the reductant, laser excitation at 253.323 nm and fluorescence measurement at 303.907 nm, the LOD was 0.1 ng mL^{-1}. Quantitative recoveries were obtained for a 20 ng mL^{-1} spike in NIST SRM 1643e (trace elements in water) for which there is no certified Ge concentration. The MIP-AES LOD for Ni was improved[106] by using 70% *m/v* formic acid as carrier and diluent solution to generate volatile $Ni(CO)_4$. The LOD of 0.3 µg L^{-1} was 80-fold better than that obtained using conventional nebulisation. Results for the Chinese CRM (BMEMC) GBW(E)080405 (natural water) agreed with the certified values.

The accurate *determination of mercury* in many liquids (groundwater, hydrothermal fluids and acid mine drainage) can be limited because the high levels of H_2S present can poison the gold traps used to preconcentrate Hg prior to CV-AFS analysis. This problem was resolved[16] by using a series of impingers. The first contained an alkaline trap with $NaBH_4$ to convert H_2S to the S^{2-} ion which did not then react with the $KMnO_4$ solution used to trap Hg in the following two impingers. The ability to trap 98% of the volatile Hg present in a 25 L sample in a few mL of $KMnO_4$ was a big advantage for field work as only the trapping solution and not 25 L of sample needed to be transferred to the laboratory. Determination of Hg speciation in oil production waters was simplified[107] by using a UV reactor instead of more complex extraction procedures. After cold VG with $SnCl_2$, inorganic Hg was detected by a "portable" long-path-length Zeeman AAS instrument. The total Hg concentration was then determined using the same method after UV photoreduction of the sample. The CH_3Hg^+ concentration was reported as the difference between total and inorganic concentrations. The LOQ was 12 ng L^{-1}. Results compared well with those obtained using the standard GC-CV-AFS method. The authors concluded that the portability of the instrumentation coupled with the reduced complexity of the sample preparation meant that this method could easily be employed on oil production platforms.

3.5.3 Inductively coupled plasma atomic emission spectrometry

The joys of *heating various parts of the instrumentation* have been rediscovered. Heating the spray chamber resulted[108] in a 10-fold improvement in LODs. Heating a pre-evaporation tube between the torch and a multimode sample introduction system (a spray chamber that can also be used for HG) improved[109] sensitivities for some elements in both axial and radial viewing modes but improvements in LODs were less marked suggesting that background levels had also increased.

The *severity of possible matrix effects* has been assessed[110] during the analytical run by applying a PCA-based machine-learning algorithm to background signals from nine species of Ar, H and O that occur in a plasma. When applied to the determination of Cd, Co, Cr and Pb in seawater, this procedure could be used to identify when an external calibration was not applicable. This proof-of-concept was designed to inform decisions on calibration strategies for complex matrices and so could also be applied to other matrices. It was perhaps unsurprising that the best results were obtained when seawater was diluted at least 10 times before analysis. This algorithm should help inexperienced operators improve their results whilst learning the limits of their instrumentation. It remains to be seen if the human operator or instrument will learn first.

3.5.4 Inductively coupled plasma mass spectrometry

3.5.4.1 ***Total elemental concentrations by ICP-MS.*** Tables 1 and 2 testify to the fact that many researchers use microcolumns or other *preconcentration techniques* to improve LODs. No matrix removal occurs during freeze drying which can be used if precautions are taken to correct for matrix effects that can occur even in relatively clean waters. Using IDA with freeze drying preconcentration and ICP-MS with CCT, workers based in Japan quantified[111] 52 elements in tap water, groundwater and the NRCC CRM SLRS-5 (river water). Freeze drying reduced sample volume from 50 to 1 mL. The samples were then thawed, split into aliquots and acidified with various reagents to prevent elemental losses or coprecipitation of insoluble residues. Results agreed well with the certified values of the CRM and with results obtained by analysis without preconcentration. The need to be aware that freeze drying can introduce contamination was demonstrated by the fact that the method LODs of 0.0009 (In) to 89 pg g^{-1} (K) were heavily dependent on the blank concentrations for some elements. Not surprisingly, no data for the volatile elements Hg and Os could be presented as they were lost during the freeze-drying process.

Two *fully automated sample introduction systems* are available commercially for use with ICP-MS. One system[112]used a proprietary low-pressure anion-exchange column in the determination of total metal concentrations in waters (and other matrices) and Cr speciation. The LOD of 0.007 µg L^{-1} for Cr^{VI} was considerably better than the 0.3 µg L^{-1} achievable using HPLC-ICP-MS. The other system[113] was specific for trace elements in seawater and has been available for longer. Extensive testing over several years has shown it to be suitable for trace element analysis in Southern Ocean samples. The preconcentration factors were 10 for rain water or sea ice, 40 for typical seawater and 70 for remote open ocean seawater (Southern Ocean). Quality control used in-house RMs and the NRCC CRM NASS 6 (seawater). Recoveries for most elements were >98% but those for Ga and Ti were only 70 and 80%, respectively.

The *determination of non-metals* continues to be of interest. In the ICP-MS/MS determination of total P concentrations in river, lake, rain and seawaters[114], all ions with *m/z* 31 selected in the first quadrupole were reacted with a 2.5 mL min^{-1} flow of O_2 to convert P^+ ions to PO^+ ions for detection in the second quadrupole at *m/z* 47. By shifting the mass of P away from the interfering ions $^{15}N^{16}O^+$, $^{14}N^{16}O^1H^+$ and $^{12}C^{18}O^1H^+$, the BEC dropped to 0.2 µg L^{-1} from the 4.7 µg L^{-1} obtained without the shift. The corresponding LOD was 8 ng L^{-1}. The method was faster, more sensitive and less prone to interference from DOM than the existing US EPA colorimetric method. A new method for the determination of Br and I in saline waters used[115] a cation-exchange resin to remove matrix interferences such as those arising from calcium, magnesium, potassium and sodium. The reduced requirement to dilute samples led to improved MDLs. Isobaric interferences (*e.g.*$^{40}Ar^{39}K$ and $^{40}Ar^{38}Ar^1H$) were removed by KED in the collision cell. Following matrix removal, procedural blanks were 0.78 and 0.02 µg L^{-1} for Br and I, respectively, and the corresponding LODs were 0.11 and 0.001 µg L^{-1}. Accuracy was confirmed by quantitative spike recoveries from lake and salt lake waters, oil field water and the NRCC CRM CASS 5 (near shore seawater).

Trace element concentrations of *microplastics* recovered from surface waters and waters collected from beaches were determined[116] by ICP-MS and a mercury analyser based on AAS. The plastic pellets (*ca.* 0.1 g) were digested using mixtures of HF-HNO_3 and HNO_3-HCl. The Ba, Ce, Cr, Ni, Pb, Rb, Sr and Zr concentrations were higher in degraded white plastics than in new white plastics and Hg concentrations highest in secondary microplastics produced by weathering of plastic debris. The authors confirmed that the surface degradation of microplastics supported adsorption of metals and so trace elements could accumulate and be transported over long distances.

3.5.4.2 ***Single particle ICP-MS.*** Work continues to improve *the applicability of sp-ICP-MS to real samples* as many studies in the past have been on artificial samples. The performance of sp-ICP-MS for analysis of soluble ZnO NPs has been improved[117] by cleaning the samples on a Chelex 100 resin column. This successfully lowered the dissolved-metal background and increased the S/N by a factor of 5. Without the column, nearly 82% of the NPs in the sample was masked by the dissolved-Zn background signal. As a consequence, the size LOD was improved from 53 to 8 nm. Losses of NPs on the column were <10%. It was reported that in real samples "most of detected Zn-containing particles were actually larger colloidal particles (up to ~µm), with a relatively small proportion of Zn". Some matrix effects during the mass quantification of NPs in complex matrices were corrected[118] by introducing Au- and Cs-containing microdroplets into the sample aerosol stream after the spray chamber. As the metal concentrations in the droplets and the relative size and masses of the droplets were known, the procedure effectively added an IS. Addition before and after sample acquisition made it possible to correct for acid-matrix effects and space-charge effects caused by single-element matrices and high-salt matrices. However, correction for matrix effects caused by the composition of the NPs themselves (particle-related matrix effects) could not be made. It was thought that metal-containing microdroplets could be used as matrix-independent mass calibrants for NPs.

Researchers are starting to use *sp-ICP-MS as a routine tool* for investigating the sources and fate of NPs in waters. The distribution of corrosion-related NPs in tap water was studied[119] in 50 samples from three separate buildings. Particles containing Fe, Pb and Sn had mean concentrations of 88, 1.2 and 1.8 ng L^{-1}, representing 15, 0.4 and 10% of the total concentrations, respectively. No silver or titanium NPs were detected in any of the samples. In order to analyse Cu-containing NPs successfully, the sample introduction system had to be modified to reduce the interaction of copper complexes with the uptake tubing. Best results were obtained in free aspiration mode as the background signal was reduced from 6000 to 4000 cps. Under these conditions, Cu particles were detected in half of the samples with a mean concentration of 69 (range 15-136) ng L^{-1}. The authors ascribed these values to the fact that although the building was certified to have a low water consumption, the pipes had a normal bore size so water was in contact with the pipes for longer and consequently Cu levels increased. They concluded that metal particles should be studied in drinking water as they may represent a significant fraction of the total element concentrations. Isotopically labelled NP tracers were proposed[120] for studying the fate, behaviour and toxicity of NPs in aquatic matrices. Quantum dots isotopically labelled with ^{111}Cd, ^{77}Se and ^{68}ZnS were added to samples of river, estuarine and seawaters. In ultrapure water and dilute HNO_3, the LOQs for the analytes in the quantum dots were lower than those for dissolved elements. The LOQs in real samples were between 10- (Zn) and 250-fold (Se) higher due to the natural presence of these elements in the samples. Despite this, the authors considered these limits to be within the range of expected environmental concentrations. They concluded that as LOQs can be estimated from the background elemental concentrations in a given water body, tracers could be added at environmentally relevant concentrations.

3.5.4.3 ***Isotope analysis by ICP-MS.*** *A novel approach to isotope dilution analysis*[121] could be applied to mono-isotopic elements. Using Y as a model element, isotopically labelled O_2 gas was introduced into a reaction cell to generate the molecular ions $^{89}Y^{16}O$ and $^{89}Y^{18}O$. Silver was added as a third, multi-isotopic element, to correct for mass bias and instrumental fluctuations as the isotope at *m/z* 105 had the same nominal mass as $^{89}Y^{16}O^+$. The Y concentration was then calculated from the intensity ratios measured at *m/z* 105 and 107 and the mass abundances of ^{16}O, ^{18}O and ^{107}Ag. Analysis of the JSAC CRM 0302-3C (river water) (not certified for Y) using the gas IDA method gave a value of 0.00415 ± 0.00003 ng g^{-1} which agreed well with values obtained by conventional ICP-MS analysis.

The main focus of the isotopic analysis of water samples as reported in the literature remains the *determination of stable isotope ratios* in seawater. Janssen *et al.*[122] generated Hg^0 from a 250 mL sample and subsequently trapped it on a gold bead. The mercury was then thermally desorbed and trapped in 2 mL of a mixed HNO_3-BrCl (3+1) trapping solution for analysis by CV-MC-ICP-MS. Sample throughput for the determination of $\delta^{202}Hg$ in seawater was increased threefold in comparison to a previously used preconcentration and separation method. The $^{53}Cr/^{52}Cr$ isotope ratio in Pacific Ocean water was measured[123] after the conversion of all the Cr present in acidified samples to Cr^{III}. The Cr was then preconcentrated using $Mg(OH)_2$ coprecipitation and separated from the matrix using a series of Biorad AG 1-X8 SAX columns prior to MC-ICP-MS analysis. It was possible to obtain a full water-column Cr-isotope-ratio profile, at a Pacific station, for the first time. The authors considered that slight adjustments to the method would allow redox species-specific isotope ratios to be obtained.

3.5.5 X-ray fluorescence spectrometry

A review on the use of *TXRFS for the analysis of waters*[124] (20 references), assessed improvements arising from the use of low-angle XRF viewing and considered sorption and microextraction processes that are compatible with this instrumentation. A multivariate calibration strategy was designed[125] to eliminate matrix effects during the determination of Al, As, Cd, Co, Hg, K, Ni and Pb in natural waters. The linear range was 0.05-2.00 mg L^{-1} and recoveries from spiked samples were quantitative.

Portable XRF instrumentation for in situ measurements has received a lot of attention this year. By passing 50 mL of water adjusted to pH 4 through a Ti-loaded SAX disk using a plastic syringe in the field, it was possible[126] to preconcentrate As^{III}, As^{V}, Cr^{VI}, Se^{IV} and Se^{VI} sufficiently to make them detectable by a pXRF instrument. The LODs were 1 µg L^{-1} for all the analytes. Results for the SCP Science EnviroMAT RMs EP-L (drinking water) and ES-L (ground water) agreed well with the reported values and results for spiked mineral waters agreed with those obtained by ICP-AES. No preconcentration was necessary for the elemental analysis of metal-laden waters from mine tailings[127]. A total of 390 samples was analysed for Ca, Cu, Fe, K, Mn, Pb and Zn by pXRFS in the field and by ICP-AES in the laboratory. The two instruments showed near perfect agreement when using the XRF instrument in multiple-stacked-beams acquisition mode; poorer correlation was obtained with single-beam acquisition. This demonstrated the need to calibrate the instrument specifically for water samples. By waterproofing a portable instrument with an X-ray-transparent film, it was possible[128] to immerse the instrument fully in water. Exploitation of the full X-ray penetration depth in water resulted in LODs of 21 and 28 ppm for Cu and Pb, respectively.

4 Analysis of soils, plants and related materials

4.1 Review papers

Reviews on *speciation of specific elements* included that by Hellmann *et al.*[129] which provided a useful overview (230 references) of analytical methods for speciation of Hg in sediments. Sample storage and pretreatment, CRMs and QC, species extraction, pre-concentration, separation and detection were all covered. AlChoubassi *et al.*[130] (52 references) described advances in methods for Fe speciation in plants and noted the growing popularity of HPLC separation followed by dual ICP-MS and ESI-MS detection. Seby and Vacchina[131] (161 references) included soils in their review of approaches for the determination of Cr^{VI} in environmental, industrial and food samples. Comments on analytical methodology were included in reviews focussed on ^{90}Sr in the environment[132] (122 references) and on the redox chemistry of V in soils and sediments[133] (140 references).

A comprehensive review[134] (199 references) of *recent advances in LIBS and XRF analysis of plants* concluded that a combination of the two techniques represented a promising approach for routine crop nutrition diagnostics.

4.2 Reference materials

In *the development of new CRMs*, BMEMC GBW 07481 (Arctic marine sediment) was certified[135] for 68 elements and components following characterisation by nine Chinese laboratories. Seven new candidate CRMs relevant to analyses undertaken in Saudi Arabia[136] were agricultural soil, industrial soil, urban street dust, sediment, dates, date palm leaves and fish.

Supplementary information on the isotopic composition of commercially available CRMs has been provided. As the IAEA CRM 375 (Chernobyl soil) is no longer available, ^{129}I activities and ^{129}I/^{131}I isotope ratios were determined[20] in NIST SRMs 8704 (Buffalo River sediment) and 2710a (Montana soil), and IAEA CRMs SL-1 (lake sediment) and 385 (Irish Sea sediment) using AMS and TIMS. High precision Cd isotope ratios were obtained[137] for soil, sediment and manganese module RMs by MC-ICP-MS using both SSB and double-spike mass-bias-correction methods. Separation of Cd from matrix components (>97.8% recovery) using AG MP-1M strong anion-exchange resin eliminated possible spectral interference from Sn.

4.3 Sample preparation

4.3.1 Sample dissolution and extraction

A comparison of *methods for extracting Ca, K and Mg from soil and plant samples* included[138] various dry ashing, acid digestion and MAE procedures. Analyte recoveries for three soil and one plant CRM were determined by FAAS and the insoluble residues characterised using XRD and SEM-EDS. As would be expected, extraction efficiencies varied markedly between analytes, methods and substrates. Recoveries as low as 15% were obtained for soil K when there was no HF in the extractant.

Two *low-temperature fusion methods for the determination of Pu in soil and sediment* by SF-ICP-MS were proposed[139] for applications in nuclear emergencies. The use of NH_4HSO_4 (melting point 147 °C) or NH_4HF_2 (melting point 125 °C) as flux meant a hot plate could be used instead of a furnace and as a result the procedures could be performed in just 30 minutes.

Acid dissolution and extraction methods for specific elements in soil and sediment included a procedure[140] for the determination of B. If Rh was used as IS, digestion (30 minutes, 190 °C) with HNO_3–HF (1+1) in a PTFE-lined stainless-steel bomb followed by dilution in ammonia to mitigate memory effects and avoid corrosion of the ICP-MS sample introduction system gave complete recovery of B from three CRMs. In a similar method[141], for the determination of Br and I, digestion for only 15 minutes at 140 °C was required. The IS in this study was Te. Extraction in high-purity 5% *v/v* ammonia solution in closed PTFE bombs for 6 h at 190 °C was recommended[142] for the determination of I in soils and sediments by ICP-MS. An article[143] in Japanese with English abstract described the removal of the REEs Gd, Nd and Sm from soil samples by cation-exchange so that As and Se could be determined free of doubly charged REE-ion interferences.

