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

JEFFREY R. BACON[a]*, OWEN T. BUTLER[b], WARREN R.L. CAIRNS[c], OLGA CAVOURA[d], JENNIFER M. COOK[e], CHRISTINE M. DAVIDSON[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, SK17 9JN, UK

[c]CNR-ISP and Universita Ca' Foscari, Via Torino 155, 30123 Venezia, Italy

[d]School of Public Health, University of West Attica, Leof Alexandras 196, 115 21 Athens, Greece

[e]British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK

[f]Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, UK

[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 this review period included: a new in situ method for measuring resuspended road dust arising from vehicular movements; new ink-printed filter reference materials for black- and elemental- carbon measurements; coupling of a *scanning mobility particle sizer to a single-particle-ICP-MS instrument for improved nanoparticle characterisation; developments in total-reflection XRF spectrometry for trace analysis and evaluation of vibrational spectroscopic techniques for measuring respirable crystalline silica in the workplace.*

The increasing availability of ICP-MS/MS instruments is revolutionising the analysis of environmental samples such as waters for trace elements. The advent of mass shift mode makes some elements such as P and S much easier to quantify and allows the REEs and some radioisotopes to be determined at much lower concentrations than previously possible. Advances in vapour generation methods are mostly limited to photochemical and chemical vapour generation as reflected in the new table listing the main advances. Solid or liquid phase extraction prior to analysis remains of great interest, although a notable trend is the synthesis of new materials rather than optimisation of readily available commercially available chelating agents and columns. The analytical effort presented in a paper is sometimes much less than the effort put into the synthesis of the materials so one wonders about the likelihood of methods actually being used and results replicated.

Notable in the analysis of soils and plants was the unusually large number of review articles - possibly because practical research was hampered by the Covid-19 epidemic. Areas of continued growth were research on nanoparticles, the application of high-resolution continuum source AAS for multielement analysis, the development of miniaturised, AES instruments that may ultimately be field-portable and application of LIBS to the analysis of plant materials.

A concerted effort to characterise natural minerals that are sufficiently homogeneous to act as reference materials in the microanalysis of geological materials has resulted in the availability of new materials for isotope ratio determinations. Tied to this has been research into U-Pb dating of zircon and a variety of other accessory minerals by LA-ICP-MS and SIMS.

New chemometric models have been developed to handle the complex LIBS data arising from the analysis of geological matrices in the field and during ore processing. Studies on the use of ICP-MS/MS to reduce polyatomic interferences in geological applications were widespread, reflecting the availability of such instruments. In contrast, the potential offered by integrating LIBS data with those from LA-ICP-MS has only just started to be explored but is likely to increase with the development of commercial instruments.

1 Introduction

This is the 38th annual review of the application of atomic spectrometry to the chemical analysis of environmental samples. This Update refers to papers published approximately between August 2021 and June 2022 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 critical insights into developments in instrumentation, methodologies and data handling that represent significant advances in the use of atomic spectrometry in the environmental sciences.

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

2 Air analysis

2.1 Review papers

It was concluded[7] in a *review* (59 references) of analytical techniques for determining the elemental content of APM that whilst direct analysis of filter samples by XRFS could potentially replace ICP-based approaches, new filter-based calibrants were required. Similarly, new calibrants and autosamplers were required if the potential of LA-ICP-MS were to be exploited. In a comprehensive review (167 references) of techniques for the chemical characterisation of indoor-air particles, the authors highlighted[8] the challenges posed by noise effects and space requirements associated with indoor sampling and the need for handling and interpreting large complex data sets. They also suggested that there is a need for closer collaboration between scientists making indoor and those making outdoor measurements, as well as with epidemiologists and toxicologists. It was concluded[9] in a review (39 references) of recent developments in the determination of the chemical composition of $PM_{2.5}$ that new representative RMs and new portable analytical systems for *in situ* measurements are needed. As vehicle engines become cleaner and tailpipe emissions decrease, attention is now focusing on the contribution of non-exhaust emissions, *e.g.* road dust, as pollutant sources. An editorial review paper (35 references) presented[10] 16 themed papers that discussed the sources, composition, accumulation, pathways, impact and management of road dust in urban and industrial environments. Similar topics were discussed[11] in a review (257 references) in which it was noted that to date there have been few source-specific studies and that current toxicological and epidemiological evidence did not provide a clear picture of the health risks posed.

2.2 Sampling techniques

An eclectic mix of new *sampling platforms* has been reported. The "SCAMPER" (System for the Continuous Aerosol Measurement of Particle Emissions from Roads) system measured[12] road-dust resuspension values by determining the PM_{10} concentrations both ahead of a vehicle, through use of an isokinetic sampling inlet attached to an OPC mounted on or near the bonnet, and in the vehicle's wake, through use of a second OPC unit mounted on a flatbed trailer towed behind. The "CC-TRAIRER" (Climate Change-TRailer for AIR and Environmental Research) system was[13] a small towed-caravan with OPCs for PM_1, $PM_{2.5}$, PM_4 and PM_{10} measurements, NOx and O_3 gas analysers and a filter sampler for gravimetric and chemical analysis. Information on power requirements, cabin climate control and data transmission systems were summarised and a useful tabulation given of mobile laboratory equipment used in 16 other air monitoring studies. The sampling of emissions from cooling towers is challenging due to concerns over accessibility and working at heights. A unique pallet-based system incorporated[14]: a phase Doppler interferometer to measure size and velocities of emitted droplets; a sampling manifold that included a drier unit to capture both $PM_{2.5}$ and PM_{10} particles on filters for laboratory-based XRF analysis; and both APS and OPC instrumentation for monitoring particles in real-time.

Brown *carbon* particles contribute to global warming because they can absorb sunlight at relevant wavelengths but understanding of their prevalence and impact is limited by the lack of atmospheric measurements. Systems that utilised either a particle-into-liquid sampler (two variants examined) or a mist chamber sampler coupled to an absorption spectrometer were evaluated[15] for use on-board a survey aeroplane. A new instrument developed for ground-based black carbon measurements consisted[16] of a CEN-compliant PM-filter-based sampler (with either a $PM_{2.5}$ or PM_{10} inlet) together with an integral optical module that enabled passing particles to be monitored prior to their deposition on a filter. The analysis of filter samples in the laboratory for EC and OC enabled calculation of a MAC value for each specific sampling location so that the black carbon absorbance measurements at 635 nm could be converted to the equivalent mass concentrations.

Two *new air sampler designs* of note were reported. The Versatile Aerosol Concentration Enrichment System (VACES) enabled[17] simultaneous sampling of ultrafine particles both on filters and in a liquid suspension for subsequent chemical and toxicity measurements. The Time Resolved Atmospheric Particle Sampler (TRAPS) coupled[18] a rotary cascade impactor to an OPC so that both coarse particles (1 µm) and fine particles (0.1 µm) could be monitored at high temporal resolution.