With the aim of complying with the principles of green analytical chemistry, a *MAE method for sediments* used[144] only dilute (1M) H_2O_2 and just 400 µL of *aqua regia* per 0.2 g of sample. Extraction was performed at 180 °C for 30 minutes. Recoveries from the CRMs LGC 6187 (river sediment) and RTC CRM 015-050 (freshwater sediment) were 80-124% for Ba, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn.

Methods proposed for *speciation analysis in soil and sediments by HPLC-ICP-MS* reflected an increased awareness of the need to avoid or correct for species interconversion during extraction. An MAE procedure for As used[145] 0.3 M $(NH_4)_2HPO_4$ and 50 mM EDTA to achieve baseline separation of As^{III}, As^{V}, MMA and DMA in 12 minutes without species interconversion. The LODs were 0.03-0.11 ng g^{-1}. In a UAE method for the determination of Cr^{VI} in sediments, 0.4 M $MgCl_2$ was added[146] to 2% NaOH and 3% Na_2CO_3 to prevent Cr^{III} oxidation. Extracts were spiked with enriched $^{50}Cr^{VI}$ and $^{53}Cr^{III}$ to investigate possible species interconversion. The method LOD for Cr^{VI} was 1.25 µg kg^{-1} when using ID-HPLC-ICP-MS. Good agreement was obtained between measured (129 ± 6 mg kg^{-1}) and certified (130 ± 2.31 mg kg^{-1}) values for RTC CRM 041 (chromium (VI) in soil). An alkaline solution of 10% *v/v* NH_4OH at 150 °C for 3 h was used[147] to extract readily mobilisable I species from soils. Transformation between IO_3^- and I^- was decreased by adding 0.5 mM EDTA before extraction. The LODs were 0.03 and 0.025 µg g^{-1} for IO_3^- and I^-, respectively. Spike recoveries ranged from 85 to 115%.

A *non-chromatographic speciation procedure* used[148] samples spiked with inorganic Hg and MeHg for selective extraction of MeHg from heavily contaminated soils for determination by CVG-ICP-MS. An UAE in 5% *v/v* HNO_3 maximised recovery of the organic species with minimal co-extraction of inorganic forms. Any inorganic Hg in the extract was precipitated as

HgS by addition of 0.35 M $(NH_4)_2S$ prior to CVG using 1% (*m/v*) $NaBH_4$. Results for RMs IRMM ERM CC580 (estuarine sediment) and Sigma-Aldrich SQC 1238 (methylmercury in sediment) were in agreement with certified values. Selective determination of TBT in sediment in the presence of MBT, DBT and inorganic Sn was achieved[149] by use of 0.1 M EDTA and 0.5% *w/v* DPC as masking agents to prevent ethylation of the non-target species. EthylTBT was then sorbed onto a SPME fibre for TD and MIP-AES detection.

A protocol for *preconcentration of Hg from sediment digests and water samples for isotopic analysis by MC-ICP-MS* involved[122] Hg reduction, gold trap amalgamation, rapid (40 minute) TD and chemical trapping in just 2 mL of an oxidising 40% (3:1 HNO_3+BrCl) aqueous solution. The method tripled sample throughput relative to that of traditional procedures and allowed isotopic analysis to be performed in samples containing lower concentrations of Hg without compromising accuracy or precision.

The need for improved (and ultimately harmonised) *analytical methods for extraction of nanomaterials from environmental samples* was addressed in a study[150] that compared four extractants over a range of pH values and concentrations for the isolation of natural nanomaterials from topsoil for characterisation by various analytical techniques, including ICP-MS. Extraction with 10 nM $Na_4P_2O_7$ at pH 9-10 was 2-12 times more effective than those with other extractants (NaOH, Na_2CO_3 and $Na_2C_2O_4$).

Interest in *methods for evaluating the availability or mobility of metals in soils and sediments* remains strong. The Mehlich-1 extraction procedure, widely used to predict the phytoavailability of nutrients in soil, was optimised[151] using Box-Behnken-type response-surface methodology. Optimal extraction of Cu, Cd, Cr, Mn, Ni and Zn occurred when 2 g samples were stirred in 43 mL extractant for 14 minutes. A free-ion-activity model based on the Cd, Cu, Ni, Pb and Zn concentrations in soil extracts predicted[152] uptake into spinach. The robustness of two standard methods[153] to estimate mobility of metals in soil, ISO 14870:2001 (extraction of trace elements by buffered DTPA solution) and French standard NF X 31–120:2003 (extraction by means of ammonium acetate in the presence of EDTA), was evaluated using a Youden and Steiner factorial design. Both methods were insensitive to minor changes (±10% of the prescribed value) in shaking rate, shaking time and solid:liquid ratio. A previously reported seven-step sequential-extraction procedure was compared[154] with the BCR procedure for estimating the bioavailabilities of As, B, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn to plants collected near boron mines in Turkey. Although the two procedures yielded similar results, the authors claimed the more elaborate procedure was superior because it could fractionate elements associated with manganese oxides, amorphous iron minerals and crystalline iron minerals. These claims need to be verified as it is long established[155] that sequential extraction procedures are rarely mineral-phase specific.

The use of DGT for sampling PTEs in soil and sediment porewaters for analysis by LA-ICP-MS remains popular. The binding capacity of Chelex-100 (100 µm bead diameter) was superior[156] to that of the resin SPR-IDA (10 µm, supplied as 10% *w/v* aqueous suspension) for Fe and Mn but its larger bead size limited the spatial resolution that could be obtained. The pragmatic solution adopted involved grinding of the Chelex resin in a ball mill and then supporting it on a gel similar to that typically used in the SPR-IDA approach. Deployment[157] of arrays of miniaturised DGT probes (864 individual samplers housed in 72 arrays) allowed a detailed study to be conducted of the field-scale heterogeneity of As, Fe, P and S in a paddy field in Nanjing, China. Different combinations of gels were used to collect both cationic and anionic species. An article[158] in Chinese with English abstract claimed a mixed CeO_2/ZrO_2 binding-medium provided better performance for the measurement of As species in sediments and waters than either of the individual components used alone.

Several MAE methods applicable to plants have been published. Researchers in India[159] reported that it was possible to extract Cr species from various types of leaf powder using 0.1 M EDTA, 1% tetrabutyl ammonium bromide and “a little HF” in a domestic microwave oven for analysis by ICP-AES. Workers in Brazil[160] compared water-bath, digestion block, MAE under medium pressure and MAE under high pressure. Unsurprisingly, the high pressure MAE gave the best recoveries (85-113%) for As, Cd, Cu, Fe, Ni, Pb, Se and Zn from BCR CRM 670 (aquatic plant). Pressure-assisted and microwave-assisted enzymatic hydrolysis procedures were optimised[161] for Se speciation in plant-based foods by HPLC-ICP-MS. The procedures were rapid, taking only 7 and 12 minutes, respectively. The LODs were 0.014-0.599 $\mu g\ g^{-1}$. To address the lack of suitable sample-pretreatment procedures for measurement of $\delta^{11}B$ in plants by MC-ICP-MS, a three step approach was developed[162] that involved dry ashing, dissolution of the residue in 0.5 M HNO_3, removal of interferents by cation-exchange chromatography and microsublimation of $B(OH)_3$. The method had a low procedural blank (0.70 ± 0.09 ng) with good overall B recovery (97 ± 11%) and, importantly, gave $\delta^{11}B$ values for BCR CRM 679 (white cabbage) and NIST SRM 1547 (peach leaves) consistent with those measured in previous studies.

4.3.2 Preconcentration procedures

Preconcentration procedures for specific analytes continue to be developed. Methods for the analysis of soils, plants or related materials, or those developed for other sample matrices that used soil or plant CRMs for validation, are summarised in Tables 3 (liquid phase extraction methods) and 4 (solid phase extraction methods).

[Tables 3 and 4]

4.4 Instrumental analysis

4.4.1 Atomic absorption spectrometry

Reports of *advances in HR-CS-ETAAS* included a comparison[163] of three sample preparation procedures and four matrix modifiers for the determination of Hg in soil and sewage sludge CRMs. The procedures were: slurry sampling; microwave-assisted digestion with HNO_3 + HF according to US EPA Method 3052; and acid leaching with *aqua regia* according to US EPA Method 105. Novel gold- and palladium-NP modifiers were compared with more conventional gold and platinum solutions. Both slurry and *aqua-regia*-leaching procedures gave results in good agreement with certified values when gold NPs were used. A method for direct determination of As in soil was based[164] on the use of zirconium as a permanent modifier, a pyrolysis temperature of 1000 °C and an atomisation temperature of 2200 °C. The LOD was 0.04 ng g^{-1}. Results for CRMs BCR142 (light sandy soil) and NRCC PACS-2 (marine sediment) agreed with the certified values according to a t-test at 95% confidence.

A FAAS method for the determination of Co in soil incorporated[165] PVG and a novel batch gas-liquid separator. The LOD of 8.7 µg L^{-1} was an improvement of over an order of magnitude when compared to that achievable using conventional nebulisation. Spike recoveries were 98.9-107%.

4.4.2 Atomic emission spectrometry

An ICP-AES method for trace element quantification in medicinal plants involved[166] multi-wavelength calibration (at least four lines per analyte) and a variant on *standard addition* in which just two solutions were analysed. These solutions were 1 + 1 *v/v* mixtures of (a) sample + known concentration of analyte and (b) sample + blank. Recoveries for Cd, Cu and Ni from NIST SRM 1570a (spinach leaves) were close to 100%. An improved method for determination of P in soil used[167] the standard addition calibration for one sample to quantify the analyte in other samples. Although the method appeared to work well for soils of similar provenance, whether it is more widely applicable has yet to be demonstrated.

A portable instrument was developed[168] for the *determination of organomercury in sediment*. A PDMS/Carboxene SPME fibre accumulated analyte species from the gas phase, which were then transferred to a TD unit and swept into a digitally-controlled, rotating-field (10 kHz) helium microplasma. A small spectrometer with a CCD recorded the emission spectrum and transferred the data to the USB port of a notebook computer for processing. The instrument was first used to screen for any volatile organomercury compounds emanating from the sediments. Samples were then subjected to MAE. Total Hg, inorganic Hg and MeHg were determined in aliquots of the extract by addition of 5% $NaBH_4$, 3% $SnCl_2$ and 36.5% NaCl, respectively, to transfer the desired species into the headspace for collection on the SPME fibre. The LODs were 0.2 µg kg^{-1} for total and inorganic Hg, and 0.7 µg kg^{-1} for MeHg.

4.4.3 Atomic fluorescence spectrometry

A new method[169] for the *determination of trace levels of MeHg in plants by GC-AFS* was applied to cyanobacterial mats from the Antarctic Peninsula. Samples were subjected to enzymatic hydrolysis with cellulase for 24 h at 40 °C, UAE of MeHg into 6 M HCl, derivatisation with sodium tetraethylborate and preconcentration in hexane. Use of the enzyme to decompose the sample matrix avoided formation of a precipitate in the organic phase during extraction.

4.4.4 Inductively coupled plasma mass spectrometry

Chromatographic separation coupled with ICP-MS was used[170] to determine As^{III}, As^{V}, MMA and DMA in herbal tea leaves and infusions from Brazil. Concentrations in 28% of leaves exceeded regulatory guidelines. Although transfer from leaves into infusions was limited, herbal tea consumption was identified as an important contributor to As uptake in children. A detailed evaluation[171] of the fate of Zn in lettuce used several techniques. First, sp-ICP-MS was used to study uptake of zinc NPs from a hydroponic solution. No difference in accumulation rates was found when either zinc NPs or $ZnCl_2$ were added because the NPs dissolved rapidly in the growth medium. Next, a three-step sequential-extraction procedure (10 mM ammonium acetate at pH 6.8; 4% pectinase at pH 4.5; 4% cellulose at pH 4.5) was applied to the plant tissue and SEC-ICP-MS used to fractionate the Zn species in the extracts. The fractions obtained by SEC were further separated by HILIC and the column effluent split and analysed in parallel by ICP-MS and ESI-MS/MS. Nicotianamine was the major Zn-binding ligand in lettuce leaves.

Other developments in *on-line liquid-sample introduction to ICP-MS* have been reported. The ultimate goal of a FFF-ICP-MS method[172] for the determination of particulate C in charcoal-spiked soil samples was to monitor C, P and metals in natural and engineered particulate matter in environmental systems. The loss of sensitivity in FI systems typically caused by diffusion of the injected sample aliquot into the carrier liquid was avoided[173] in a segmented-flow FI-ICP-MS method by introducing a 50 μL sample plug in the middle of a 1 mL plug of air. This improved the LOD 2 to 3-fold and sample throughput 5-fold in comparison to values achievable by conventional FI-ICP-MS. This enabled the successful determination of Fe, Mn and Zn in a sample containing just 60 μg of plant protein in a total volume of 150 μL.

The importance of determining the bioaccessible PTE fraction in environmental samples led to the development of stable isotope *ID-ICP-MS methods* for determining Cd [174] and Cr [175] in marine sediments. The samples were equilibrated with either a ^{111}Cd- or a ^{53}Cr-enriched 1 M HCl spike using ultrasonic agitation and the results validated by comparison with Cd or Cr concentrations extractable in the first three steps of the BCR sequential extraction procedure. In another study[176], a ^{110}Cd spike was equilibrated with soil suspended in three different electrolytes (0.01 M $CaCl_2$, 1 M NH_4NO_3, 1 M HN_4Cl). All three electrolytes gave similar estimations of the labile Cd pool.

The sensitivity of a *ferric-ion-assisted PVG method*[102] for the determination of Bi in sediment and water samples was 30-fold better than that achievable using direct solution nebulisation. The LOD of 0.3 ng L^{-1} represented a significant improvement over those obtained using, for example, HG-AFS, HG-ICP-MS, PVG-AFS or non-ferric-ion-assisted PVG-ICP-MS.

An *ETV-ICP-MS method for the direct determination of Hg in soil* was calibrated[177] using NIST SRM 2709 (San Joaquim soil). The reproducibility was <21% (n=3) and the LOQ 3.1 ng g^{-1} for a sample mass of 0.5-5.0 mg. Results for NIST SRM 1645 (river sediment) and NRCC CRM MESS 3 (marine sediment) were within 13% of certified values.

Direct application of LA-ICP-MS to samples of suspended sediment collected on filters is challenging because the sample is not homogeneously distributed and is of variable thickness. The complete removal of the fine particulate material from the filter for pelletisation is impractical so, to overcome these difficulties, sediment-loaded filter samples were milled[178] intact, pressed into "filter pellets" and analysed. Calibration pellets were created by milling together equal masses of CRMs and blank filters. Quantification of 17 elements allowed the various catchments contributing sediment to the Ruvu River system in Tanzania to be delineated.

Work on *calibration strategies for the analysis of plants by LA-ICP-MS* included a comparison[179] of ^{12}C, ^{13}C, ^{28}Si and ^{31}P as ISs for mapping the elemental distributions of Ag, Cu and Mn in soybean leaves cultivated in the presence or absence of silver NPs. The use of ^{13}C was preferred as it provided best precision and the most homogeneous images. Other workers[180] also used a ^{13}C IS, in combination with spiked-agarose-gel in-house calibrants, for the analysis of food samples. Recoveries for the analysis of NIST SRM 1573a (tomato leaves) were 84-122% for a suite of 19 analytes. The inclusion of pulverised leaves of *Eremanthus erytropappus* as a matrix-matched QC sample was recommended[181] when analysing plants belonging to the Atlantic and Cerrado Forest biomes of Brazil.

Advances in *LA-ICP-MS methods to study the behaviour of NPs in plants* included a procedure designed[182] to overcome difficulties in imaging silicon NPs caused by the high Si background. The plant *Ocimum basilicum* was exposed to NPs with a yttrium core and a silicon coating and the response for ^{89}Y quantified. A LA-sp-ICP-MS method[183] previously developed for the *in situ* characterisation of NPs in biomaterials was applied to gold NPs taken up from hydroponic solution by sunflower roots. By optimising parameters such as laser fluence, beam diameter and dwell time, it was possible to determine not only the distribution of Au in root cross sections but also the number of NPs present and their size.

The ability of a current-generation quadrupole ICP-MS instrument to determine *Pb isotope ratios in urban soil* was thoroughly assessed[184] through comparison with analysis by MC-ICP-MS. The optimised parameters included: sample dilution to match the Pb concentration with that of a solution of NIST SRM 981 (common lead isotopic standard); dead time correction factor; quadrupole dwell time; and number of scans per sample. Both internal (Tl) and external (NIST SRM 981) mass bias corrections were applied. Although not able to match the precision of MC-ICP-MS, the protocol could provide results that were considered fit for purpose without having to extract the Pb from the soil digest.

New ICP-MS/MS methods are being increasingly reported as instrumentation becomes more widely available. Procedures of note included the determination of ^{90}Sr in soil[185], Pu isotope ratios in environmental samples containing high levels of U[186], ^{226}Ra in rock, soil and water[187] and, in Chinese with an English abstract, As, Cd, Cr, Hg, Ni, Pb, Sb and Sn in activated clay[188]. The advantages of coupling chromatography with ICP-MS/MS are beginning to be explored. For example, a HPLC-ICP-MS/MS procedure[189] for determining Cr speciation in alkaline extracts of soil gave LODs of 0.08 and 0.09 μg L^{-1} for Cr^{III} and Cr^{IV}, respectively. Reliable Cr^{VI} spike recovery could be obtained from soils with low OM content (2.8%) but the presence of 18% OM led to losses due to reduction of Cr^{VI} to Cr^{III}.

4.4.5 Laser-induced breakdown spectroscopy

Progress in the use of *high-spatial-resolution imaging by μLIBS* was reviewed[190] (95 references). The various applications highlighted included a study on Ca distribution in sunflower stems in which crater diameters as small as 100 nm were achieved.

Although one of the advantages frequently claimed for LIBS is that it requires no sample preparation, several studies explored *methods of sample pretreatment for LIBS analysis* in order to improve analytical performance. Donaldson and Yan[191] approached this from a purely theoretical perspective by using a 2D COMSOL model to simulate the effects of LA on soil samples with different physical characteristics. Popov *et al.*[192] studied the effects of soil moisture (amongst other parameters) on emission intensity for Fe and Mn, and concluded that samples should be dried as well as pelletised prior to LIBS analysis to improve accuracy. In contrast, Khumaeni *et al.*[193] recommended adding a small amount of water to soil samples and 'painting' a thin layer onto a metal substrate for the determination of C. An assessment[194] of the feasibility of determining N in soil using portable LIBS established that, whereas pelletisation might be challenging on a remote robotic rover (for example, on the surface of Mars), simply milling to a particle diameter of <100 μm gave results that correlated well with those obtained by microanalysis using a commercial CHN analyser. Carvalho *et al.*[195] improved precision in the determination of Al, Ca, Fe, Mg, Si and Ti in soil by converting samples into glass beads using a lithium borate fusion method. Yi *et al.*[196] used what they rather grandly termed a "solid-liquid-solid transformation" (extraction with 0.1 M HCl then evaporation of the extract onto a glass slide) to determine Cd and Pb in soil. The LODs in the dried extracts were, unsurprisingly, superior to those achievable with pressed soil pellets.

Various methods for *improving sensitivity in LIBS analysis of soils and plants* have been reported. A secondary (tuneable) laser is used selectively in LIBS-LIF analysis to re-excite a transition of the analyte element in the ablation plume. A method for Pb in soils[197] used a homemade CW-DL to achieved a two-fold increase in intensity of the Pb I 405.78 nm transition. In a procedure for Sb in soils[198], spectral interference from Si was eliminated through selective enhancement of the Sb I 287.79 nm line. An alternative approach to improving sensitivity involved[199] application of a magnetic field to confine the ablation plume and increase emission intensities. The LOD for Cr was improved from 20 to 8 mg kg^{-1}. Application of 80 nm diameter silver NPs to the surface of lettuce leaves significantly enhanced[200] LIBS peak intensities and so allowed the determination of both Cd and the organophosphate insecticide chlorpyrifos (based on P emission at four wavelengths).

The limitations of univariate calibration have prompted continued interest, in particular in China, in the exploration of *chemometric methods for processing LIBS spectral data*. Soils were analysed for: Cr, Cu, Ni and Pb using PCR and Lasso[201]; K using CNNs[202]; and Cd using PLSR and LS-SVM[203]. In the last study, analysis under an argon atmosphere was considered preferable to analysis in air. Plants were analysed for: B, Ca, Fe, K, Mg and Zn in *Panax notoginseng* using PLSR, LS-SVM and Lasso[204]; Cd in tobacco roots using PLSR and SVM[205]; Cu in tobacco leaves using PLSR and ELM[206]; and Cd in lettuce using PLSR[207].

High resolution multielement LIBS maps were produced[208] across cross-sections of the soil-rhizosphere-root interface, using switchgrass (*Panicum virgatum*) grown in sandy loam Alfisol as a test sample. The 17 elements imaged successfully at a resolution of *ca.* 100 µm included: analytes characteristic of organic matter (C, H) and soil minerals (Al, O, Si); macronutrients (K, Mg, P); and micronutrients (Fe, Mn, Zn). The ability of LIBS to map light elements was exploited[209] in a study of Li uptake in *Podocarpus macorophyllus* leaves.

The development of *classification models based on LIBS data* has continued. In this approach, spectral information indicative of the parameter to be sensed (often arising from multiple species in the sample) is selected and subjected to chemometric algorithms. For example, hypothesising that imbalance in Ca, K and Mg concentrations was associated with soybean's susceptibility to green stem and foliar retention syndrome, Ranulfi *et al.*[210] created an early diagnostic tool using representative emission lines for these elements that discriminated sick from healthy leaves. Ponce *et al.*[211] applied PCA to 38 atomic and molecular emission lines to detect the onset of citrus-greening disease in asymptomatic fruit trees, thereby allowing the trees to be removed before the infection spread. Chemometric procedures for the automated selection of optimal spectral peaks were used[212] in the construction of PLS-DA models for classification of Chinese tea leaves. Over 99.5% of 600 samples of six varieties of tea were classified correctly. Differentiation of willow, pine and poplar was achieved[213] by analysis of bark using a LIBS variant in which fs laser filamentation allowed a beam of almost constant energy to be projected over a distance of several metres for remote analysis of rough surfaces.

In *data fusion models,* outputs from complementary analytical techniques are combined to generate proximal information. Of particular interest is the combination of data that can be generated in the field. Bricklemyer *et al.*[214] evaluated LIBS and VIS-NIR DRS to estimate C species in intact soil cores. Inorganic C was best predicted by LIBS, SOC by VIS-NIR DRS and total C by integration of LIBS and NIR data. De Olivena *et al.*[215] applied the same two techniques to estimate the nutritional status of *Bracharia* forage. When incorporated into a single model, the VIS-NIR DRS results helped compensate for sample matrix variability and so improved accuracy for the LIBS determination of Ca, Fe, K, Mg and Mn. Xu *et al.*[216] assessed LIBS, VIS-NIR DRS, MIR spectroscopy and pXRFS both individually and in various combinations for prediction of six key properties (SOM, total N, available N, available P, available K and pH) that affect soil fertility. The predictive capability decreased in the order MIR>VIS-NIR>LIBS>pXRFS. Interestingly, combining the outputs of the individual VIS-NIR, MIR and LIBS models using Bayesian-model averaging gave more accurate predictions than data fusion.

4.4.6 X-ray spectrometry

An informative *review article* [217] (98 references) of elemental imaging in plants by SR-based XRF microscopy included current uses and future opportunities such as high-throughput screening in molecular biology and time-resolved *in vivo* analysis of living plants. The applications, advantages and limitations of XAS and XRFS for imaging Se in living systems were discussed[218] (73 references). A review[68] (66 references) of the use of SR and other approaches to characterise radioactive microparticles emitted from the Fukushima Daiichi Nuclear Power Plant accident included information on the capabilities of µXRFS, XANES, XRD, PIXE and SEM-EDS.

Methods for the analysis of plants or soils using EDXRFS have been developed or improved. A procedure[219] for simultaneous determination of As, Hg, Sb and Se in powdered plant leaves was proposed as a labour-saving alternative to techniques based on HG or VG. The LODs were 2.3, 1.6, 20 and 3.6 mg kg^{-1} for As, Hg, Sb and Se, respectively. Recoveries were 89.9-97.2% of concentrations determined by HG-AAS. With the goal of widening the applicability of the technique, workers at the JRC in Geel developed[220] an EDXRF method that could be applied to a wide range of organic and inorganic matrices using a single calibration curve for each element. The curves were constructed using CRMs and RMs covering a variety of matrices and analyte concentrations. An algorithm based on full-spectrum LS multivariate calibration was proposed[221] as an alternative to the fundamental parameter method for the determination of Cu, Fe, Ni, Ti and Zn in soil. The feasibility of analysing seed coats, seedlings and leaves of *Phaseolus vulgaris* (common bean) exposed to CuO, Fe_3O_4 and ZnO NPs was demonstrated[222] in a scoping study with the aim of assessing the potential of EDXRFS for investigating uptake of trace elements from nanoparticle-based fertilisers. A key goal in this research area is to determine the extent to which the NPs are taken up intact and the extent to which they dissolve in the soil or rhizosphere thereby releasing ions into solution for subsequent root uptake.

A*dvances in WDXRF methodology for soils and plants* included a rapid method[223] for determination of Si developed using *Equisetum arvense* (horsetail) and *Urtica dioica* (nettle). Samples were calcined at 700 °C and then converted into fused beads for analysis. The linear range was 6-55% SiO_2. There were no significant differences between measured and certified values for the NACIS CRM NCS DC73349 (trace elements in bush branches and leaves). A procedure for the rapid screening for F in contaminated soil had[224] an LOD of 52 mg kg^{-1} and a linear range extending up to 5%. Measured concentrations for USGS SDC-1 (mica schist) and NIST SRM 694 (phosphate rock) were within 3% of the certified values (600 and 32,000 mg kg^{-1} F, respectively) but recoveries for 15 soil samples collected in the vicinity of a HF spill were more variable.

The ability of benchtop µXRFS instruments to produce *detailed spatial images of trace element distributions in fresh or living plants* was highlighted in interesting case studies presented by Rodrigues *et al.*[225] and Capobianco *et al.*[226]. In the latter study, PCA was used to determine correlations between the distributions of essential elements and As in tobacco seedlings exposed to arsenate.

A challenge for *synchrotron-based µXRF analysis of living plants* is radiation damage and dehydration caused by prolonged exposure of the sample to X-rays. Improved detector efficiency allowed Blamey *et al.*[227] to reduce dwell time. This made possible the first microscopic-scale quantification of both spatial and temporal changes in the concentrations of multiple elements in the same area *Vigna unguiculate* (cowpea) leaves. No tissue damage was observed. The analysis of cross-sections of *Pinus radiate* (Monterey pine) revealed[228] a cyclic seasonal change in the tree's uptake of Si.

Factors affecting the accuracy of soil and sediment analysis by pXRFS were the focus of several studies. The decrease in analyte peak intensity that occurs with increasing moisture content[229-231] and the effect of sample thickness[230] were investigated. Three closely related articles examined the effects of moisture[232], organic matter[233] and packaging[234] on the determination of Al_2O_3, Fe_2O_3, P_2O_5, SiO_2, and TiO_2.

Approaches previously developed for soil analysis were adapted for the pXRFS analysis of 74 compost samples from the USA and Canada with the aim of using the elemental data to develop *methods of proximal analysis*. Comparison with established laboratory-based methods yielded R^2 values of 0.8 for salinity[235], 0.63 for pH[235] and 0.90 for CEC[236]. Copper and Zn concentrations gave the best prediction of CEC. In a study[237] of soil from the Great Hungarian Plain, Rb concentrations were better predictors for soil clay content and salinity than K concentrations, possibly since Rb is less affected by plant metabolism. A data fusion approach[238] combined FT-NIR spectroscopy data and pXRFS data to predict nutrient status in olive leaves. Whereas predictions for concentrations of Ca, K and Mn were quantitative and those for N and P semi-quantitative, models for B and Mg were less satisfactory and levels of Zn could not be predicted at all. Since both techniques are field portable, this approach shows great promise for on-site determination of nutrient levels in crops, thereby allowing more targeted fertiliser application to be made.

4.4.7 Other techniques

A short review[239] (34 references) of recent methodologies to study SOM included *developments in IRMS*, pyrolysis GC-MS and NMR spectroscopy. A novel LA-IRMS system allowed[240] $^{13}C/^{12}C$ isotope ratios in solid samples to be measured with a spatial resolution of 10 μm. This was an order of magnitude improvement on what could be achieved by previous methods. Application to soil and plants revealed a marked $\delta^{13}C$ gradient across the rhizosphere, with root exudates diffusing distances of up to 300 μm into the surrounding soil. In an international intercomparison[241] of the use of cryogenic extraction systems in soil-water isotopic-analysis, the large differences between laboratories for δ^2H and $\delta^{18}O$ results were attributed to isotopic fractionation during the extraction procedure because all samples were analysed by the same IRMS instrument and off-axis ICOS procedures in a single facility

A procedure[242] for the *determination of* $^{135}Cs/^{137}Cs$ *by TIMS* used AMP-PAN resin followed by anion- and cation-exchange steps to remove matrix interferents, particularly Rb which inhibits ionisation. The precision was <10% for samples containing as little as 10 fg ^{137}Cs. Results for analysis of IAEA CRMs 372 (grass) and 330 (spinach) were similar to values reported in the literature for other, Chernobyl-derived, CRMs.

5 Analysis of geological materials

5.1 Reference materials

Well-characterised RMs are crucial in geochemical analysis. This section focuses on newly developed RMs and the further characterisation of established RMs to provide additional information on their elemental and isotopic compositions.

An *annual bibliographic review*[243] (23 references) provided an overview of papers published in 2017 in the fields of geochemistry, analytical chemistry, palaeoclimate research and environmental sciences and contained analytical data for geological RMs used for calibration or QC. The characterisation of new RMs was also covered. All the publications listed in this review and their analytical data can be found in the GeoReM database.

Several *new certified RMs for bulk analysis* are now available. Thirteen Chinese laboratories[244] participated in an interlaboratory exercise to certify three Mo ores (GMo-1 to GMo-3) and one Mo concentrate (GMo-4). A variety of analytical techniques was used in certifying the mass fractions of up to 26 elements and oxides. The certified values and uncertainties for Mo in the three ores and concentrate were 0.066 ± 0.003, 0.15 ± 0.01, 0.54 ± 0.02 and 50.08 ± 0.14 wt %. Their bulk compositions were determined after high pressure digestion and conventional PGE separation, while their PGE distributions were assessed by LA-ICP-MS. The RMs were then used to test the accuracy of different procedures for chemical separation of base metal sulfide grains and digestion of single grains.

Several *new RMs for isotope ratio determinations* were developed and characterised. Vogl *et al.*[245] described the certification of ERM-EB400, a bronze material, and ERM-AE142, a Pb solution, for Pb isotope ratios. Both materials were designed so that the Pb isotope ratios fell within the naturally occurring range and so provide analysts in many scientific fields, including geochemists, with an independent means of validating their analytical procedures and acting as QC materials. The Chinese Academy of Geological Sciences in collaboration with other institutes prepared[246] a basaltic RM (CAGS-Basalt) and three single-metal solution RMs (CAGS-Cu, CAGS-Fe and CAGS-Zn) to act as secondary RMs for Cu, Fe and Zn isotope ratio determinations. A pyrrhotite sample, YP136, collected from northern Finland was proposed[247] as a new candidate RM for *in situ* S isotope determinations by SIMS. Internal growth and other zoning was excluded by examination of thin sections by polarised microscopy, back-scattered-electron image analysis and WDS mapping. More than 100 grains were analysed by SIMS amounting to 318 spot measurements that gave a repeatability of 0.3‰ (2s) for $^{34}S/^{32}S$. The $\delta^{34}S$ value determined by IRMS was 1.5 ± 0.1‰ (2SD, n = 11).

There is ongoing interest in the *determination of additional compositional information for existing RMs*. A study by Kirchenbaur *et al.*[248] determined In and Sn mass fractions in 16 basaltic, ultramafic and sedimentary geological RMs by ID-MC-ICP-MS. Optimisation of the digestion and ion-exchange separation conditions provided high yields, low procedural blanks and low analytical uncertainties (<3% 2u). Mass fractions of Br, Cl, F and I reported[249] for eight USGS, GSJ and NIST powdered-rock RMs were in agreement with previously published data. In addition, new F mass fractions were measured in five silicate glass RMs (NIST SRMs 610 and 612 and USGS RMs BHVO-2G, BCR-2G and BIR-1G). The F mass fractions were determined by SHRIMP analysis, while Br, Cl and I were measured by the noble-gas method. Five in-house biotite RMs used for O isotope measurements at the University of Lausanne, together with the RM NBS 30 (biotite), were investigated**[250]** for their H_2O, Cl and F contents by SIMS in negative ion mode. In addition, the homogeneity of all six materials was assessed. There was no detectable dependency on crystal orientation at the level of homogeneity of the RMs so the *in situ* determination of contents in randomly oriented grains in thin sections was possible. Accuracy was 15 and 3% (1SD) for Cl and F contents, respectively and was estimated to be 3-4% (1SE) for H_2O measurements. Valuable recommendations for the analysis of biotite unknowns were provided.