The sampling of *volatile metal(loid) species* remains a challenge. The microbial-mediated volatilisation of Sb is a poorly understood component of its biogeochemical cycle, so a study was undertaken[19] to ascertain suitability of sampling methods to trap volatile Sb. Although sampling into impingers containing HNO_3/H_2O_2 best preserved volatile trapped Sb species, preconcentration onto solid-phase traps containing $AgNO_3$-impregnated silica gel was preferable for remote locations and for achieving a lower method LOD. The performance of both KCl-impregnated sorbent traps and KCl-liquid impinger samplers, widely used to trap gaseous oxidised mercury (GOM), were evaluated[20] using a novel ^{197}Hg radiotracer procedure. Reduction of some of the collected Hg^{2+} species to Hg^0 resulted in losses from the sorbent traps even when spiked only with a mass (<1 ng) typical of that collected when clean ambient air is sampled. In contrast, a positive GOM bias observed when spiked KCl-liquid impingers were used was attributed to a small portion of the co-sampled gaseous elemental mercury (GEM) being oxidised. Atmospheric GEM concentrations far exceed GOM concentrations so this finding suggests that the use of impinger-based samplers for GOM is not appropriate.

2.3 Reference materials, calibrants and interlaboratory comparisons

It is encouraging to see development of *new reference materials for air analysis*. New multielement RMs for XRFS analysis were prepared[21] by re-aerosolisation onto PTFE filters of small quantities (0.5 and 5.5 mg) of either NIST SRM 2583 (trace elements in indoor air (nominal mass fraction of 90 mg kg^{-1} Pb)) or NIST SRM 2584 (trace elements in indoor air (nominal mass fraction of 1% Pb)). A procedure for preparing filter-based RMs for the measurement of both black carbon and brown carbon by optical techniques and for measuring OC and TC fractions by combustion techniques involved[22] a novel approach in which a commercially available inkjet printer was used to print ink containing organic and inorganic components onto filter media at programmable print densities. In order to address the lack of RMs for studies using the oxygen-isotope mass-independent fractionation signal, a useful metric for probing the pathways of atmospheric sulfates, purified O_3 was reacted[23] with sodium sulfite to produce three ^{17}O-enriched sulfate candidate RMs that were analysed using a pyrolysis method calibrated using USGS RM 35 (nitrogen and oxygen isotopes in sodium nitrate).

Testing of a mini inverted *soot* generator revealed[24] that soot particles from the combustion of propane had higher EC:TC ratios and absorbed more light than particles generated from the combustion of ethylene. The coupling of a micro smog chamber to a miniCAST 5201™ soot generator made[25] it possible to generate stable and reproducible model aerosols that mimicked combustion particles found in ambient air. The particles produced ranged from “fresh” soot (typically < 100 nm in size, SSA < 0.05, AAE *ca.* 1 and EC:TC >0.9) to “aged” soot (up to 200 nm in size, SSA up to 0.7, AAE up to 1.7 and EC:TC <0.1) and will be useful for method standardisation and intercomparison exercises.

The provision of *new isotopic data for existing RMs* is beneficial for supporting the growing interest in the use of isotopic fingerprinting in source apportionment studies. A high-yielding (82-97% recoveries) column-based chromatographic procedure was used[26] to isolate Hf, Nd and Sr from NIST SRM 1633b (coal fly ash), 1648a (urban particulate matter) and IRMM CRM BCR 723 (vehicular road dust) for isotopic analysis by MC-ICP-MS. Provisional Hf^{176}/Hf^{177}, Nd^{143}/Nd^{144} and Sr^{87}/Sr^{86} data were reported. Similarly, the NIST SRM 1648a (urban particulate matter) and NIST SRM 1649a (urban dust) were analysed[27] by MC-TIMS and MC-ICP-MS to determine the Am, Np, Pu and U contents and isotopic ratios. The high Np, Pu and U concentrations measured in these two SRMs are indicative perhaps of the legacy of atmospheric fall-out of radioactive particles from nuclear bomb tests.

2.4 Sample preparation

Innovations in sample preparation are always welcome. The coupling of a microextraction assembly directly to an ICP-MS instrument enabled the direct isotopic analysis of either Pu[28] or U[29] particles collected on cotton swabs for rapid nuclear-safeguarding purposes. A flow of 2% (*v/v*) HNO_3 solvent rinse flushed deposited actinide material from a swab directly into the ICP-MS instrument for analysis. Validation involved the successful analysis of several Pu and U CRM particles that had been deposited on test swabs using a particle manipulator. Although stable Hg isotope measurements are used in environmental tracer studies, the acid digestion of samples remains fraught with potential problems of analyte loss and cross-contamination. To overcome these problems, a combustion-based analyser was modified[30] to enable the thermal release of Hg and trapping in a solution of 10% HCl-BrCl (5:1 *v/v*) prior to analysis by CV-MC-ICP-MS. No appreciable carryover was noted as blank values were <1% of the concentration of Hg introduced. Recoveries were >90% and samples were processed in <15 min. The isotopic data for several CRMs were statistically indistinguishable from the reported values. Gravimetric analysis of air filter samples remains a tedious and time-consuming activity but the development of robotic systems has made unattended automated operations a reality. The development of AIRLIFT extended[31] measurement operations beyond just filter weighing. The system consisted of a sealed environmentally-controlled chamber, a 6-axis articulating robotic arm, a 6-place balance for filter weighing and an optical measuring system for determining black carbon content. Up to 240 filters could be processed in a day with an estimated four-fold reduction in labour requirement.

Two studies on *sample preparation for XRFS* are noteworthy. In the first, a stirring device ensured[32] that ZnO NPs remained suspended in water whilst being interrogated in an X-ray beam. Otherwise, agglomeration and sedimentation occurred rapidly as indicated by a 2.5%

per min reduction of the fluorescence signal. In the second study, a casting procedure for the analysis of a SiO_2 powder involved[33] dispersing a measured quantity of SiO_2 in a known amount of epoxy resin that was then poured into a plastic X-ray sample cup and cured to prepare sample discs. The good linearity ($R^2 = 0.997$) for test discs (30 mm diameter, 5 mm thickness) doped with 1 – 5% (*m/m*) SiO_2 indicated that this approach could be a useful alternative to methods involving either fused beads or pressed pellets.

2.5 Instrumental analysis

2.5.1 Atomic absorption and emission spectrometries

A review (154 references) on *the use of AAS* considered[34] papers published in the period 2000-2020. The review focussed on the use of line source ETAAS and CS-ETAAS for elemental determinations in various matrices and included references to six application papers in which the concentrations of the elements Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in APM were determined. A new method for the determination of Hg^0 in workplace air involved[35] sampling onto a graphitic sorbent from which Hg^0 was released thermally within a combustion-based analyser for analysis by AAS. Recoveries from spiked sorbents were *ca.* 100%. The LOQ of 0.44 ng corresponded to 29 ng m^{-3} for a nominal air sample volume of 15 L.