Work to obtain *new isotopic information for existing geological RMs* provided much valuable information. The focus of research by Brett *et al.*[251] was the determination of Tl mass fractions and stable Tl isotope ratios in 16 geological RMs with Tl contents spanning three orders of magnitude. They reported the first ε^{205}Tl (relative to NIST SRM 997) data for many of the rock and mineral RMs analysed and the first Tl mass fractions for USGS RM COQ-1 (carbonatite), CRPG RMs ISH-G and MDO-G (trachytes) and all the mineral RMs involved in the study. The $\varepsilon^{205}\text{Tl}_{\text{SRM997}}$ results for the 16 RMs were in the range -3.4 to +1.8. All the RMs except G-2 were deemed to be suitable as matrix-matched Tl isotope RMs as long as a test portion of at least 100 mg was taken. Prompted by the lack of suitable RMs for the determination of N mass fractions and δ^{15}N in low-N (200 µg g^{-1}) silicate rocks, Feng *et al.*[252] selected USGS RMs BCR-2 and BHVO-2 (basalts) for an interlaboratory comparison. A newly developed method based on high-temperature sealed-tube combustion coupled to continuous-flow IRMS gave N-isotope data more positive than published EA-IRMS data for the same materials. The authors suggested that the EA-IRMS method underestimated the N mass fraction due to incomplete release of N and high blanks so making it unsuitable for the determination of δ^{15}N in silicates. As the primary NIST standard Zn solution JMC 3-0749L is nearly exhausted, the NIST SRM 683 (pure Zn metal nugget) was identified[253] as having potential to be a new international RM for Zn isotope measurements. The Zn isotope composition and homogeneity of NIST SRM 683 were assessed by analysing five Zn metal nuggets at three different laboratories by MC-ICP-MS using a double-spike protocol. The NIST SRM 683 was homogeneous within an analytical precision of 0.04‰ and had a δ^{66}Zn value of 0.12 ± 0.04‰ (n = 295) at the 95% confidence level relative to the JMC 3-0749L Zn reference standard (JMC-Lyon). Based on these findings, and the fact that it is much more abundant than previous primary RMs, NIST SRM 683 was proposed as the future "zero-point" RM for Zn isotope measurements. Motivated by a renewed interest in K isotope geochemistry, Xu *et al.*[**254**] investigated 23 RMs for their δ^{41}K compositions. The samples (sedimentary, igneous and metamorphic rocks) had δ^{41}K values of -0.562 to -0.253‰ as measured by MC-ICP-MS after cation-exchange chromatography. A study of the Sm-Nd isotopic compositions of 12 mineral RMs (apatite, monazite, titanites and eudialyte) reported[**255**] ^{143}Nd/^{144}Nd and ^{147}Sm/^{144}Nd values acquired over four years by LA-MC-ICP-MS. External reproducibilities of <0.06‰ (2SD) for ^{143}Nd/^{144}Nd and 2.5‰ (2SD) for ^{147}Sm/^{144}Nd demonstrated the potential of these materials as candidate RMs for *in situ* Sm-Nd isotopic determinations.

5.2 Sample preparation, dissolution, separation and preconcentration

Sample preparation for bulk analysis by LA-ICP-MS commonly involves the use of fused glasses or pressed powder pellets. In a study[**256**] to evaluate the merits of these preparation strategies for granitic rocks, ultrafine powder particles produced by wet milling a suite of granitic RMs were pressed into pellets. The 6.6% abrasion of the agate milling balls resulted in sample dilution but contamination was negligible except for SiO_2. The homogeneity of flux-free glasses was improved by grinding an initial fused glass a second time and re-melting the resulting powder to obtain compositionally homogeneous glasses. The LA-ICP-MS results indicated that Pb and Sn were depleted (<30%) during fusion and results for Cu and Ni could also be compromised. The better homogeneity for the fused glasses (spot size 50 µm) than for the powder pellets (spot size 90 µm) was attributed to large crystal fragments of minerals such as biotite remaining in the ultrafine powder even after extensive milling. Zhang *et al.*[**257**] reported a novel method of fusion of peridotites with synthetic albite ($NaAlSi_3O_8$) to prepare homogeneous glasses suitable for the determination of trace element contents by LA-ICP-MS. To minimise the effects of volatilisation, contamination and metal segregation, the peridotite powders were fused with albite (1 + 2) in a molybdenum-graphite assembly at atmospheric pressure and 1500 °C for 10 minutes before quenching. The elemental compositions of two USGS peridotite RMs (PCC-1 and DTS-2B) prepared as albite glass were within 10% of the published values for most elements but deviations of up to 20% were observed for Pb, REEs, Ta, Th and U. Benefits compared to wet chemistry digestion were complete sample fusion, particularly of resistant minerals such as spinel and rutile, long-term conservation of the resulting sample material and much reduced preparation times.

Several contributions focused on the *evaluation and improvement of digestion techniques*. A rapid acid digestion for the simultaneous determination of B and I in soils and sediments involved**[141]** HNO_3 + HF with ammonia dilution. Complete recoveries of Br and I were obtained from IGGE RMs GSD-2 (sediment) and GSS-24 (soil) by digestion for 15 minutes in a PTFE-lined stainless-steel bomb at 140 °C. The use of ammonia to dilute the resultant slurry had the advantages of stabilising the Br and I signals and eliminating the memory effects often observed in their measurement by ICP-MS. A MAD method employing NH_4HF_2 and HNO_3 was evaluated**[258]** using 21 silicate rock RMs of felsic to ultramafic composition and measuring their trace element content by ICP-MS. The entire dissolution procedure occurred in a closed vessel system and took up to 4 h. Satisfactory recoveries for 41 elements were obtained from most matrices; important exceptions being Hf and Zr in USGS RMs G-2 (granite) and GSP-2 (granodiorite), even though a complete digestion was achieved for four other felsic RMs. The difference in Hf and Zr recoveries for specific RMs was attributed to the presence of resistant minerals such as zircon. The importance of carrying out a comprehensive characterisation of the mineral phases of a material to optimise the digestion protocol was emphasised. In a novel approach**[259]**, refractory ore samples were decomposed in a mixture of Na_2O_2/Na_2CO_3 in a corundum crucible by adding a piece of wet filter paper and heating in a microwave oven at 600 W for 15 minutes. The energy released by the reaction of water with the Na_2O_2 was key to achieving complete dissolution. The precisions for Cr, Fe, Mo, Ti and W concentrations determined by ICP-AES were better than 6% (RSD) and the results for all elements except Cr were in good agreement with those obtained from a traditional fusion method.

For the *determination of Au* in a wide variety of mineral matrices by MIP-AES, Helmeczi *et al.***[260]** compared different open-vessel acid digestion techniques and investigated the use of different solvents for preconcentration. Whereas acid treatment with HNO_3–HCl (5 + 1) gave an average Au recovery of 97% after 35 minutes, focussed IR digestions delivered higher recoveries (95-104%) in a shorter time (15 minutes). Solvent extraction with 2-octanone was preferred over the use of MIBK or 2-ethylhexanol because of the greater sensitivity which resulted in accurate Au determinations by MIP-AES except for samples with high Fe contents. A low-cost method**[261]** based on the use of N, N-diethyl-N'-benzoylthiourea as a selective chelating agent and Amberlite XAD-16 as solid sorbent was developed for the selective preconcentration of Au from ore samples. A preconcentration factor of 6.7 was achieved and Au concentrations as low as 0.015 μg mL^{-1} detected by FAAS. To validate the proposed method, a copper ore (Cyprus Mining Company, Northern Cyprus) and CCRMP CRM MA-1b (gold ore) were analysed, yielding results in agreement with given values.

5.3 Instrumental analysis

5.3.1 Dating techniques

A critical review[262] (191 references) of recent advances in *U-Th-Pb geochronology by LA-MC-ICP-MS* highlighted improvements in spatial resolution, calibration of ion counter drift, common lead correction, elemental fractionation and making allowance for differences between RM and sample matrices. The review also considered the LASS methods published for the simultaneous measurement of multiple isotope systems and trace element concentrations in geological samples, including the various accessory minerals, isotope systems and instrument configurations used in LASS techniques. Potential areas for future work were proposed.

Chemical abrasion combines high temperature annealing with a partial dissolution step and is commonly used in zircon geochronology to minimise the loss of radiogenic Pb from parts of a crystal affected by radiation damage. This loss would otherwise bias the $^{206}Pb/^{238}U$ age determined. Widmann *et al.*[263] presented an experimental approach to quantify how CA affects the crystal structure and the chemical composition of zircon and its U-Pb age. This is an important contribution since up until now different laboratories have adopted different reaction conditions with no detailed understanding on how the CA temperature and duration affected the radiation-damaged zones. Experiments were performed under different temperature-time conditions using fragments of the Plešovice zircon and changes in trace element concentrations, lattice order and U-Pb age were monitored. The most reliable U-Pb results were achieved when Plešovice zircon was treated by CA at 210 °C for 12 h. It was also demonstrated that the Plešovice zircon can no longer be considered to be homogenous given the level of precision now achievable by LA-ID-TIMS dating.

An area of major activity is *U-Pb zircon geochronology by LA-ICP-MS*. Mukherjee *et al.*[264] studied the precision and accuracy of U-Pb zircon geochronology when using small spot sizes as well as the extent to which short ablation times affect downhole fractionation. Six reference zircons were systematically analysed using four different spot sizes (7 to 20 µm) and fluence combinations (3 to 6 J cm^{-2}). Each sample was ablated for 30 s and ablation signals of different duration were processed. The most accurate ages were obtained by excluding the initial 2 s of unstable ablation and then integrating only the next 10 to 15 s of the ablation signal (corresponding to 50 to 75 laser pulses), thereby restricting the extent of downhole fractionation and time-resolved Pb/U variations between different zircons. This methodology yielded concordant U-Pb ages with an accuracy and precision better than 1.4% when using LA-SF-ICP-MS. A study of detrital zircons demonstrated**[265]** that the complete history of a polyphase crystal may not be obtained if only cores or only rim overgrowths were ablated so both should be analysed when possible. It was recommended that the single-analysis concordia age should be used to present the U-Pb data rather than single isotope ratio ages, as the concordia age provided the best precision through geological time and the precision varied less with age. Pullen *et al.*[266] developed a methodology for optimising the precision, accuracy, efficiency and spatial resolution of U-Pb and Pb-Pb ages when dating detrital zircons by LA-SC-ICP-MS. Such studies typically involve the analysis of many hundreds of crystals. The approach corrected for the nonlinearity of the detector as well as element- and mass-dependent fractionation and instrumental drift by using a suite of three zircon RMs with known isotope ratios determined by ID-TIMS but with differing Pb and U concentrations. Age offsets were typically better than ±2.0% for individual measurements of small volumes (10 µm depth × 20 µm diameter) of material. Although the authors claimed a high sample throughput, their experiments were performed on RMs only and no indication of the actual throughput of unknown detrital zircons was presented. To improve the efficiency of preparing zircons for dating, Isozaki *et al.*[267] developed an automatic zircon separator that picked out automatically 100 µm-sized zircon grains from a heavy mineral fraction prepared by conventional separation procedures. The separator targeted mineral grains using optical recognition, mechanically captured individual grains with micro-tweezers and placed and aligned the grains on a receiving tray with registered coordinates. Automatic zircon separation was combined with direct ^{207}Pb/^{206}Pb dating of unpolished zircons by LA-ICP-MS prior to high-resolution U-Pb dating by LA-MC-ICP-MS of mounted and polished grains.

There is considerable interest in *U-Pb dating of additional U-bearing accessory minerals*. An ultrafast U-Pb dating method[268] by LA-ICP-MS was applied to zircon, apatite, rutile and titanite RMs using repetition rates of >50 Hz. Ablation was performed in a fast-washout 2–volume cell fitted with a rapid aerosol-introduction-system that was capable of resolving individual LA pulses at fast sampling rates. Analysis time for each laser spot (18 – 47 μm diameter) was about 8 s, which included about 5 s for ablation. With this approach, spot analyses of >1000 grains could be performed in less than 3 h. Accuracy and precision were <1% (2SD) for pre-Cenozoic RMs and <2% for younger RMs and therefore comparable to those obtained using conventional LA-ICP-MS protocols. Luo *et al.*[269] investigated the effect of the addition of oxygen, nitrogen and water vapour either before or after the ablation cell on the accuracy of U-Pb measurements of zircon, monazite, titanite and xenotime by LA-ICP-MS when using the non-matrix-matched RM NIST SRM 610 for calibration. The addition of small amounts of water vapour (*ca.* 0.004 mL min^{-1}) before the ablation cell significantly suppressed matrix effects by about a factor of 10 but no such effect was observed when oxygen or nitrogen was added. Comparable results were obtained with 193 nm excimer laser and 213 nm Nd:YAG LA systems and were consistent with observations made over many years that wet plasma conditions reduce matrix effects. The U-Pb dating of baddeleyite, a key mineral in the geochronology of mafic rocks, requires matrix-matched RMs for calibration when using ns LA-ICP-MS. A comparison[270] of U-Pb data generated by ns-LA-ICP-MS and fs-LA-ICP-MS in spot and line scan modes came to the conclusion that elemental fractionation occurred with both LA systems when using a zircon RM for calibration. Although line scans were not affected by downhole fractionation, they still yielded discordant ages. Spot analysis and matrix-matched calibration were recommended to obtain high-precision concordant U-Pb ages in baddeleyite. A U-Pb geochronological study[271] of hydrothermal hematite employed LA-ICP-MS, SHRIMP and ID-TIMS analyses and an *in situ* grain-microsampling technique to assess the suitability of hematite for dating ore formation within iron-oxide-rich mineral systems. The results indicated that hematite could be a useful U-Pb mineral geochronometer if careful sample petrography, screening and data interpretation were applied.

In a new approach[272] to *U-Pb dating of carbonates by LA-ICP-MS*, polished rock fragments were mapped for key elements and Pb and U isotopes. One pixel in the map corresponded to one time slice of the time-resolved signal. From these 2D elemental and isotopic maps, pixels corresponding to likely homogeneous age domains could be isolated by applying suitable selection criteria and pooled into pseudo-analyses. This generated the largest possible spread of the data points on isochron diagrams. Depending on the U concentration, ^{238}U/^{204}Pb ratio and age of the sample, this approach could yield a precision of ±1% or better for analyses employing quadrupole instruments. In a non-matrix-matched U-Pb-dating-method[273] for calcite using LA-MC-ICP-MS, 2D elemental maps were constructed to identify areas with elevated ^{238}U concentrations and high ^{206}Pb/^{208}Pb ratios for U-Pb isotopic analysis. To minimise downhole fractionation during the U-Pb measurements, the aspect ratio of the craters was kept low (spot size 100 µm, depth 50 µm). Calibration with NIST SRM 612 (synthetic silicate glass) yielded an age for the carbonate RM WC-1 that agreed within the uncertainty of its published age.

In an improved measurement protocol**[274]** for *U-Th dating,* the effect of plasma instability was reduced by measuring low abundance isotopes on the axial EM of a MC-ICP-MS instrument operated in peak-jumping mode and with short integration times. The ionisation and transmission efficiencies were *ca.* 3% for both Th and U. This, together with significantly reduced procedural blanks, enabled analytical precisions of ±1.4 yr (2SD) to be achieved for corals as young as *ca.* 10 years old using a sample mass of only *ca.* 40 mg. A processing protocol**[275]** for MC-ICP-MS data written in MATLAB was applicable to studies of ^{230}Th-U geochronology. This protocol consisted of two interactive programmes, the first designed for graphical presentation of the raw data and outlier filtering, and the second to enable data reduction, age calculations and data storage.

A new approach was proposed**[276]** to overcome the drawbacks of conventional *K-Ar dating* by NAA and current unspiked K-Ar dating methods. The new method involved laser fusion on multiple microaliquots of a sample and the construction of an inverse isochron. Almost complete extraction of Ar from the samples was achieved and accurate and precise K-Ar ages obtained for RMs Fish Canyon sanidine and B4M muscovite. This approach could be employed in a modern ^{40}Ar/^{39}Ar laboratory without any special equipment and provided an alternative to methods requiring access to a nuclear reactor. A new analytical system (KArMars) was developed[277] to investigate the feasibility of *in situ* K-Ar dating on Mars. The system was based on UV LA with LIBS for K measurement and quadrupole MS for Ar determinations. Calibration of the LIBS and quadrupole MS systems and improved quantification of the ablated mass were investigated through the development of RMs whose chemistry and ^{40}Ar yields were determined independently. Using multiple ablations and an isochron approach, the KArMars system provided ages with an accuracy and precision of *ca.* 10% for a wide range of rock compositions.

Using an established gentle stepwise-crushing technique, Xiao *et al.***[278]** determined the *^{40}Ar/^{39}Ar geochronology* and geochemical composition of gases released from fluid inclusions in ore minerals such as wolframite and cassiterite. A combination of quadrupole MS, microscopic observations and Raman spectroscopy was used to reconstruct the hydrothermal activities recorded in mineral-hosted fluid inclusions. Gases released during each crushing stage changed progressively from large vapour-rich secondary-fluid-inclusions (SFIs) through large aqueous

SFIs to small primary-fluid-inclusions, each of which had distinct ^{40}Ar/^{39}Ar compositions and corresponding ages.

5.3.2 Atomic emission spectrometry

Determination of the trace element compositions of ore samples by ICP-AES can be challenging because of interfering emission lines originating from the complex matrices. Zybinsky *et al.*[279] developed software to calculate the mathematical corrections required to resolve spectral interferences when measuring the REE contents of Nb-REE ores. Preparation of calibration solutions that did not contain mutual interferences, sample preparation and spectrum analysis were key considerations in the analytical procedure. A list of recommended analytical emission lines was given. Another study focussed[280] on how matrix complexity affects the measurement of PGEs by ICP-AES. Sources of PGEs now include low-grade ores and recycled automotive catalytic converters with high concentrations of elements such as Al, Fe and Si. Sample matrices containing PGEs and interfering elements at varying concentrations were prepared from standard stock solutions to mimic the composition of natural PGE ores and catalytic converter slags. If the matrix contained Al, Ca, Cr, Cu, Fe, Mg, Mn, Pb and Si then, depending on the combination of parameters, the PGE concentrations were usually underestimated. A set of guidelines for selecting PGE emission lines was given. A novel liquid-cathode GD was constructed[281] as a miniaturised excitation source for AES to determine Cd, Cu and Pb in ore digests. It had a higher discharge stability, smaller sample loss and lower energy consumption than previous systems of this type. The recoveries for Cd, Cu and Pb were 79-115% although statistical analysis indicated that results were comparable with those from ICP-AES analyses. The long-term aim was to develop a portable analytical instrument for continuous monitoring.

5.3.3 Laser-induced breakdown spectroscopy

Díaz *et al.*[282] explored *the effect* of *laser wavelength and irradiance* on the performance of LIBS analyses when determining Ag and Au in pressed pellets prepared from ores and mineral samples doped with Au. Two Nd:YAG lasers operating at 1064 and 355 nm wavelengths were carefully aligned and combined into the same beam path. A range of beam irradiances was achieved by varying the beam energy at constant spot size. Figures of merit such as LOD did not vary significantly between the 1064 and 355 nm ablations but the improved repeatability (50%) at shorter laser wavelengths indicated better ablation behaviour. Higher laser energies and optical setups that produce large sampling areas were recommended to improve the quantification of Au by LIBS.

There is much ongoing interest in *elemental imaging* by LIBS. A review[283] (151 references) on recent advances and applications of LIBS-based elemental imaging for laboratory applications described the more common experimental configurations and various data processing methodologies. The wide variety of LIBS mapping applications included paleoclimate studies, mineralogy and ore formation. A complex hydrothermal ore sample containing five different mineral phases (galena, sphalerite, chalcopyrite, quartz and ankerite) was employed**[284]** to evaluate the use of megapixel LIBS for the geochemical characterisation of minerals. By using megapixel LIBS with a new methodology for data treatment of multiphase materials, it was possible to demonstrate that the technique was capable of detecting and imaging La and Y in carbonates and substitution elements in various mineral phases at the μg g^{-1} level. For example, Cd could be detected in sphalerite, Ag, Bi and Sb in galena, Al and Be in quartz and Sn in chalcopyrite. Rifai *et al.***[285]** demonstrated the capabilities of a new benchtop LIBS platform developed to meet the needs of the mining industry for fast *in situ* measurements of the chemical composition of drill cores and thereby to provide the foundation for rapid core logging. Several elements in geological samples and drill cores were mapped quickly and simultaneously and their distributions visualised on the same image using new software. Another study focussed**[286]** on the elemental mapping and geochemical characterisation of hydrocarbon-bearing shales by LIBS. Five samples of Marcellus shale were analysed using an 81 x 81 grid pattern covering an area of 8 x 8 mm to construct 2D elemental maps. The ability of LIBS to detect most of the elements of interest, including C and H, together with the possibility of making *in situ* measurements using a downhole LIBS sensor currently under development, could potentially offer a distinct advantage over current techniques used in shale gas exploration.

Various applications of handheld LIBS included its use**[287]** to discriminate between the elemental composition of a fragment of the Agoudal meteorite, a sample suspected to be a meteorite and industrial pig iron. Qualitative data for the major elements Co, Fe and Ni and the trace elements Ga and Ir were sufficient to differentiate a genuine meteorite sample from ordinary terrestrial rocks or man-made objects. It was concluded that handheld LIBS was a promising technique for fast, reliable, non-destructive, in-field chemical analyses to identify rocks that are likely to be of extraterrestrial origin. Comparison of quantitative data obtained by handheld, portable and benchtop LIBS systems in the analysis of a weathered limestone fragment from a stone monument indicated**[288]** that the relative differences between all three techniques were <25% for

Al, Fe, K, Mg, Na and Si but around 50% for C and Ca. Although the benchtop and portable systems had a double-pulse setting that improved the sensitivity, the main elemental composition of the two distinct layers (a superficial black crust and limestone rock) could be rapidly identified and quantified with the handheld LIBS instrument.

Data processing methods were discussed**[289]** in a paper on improving the accuracy of iron ore analysis by LIBS. To overcome challenges posed by nonlinear self-absorption and matrix effects, a hybrid model of sparse partial least squares (SPLS) and least-squares support vector machine (LS-SVM) was proposed for the determination of Al_2O_3, CaO, Fe, MgO and SiO_2 in iron ores. The hybrid model provided better data than either the SPLS or LS-SVM model used alone. A method of automatic spectral peak identification with linear discriminant analysis (ASPI-LDA) was developed**[290]** to improve the capability of standoff LIBS to categorise rock types. Rather than identifying rocks manually one-by-one, the new procedure allowed automatic and rapid identification of rock types to be made so ASPI-LDA combined with a compact spectrometer was considered to be a promising technique for remote detection and direct *in situ* analysis. Dong *et al.***[291]** demonstrated the importance of the molecular spectra of CN and C_2 for the quantitative LIBS determination of the C content of coal. A combination of carbon atomic and molecular emissions with both PLS regression and support vector regression correction improved the measurement accuracy.

Much of a review**[292]** (212 references) on *new trends of LIBS in cultural heritage and archaeology* was applicable to geological studies. Materials of interest included metals, pigments, pottery, glass, rocks and gemstones. The combination of LIBS with other analytical techniques was also discussed.

5.3.4 Inductively coupled plasma mass spectrometry

5.3.4.1 ***ICP-MS instrumentation.*** There have been some interesting *developments in sample cell design and transport technologies for LA-ICP-MS*. Craig *et al.***[293]** reported the use of a MC-ICP-MS instrument coupled to a commercially available rapid-response LA cell and sample transport system for the measurement of Hf and Pb isotope ratios in geological materials. When tuned for maximum signal, the ion yield for Pb of 6.5% was more than double that of a conventional LA-MC-ICP-MS configuration. This increase in sensitivity resulted in improved precision for Pb isotope ratios when ablating MPI-DING glass RMs and better spatial resolution for Hf isotope ratio analysis of reference zircons. The influence of Ar and He carrier gasses on signal intensities in 193 nm ArF excimer LA-ICP-MS was reassessed**294** by studying the influence of carrier gas composition at different positions in the ablation cell. When a modified version of a standard cylindrical ablation cell was used, gas flow rates depended on the location in the ablation cell. This in turn affected the signal intensities obtained in different ablation atmospheres. The pronounced enhancement in sensitivity when using He as carrier gas was found to be mainly due to more effective vaporisation of the aerosol particles in the ICP rather than enhanced transport efficiency of small particles away from the ablation site. Xie *et al.***295** designed a new sample cell to give a homogeneous gas flow over the sample surface and thereby reduce differences in particle transport efficiencies at different ablation sites for isotopic measurements by LA-MC-ICP-MS. The effect of sampling position was negligible at a carrier gas flow rate of 1 L min^{-1}. Measurements of the Fe isotopic composition of an in-house pyrite RM obtained at various positions in the new LA cell were consistent with those achieved by solution methods (95% confidence limit).

The use of *ICP-TOF-MS for elemental and isotopic analyses* has particular advantages when combined with LA sampling. Gundlach-Graham *et al.***296** used LA-ICP-TOF-MS with a low dispersion ablation cell to generate large format (4 x 2 mm), high dynamic range (1–106 µg g^{-1}) and quantitative multi-elemental 2D compositional maps of a mineralogically complex fault rock from Italy. Data were acquired in a few hours. It was possible to assign mineral phases directly from LA-ICP-TOF-MS data, with good agreement between the elemental mass fractions determined by LA-ICP-TOF-MS imaging with 100% normalisation quantification and those determined employing conventional LA-ICP-MS spot analysis with ^{29}Si as the IS. The elemental images provided unique insights into the genesis of the fault system. Direct isotopic analysis of individual µm-sized U-containing reference particles by LA-ICP-TOF-MS exploited**52** the very high temporal resolution of the technique and gave quasi-simultaneous measurement of all nuclides. Internal and external precisions of 0.2-0.4% could be achieved for ^{235}U/^{238}U measurements when both isotopes had the same abundance. For materials with more natural U isotopic signatures, the precision was 4-5%. Although ^{234}U/^{238}U and ^{236}U/^{238}U were measured successfully, the precision was limited when the abundance of the minor isotope was very low (in the 10^{-5} range). The potential of ICP-TOF-MS in combination with collision/reaction cell technology was evaluated**297** using a range of sample introduction schemes including high- and low-dispersion LA and microdroplet generation. Hydrogen was used as the reaction gas and He as the collision gas. The sensitivity for intermediate- and high-*m/z* elements was improved by a factor of 1.5 to 2 with small flow rates of H_2 and He (or a mixture of both gases). Use of H_2 as the reaction gas made it possible to suppress background species such as Ar^+ and Ar_2^+

selectively. The LODs for many of the elements contained in NIST SRM 610 (trace elements in glass) were improved by a factor of two to four.

5.3.4.1 ***Trace element determinations by ICP-MS.*** A procedure[298] for the determination of *Ca and Mg concentrations in foraminifera calcite* combined an automated on-line dual-dilution manifold with different octopole conditions (no gas or H_2) to optimise the acquisition of Ca and Mg signals by quadrupole ICP-MS. This strategy, which included the on-line addition of Sc as an IS, and the ability to analyse two dilutions of each sample minimised memory effects and effectively mitigated matrix effects and instrumental drift. The instrumental LOD for Mg/Ca was 0.6 nmol mol^{-1} for sample sizes of only 20 µg. The method was validated using RMs (LGC ECRM-752-1, limestone; Chinese RM CMSI-1767, limestone; and BAM-RS3, calcium carbonate) with Mg/Ca ratios in the 0.8 to 5.7 mmol mol^{-1} range. Repeatabilities were 0.3 - 0.7%.

The use of *solid-sampling electrothermal-vaporisation ICP-MS* for the determination of As, Sb, Se and Te in coal overcame[299] the difficulties of digesting this type of material. Operational parameters evaluated included the furnace temperature programme, mass of Ir modifier, oxygen flow rate in the pyrolysis step and carrier and bypass gas flow rates. Whereas it was possible to use aqueous standard solutions to calibrate As, Sb and Te determinations, coal CRMs were required to calibrate the determination of Se. No statistical difference was observed between results obtained by SS-ETV-ICP-MS and those obtained by ICP-MS after sample digestion. Data for NIST coal SRMs agreed with the certified values. The SS-ETV-ICP-MS LOQs of 0.03, 0.01, 0.03 and 0.006 µg g^{-1} for As, Sb, Se and Te, respectively, were lower than those obtained using decomposition methods.

A novel approach[300] was adopted for *in situ* trace element determinations when *analysing melt inclusions by LA-ICP-MS*. Instead of ablating an entire melt inclusion along with the host mineral, melt inclusions were exposed by polishing the sample surface so that the melt inclusion could be ablated without the host material. This reduced the uncertainty associated with measured concentrations because no deconvolution of the mixed ablation signal was necessary. In contrast, Yang *et al.*[301] developed a new quantification strategy for deconvoluting LA-ICP-MS signals from ablated melt or fluid inclusions from those from the host material. Varying proportions of the target and host material were ablated and the resulting mixtures defined a linear trend for which the end points could be determined if the concentration of at least one element was known independently for both phases. Results provided by the two linear-regression deconvolution methods proposed in this study were within ±15% of compositions derived from traditional data quantification. One advantage of this new approach was that it enabled accurate quantification of features smaller than the laser spot size to be made. In the *in situ* quantification of Cl and S in melt inclusions, glasses and minerals by LA-ICP-MS, a correction procedure**302** accounted for signals enhanced by mobilisation of Cl and S contamination from the walls of the ablation cell and transfer tubing. For accurate results down to a few hundred μg g^{-1} for both elements to be achieved, it was essential that the ICP-MS instrument had relatively low backgrounds for Cl and S and that instrument-specific corrections be established using samples with known Cl and S contents.

Branson *et al.***303** developed a *new data-analysis-package for processing LA-ICP-MS data*. The emphasis of this Python-based open-source package (LAtools) was on ensuring that the reduction of trace element data from complex, heterogeneous samples was fully reproducible while at the same time operating with efficacy similar to that of existing software. It was recommended that a series of analytical parameters additional to the LA-ICP-MS data (*e.g.* laser repetition rate, spot size, gas flow rate) should be included in any publication in order to increase the transparency and reliability of the LA-ICP-MS data.

5.3.4.3 ***Isotope ratio determinations by ICP-MS.*** Much research effort continues to be devoted to the *measurement of isotope ratios by MC-ICP-MS* and other techniques. Relatively modest developments such as modified column chemistry or instrument configuration are summarised in Table 5.

[Table 5]

Several *reviews on isotope ratio measurements by ICP-MS* were noteworthy. Yang *et al.***304** (176 references) summarised models available to correct for isotopic fractionation in MC-ICP-MS measurements. Models for mass-dependent fractionation were considered together with the latest findings on the causes of mass-independent fractionation. It would appear that this is a more frequent phenomenon than previously thought and the implications of this for several of the models commonly used for correcting for mass bias was outlined. A flow chart for the selection of an appropriate mass bias correction model was provided to assist the reader in implementing a suitable measurement strategy to obtain accurate isotope ratios. Emphasis was placed on the importance of accounting for all possible sources of uncertainty so that a meaningful comparison could be made of isotope ratio results obtained by different research groups. On a related theme, another review**305** (53 references) focussed on practical considerations in the use of the double-spike technique to correct for instrumental mass bias. The advantages of this technique over other methods such as sample-calibrator bracketing were emphasised. Of particular advantage was the ability to eliminate mass-dependent fractionation during sample processing and measurement if the double spike was added beforehand. The detailed description of how to design and calibrate a suitable double-spike and optimise analytical strategies was aimed at researchers new to the subject. A review**[306]** (87 references) of current research and instrumental developments in the application of LA-ICP-MS to the isotope ratio analysis of hard and soft biological tissues is of direct relevance to geoanalysis. Limitations to obtaining accurate and precise isotope ratios were highlighted, an overview of recent applications provided and an outlook on potential future developments given.

Research into specific *MC-ICP-MS instrument configurations* included a study**[307]** of four different sample and skimmer cone combinations and their effect on the accuracy and precision of Mg isotope measurements in wet-plasma mode. The performance of the Jet sample cone combined with an H skimmer cone was regarded as outstanding for its good accuracy and best precision and was therefore recommended for this particular application. In the context of U-series disequilibria measurements by MC-ICP-MS, Scott *et al.***[308]** evaluated the use of retardation energy filters combined with ion counting detectors. A systematic bias for $^{234}U/^{238}U$ and $^{230}Th/^{232}Th$ measurements occurred when a retarding potential quadrupole (RPQ) lens was not used. Each RPQ combined two charged lenses (decelerator and suppressor) that could be tuned to achieve the best abundance sensitivity while at the same time maximising ion transmission. The use of RPQs in the ion counting system was always recommended when measuring isotope ratios of the order of $\leq 10^{-5}$ in order to minimise the background. The RPQ configuration made it possible to measure ^{210}Pb in geological samples with low concentrations of common Pb (*e.g.* carbonates and silica sinter) as well as ^{226}Ra concentrations in rock RMs. New ^{226}Ra, Th, $^{230}Th/^{232}Th$ and U data were presented for 10 USGS geological RMs and AThO, a rhyolite from Iceland. To overcome interferences from scattered ions and peak tailing of the intense $^{40}Ar^+$ and $^{40}Ca^+$ ion beams when making high-precision stable Ca isotope measurements by MC-ICP-MS, Li *et al.***[309]** designed a so-called "dummy bucket" to trap $^{40}Ar^+$ and $^{40}Ca^+$. The dummy bucket consisted of a metal box with the same external dimensions as a normal FC and was installed at the low mass side of a grounded baffle plate of the lowest-mass mechanically adjustable FC. The $^{40}Ar^+$ and $^{40}Ca^+$ ion beams were assigned to the dummy bucket and the charges released via the attached grounded baffle plate in front of the bucket. Long-term external precisions based on repeated measurements of standard solutions and rock RMs were better than ±0.07‰ (2SD) for $\delta^{44}Ca/^{42}Ca$ and ±0.10‰ (2SD) for $\delta^{43}Ca/^{42}Ca$, respectively. Other possible interferences could be removed by using efficient chemical separation or be resolved at a high operating resolution of 2500.

5.3.5 Secondary ion mass spectrometry

A personal reflection on *the past, present and future of SIMS* was presented in a detailed contribution by Shimizu[310]. He recounted how he became involved with SIMS in the early days of its development in the 1970s and helped to develop some significant geochemical applications over four decades, reflecting his fundamental curiosity about nature.

In a new *sample preparation technique*[311], specimens were mounted using an alloy of *ca.* 52% tin and *ca.* 48% bismuth rather than epoxy resin which degases readily under ultra-high vacuum conditions. The use of the tin alloy mounts together with an automatic liquid-nitrogen refilling-system significantly improved the vacuum conditions by about one order of magnitude. Compared to the indium mounts commonly used for ultra-high vacuum measurements, tin alloy mounts were easier to polish to give the relief of <2 µm essential for high-precision isotope analysis by SIMS. The spot-to-spot reproducibility of 0.15‰ (1SD) for O_2 isotope ratios was comparable with that obtained using routine epoxy mounts. This novel preparation method was ideal for measuring water content in olivine or other anhydrous minerals.