A review (130 references) on the *use of LIBS* for online measurements of air pollutants showcased[36] the analysis of APM and the determination of S and halogens in gaseous VOCs. Further developments in the application of LIBS and SIBS to the analysis of APM are summarised in Table 1.

Insert Table 1

2.5.2 Mass spectrometry

2.5.2.1 Inductively coupled plasma mass spectrometry: A *review* (80 references) on the application of ICP-MS/MS to environmental studies included[37] analyses of atmospheric particles, NPs and road dusts. Other pertinent reviews were on the application of FFF-ICP-MS to the characterisation of engineered metal NPs (103 references)[38] and on advances in sp-ICP-MS (301 references)[39].

Although papers that advocate use of *LA-ICP-MS* for the analysis of APM collected on filter samples have been published in recent years, a more critical insight has now been presented[40]. Useful conclusions reached were that: the NIST RM 8785 (air particulate matter on filter media) was unsuitable as a LA calibration standard; analysing a representative portion of a filter in minimal time required a judicious selection of laser beam size and ablation area; and use of less energetic 213 nm lasers was preferable to the use of 193 nm lasers because this minimised the ablation of the quartz filter media itself and thus reduced background elemental contributions to the analytical signal. It was noted that further instrumental developments were required before this approach could be deployed routinely. These included: lasers with increased beam sizes for increased filter ablation coverage; ablation cells with faster wash-out characteristics; and autosamplers for the automated processing of filter samples.

The *coupling of a SMPS to a sp-ICP-MS instrument* for improved interrogation of NPs involved[41] connecting a differential mobility analyser unit, in which charged aerosol particles in a flow of N_2 gas were separated by means of their electrical mobility, to a modified RDD. The latter enabled both the aerosol particle stream to be diluted and an Ar carrier gas to be introduced to sustain the ICP-plasma. A sample splitter placed after the RDD allowed aerosol to be sent both to a CPC (to count particles) and to the sp-ICP-MS instrument (to provide data on particle size, count and mass distributions). The novelty of this configuration was that the switching between N_2 and Ar gas flows could be carried out downstream of the differential mobility analyser thereby enabling this device to work efficiently. This had not been possible in previous studies in which Ar carrier gas was used throughout.

Further ICP-MS applications are summarised in Table 2.

Insert Table 2

2.5.2.2 Mass spectrometry techniques other than ICP-MS: *New and improved instrumental approaches* are always welcome. Use of a new sampling inlet, the Soot Particle Agglomeration Inlet, made[42] it possible to analyse NPs by aerosol mass spectrometry. This had not previously been possible because the small size of the particles made them undetectable. The NPs were passed initially through a soot chamber so that they agglomerated on the surface of larger soot particles and so became detectable. A possible application could be the analysis of particles <23 nm in size emitted from engines for which there is growing regulatory interest. A new QMS method for the quantification of sea-salt particles employed[43] a graphite particle collector and a CO_2 laser ionisation system so that high desorption temperatures (up to 930 ºC) could be achieved. The prototype system was equipped with an inlet optimised for the sampling of <1 μm particles so further development is required to design an inlet which can sample larger sea-salt particles effectively.

Identifying *sources of actinide-containing particles* collected on swab samples is important for nuclear safeguarding purposes. A new thermal ion emitter improved[44] U ionisation efficiencies in a new procedure in which particles of interest were initially identified using SEM-EDS and then transferred by a micromanipulator for TIMS analysis. The relative errors for 13 certified U particles (1.3 – 4.7 µm in size) were <2.7, <1.1 and <4.5% for $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$, respectively. The corresponding RSDs were 1.6, 0.5 and 3.3%.

2.5.3 X-ray spectrometry

Although the sensitive *TXRFS and allied techniques* have potential in air pollution studies because elemental concentrations in APM can be in the low ng m^{-3} range, attenuation and depth effects can arise from the analysis of overloaded samples. Experiments into the use of a grazing incidence set-up at a synchrotron facility made[45] it possible to extend the quantifiable range of TXRFS. This approach could, it was suggested, be transferable to portable TXRFS units for field operations. Researchers at the University of Brescia used[46] their proprietary SMART STORE® sample preparation procedure to encapsulate and thereby sandwich Pb-containing calibrant filters between transparent PP film sheets in order to produce ideal flat samples for TXRFS analysis. Filters were analysed under grazing incidence conditions which enabled a broader sample area to be illuminated and hence enhancement of the fluorescence emission. The LOD of 0.0065 µg cm^{-2} provided potential for trace measurements in ambient air. Further work will consider other elements of regulatory interest such as As, Cd, Hg and Ni. By sampling onto 20 x 20 mm polished Si wafers using a 7-stage May-type cascade impactor sampler, it was possible[47] to use portable TXRFS to quantify the elemental composition of size-fractioned particles 70 nm to 10 µm in size. The LODs were as low as *ca.* 0.1 ng m^{-3}. The optimum sampled air volume of *ca.* 4 m^3 (4 h sampling at 16.7 L min^{-1}) balanced the need for timely measurements to track short-lived pollution episodes with the need for sufficient sample mass for analysis. Complementary TXRFS and XANES measurements undertaken at a synchrotron facility provided useful morphological information to support source identification and apportionment studies.

The application of *SEM-EDS,* a well-established technique for the determination of the elemental composition of imaged particles, was reported in two aerosol-related studies. In the first[48], the analysis of 98 TSP dust samples from various ore processing operations within a nickel refinery plant generated compositional data for individual particles. Process-specific emission sources could be identified so plant operatives could implement dust control systems optimised for location and activity. Future work will examine the composition and morphology of fine (< 2.5 µm) and ultrafine (<100 nm) particles because these can be inhaled by workers and may have different toxicities than larger TSPs. From an occupational exposure perspective, it will be interesting to compare new particle data with elemental fractionation data generated using the industry-specific Zatka leaching protocol, which involves the sequential leaching of air filter samples in extractants of increasing potency and subsequent analysis by ICP spectrometry. In the second publication[49], use of the SEM-EDS technique helped elucidate the morphology, chemical composition and wear alteration of brake assembly components (pads and discs) and of released particles. Findings will help the industry to optimise pad components for more efficient operation whilst simultaneously minimising emitted wear particles, the presence of which in the urban atmosphere is of growing concern.

Other applications of XRFS to the analysis of APM are presented in Table 3.

Insert Table 3

2.5.4 Other techniques

New ways of measuring exposure to *diesel fumes* included the first use of micro-Aethalometers™ sensors to measure[50] the exposure of workers to black carbon in the harsh environment of a platinum mine. From a process-control perspective, the fast measurement response rate of this sensor was beneficial for assessing the magnitude of the often-transient emissions from various engines employed in the mine. However, from a worker's exposure perspective there remains a need to convert transient black carbon data to equivalent time-weighed EC data as this latter metric underpins workplace diesel fume exposure limits. Both the OC and EC contents of DPM collected on filters were predicted[51] by FTIR analysis. Spectral measurements in the region between 3000 and 2800 cm^{-1}, associated with the stretching of aliphatic CH_2 and CH_3 functional groups, were used to estimate OC content. The EC content was estimated by integrating the absorbance in the 4000-3796 cm^{-1} spectral region associated with a broad $\pi \rightarrow \pi^*$ transition in the aromatic ring structures. Analysis of the same filter samples by the existing NIOSH 5040 TOA combustion method enabled a TOA-FTIR linear regression model to be developed and hence a means of cross-calibration. Further work is however required to test this FTIR approach in other environments in which DPM is emitted and assess its potential for timely measurements in the workplace using portable instruments. This would contrast with TOA measurements which require filter samples to be shipped to a laboratory for analysis. The sub-μm size of DPM results in deep penetration of the particles into the lung and its large surface area facilitates transport of toxic gases into the lung as species condensed on particle surfaces. There is therefore growing interest from a health perspective in looking at new metrics such as particle surface area. Black carbon measurements were undertaken[52] in different locations in Helsinki using an Aethalometer™ and lung deposited surface area (LDSA) measurements were made using an ELPI+™ instrument. The average LDSA per black carbon mass determined in DPM sampled in the harbour region was 2.4-2.7 times the value determined in particles from a road traffic environment. This finding indicated that the make-up of emitted particles depended upon the type of diesel engines used, their mode of operation and the fuels consumed, and their subsequent interaction with other airborne species.

The portability of *vibrational spectroscopic* techniques such as FTIR spectrometry makes it possible to undertake occupational RCS measurements in workplaces. Such measurements are, however, prone to interferences from other minerals co-sampled onto air filter samples. In a comparative testing[53] of FTIR and XRD methodologies using 253 air filter samples from representative activities such as road construction and tunnelling, coal mining and kitchen benchtop manufacturing, the FTIR results were on average 9% higher than the XRD data. This discrepancy was largely attributed to spectral interferences around the 800 cm^{-1} region where characteristic Si-O stretches are measured. The authors recommended that, to obtain better FTIR data, spectra should be examined for potential matrix interferences, a peak height ratio method should be used for quantification and filters should not be overloaded. In order to minimise such interferences, a PCR chemometric model was developed[54] using coal dust mixtures on filter samples and verified by comparison with the results from XRD analyses. This model allowed quartz to be measured in several coal dust types with a LOD of 5 μg per filter and met the method performance requirements set out in ISO 20581 if airborne silica concentrations of 100 μg m^{-3} were to be sampled using a nominal 500 L sample volume. Further work will examine the wider applicability of chemometric models for predicting quartz contents in other workplace dusts and whether such models can be used universally with different portable FTIR instruments. In a Raman-based method, test RCS aerosols were sampled[55] onto a small 1.5-mm filter spot and analysed either with a hand-held instrument (*ca.* 0.5 kg) or a larger probe-based portable unit (*ca.* 5 kg). The best LOQ of 17 μg m^{-3} was attained for a nominal 24 L air sample collected at a flow rate of 0.4 L min^{-1} over 60 min using the handheld instrument. Results were within 23% of those obtained using a reference XRD method. Future studies will assess instrumental performance on real-world RCS samples.

3 Water analysis

3.1 Reviews

A review[56] (210 references) on the *determination of phosphorus and its species in environmental samples* highlighted the use of DGT samplers for *in situ* sampling of water and pore water in soils and sediments and the use of ETAAS, ICP-MS, ICP-AES for subsequent analysis.

A review (291 references) on the *characterisation of nanomaterials in the environment* covered[57], amongst other topics, the preconcentration of nanomaterials from aqueous samples, their quantification by sp-ICP-MS and XRFS and their characterisation by techniques such as FFF-ICP-MS and LA-ICP-MS. A more specific review (74 references) on the trends and challenges in determining engineered NPs in seawater drew[58] the reader's attention to the important fact that the main limitation of many studies is the use of spiked samples at concentrations much higher than those found in real samples. Of note was the table on atomic spectrometric methods used and the sample preparation procedures required prior to analysis.

3.2 Sample preconcentration

Two useful reviews on *analytical sample preparation* were published. The first (157 references) focussed[59] on the use of MOFs (a type of coordination polymer with an inorganic metal centre surrounded by organic ligands) as specific adsorbents for trace elements in environmental and food matrices. The second review (146 references) covered[60] sample preservation, storage and extraction techniques for the elemental speciation analysis of environmental samples.

An *electrodialytic enrichment device* for the preconcentration of trace ions from ultrapure water before analysis by ICP-MS generated[61] an effluent with a tenfold trace element enrichment. As part of the procedure, the effluent was acidified with HNO_3, thereby making QC easier. The “waste” water that had been stripped of trace elements was recycled to make the analytical blanks and standards.

Tables 4 and 5 present the most significant advances in analyte preconcentration using SPE or LPE for water analysis.

Insert Tables 4 and 5

3.3 Speciation analysis

A review (60 references) on the *determination of* Se^{IV} by CVG coupled with AFS detection covered[62] all the main chemical strategies for reducing Se^{VI} to Se^{IV} together with species-specific preconcentration methods. This paper demonstrates that there are now a sufficient number of analytical methods for this application.

An investigation on the *preservation of As species in water* established[63] that the bottle type had little effect on species stability and that acidification of the samples to 0.018M HCl or 0.019M HNO_3 was sufficient to preserve the original sample composition for up to 12 weeks. The use of HNO_3 was preferred over that of HCl in order to to avoid polyatomic interferences when using ICP-MS. It was suggested that HNO_3 had no oxidising effect but this assertion was unfortunately not tested on real samples. It should be noted that chromatographic separations typically separate chloride from As species and that most ICP-MS instruments these days have collision cells that successfully remove the $ArCl^+$ interference so HCl can in fact be used without the risk of species oxidation by HNO_3. A different approach was adopted[64] for groundwater samples with significant concentrations of iron sulfide and oxide minerals. To overcome the problem of a >60% reduction in As^{III} concentrations that occurred after 36 h of collection, samples were preconcentrated on-site onto strong cation- and anion-exchange cartridges. Recoveries of As species were quantitative when the Fe^{2+} concentrations were <10 mg L^{-1}.