Matrix effects remain a key issue for SIMS analyses. Schicchitano *et al.*[312] investigated matrix bias related to Mg/Fe variations when measuring oxygen isotope ratios in olivines by SHRIMP analysis. The observed matrix bias was +0.7‰ to -2‰ for olivines with forsterite contents of 74-100 mol%. The correction scheme developed, based on a quadratic function of the minor fayalite content, was applied to chemically zoned olivine crystals from a partly serpentinised dunite to identify the source of the serpentinising fluids. The matrix-dependent bias that occurs when determining Li mass fractions in silicate glasses by SIMS was quantified[313] by analysing a range of silicate glass RMs. A clear correlation of the relative ion yield (RIY) for Li with SiO_2 mass fractions was evident; in silica-rich matrices the RIY for Li was about 40% higher than in matrices with low silica contents. In addition to their own measurements, the researchers evaluated published Li mass fraction data by comparing results obtained by SIMS with those obtained by other techniques such as ICP-MS and LA-ICP-MS. The differences were especially striking for basaltic and ultramafic samples for which published SIMS data differed by up to 40% from data derived by other techniques. Updated preferred values for several MPI-DING and

USGS RMs were proposed together with valuable recommendations for the quantification of Li mass fractions by SIMS.

Other *geological applications of SIMS* included a study**[314]** to determine abundances of the short-lived radionuclide ^{10}Be ($t_{½}$ = 1.4 Ma) in meteoritic samples. It was necessary to determine the relative sensitivities of B and Be so that ^{9}Be/^{11}B ratios could be measured and then initial ^{10}Be/^{9}Be ratios estimated. Five synthetic melilitic glasses were doped with trace amounts of B and Be to give varying Be/B ratios and were analysed together with NIST SRM 610 (glass) by nanoSIMS and LA-ICP-MS. The Be/B relative sensitivities of the melilitic glasses were identical to that of the NIST 610 glass, indicating that matrix effects were insignificant for Be-B measurements. These findings were important for determination of accurate initial abundances of ^{10}Be to provide information on the astrophysical conditions in the Early Solar System. A novel protocol**[315]** for *in situ* N-abundance and isotope analyses of basaltic glasses by high-mass-resolution SIMS was capable of resolving significant isobaric interferences. Twelve (C-)N-bearing synthetic basaltic glasses with N concentrations between <1 and 18,443 ± 966 µg g^{-1} were prepared as RMs for the study. By targeting the AlN^{-}, CN^{-}, NO^{-} and SiN^{-} secondary molecular ions, N abundances were determined down to the µg g^{-1} level in both carbon-bearing and carbon-free glasses. Analytical precision and reproducibilities of 11‰ and 10-17‰ (2SD) were achieved for $^{15}NO^{-}/^{14}NO^{-}$ measurements in glass RMs containing ≥100 µg g^{-1} N. This new analytical protocol could help to improve our understanding of the N characteristics of the deep Earth and other planetary interiors as it enabled, for the first time, the study of the concentration and isotopic composition of N trapped within µm-sized silicate phases such as melt inclusions in terrestrial and extraterrestrial samples. Jones *et al.***[316]** developed a methodology for extracting accurate 3D isotopic information from pyrite (FeS_2) minerals in thin sections using SIMS-based ion imaging. The protocol allowed the spatial variability of δ^{34}S across individual grain surfaces to be determined and enabled the 'true' size of grains to be estimated from the apparent size by assessing rates of radius change with depth. This technique could be applied to SIMS-based elemental and isotopic ratio measurements of a range of minerals in thin sections.

5.3.6 Other mass spectrometric techniques

Three separate contributions involved the coupling of *elemental analysers to IRMS systems* for the determination of δ^{2}H in different matrices. In all three systems, water was reduced to H on a column packed with chromium and operated at high temperature. A rapid method**[317]** for determining δ^{2}H in water extracted from micro-inclusions in minerals such as quartz was calibrated using three aqueous RMs (VSMOW, GISP, W-62001) and validated by analysing new phyllosilicate RMs USGS57 (biotite) and USGS58 (muscovite) intended to be replacements for NBS 30. Advantages of the new method were the small minimum sample size of *ca.* 20 mg and the high throughput of about 30 samples per day. The reproducibility was <3‰. An improved method for the determination of H isotope ratios of aqueous inclusions in halite employed[318] CF EA-pyrolysis-IRMS. Analysis of Precambrian halite samples with low H concentrations (30-300 $\mu g\ g^{-1}$) yielded δ^2H_{VSMOW} values ranging from -89 to -38‰ with an average SD of ±5.4‰. Greenwood[319] employed EA-IRMS for the measurement of H mass fractions and δ^2H in apatites. The ability of chromium to bind with P in the reactor conferred an advantage over TC-EA methods as it prevented clogging of the instrument by elemental P. The importance of removing adsorbed moisture from nominally hydrous minerals and glasses was demonstrated.

The presence of nitrate can affect the accuracy of *oxygen isotope ratio measurements in carbonates* by IRMS because isobaric interferences are created during the phosphoric acid digestion step at 72 °C. Hu *et al.*[320] used a low-temperature (25 °C) phosphoric acid digestion method to decrease the production of NO_2 during CO_2 extraction from nitrate-rich samples such as speleothems and evaporites. Subsequent measurements of $\delta^{13}C$ and $\delta^{18}O$ by CF IRMS yielded accuracy and precisions for nitrate-doped carbonate RMs that were indistinguishable from those of the undoped RMs.

Pulsed-direct-current GD-TOF-MS was used[321] to quantify concentrations of 24 major and trace elements in ore samples directly. Benefits of this technique included low spectral interferences and LODs and a minimal amount of sample pre-treatment as the measurements were performed on pressed powders. For quantification, RSFs were determined using two RMs (NIST SRM 2782 (industrial sludge) and a gabbro, SGD-1A, from the Institute of Geochemistry in Irkutsk, Russia) and Fe as IS. The method was validated by analysing an ore sample previously characterised by different techniques. Any differences between GD-TOF-MS data and those obtained by ICP-AES were attributed to shortcomings in the microwave digestion procedure and spectral interferences affecting the ICP-AES measurements.

5.3.7 X-ray spectrometry and related techniques

The advent of pXRF instruments has revolutionised *mineral exploration*. McNulty *et al.*[322] compared pXRFS data from powdered samples and the flat cut surface of a drill core with those obtained by conventional laboratory-based XRFS. Trends in Ti/Zr ratios observed from the laboratory-based analysis were reproduced by pXRFS measurements on both pressed pellets and the intact drill core. Analysis of unprepared drill core samples rather than powders made no significant difference to accuracy or precision. In this case study, hydrothermally altered rock types could be identified by their Ti/Zr ratios so pXRFS could be considered a time- and cost-efficient alternative to laboratory-based XRFS for many key lithogeochemical elements when used together with geological observations. A routine pXRF sampling methodology and data processing procedure was proposed. The importance of a multi-technique approach was demonstrated[323] in a study of drill cores of contrasting textures, chemistry and mineralogy. The samples were analysed by a number of techniques including pXRFS in mining and soil modes, portable IR analysis and laboratory-based techniques (Raman spectroscopy, XRD analysis, ICP-AES and XRFS). Surface roughness had only a minor effect on the signals gathered by the portable instruments so clean drill core surfaces could be analysed without the need for commonly practiced core cutting. However, precise calibration based on ore- and mine-specific RMs was considered mandatory, especially for pXRFS.

Synchroton-based XANES was used[324] to measure Fe^{2+} and Fe^{3+} directly on three tourmaline samples (dravite, povondraite and oxy-schorl) to complement the chemical characterisation by EPMA. Better knowledge of the Fe oxidation states was required to avoid the considerable errors in structural formulae and classification that occurred when it was assumed that all Fe existed as either Fe^{2+} or Fe^{3+}. In an evaluation[325] of bulk and microfocused synchrotron-XANES for investigating V speciation in marine sediments, the S/N ratios of the XANES spectra were too poor to allow accurate quantitative analysis. Scanning XRF microscopy, used to image elemental distributions in the sediment sample with the aim of identifying host phases of vanadium, was limited in its ability to distinguish between Ti and V because of the close proximity of their fluorescence emission lines. Cautious interpretations were required as well as rigorous QC measures.

Two *regression models for XRFS* – ordinary linear regression (OLR) and uncertainty-weighted linear regression (UWLR) – were compared in a study[326] of 59 geochemical RMs and a procedural blank. The UWLR model was preferred for routine calibrations of XRFS analytical procedures because it generally gave lower uncertainties or narrower confidence intervals than those of the OLR model.

6. Glossary of terms

2D	two dimensional
3D	three dimensional
AAS	atomic absorption spectrometry
AB	arsenobetaine
AEC	anion exchange chromatography
AES	atomic emission spectrometry
AFS	atomic fluorescence spectrometry
AMP-PAN	ammonium molybdophosphate-polyacrylonitrile
AMS	accelerator mass spectrometry
amu	atomic mass unit
ANOVA	analysis of variance
APCI	atmospheric pressure chemical ionisation
APDC	ammonium pyrrolidine dithiocarbamate
ASU	Atomic Spectrometry Update
ATR	attenuated total reflectance
AVEC	attenuation versus evolved carbon
BAM	Bundesamt für Materialforscung und Prüfung (Germany)
BCR	Community Bureau of Reference (of the Commission of the European Communities)
BEC	background equivalent concentration
BMEMC	Beijing Municipal Environmental Protection Monitoring Center
BP	bulk particle
BSE	back-scattered electron
C_{18}	octadecyl bonded silica
CA	chemical abrasion
CCD	charge coupled detector
CCRMP	Canadian Certified Reference Materials Project
CCT	collision cell technology
CE	capillary electrophoresis
CEC	cation exchange capacity
CF	continuous flow
CFA	continuous flow analysis

CIMS	chemical ionisation mass spectrometry
CLD	chemiluminescence detection
CNN	convolutional neural network
CNT	carbon nanotube
CPE	cloud point extraction
cps	counts per second
CRM	certified reference material
CRPG	Centre de Recherches Petrographiques et Geochimiques France
CS	continuum source
CSDFME	continuous sample drop flow-based microextraction
CT	computed tomography
CTAB	cetyl trimethylammonium bromide
CV	cold vapour
CVG	chemical vapour generation
CW	continuous wave
DA	discriminant analysis
DART	direct analysis in real time
DBT	dibutyltin
DDTC	diethyldithiocarbamate
DE	detection efficiency
DL	diode laser
DGA	diglycolamide
DGT	diffusive gradient in thin films
DLLME	dispersive liquid liquid microextraction
DMA	dimethylarsonic acid
DME	dispersive microextraction
DMF	dimethylformamide
DOC	dissolved organic carbon
DOM	dissolved organic matter
DPC	diphenylcarbazone
DRI	Desert Research Institute (USA)
DRS	diffuse reflectance spectrometry
DTPA	diethylenetriaminepentaacetic acid
EA	elemental analyser
ED	energy dispersive

EDB	electrodynamic balance
EDTA	ethylenediaminetetraacetic acid
EDXRF	energy dispersive X-ray fluorescence
EDXRFS	energy dispersive X-ray fluorescence spectrometry
ELM	extreme learning machine
EM	electron multiplier
EN	European Committee for Standardisation
EPMA	electron probe microanalysis
ERA	Environmental Research Associates
ERM	European reference material
ESI	electrospray ionisation
ETAAS	electrothermal atomic absorption spectrometry
EtHg	ethylmercury
ETV	electrothermal vaporisation
EU	European Union
EUSAAR	European Supersites for Atmospheric Aerosol Research
FFF	field flow fractionation
FAAS	flame atomic absorption spectrometry
FC	Faraday cup
FFF	field flow fractionation
FI	flow injection
FIA	flow injection analysis
FT	Fourier transform
FTIR	Fourier transform infrared
GAW	Global Atmosphere Watch
GC	gas chromatography
GD	glow discharge
GLS	gas liquid separator
GPS	global positioning system
GRIP	Greenland Ice Core Project
GSJ	Geological Survey of Japan
HEN	high efficiency nebuliser
HFSE	high field strength element
HG	hydride generation
HPLC	high performance liquid chromatography

HG	hydride generation
HILIC	hydrophilic interaction liquid chromatography
HME	hydrophilicity microextraction
HPLC	high performance liquid chromatography
HR	high resolution
HREE	heavy rare earth element
IAEA	International Atomic Energy Authority
IAG	International Association of Geoanalysts
IAPSO	International Association of the Physical Sciences of the Ocean
IC	ion chromatography
ICOS	integrated cavity output spectroscopy
ICP	inductively coupled plasma
id	internal diameter
ID	isotope dilution
IDA	isotope dilution analysis
IEC	ion exchange chromatography
IGGE	Institute of Geophysical and Geochemical Exploration
IGI	Institute of Geochemistry, Irkutsk (Russia)
IMEP	International Measurement Evaluation Programme
INAA	instrumental neutron activation analysis
INCT	Institute of Nuclear Chemistry and Technology (Poland)
IOM	Institute of Occupational Medicine (Scotland)
IPGP	Institut de Physique du Globe de Paris
IR	infrared
IRA	isotope ratio analysis
IRMM	Institute for Reference Materials and Measurements
IRMS	isotope ratio mass spectrometry
IS	internal standard
ISBN	international standard book number
ISM	incremental sampling methodology
ISO	International Organization for Standardization
JIS	Japanese Industrial Standards
JMC	Johnson Matthey Corporation
JRC	Joint Research Centre (of the European Commission)
JSAC	Japan Society for Analytical Chemistry

KED	kinetic energy discrimination
LA	laser ablation
LASS	laser ablation split stream
Lasso	least absolute shrinkage and selection operator
LDI	laser desorption ionisation
LGC	Laboratory of the Government Chemist (UK)
LIBS	laser-induced breakdown spectroscopy
LIF	laser-induced fluorescence
LIFS	laser-induced fluorescence spectrometry
LLE	liquid-liquid extraction
LLME	liquid liquid microextraction
LOD	limit of detection
LOQ	limit of quantification
LPME	liquid phase microextraction
LREE	light rare earth element
LS	least squares
MAD	microwave assisted digestion
MAE	microwave-assisted extraction
MBT	monobutyltin
MC	multicollector
MDL	method detection limit
MeHg	methyl mercury
MIBK	methyl isobutyl ketone
MIL	magnetic ionic liquid
MIO	magnetic iron oxide
MIP	microwave induced plasma
MIR	mid infrared
MLLE	micro liquid-liquid extraction
MMA	monomethylarsonic acid
MP	microwave plasma
MPI	Max Planck Insitute
MRM	multi reaction monitoring
MS	mass spectrometry
MS/MS	tandem mass spectrometry
MSPE	magnetic solid phase extraction

MU	measurement uncertainty
MWCNT	multiwalled carbon nanotube
m/z	mass to charge ratio
μLIBS	micro laser-induced breakdown spectroscopy
μXRF	micro X-ray fluorescence
μXRFS	micro X-ray fluorescence spectroscopy
NAA	neutron activation analysis
NACIS	National Analysis Centre for Iron and Steel
NBS	National Bureau of Standards
NCS	National Analysis Center for Iron and Steel (China)
Nd:YAG	neodymium doped: yttrium aluminium garnet
NF	Normes Françaises
NIES	National Institute for Environmental Studies
NIOSH	National Institute of Occupational Safety and Health
NIR	near infrared
NIST	National Institute of Standards and Technology
NMIJ	National Metrology Institute of Japan
NMR	nuclear magnetic resonance
NP	nanoparticle
NRCC	National Research Council of Canada
NRCCRM	National Research Centre for Certified Reference Materials (China)
NTIMS	negative thermal ionisation mass spectrometry
NWRI	National Water Research Institute
OM	organic matter
PAH	polyaromatic hydrocarbon
PCA	principal component analysis
PCR	principal component regression
PDA	photodiode array
PDMS	polydimethylsiloxane
PFA	perfluoroalkyl
PFAS	perfluoroalkyl substance
PGE	platinum group element
PhHg	phenylmercury
PIXE	particle-induced X-ray emission
PLS	partial least squares

PLSR	partial least squares regression
$PM_{2.5}$	particulate matter (with an aerodynamic diameter of up to 2.5 µm)
PM_4	particulate matter (with an aerodynamic diameter of up to 4.0 µm)
PM_{10}	particulate matter (with an aerodynamic diameter of up to 10 µm)
ppb	parts per billion (10^{-9})
ppm	parts per million (10^{-6})
ppt	parts per trillion (10^{-12})
PSL	polystyrene latex
PTE	potentially toxic element
PTFE	poly(tetrafluorethylene)
PTR	proton transfer reaction
PVC	poly(vinylchloride)
PVG	photochemical vapour generation
pXRF	portable X-ray fluorescence
pXRFS	portable X-ray fluorescence spectrometry
QA	quality assurance
QC	quality control
QCL	quantum cascade laser
QCLAS	quantum cascade laser absorption spectrometry
RCS	respirable crystalline silica
RDD	rotating disc dilutor
REE	rare earth element
rf	radiofrequency
RIMS	resonance ionisation mass spectrometry
RM	reference material
RP	reversed phase
RMSEP	route mean square error of prediction
RSD	relative standard deviation
RSF	relative sensitivity factor
RTC	Resource Technologies Corporation
SAEME	surfactant-assisted emulsification microextraction
SARM	South African Reference Material
SAX	strong anion exchange
SAXS	small angle X-ray scattering
SBET	simplified bioaccessibility extraction test