Species-selective preconcentration can be used to improve the sensitivity of speciation methods. Turbulent flow chromatography is a commercial and patented SPE method typically used in clinical analysis to separate low- and high-molecular-weight fractions by diffusion-controlled mass transfer instead of by chemical interaction with a stationary phase. It was tested[65] for the preconcentration and fractionation of Gd in surface waters. All low-molecular-weight compounds were retained at loading flow rates above 1 ml min^{-1} whereas compounds of 5.7 kDa and above were not. The recovery of low-molecular-weight Gd species from the samples (92 ± 5%) was a slight improvement over the 87 ± 4% achievable using standard cation-exchange SPE preconcentration cartridges. The mercury species Hg^{2+}, $MeHg^+$ and $EtHg^+$ were selectively extracted[66] offline from sea, lake and river waters onto a C_{18} column functionalised with 12.5 µg of dithizone. Once extracted, the immobilised species were stable for up to 10 days. The column was then mounted onto the HPLC injection valve for elution and HPLC-ICP-MS detection. The LODs for 50 mL samples ranged from 0.007 ($EtHg^+$) to 0.02 (Hg^{2+}) ng L^{-1}.

The *fractionation of trace elements in waters and soil porewaters* remains an important topic. An investigation into the environmental bioavailability of Co, Fe, Pb, U and Zn at a mine reclamation site used[67] DGT to sample extractable metals from soils and ICP-MS pore-water analysis to estimate their lability and biotoxicity. Although the metals were highly labile and so potentially had high toxicity, analysis of tree core samples, surprisingly, revealed little uptake into the xylem of nearby trees. Dissolved As^{III}, Sb^{III}, and Se^{IV} concentrations within a river catchment were successfully mapped[68] using a DGT sampler loaded with aminopropyl and mercaptopropyl bi-functionalised mesoporous silica spheres. The time-weighted average data obtained were comparable to data from high frequency sampling and HPLC-ICP-MS analysis. The spatial resolution that can be obtained with these samplers was exploited to follow redox-constrained spatial-patterns of these analytes associated with root penetration. Results obtained using passive DGT sampling and ICP-MS detection for the labile forms of Cd, Ni and Pb in transitional and coastal waters were compared[69] with those obtained by standard ASV analysis. Although the concentrations of labile Cd and Pb obtained by the two methods were highly correlated, the values obtained for Pb by ASV were always similar to or lower than the results obtained by DGT-ICP-MS. As ASV cannot be used to determine the labile fraction of Ni due to the irreversible reduction of Ni at the electrode, this new method had a considerable advantage for the analysis of estuarine waters.

3.3.1 Instrumental speciation: A review (103 references) of *FFF-ICP-MS for the determination of engineered NPs in the environment* covered[38] the separation theory of FFF and application to the determination of engineered NPs in wastewaters, environmental waters, soils and organisms.

Although the *combination of HPLC with ICP-MS for elemental speciation* is facilitated by the ease of interfacing these two instruments, HPLC mobile phases containing large amounts of organic solvents are often incompatible with ICP-MS. To overcome the problems of high reflected power and carbon deposition on the interface, dimethyl carbonate was used[70] as an organic-mobile-phase modifier for the RP chromatography of a series of Br-, Cl- or S-containing organic compounds in urine. A 10% *v/v* concentration of dimethyl carbonate had an elution capacity equivalent to 23 and 48% *v/v* concentrations of acetonitrile and methanol, respectively, but didn't require the addition of oxygen to the plasma. Use of this mobile phase might also have potential for water samples but it is less miscible with water so the maximum useable concentration of dimethyl carbonate in a mobile phase is 10% *v/v*.

As ICP-MS is a multi-elemental detector, it is always gratifying to see the development of *multi-elemental separations*. The species Cd^{II}, Cr^{III}, Cr^{VI}, Hg^{II}, $MeHg^+$, $EtHg^+$, Pb^{II}, TEL and TML were preconcentrated[71] on a C_{18} SPE column modified with 10 mM 2-hydroxyethanethiol and then eluted with 5 mM cysteine onto a C_{18} HPLC column from which separation of all the analytes was achieved in 8 min using the eluent as the mobile phase. The LODs ranged from 0.001 ($MeHg^+$) to 0.007 (TML). Accuracy was verified by spike recoveries from real samples and by analysis of the Chinese RMs GBW08602 (Cd in water), GBW08603 (Hg in water) and GBW08601 (Pb in water). The separation and quantification of 5 Gd MRI contrast agents by IC-ICP-MS used[72] the PrepFast sample introduction system fitted with a proprietary polymer-based IC column functionalised with quaternary ammonium alkyl groups. Complete separation in less than 2 min was achieved with a gradient of ammonium nitrate buffers at pH 9.2. The LODs of 11 (gadoterate) to 19 (gadobenate) pM were sufficient for the monitoring of these compounds in a river in Germany.

The Re^{VII} and Re^{IV} species have similar physicochemical properties and electrophoretic behaviour to ^{99}Tc and so were determined[73] by *CE-ICP-MS/MS* in simulated contaminated groundwater samples as stable analogues of ^{99}Tc. The CE-ICP-MS interface added a sheath liquid to the CE flow to increase the flow rate for ICP-MS analysis. The LODs were 0.01 (Re^{VII}) and 0.02 (total Re) µg L^{-1}. The authors considered this method to be a promising candidate method for monitoring ^{99}Tc species in contaminated groundwater.

3.4 Instrumental analysis

3.4.1 Atomic absorption spectrometry. A review (154 references) of *simultaneous or sequential multi-elemental AAS analysis* over the last 20 years included[34] relatively few examples of water analysis but was still a useful summary of the state-of-the-art. The determination of Cd, Mn and Zn in gas-field-strata waters by sequential FAAS was improved[74] through a sequence of steps involving evaporation and redissolution under sonification with HNO_3, Triton™ X-100 and acetyl acetone. The LODs were 4 (Mn and Zn) and 7 (Cd) µg L^{-1}. The method was validated by spike recoveries and ICP-AES analysis of the same samples. Undiluted seawater was successfully analysed[75] for Cu and Mn by HR-CS-ETAAS, use of which allowed more accurate background correction to be made than possible with low-resolution line source instruments. When optimised pyrolysis and atomisation temperatures were used, the LODs were 0.07 (Mn) and 0.6 (Cu) µg L^{-1} for a 20 µL sample injection. The method was validated by spike recoveries.

The *determination of As^{III} by FAAS* with a quartz tube atomiser was improved[76] by using a Pt-coated tungsten coil heated at 60 °C to trap arsine gas after HG. The LOD of 0.016 µg L^{-1} was a considerable improvement over that (0.26 µg L^{-1}) achievable without the coil. Results for the NIST SRM 1640a (trace elements in natural water) and the SCP science RM EnviroMAT (drinking water high) were not significantly different from the certified values at the 95% confidence level.

3.4.2 Atomic fluorescence spectrometry. The *quantification of mercury and its species* remains one of the main applications of AFS. Dissolved elemental, reactive and total Hg mercury fractions were determined[77] in seawater using an on-ship FI dual-channel purge-and-trap CV-AFS system. The method was validated using the IRMM CRM BCR-579 (coastal seawater). The LOD was 0.05 ng L^{-1}. A commercially available instrument designed specifically to automate the laborious US EPA method 1630 (methyl mercury in water by distillation, aqueous ethylation, purge and trap and cold vapour atomic atomic fluorescence spectrometry) was investigated[78] for the determination of MeHg in seawater. The Hg^{2+} and $MeHg^+$ species were ethylated using tetraethyl borate, trapped on Tenax® and determined by GC-AFS. Automation of the method meant that up to 72 samples per day could be analysed and gave an LOD of 0.0004 ng kg^{-1} (as Hg). The method was validated by gravimetric spiking, participation in the GeoTraces laboratory intercomparison exercises and analysis of IRMM CRM BCR-579 (coastal seawater).