SBME	solvent bar micro-extraction
SC	single collector
SCF	supercritical fluid
SD	standard deviation
SDD	silicon drift detector
SDS	sodium dodecyl sulfate
SE	standard error
SEC	size exclusion chromatography
SEM	scanning electron microscopy
SEM-EDS	scanning electron microscopy energy dispersive (X-ray) spectrometry
SF	sector field
SFOD	solidification of a floating organic droplet
SHRIMP	sensitive high resolution ion microprobe
SI	Système International (d'unités)
SIMS	secondary ion mass spectrometry
SLME	solid liquid microextraction
SMPS	scanning mobility particle sizer
S/N	signal-to-noise ratio
SOA	secondary organic aerosol
SOC	soil organic carbon
SOM	soil organic matter
sp	single particle
SPAMS	single particle aerosol mass spectrometry
SPE	solid phase extraction
SPME	solid phase microextraction
SPR	suspended particulate reagent
SPS	Spectrapure Standards
SQT	slotted quartz tube
SR	synchrotron radiation
SRM	standard reference material
SS	solid sampling
SSB	sample standard bracketing
SSID	species specific isotope dilution
SSME	supramolecular solvent microextraction
SVM	support vector machine

TA	thermal annealing
TBT	tributyltin
TC	total carbon
TD	thermal desorption
TEM	transmission electron microscopy
TEOM	tapered element oscillating microbalance
TGA	thermal gravimetric analysis
TIMS	thermal ionisation mass spectrometry
TMAH	tetramethylammonium hydroxide
TML	tetramethyllead
TOF	time-of-flight
TXRF	total reflection X-ray fluorescence
TXRFS	total reflection X-ray fluorescence spectrometry
UACPE	ultrasound-assisted cloud point extraction
UA	ultrasound-assisted
UAE	ultrasound-assisted extraction
UAEME	ultrasound-assisted emulsification microextraction
UBMG	unified bioaccessibility method (gastric fluid only)
UME	National Metrology Institute of Turkey
USB	universal serial bus
US EPA	United States Environmental Protection Agency
USGS	United States Geological Survey
USN	ultrasonic nebuliser
UV	ultraviolet
UV-VIS	ultraviolet-visible
VG	vapour generation
VIS-NIR	visible near infrared
VIS-NIRS	visible near infrared spectrometry
VSMOW	Vienna Standard Mean Ocean Water
WDS	wavelength dispersive spectrometry
WDXRF	wavelength-dispersive X-ray fluorescence
WDXRFS	wavelength-dispersive X-ray fluorescence spectrometry
WHO	World Health Organisation
WMO	World Metrological Organisation
XANES	X-ray absorption near-edge 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. Preconcentration methods using solid phase extraction for the analysis of water

Analytes	Matrix	Substrate	Coating or modifier	Detector	LOD in µg L^{-1} (unless stated otherwise)	Validation	Reference
Ag, Cd, Co, Fe, Ni, Pb, Zn	water	pencil lead, CNTs, polypyrrole	1, 10 phenanthroline	ICP-MS	0.012 (Ag)-0.163 (Fe)	HPS CRM TMDW (trace metals in drinking water)	327
As^{III} or As^{V}	water	graphene oxide	polyethylenimine	HG-MIP-AES	1.3 (As^{V}) -1.8 (As^{III}) ng L^{-1}	NIST SRM 2669 (arsenic species in frozen human urine) and spike recovery	328
As^{III} and As^{V}	tap water and synthetic seawater	CeO_2/ZrO_2 mixed binding gel	none	HG-AFS	0.06 (As^{III}) and 0.08 (As^{V})	not reported in abstract, paper in Chinese	158
As^{V}, Cd, Co, Cr^{III}, Cu, Ge, Ni, Pb, Sb, Se^{IV}, Sn, Ti, U, V, W, Zn, Zr	seawater	InertSep ME2 chelating resin	$Fe(OH)_3$ *in situ* coprecipitate	ICP-MS	0.1 (Sb) to 7.4 (Ti) ng L^{-1}	spike recovery	329
As^{III}, Au^{III}, Bi^{III}, Co^{II}, Hg^{II}, Ni^{II}, Pb^{II}, Se^{IV}	water	graphene membranes on glass support	APDC	TXRFS	0.15 (Se) to 0.5 (Bi)	Merck CRM QC1187(Trace Metals-ICP Sample 1) and CRM QC1014 (Trace Metals AA Sample 1)	330
Cd	tap water	mesoporous silica	CTAB and a doubly imprinted polymer	ETAAS	0.001	spike recovery	331
Cd	water and oysters	$CoFe_2O_4$ magnetic NPs	none	FAAS	0.24	NIST SRM 1566b (oyster tissue) and spike recovery	332
Cd, Co, Cu, Fe, Mn,	ground and waste water	particulate polyethylene	sintered Presep® PolyChelate	ICP-AES	0.007 (Cd) to 0.160 (Zn)	SCP science RMs EnviroMAT ES-L-1	333

Mo, Ni, Pb, Ti, V, Zn						(ground water) and EU-L-3 (waste water)	
Cd, Pb	bottled and tap water	Fe_3O_4 coated with SiO_2	thiol-rich polyhedral oligomeric silsesquioxane	ICP-AES	0.08 (Cd) and 0.12 (Pb)	BMEMC GBW08608 (natural water)	334
Cd, Pb	water	graphene oxide coated with metallic Ag	Triton X-114	ETAAS	2 (Cd) and 30 (Pb) ng L^{-1}	NIST SRM 1640a (trace elements in natural water), IRMM ERM-CA011b (hard drinking water), Environment Canada CRM TMRain-04 (simulated rain water), and RMs TM-25.4 (low level fortified lake water) and TM-23.4 (fortified lake water)	335
Cd, Cu, Pb	water	magnetic Ambersorb-563 resin	1-nitro-2-naphthol-3, 6-disulfonic acid disodium salt	FAAS	1.4 (Cd) to 5.8 (Cu)	NWRI EC CRM TMDA-53.3 (fortified water) and spike recovery	336
Cd, Cu, Ni, Pb	waste water	graphene nanoplatelets	none	ETAAS	0.4 (Cu) to 5.4 (Pb)	HPS RM CWW-TM-E (waste water)	337
Co, Hg	tap, mineral and lake waters	Fe_2O_3 NPs	*Pleurotus eryngii* (fungus)	ICP-AES	0.01 (Co) and 0.06 (Hg)	NIST SRM 1643e (trace elements in water), SCP science RM EU-L-2 (waste water), NWRI EC RM NWTM-15 (fortified water)	338
Co, Ni	tap, well and river water, tea and spinach leaves	sodium dodecyl sulphate-coated Fe_3O_4 NPs	2-nitroso-1-naphthol	FAAS	0.09 (Ni) and 0.4 (Co)	spike recovery	339
Cr^{III}	natural water	nanographite	Al_2O_3	EDXRFS	0.04	NIST SRM 1640a (trace elements in natural water)	340

Cr	bottled, tap, river and sea water	microcrystalline cellulose	Triton X-100 and CPE	ETAAS	6 ng L^{-1}	Environment Canada CRM TMRain-04 (simulated rain water), Environment Canada RMs TM-25.4 (low level fortified lake water) and TM-23.4 (fortified lake water), NIST SRM 1640a (trace elements in natural Water) and NRCC CRM NASS 6 (seawater)	341
labile Cr^{III} and Cr^{VI}	river water	ZrO_2 binding gel as a DGT sampler	none	HPLC-ICP-MS	0.05 (Cr^{III}) and 0.02 (Cr^{VI})	comparison with an in-house standard method	342
Er	water	graphene oxide nanosheets collected by Fe_3O_4 microparticles	3-hydroxy-N'-[(1Z)-pyridin-2-ylmethylidene]naphthalene-2-carbohydrazide	HR-CS-ETAAS	6 ng L^{-1}	analysis of an unspecified reference solution and spike recovery	343
Fe^{II} and Fe^{III}	water and seawater	3D printed acrylate resin	none	ICP-MS	1-2 ng L^{-1} (Fe^{III}) and 1 ng L^{-1} (Fe^{II})	NRCC CRM SLEW-3 (estuarine water), and NIST SRMs 1640a (natural water) and 1643e (trace elements in water)	344
Hg	water	PVC membrane	dithizone	TXRFS	0.3	spike recovery	345
Hg	water	silica wafer	gold NPs	TD-GC-AFS	0.8 ng L^{-1}	NRCC CRM ORMS-5 (elevated mercury in river water)	346
Hg^{2+} and MeHg	water and fish	polypropylene hollow fibre	toluene (MeHg) and DDTC plus 1-octanol (Hg^{2+})	ETAAS	0.06 (MeHg) and 0.14 (Hg^{2+})	spike recovery (water) and NIST SRM 1566b (oyster tissue)	347
Hf, Nb, Ta, Zr	seawater	UTEVA® resin	none	ICP-MS	0.03 (Ta) to 0.15 (Zr) pmol kg^{-1}	spike recovery and comparison with standard method	348
Pb	tap, river and well	graphene oxide	4-(2-pyridylazo)resorcinol and Fe_2O_3	ETAAS	0.18 ng L^{-1}	ERA QC solution concentrate 1340	349

	water plus fruit juices					(metals in clean water)	
^{226}Ra	natural water	Analig® Ra-01	none	ICP-MS/MS	68 mBq L^{-1} (Scott Spay Chamber), 8 mBq L^{-1} (heated nebuliser system)	spike recovery	350
REEs	tap and river water	calcium alginate microparticles	none	ICP-MS	0.01 (Tb) to 0.03 (Yb)	spike recovery	351
REEs	tap, river and seawater	silica	pyrolised lignin	ICP-MS	0.4 to 0.6 ng L^{-1} (for unspecified elements)	spike recovery	352
Rh, Pd, Pt	seawater	NOBIAS chelate-PA1 resin	none	ICP-MS	16.5 (Pt) to 26.9 pg L^{-1}	spike recovery	353
Se^{IV}	natural water	fused silica capillary	ethylenediamine modified poly(glycidyl methacrylate-ethylene dimethacrylate)	ICP-MS	14 ng L^{-1}	BMEMC GBW(E)080395 (environmental water)	354
Se	rain, tap, underground and seawater	nanosilica	APDC	ETAAS	1.4 ng L^{-1}	NIST SRM 1643e (trace elements in water)	355
Th^{IV}, U^{VI}	tap, river and lake water	Fe_2O_3 NPs	*Bovista plumbea* (fungus)	ICP-AES	0.02 (both elements)	NRCC CRM CASS 4 (near shore seawater) and NWRI EC RM NWTM-15 (fortified water)	356
Tl^{I}	water	aminodibenzo-18-crown-6 functionalised Fe_3O_4 NPs	metal organic framework MIL-101(Cr)	ETAAS	1.5 ng L^{-1}	NIST SRM 1643d (trace elements in water) and spike recovery	357
U^{VI}	water	3D printed polymeric device	TEVA® resin and Aliquat®336 (trioctylmethylammonium chloride)	ICP-MS	0.032 ng (from a 30 mL sample) (1 ng L^{-1})	intercomparison water sample CSN/CIEMAT 2011	358

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

Analytes	Matrix	Method	Reagents	Detector	LOD in µg L^{-1} (unless stated otherwise)	Method validation	Reference
silver NPs	waste water	CPE	Triton X-114, EDTA and $Na_2S_2O_3$	ETAAS	0.04	spike recovery comparison with sp-ICP-MS	359
silver NPs	environmental water samples	DLLME	acetonitrile/water and 1-octanol and $Na_2S_2O_3$	FAAS	6.5	spike recovery	360
silver and gold NPs	mineral, tap, river and seawater	CPE	Triton X-114 and $Na_2S_2O_3$	TXRFS	0.3 (Ag) and 0.2 (Au)	spike recovery	361
Ag, Cd, Pd	tap, river, waste and hyper saline water	SBME	Cyphos® 101 ionic liquid (trihexyl(tetradecyl)phosphonium chloride)	ICP-MS	7 ng L^{-1} (Pd) to 21 ng L^{-1} (Ag)	spike recovery	362
Be	effluent, seawater and tap water	CPE	Triton X-114 and graphene oxide micro-suspension	ICP-AES	0.005	NIST SRMs 1640, 1640a and 1643e (trace elements in water)	363
Cd	drinking and ground water	DLLME	APDC, Triton X-114 and 1-butyl-3-methylimidazolium hexafluorophosphate	FAAS	0.05	NIST SRM 1643e (trace elements in water)	364
Cd, Cu	tap water	DLLME	decylguanidinium chloride, N,N-	FAAS	0.3 (Cu) and	spike	365

			bis(salicylidene)thiocarbohydrazide and lithium bis[(trifluoromethyl)sulfonyl]imide		0.5 (Cd)	recovery and a drinking water round robin control sample.	
Cr^{VI} and total Cr	mineral water	UAE	tributylphosphate and $KMnO_4$	ETAAS	0.85 ng L^{-1}	spike recovery	366
Co, Ni	surface, well and river water	LLME	3-picoline (3-Methylpyridine), NaCl	ETAAS	2.2 (Ni) and 3.8 (Co) ng L^{-1}	spike recovery and NRCC CRM SLRS-4 (river water)	367
Cu	tap, river and well water	air assisted LLME	Triton X-100, Fe_3O_4 NPs, 1-hexyl-3-methylimidazolium hexafluorophosphate	ETAAS	0.5	spike recovery	368
Eu, Gd, La, Nd, Yb	tap, ground and seawater	vortex-assisted DLLME	butan-1-ol, 1-(2-pyridilazo)2-naphthol and NaCl	ICP-AES and ICP-MS	ICP-AES 0.3 (Eu) to 1.0 (Nd). ICP-MS 3.0 (Gd) to 4.0 (Nd) ng L^{-1}	NRCC CRM CASS-4 (near shore seawater) and spike recovery	369
Hg^{2+}, CH_3Hg^+	waste water	sequential CPE	potassium-iodide and methyl green (Hg^{2+}) and APDC (CH_3Hg^+), Triton X-114	CV-AFS	0.007 (Hg^{2+}) and 0.018 (CH_3Hg^+)	spike recovery and BMEMC GBW08603 (water)	370
Sb	bottled, river and tap water	single drop LLME	N-benzoyl-N-phenylhydroxylamine and 1-butyl-3-methylimidazolium hexafluorophosphate	ETAAS	0.01	spike recovery	371
Sb, Sn, Tl	potatoes, carrot, beetroot, canned beans, canned	ultrasound-assisted CPE	Triton X-114, SDS and 1-(2-pyridylazo)-2-naphthol	ICP-AES	0.007 (Sn) to 0.01 (Tl)	NIST SRM 1643e (trace elements in water), EC RM TMDA-52.3	372

	tomatoes, spinach and water					(fortified Lake Ontario water)	
V	river and drinking waters tomato, spinach and potato	LLME	bromo-2-pyridylazo)-5-diethylaminophenol, decanoic acid and 1 M H_2SO_4	ETAAS	0.008	NRCC CRM SLRS-4 (river water) and NIST SRM 1515 (apple leaves)	373

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

Analyte(s)	Sample matrix	Method	Reagent(s)	Detector	LOD (μg L^{-1}, unless otherwise stated)	RMs or other validation	Reference
silver NPs	soil, water	CPE	sodium thiosulfate, Triton X-114	TXRFS	<1	comparison with sp-ICP-MS and ICP-AES	374
gold NPs, silver NPs,	soil, water	CPE	sodium thiosulfate, Triton X-114	TXRFS	0.3 for Ag, 0.2 for Au	spike recovery	361
As, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, P, Zn	forage grass	UAE	deep eutectic solvents based on citric acid, malic acid and xylitol	ICP-AES, ICP-MS	Not reported	NIST SRMs 1573a (tomato leaves) and 1570 (spinach leaves)	375
Au^{III} (discriminated from gold NPs)	soil, water	SAEME	cetyltrimethylammonium bromide, 1,2-dichloroethane	TXRFS	0.05	spike recovery	376
Cd	tea, water	UAEME	trichloroethane	FAAS	0.17	NIST SRMs 1573a (tomato leaves)	377
Cd	lettuce, potato, rice, water	DLLME	ionic liquid based on 1-chloroethyl-3-methylimidazolium chloride functionalized with 8-hydroxyquinoline	FAAS	0.55	spike recovery	378
Cd	liquid and solid samples	DLLME	2-[(4-phenylpiperazine-5-thioxo-4,5-dihydro-1,3,4-oxadiazole-2-yl)methyl]-5-methyl-4-[2-(1H-indole-3-yl)ethyl]-2,4-dihydro-3H-1,2,4-triazole-3-one, chloroform, methanol	FAAS	0.69	NWRI TMDW (drinking water), RTC SA-C Sandy Soil C	379
Cd	bean, cabbage, cornflour, water	UAEME	1-(2- thiazolylazo)-p-cresol	FAAS	0.60	NIST SRMs 1573a (tomato leaves), NIES 10d (rice flour)	380
Cd, Hg, Pb	plants, soil	DLLME	deep eutectic solvent based on 1-decyl-3-methylimidazolium	ETAAS	0.01–0.03 μg kg^{-1}	BMEMC GBW 08303 (polluted farming soil)	381

			chloride and 1-undecanol				
Cd, Pb	chilli pepper, tea, tobacco	CPE	2-[(6-morpholin-4-ylpyridin-3-yl)amino]-N'-(4 -oxo-3-phenyl-1,3 thiazolidin-2-ylidene) acetohydrazide, Triton X-114	FAAS	0.6 for Cd, 1.2 for Pb	RTC SA-C Sandy Soil C	382
Co, Cr, Cu, Ni, Pb	soil	DLLME	2-(2-thiazolylazo)-p-cresol, tricholoethane, methanol	EDXRFS	0.1-0.5 mg kg^{-1}	NIST SRM 2586 (trace elements in soil containing lead from paint), spike recovery	383
Co, Ni, Zn	lentils, nuts, rice, vegetables	UACPE	7-D-glucopyronosyl-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxoanthracene-2-carboxylicacid, nonylphenoxy poly(ethyleneoxy) ethanol, cetyltrimethylammonium bromide	FAAS	0.6 for Co, 0.6 for Ni, 0.5 for Zn (all µg kg^{-1})	NIST SRMs 1570a (spinach leaves) and 15481 (typical diet)	384
Cu	vegetables	LLME	deep eutectic solvent based on benzyl triphenyl phosphonium bromide and ethylene glycol, 1,5-diphenyl carbazone chelating agent	FAAS	0.13	NIST SRM 1573a (tomato leaves)	385
Pb	water	CSDFME	methanol, carbon disulfide	ETAAS	0.03	NIST SRM 1515 (apple leaves)	386
V	potato, spinach, tomato, water	HME	decanoic acid solvent, 2-(5-Bromo-2-pyridylazo)-5-diethy-laminophenol complexing agent	ETAAS	0.0075	NIST SRM 1515 (apple leaves), NRCC SLRS 4 (riverine water)	373