3.4.3 Vapour generation. *Photochemical vapour generation* is the most common methodology reported in the literature for producing volatile metal compounds from water samples. The main advances in the technique are summarised in Table 6.

Insert Table 6

Microplasmas or discharges can also be used to produce volatile metal compounds. An anodic GD was developed[79] for the CVG of Cd and Hg in waters and sediment digests prior to ICP-AES detection. The LODs of 0.3 (Cd) and 0.2 μg L^{-1} (Hg) were improvements over those achievable with pneumatic nebulisation. The VG efficiencies were 28 and 69% for Cd and Hg, respectively. Unfortunately, there was no comparison with "traditional" monoelemental CV or HG methods. A nebulised-film DBD was successfully employed[80] to vaporise 2,2,6,6-tetramethyl-3,5-heptanedione chelates of REEs prior to ICP-MS detection. The sample introduction efficiency of 51-66% gave an 8-9 fold sensitivity improvement over that achievable by nebulisation. The LODs ranged from 0.002 (Gd and Tb) to 0.328 (Y) ng L^{-1}. The accuracy of the method was checked by spike recoveries from lake and rainwaters as well as by analysis of the Chinese RM (GBW(E)082428) (multielement solution).

The inorganic, monomethyl and dimethyl Ge species in fresh and seawater samples were determined[81] following *production of volatile species by hydride generation.* The species were preconcentrated by cryotrapping and then selectively released by gradual heating of the trap. The LODs of 0.003 (DMGe) to 0.015 (iGe) ng L^{-1} achievable with ICP-MS/MS detection were low enough to provide values for these species in the NRCC CRMs CASS-4 to 6 (near shore seawater), NASS 5 and 7 (seawater) and SLRS 4 to 6 (river water). The values obtained were consistent with values previously reported for total Ge in these CRMs. The concentration of Pb in water was determined[82] by HG-MIP-AES using $K_3Fe(CN)_6$ as an additive to improve the generation of PbH_4 with $NaBH_4$. The LOD of 0.54 μg L^{-1} allowed the accurate determination of Pb in the Laboratorio Tecnólogico del Uruguay CRM MRC.INO.101 (trace elements in water).

3.4.4 Inductively coupled plasma atomic emission spectrometry. When analysing *water samples with high concentrations of solutes,* ICP-AES remains a relevant analytical technique. The determination of I in oilfield brine samples was facilitated[83] (paper in the

Chinese language) by oxidation of iodide to I_2(g) with a mix of $NaNO_2$ and HNO_3 and isolation of the vapour using a gas liquid separator. The LOD was 1.65 µg L^{-1}. Method validation was by spike recoveries from real samples. Only Ca had any appreciable matrix effect. The determination of Li in geothermal waters demonstrated[84] (paper in the Chinese language) the robustness of ICP-AES analysis. Careful matrix matching allowed the determination of Li in undiluted samples with an LOD of 0.2 µg L^{-1}. The results compared well with those obtained by ICP-MS analysis of diluted samples. When Antarctic snow samples were preconcentrated[85] by freeze drying from 20 g to a final volume of 200 µL, the resulting samples had appreciable solute contents. The determination of Al, Ba, Ca, Fe, K, Mg, Na and Sr in these small-volume samples was only possible with a low-uptake total-consumption nebulisation device. The LODs obtained at a sample uptake of 50 µL min^{-1}, ranged from 0.003 (Sr) to 0.39 (Na) µg L^{-1} and were sufficient to determine these elements in snow from the Antarctic Plateau. The method was validated by analysis of NIST SRM 1640a (trace elements in natural water).

3.4.5 Inductively Coupled Plasma Mass Spectrometry. A tutorial review (109 references) on *the use of aerosol dilution with ICP-MS* covered[86] the use of this simple sample “preparation” method for various applications including those in food, environmental, biological and clinical studies.

The optimum sample dilution of 1+9 for the *determination of REEs* in seawater samples by SF-ICP-MS was determined[87] from analyses of the NRCC CRM CASS-6 (near shore seawater). Although this method was suitable for the analysis of near-shore samples, the analysis of oceanic samples presented problems. It is suggested that these could be overcome by the use of high-efficiency heated nebulisers with aerosol desolvation. The interference effects of Ba polyatomic ions on the determination of Eu were evaluated[88] by “Pseudo ID”. Polyatomic ions were treated as surrogates for Eu ions and their contribution quantified by spiking the sample with natural abundance Eu. The LOD was 0.007 pg mL^{-1}. The method was validated by the analysis of NRCC CRMs CASS-4 and 5 (near shore seawater), NASS-5 and 6 (seawater) and SLRS 4 and 5 (river water) for which literature and information values for Eu were used.

The *determination of S* in lacustrine DOM by ICP-MS/MS was achieved[89] by measurement of $^{32}S^{16}O^+$ formed in the collision cell after removal of $^{48}Ca^+$ in the first quadrupole. The LOD was 0.2 ng g^{-1} in dried DOM. Results agreed well both with those obtained previously using FT-ICR-MS and with reference values for the IHSS RM Suwannee River fulvic acid. The same method was employed[90] for the determination of $\delta^{34}S$ in coastal seawaters and sediment pore waters. Results that were not significantly different to the certified values were obtained for the analysis of IAES RMs IAEA-S-1 (sulfur isotopes in silver sulfide), IAEA-S-2 (sulfur isotopes in silver sulfide) and the IAPSO CRM (seawater) but the precision of 1.1–1.5‰ was an order of magnitude poorer than that obtained using a MC instrument.

Seventeen water CRMs from NRCC and IRMM were analysed[91] for *REEs and technology-critical elements by ICP-MS/MS.* The MS instrument was used in combination with a commercial preconcentration-unit fitted with Nobias chelate-PA1® columns. The REEs, Sc, Ti and Y were measured in O_2 mass-shift-mode and Al, Cd, Co, Cu, Fe, Ga, In, Mn, Mo, Ni, Pb, Sn, Th, U, V, W and Zn in He-collision mode. Apart from the values obtained for Mo, Ni and U in three of the 17 CRMs analysed, the results were not significantly different from the certified values. There had been no or few results presented previously in the literature for Ga, In, Sc, Sn, Th, Ti and W in these CRMs so this paper provided the first published values for most of these elements. These new data were combined with data from an extensive literature survey to provide new consensus values for those elements without certified values.