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

Analyte(s)	Matrix	Substrate	Substrate coating	Detector	LOD (μg L^{-1})	RMs or other validation	Reference
Cd	edible plants	magnetic Fe_3O_4@chitosan composite		SQT-FAAS	0.2	NIST SRM 1573a (tomato leaves)	387
Cd	corn, lentils, liver, rice, tea, water, wheat	silver NPs		FAAS	1.1	Spike recovery	388
Cd, Cu, Pb	water	Amberlite XAD-4	*Mucor pusillus*	HR-CS-FAAS	62 for Cd, 74 for Cu, 235 for Pb	NIST SRM 1573a (tomato leaves)	389
Co, Ni	beef, chocolate, fruit, soil, vegetables, water	Amberlite XAD-4	*Geobacillus stearothermophilus*	ICP-AES	0.022 for Co, 0.025 for Ni	NWRI NWTM-15 (fortified water), NRCC DORM 2 (dogfish muscle)	390
Cr species	water	poly-3-hydroxybutyrate2-(dodecylthiocarbonothioylthio)-2-methylpropionate triester		ETAAS	0.006	BMEMC GBW 07605 (tea)	391
In, Ni	sediment, soil	bentonite clay and sonication		SS-HR-CS-ETAAS	10 for In, 260 for Ni	IAEA 433 (marine sediment); NIST SRMs 8704 (river sediment), 27091 (San Joaquin soil) and 2711a (Montana soil)	392
Pb	sediment	Pb-imprinted superparamagnetic mesoporous silica		ETAAS	0.25	IGGE GSD 3 (stream sediment), GSD 4 (pond sediment)	393
Te	Soil	magnetic cobalt particles		SQT-FAAS	15.4	spike recovery	394

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

Analyte	Matrix	Sample treatment	Technique	Analysis and figures of merit	Ref
B	rock RMs, volcanic rocks with low B contents	Study to assess cold HCl leaching for 1, 3, 5, 7 and 9 h in 2 M and 6 M HCl prior to digestion in mannitol solution, H_2O_2 and HF and anion-exchange chromatography on AGMP-1 resin. Total procedural blanks <10 ng with short duration 6 M HCl leaches.	MC-ICP-MS	SSB with NIST SRM 951 (boric acid) as the bracketing standard. External reproducibilities generally <0.6‰ (2SD). New recommended B isotopic compositions ($\delta^{11}B$) for RMs IAEA B-5 (basalt) and B-6 (obsidian) and USGS AGV-2 (andesite)	395
B	carbonate RMs	Carbonate powder dissolved in HCl with mannitol. Chemical separation in a two-step procedure involving AG 50W-X12 cation-exchange resin and AG1-X4 anion-exchange resin	MC-ICP-MS	Isotopic measurements in low-resolution mode. Reproducibility of $\delta^{11}B$ values ±0.4‰ (2SD) using SSB correction improved to <±0.2‰ by a mass discrimination correction of $^{11}B/^{10}B$ by monitoring $^{7}Li/^{6}Li$.	396
B	biogenic carbonates	Powdered RMs pressed into pellets and recrystallised in an oven under CO_2 atmosphere. Solid $CaCO_3$ samples mounted on carbon tape without embedding in resin.	LA-MC-ICP-MS	MC-ICP-MS instrument equipped with $10^{13}\Omega$ amplifiers. Sample introduction using Jet Sample and X-skimmer cones, a platinum injector, and N_2 added to sample gas to increase sensitivity. Long-term accuracy better than 0.22‰ achieved by subtraction of baseline interferences caused by matrix-specific	397

				Ca, C and O ions.	
B	biogenic carbonates	Coral and calcite fragments, and NIST glasses mounted in epoxy resin and polished. Slice of a coral polished and mounted onto a glass slide. Foraminifera cleaned ultrasonically and mounted on double-sided tape. Powdered carbonate RMs pressed into pellets.	LA-MC-ICP-MS	Three approaches tested to correct for matrix interferences: (1) matrix-matched standards; (2) relationship between $\delta^{11}B$ inaccuracy and $^{11}B/^{43}Ca$, $^{11}B/^{40}ArCa^{4+}$ or $^{11}B/Ca$ interference using three RMs with known $\delta^{11}B$ values and varying B/Ca ratios; (3) direct characterisation of interferences. Accuracy (within 0.4‰ of solution values) and external reproducibility (± 0.5‰, 2 SD) were best when applying approach 2.	398
Ca	Ca carbonates (stalagmite, coral)	Samples dissolved in 10% HNO_3, centrifuged and supernatant liquid diluted with HNO_3 for measurement without any matrix separation procedure for samples with Sr/Ca <0.1.	MC-ICP-MS	SSB with a high purity Ca standard solution to correct for mass bias; NIST SRM 987 measured to assess Sr interferences. Background interference on ^{42}Ca minimised by tuning the sweep gas and torch position. Precision was 0.08‰ (2SD, n=32) for an in-house RM and accuracy verified by interlaboratory comparison.	399
Ce	silicate rock RMs	Rock RMs dissolved in HNO_3–HF–HCl. Three columns to separate the REEs from matrix elements and then isolate Ce^{4+} from the other REEs.	TIMS	A new triple spike (^{136}Ce–^{138}Ce–^{140}Ce) method was developed for $\delta^{142}Ce$ determinations. Long-term reproducibility of new Ce RM (Ce_{LMV}) for	400

				^{138}Ce/^{142}Ce ratio was 0.02257053 ± 0.00000061 (27 ppm, 2SD, n=48).	
Cr, Ti	geological RMs, meteorites	Sample powders digested in HF-HNO_3 in Parr bombs. Chemical separation and purification of Cr and Ti in three steps: Fe removal on AG1-X8 anion-exchange resin followed by sequential Ti and Cr separations, both using AG50W-X8 cation-exchange resin. Recoveries typically 90–100% with total blanks of 3–5 ng Cr and 2–3 ng Ti.	MC-ICP-MS, TIMS	Cr isotope measurements by TIMS by SSB method using in-house Cr RM with exponential law instrumental mass bias correction. Ti isotopes by MC-ICP-MS in high resolution mode; SSB with NIST SRM 3162a (Ti solution). Instrumental mass bias corrected relative to ^{49}Ti/^{47}Ti following the exponential law.	401
Cs	RMs, marine sediments	Ashed samples leached with concentrated HNO_3. Simplified chemical separation involving initial Cs sorption using AMP-PAN resin and two-stage ion-exchange chromatography for further Cs purification. Chemical recovery of Cs was >80%.	TIMS	^{133}Cs signals collected on FCs L1 and L2, respectively, to depress the effects of scattered ^{133}Cs. Measurement precision for ^{135}Cs/^{137}Cs better than 10% for samples containing as little as 10 fg ^{137}Cs.	242
Hf, Lu, Nd, Sm	silicate rock RMs	Samples decomposed either by fusion with $LiBO_2$ flux or dissolution with HF. Sequential separation of Hf and lanthanides from matrix elements on a single column filled with cation-exchange AG50W-X8 resin. Nd, Lu and Sm further isolated from the other REE on a second column using Ln-Spec resin. Overall chemical yield was >95%. Blanks were about 40 pg Hf, 20 pg Lu, <400 pg Nd and <100 pg Sm.	MC-ICP-MS, TIMS	Determinations of Hf and Lu isotope ratios by MC-ICP-MS with ^{174}Lu-^{179}Hf spike and Nd and Sm isotope ratios by TIMS with ^{149Sm}-^{150}Nd spike. Accuracy assessed using USGS RMs AGV-2 (andesite), BHVO-2 (basalt), G-2 (granite) and W-2 (diabase).	402
Hg	igneous rock and soil RMs	RMs digested with *aqua regia* in a water bath at 95 °C for 2 h.	MC-ICP-MS	CF CVG system modified to enhance Hg signal sensitivity. NIST SRM 997 (Tl standard solution) introduced as IS for mass bias correction. LOD of 5 ng g^{-1} for	403

				Hg concentrations. Hg isotopic compositions of four USGS igneous rock RMs (BCR-2, BHVO-2, GSP-2, and GSR-2) were reported for the first time.	
K	geological RMs	Sample digestion by successive additions of concentrated HF-HNO_3, HCl-HNO_3 and HNO_3. Chemical separation of K from other matrix elements on AG50W-X8 cation-exchange resin. K solutions dried down and purification process repeated.	HR-MC-ICP-MS	Reduced rf power used to suppress Ar hydrides. High resolution mode with desolvation nebuliser system, with SSB for instrumental mass bias correction gave precisions better than 0.06‰ (95% confidence interval).	404
K	geological RMs	Samples dissolved in HF-HNO_3 using Parr high-pressure digestion vessels. Two-step ion-exchange chromatography to purify K using: (1) AG50-X8 cation-exchange resin; and (2) AG50-X8 cation-exchange resin. Procedure blank 0.26 µg; recovery *ca.* 100%.	MC-ICP-MS	MC-ICP-MS measurements under cold and dry plasma conditions. Long-term (20 months) reproducibility for $^{41}K/^{39}K$ 0.11‰ (2SD, n = 890). Range of USGS geological RMs analysed. Recommended K isotope data reported relative to NIST SRM 3141a (K solution).	405
Li	marine biogenic carbonates	Removal of organic matter by leaching before complete dissolution in dilute HCl. Chemical purification on cationic columns containing AG50-X12 resin was performed twice.	MC-ICP-MS	MC-ICP-MS with desolvating system for high sensitivity measurement; SSB used to correct for instrumental mass bias. GSJ carbonate RMs JCt-1 and JCp-1 used to assess accuracy of method; precision was <0.5‰ (2SD).	406
Mg	geological RMs	Three different Mg purification schemes developed for silicate rocks, high-Ca carbonates and carbonatites, and high-Mn samples using AG50W-X8 resin in all cases. Recovery for all purification schemes >99.1% with blanks <10 ng.	MC-ICP-MS	MC-ICP-MS in wet plasma mode and low resolution settings. SSB applied for instrumental mass bias correction. Long-term reproducibility and accuracy <0.05‰ for $\delta^{25}Mg$ and 0.06‰ (2SD) for $\delta^{26}Mg$. New Mg data for 16 USGS, GSJ and NRCCRM RMs presented.	407
Nd	basaltic RMs	New separation scheme consisting of four	TIMS	$^{143}Nd/^{144}Nd$ and $^{142}Nd/^{144}Nd$ determined	408

		extraction chromatographic stages carried out on several small columns filled with three different resins, used in successive tandem configurations, without an intervening evaporation step. Mean blank 30 pg (SD=13)		by TIMS in static MC mode; Re double-filament assembly. Mass fractionation corrected by applying the empirical exponential law and ^{146}Nd/^{144}Nd = 0.7219 as the reference ratio.	
Pa, Ra, Th, U	carbonates	Samples initially dissolved in HNO_3 and mixed ^{236}U–^{233}U–^{229}Th–^{233}Pa–^{228}Ra spike added. Two approaches to the chemical separation of Pa, Ra, Th and U from same sample aliquot were tested. The one based on a sequence of ion-exchange columns using AG 1-X8 resin yielded better results. Recoveries were 50-60% Th, *ca*. 67% Pa and *ca.* 53% Ra.	MC-ICP-MS	Correction factors for mass fractionation and ion-counter-to-FC amplification determined using a SSB approach and different RMs. Reproducibilities were 1.2% RSD for ^{231}Pa/^{235}U and 3.4% RSD for ^{226}Ra/^{230}Th.	409
Pb	Mn-Fe-rich nodules	Ultrafine powders dried at 105 °C for 1 h and pressed to pellets without adding binder.	LA-MC-ICP-MS	Two methods of mass bias correction assessed: Tl normalisation and SSB method. Precisions of <0.036% for ^{207,208}Pb/^{206}Pb and <0.066% for ^{206,207,208}Pb/^{204}Pb (2RSD).	410
Rb, Sr	geological RMs	After dissolution in HF, Rb and Sr separated from matrix elements and each other by a combination of extraction chromatography and cation-exchange using Sr-Spec and AG50W8 resins. Two aliquots prepared and an enriched ^{87}Rb-^{86}Sr spike added to one.	MC-ICP-MS	Rb and Sr concentrations determined by ID and Zr-based mass bias correction applied. ^{87}Sr/^{86}Sr ratio measured on the unspiked aliquot and raw data corrected for mass fractionation using an exponential law and normalising ratio ^{86}Sr/^{88}Sr = 0.1194	411

Re, Os, S	sulfide minerals	^{185}Re and ^{190}Os spikes added to sample powders and digested in sealed Carius tubes with inverse *aqua regia*. Os separated by CCl$_4$ solvent extraction before two-stage tandem column procedure involving AG50W-X8 cation and AG1-X8 anion-exchange resins for the separation and purification of Re and S. Recoveries were 99.8% for S and 99.7% for Re. Blanks were 2–5 pg for Re, 0.2–0.4 pg for Os and 30–50 ng for S.	ICP-MS, MC-ICP-MS, TIMS	Re concentrations determined by ICP-MS, Os isotope ratios by NTIMS using high-purity Pt filaments, and S isotopic compositions by MC-ICP-MS with SSB approach for mass bias correction. δ^{34}S values for IAEA RMs S-2 and S-3 (silver sulfide) and IAPSO Standard Seawater were consistent with certified values.	412
Sn	chondrites	Double spike of ^{117}Sn–^{122}Sn added to sample prior to digestion with HF-HNO$_3$, followed by refluxing with *aqua regia* and take up in HCl. Chemical separation of Sn performed using TRU resin.	MC-ICP-MS	Ion beams collected simultaneously in a single cycle using FCs. Results reported relative to Sn_IPGP, an in-house Sn isotope standard. Replicates of chondrite samples Jbilet Winselwan, Allende and SAH 97096 yielded repeatabilities of ±0.071‰, ±0.110‰ and ±0.040‰, respectively for δ^{122}Sn/^{118}Sn.	413
Te	Fe-Mn nodules and Jasperiod RMs	A ^{125}Te–^{128}Te double spike and ^{77}Se single spike were added to powdered samples prior to digestion in HF-HCl- HNO$_3$ at 100 °C for >12 h. Separation of Te (together with Se) from the sample matrix using thiol cotton fibre. Total procedural blanks were <19 pg for Te with recoveries of 99±7%.	MC-ICP-MS	Se and Te concentrations determined by ICP-MS and Te isotope ratios by MC-ICP-MS using double-spike method to correct for mass bias. Isotope ratios reported as δ^{130}Te/^{125}Te relative to in-house standard solution (Kanto Chemical). Analytical uncertainties (2SD) for δ^{130}Te/^{125}Te under dry and wet plasma conditions were 0.027‰ and 0.035‰, respectively.	414
Zr	geological	Samples combined with ^{91}Zr–^{96}Zr double-	MC-ICP-	Mass discriminations corrected using	415

	RMs	spike prior to dissolution and column chemistry. Comparison of two dissolution methods (Teflon bombs and Parr bombs) both involving HF and HNO_3. Separation of Zr *via* two-step ion-exchange chromatography on separate AG1-X8 and DGA columns. For USGS RM BHVO-2 (basalt) the Zr yield was *ca.* 70%.	MS	double-spike technique. Zr isotope data reported relative as the ‰ deviation of $^{94}Zr/^{90}Zr$ from the IPGP Zr standard. Precision of Zr ratios in silicate rocks was ±0.044‰ (2SD).	