In the ICP-MS/MS *determination of radioisotopes* using a commercial high-efficiency desolvating nebuliser, the ^{97}Mo isobaric interference on ^{97}Tc was eliminated[92] by adding O_2 as a reaction gas to form MoO^+ and MoO_2^+. Using ^{97}Tc as a yield tracer for ^{99}Tc, the absolute LOD was 0.9 fg (0.6 mBq). In a similar procedure, the $^{129}Xe^+$ isobaric interference on $^{129}I^+$ decreased[93] substantially when I was reacted with O_2 and measured as $^{129}I^{16}O^+$ at *m/z* 145. In this way a LOD of 11 mBq L^{-1} was achieved without the need for any sample pretreatment. The method was validated by spike recoveries from river and synthetic water samples and IDA.

A 304-reference review of *sp-ICP-MS* covered[39] all aspects from basic principles and sample preparation to analytical applications, such as the detection of NPs in various kinds of waters. Although 0.45 µm filters are often used in the preparation of samples for sp-ICP-MS, it was reported[94] that the NP affinity for filter materials differed according to the filters used. Best recoveries of NPs (>75%) were obtained when polypropylene membranes were used. Preconditioning of the filters with a multi-element solution improved recoveries by up to 80% but recoveries were dramatically dependent on the water matrix. The authors concluded that to decrease losses either their filtration protocol or centrifugation of samples at <1000 x g should be used before analysis of water samples. This finding was partially supported[95] by a study on the determination of metallic NPs in waste waters and sludges produced at water treatment plants. Samples were centrifuged at 5000 x g or less for 10 min before sp-ICP-MS analysis. Recoveries of silver NPs from spiked samples were >84%. Particle mass concentrations of <1 ng L^{-1} for cadmium NPs and *ca.* 100 µg L^{-1} for magnesium NPs were found in samples of waste waters and sludges. Most particles were <100 nm in diameter but magnesium particles could be much larger at up to 1500 nm in diameter.

Notably different approaches have been taken for the determination of *non-metallic NPs.* A review (44 references) of the use of metal tagging or labelling considered[96] this strategy to have the advantage of making the most of the detection power of ICP-MS whereas C monitoring was beset with many difficulties. The advantages and disadvantages of different kinds of tagging for polystyrene microplastic standards were discussed. In contrast, microplastics and unicellular algae have been counted and sized[97] in seawaters by ICP-MS/MS by monitoring ^{12}C and ^{13}C. Online aerosol dilution was used to reduce drift effects and to make size calibration more repeatable. The best size-LODs were obtained using ^{12}C. Size calibration using polystyrene microplastic standards made it possible to calibrate cellular masses in real samples. The measured results of 51-83 pg (equivalent to sizes of 7.6 to 10 μm) were consistent with results obtained using coulter counting, TOC analysis and microscopy. A review (151 references) of the determination of *^{137}Cs and ^{226}Ra by ICP-MS* covered [98] sample preparation, pretreatment and separation steps for a wide range of matrices, including soils, sediments and biological materials as well as several waters.

The *quantification of radionuclides in water by ICP-MS* is of increasing interest. The low instrument LODs of 0.02 (Pb) to 0.14 (U) ng L^{-1} made[99] it possible to determine stable Pb isotopes, ^{232}Th, ^{234}U, ^{235}U and ^{238}U in drinking water by SF-ICP-MS without any sample pretreatment. In contrast, the detection of ^{227}Ac in fresh and seawaters was only possible[100] following preconcentration from 30 L of sample using manganese coprecipitation and extensive column purification. As the yield was known to be <100%, ID was used for quantification by MC-ICP-MS. The method was validated against an in-house RM and spiked seawater samples and internal QC was carried out using duplicate riverwater samples The absolute LOD of 10 ag was sufficient for monitoring this radioisotope in seawater and could result in a rapid increase in the use of ^{227}Ac as a marine tracer. An automated SPE column method with UTEVA® resin was used[101] to extract Th (^{230}Th, ^{232}Th) and U (^{234}U, ^{235}U, ^{238}U) from 20 mL of sea and river waters prior to elution with 0.01 M HNO3-0.01 M HF and quantification by ICP-MS/MS. Results were not significantly different from the certificate values for the NRCC CRMs CASS-6 (near shore seawater), NASS-7 (seawater) and SLRS-6 (river water) and the IAEA CRM IAEA-443 (Irish Sea water). The LODs ranged from 0.02 (^{230}Th) to 5.89 (^{235}U) fg mL^{-1}.

A review (149 references) of the use of *"non-traditional" stable isotope ratios* in studies of the geochemical and ecotoxicological aspects of marine metal contamination included[102] the application of MC-ICP-MS to studies of contaminated marine environments. It was concluded that measurement of isotope ratios will detect changes caused by mankind and follow interactions with marine biota.

A collaborative study by two expert laboratories used various ICP-MS instruments (including SF- and MC-) to determine the trace element *mass fractions and isotope ratios in the NRCC CRM AQUA-1 (drinking water) standard.* The article provided for the first time[103] consensus or indicative values for the mass fractions of B, Cs, Ga, Ge, Hf, Li, Nb, P, Rb, Rh, Re, S, Sc, Se, Si, Sn, Th, Ti, Tl, W, Y, Zr and the REEs. In addition, six isotopic ratios were proposed for Pb and Sr. The NRCC CRM SLRS-6 (river water) was used as a control standard.

Sample preparation for isotope ratio analysis continues to receive attention. A single column method for isolating Ba from geological and water samples used[104] a Bio-Rad AG® 50W-X8

200–400 mesh column. Barium was separated from the major interference elements in geological materials, river water and gas and oil brines using a double elution procedure with 2.5 M HCl followed by 2.0 M HNO_3. The δ^{138}Ba value was determined by MC-ICP-MS. Dissolved gaseous Hg and reactive Hg fractions were purged[105] from 10 L batches of water samples after addition of acidic $SnCl_2$. The Hg^0 generated was captured on a Cl-impregnated activated-carbon-trap before thermal desorption and trapping in a 40% reverse *aqua regia* solution for determination of δ^{202}Hg, Δ^{199}Hg, and Δ^{200}Hg by MC-ICP-MS.

The *determination of $^{236}U/^{238}U$ ratios* in seawater and marine corals by MC-ICP-MS was improved[106] by adding a secondary electron multiplier to the instrument. The detector was fitted with a retarding-potential quadrupole lens that reduced the size of the ^{238}U tail signal on the ^{236}U signal, so the abundance sensitivity of ^{238}U at m/z 236 improved from 10^{-6} to 10^{-10}. As a result, the sample mass required for successful analysis (0.7 µg U) was 60- to 100-fold lower than that required for ICP-MS or AMS procedures.

3.4.6 Laser induced breakdown spectroscopy. *Several reviews* on the application of LIBS to environmental monitoring were published. One (152 references) covered[107] the period 2010-2019 and had a section dedicated to preparation and analysis of water samples. Another review (85 references) concentrated[108] more on calibration strategies for those elements (N, P and some heavy metals) that can be detected directly in contaminated liquid samples such as wastewaters and landfill leachates. A more general review (201 references) noted[109] the generally high LODs of LIBS and discussed how these might be improved for trace element detection in a large number of matrices, including environmental ones.

Research continued into *methods for improving the sensitivity of* LIBS. The determination of N concentrations in waters was achieved[110] by detecting the molecular emission of CN radicals from a dried sample spot in an Ar atmosphere. The LOQ of 1.98 µg mL^{-1} was close to the Chinese upper permissible limit for avoiding water eutrophication. The results were not significantly different from those obtained using the standard method of alkaline potassium persulfate digestion followed by UV-VIS spectrophotometry. The quantification of Pb in dried water samples was enhanced[111] by using resonant LA for interrogation of the target. Collection of fluorescence instead of atomic emission spectra provided a LOD of 2 µg L^{-1}. Adding 13 nm gold NPs to a LIBS target improved[112] the LIBS emission intensities for Cr, Cu and Pb in dried water samples by up to 26 times (Cr) and resulted in LODs of 5 (Cu) to 22 (Pb) µg L^{-1}. In a similar vein, copper oxide NPs deposited on a PTFE target increased[113] by a factor of 10 the emission intensities of Be and Cr from dried water samples and resulted in LODs of 5 and 33 µg L^{-1}, respectively.

3.4.7 X-ray fluorescence spectrometry. The determination of ^{226}Ra in water by *TXRFS* was made possible[114] by calibrating with the NIST SRM 4967A (radium standard solution) and the MCNP6.2 Monte Carlo simulation code. When Ga was used as an IS, the LOD was 0.047 Bq L^{-1}. Almost a litre of water had to be evaporated to dryness in order to overcome spectral interferences in real samples and so achieve the WHO drinking water upper limit of 1.0 Bq L^{-1} ^{226}Ra. Portable TXRFS could be used[115] to detect Cr in waters down to concentrations of 0.13 µg L^{-1} when a 200 µL sample droplet was dried onto a hydrophobic-film sample holder.

4 Analysis of soils, plants and related materials

4.1 Review papers

A useful review (275 references) summarised[116] and evaluated *analytical methods for use in the emerging discipline of agrometallomics*. Consideration was given to the determination, speciation and spatial mapping of elements in numerous types of materials of agricultural interest, not only soil and plants but also animal feed, seeds, fertilisers, pesticides, bacteria, fungi and NPs.

Nanoparticles were the topic of a comprehensive review (290 references) that covered[57] advances in methods for determination of their abundance, morphology, composition and structure in water, soil, sediment and biological samples. Laser- and plasma-based approaches for NP characterisation were included[117] in a broader review (596 references) that also covered monitoring of NP synthesis and the use of NPs for signal enhancement.

Element-or nuclide-specific reviews featured the measurement of total, inorganic and organic P in plant tissue (95 references)[118]; mapping and speciation of P in soil (105 references)[119]; speciation of As in traditional Chinese medicines, including medicinal plants (79 references#)[120]; and determination of ^{129}I concentrations and ^{129}I/^{127}I isotope ratios in environmental samples (96 references)[121].

Analytical methods for the determination of PTEs in plants were the topic of two reviews. The first (206 references) focused[122] on medicinal plants and emphasised the need for more widespread QC to ensure the products sold are fit for consumption. The second (109 references) called[123] for the development of standard methods of speciation analysis to increase reliability and comparability of results obtained by different laboratories.

4.2 Reference materials

4.2 Reference materials

Although *new or improved isotopic data for CRMs or RMs* are generally not certified, they can be valuable benchmarks for other researchers. Examples included:

- δ^{7}Li values in four soils and four sediments by MC-ICP-MS[124]
- δ^{30}Si values in 13 soils and five sediments by MC-ICP-MS[125]
- δ^{30}Si values in four soils and one plant (ERM CD281 (rye grass)) by MC-ICP-MS[126]
- δ^{44}Ca/^{40}Ca values in nine soils and five sediments by TIMS[127]
- δ^{88}Sr/^{86}Sr values in five soils and two sediments by MC-ICP-MS[128]
- δ^{87}Rb values in two soils, one loess and two sediments by MC-ICP-MS[129]
- δ^{114}Cd/^{110}Cd values in one soil and 13 sediments by MC-ICP-MS[130]
- ^{129}I/^{127}I ratios in six soils and 14 sediments by AMS[131]

Re-analysis of a suite of environmental CRMs, including some soils and sediments, produced towards the end of the 20th century for the actinide elements gave[27] results that agreed with literature or certified values but had lower uncertainties. The authors recommended that many of these CRMs should be re-certified using modern high-precision MS data.

4.3 Sample preparation

4.3.1 Sample dissolution and extraction

Studies on the *minimisation of* *contamination during dissolution* included[132] one on cross-contamination between samples arising from the use of magnetic stir bars. Elements adsorbed on Teflon-coated stir bars during the MAD of soil samples were subsequently released during microwave-assisted cleaning cycles with HNO_3 and H_2O_2 (30%). The elements Cr, Cu, Sb, Sn and Pb were detected at ppb levels in second, third and even fourth cycles. The authors suggested that microscopic cracks in the Teflon, observed with SEM/EDS, allowed penetration of elements below the Teflon surface, and they proposed the incorporation of additional bar-cleaning steps to avoid transfer of adsorbed PTEs to subsequent samples. A protocol designed to remove HF from samples following microwave digestion had[133] the aim of preventing the introduction of impurities frequently observed with open-vessel HF evaporation. The 'vessel-inside-vessel' technique involved sample digestion (with HF and HNO_3) in a small (5 mL) loosely-capped inner PFA vessel, after which HF was transferred from the inner vessel into the larger (70 mL) outer PTFE sealed vessel by means of two further microwave cycles at 500 W for 10 min. When ultra-pure water was the scavenger solution in the outer vessel, HF migration of up to 99.9% was achieved and so provided a safe closed-vessel contamination-free method of HF removal. An initial step involving soil wetting with 30% H_2O_2 at 50 °C on a hot plate prevented analyte loss from the loosely-capped inner vessel during sample digestion. The relative measurement errors ranged from -5 to +8% for all 27 elements determined in NIST SRM 2710 (siliceous soil).

Investigations into the *use of strong acids for digestion*[134] included a comparison (in the Chinese language) of the efficiency of combinations of HF, HCl, H_2O_2, HNO_3, and sample calcination for the digestion of soil standard materials IGGE GSS-1a to GSS-8a. Digestion efficiency was greatest when samples were initially calcinated at 550 °C and then digested with HF-HNO_3. The use of H_2SO_4 and H_2O_2 for MAD followed by AAS was proposed[135] as a safer and cheaper alternative to the use of HF and ICP-MS for the monitoring of trace elements in soils. Digestion (200 °C, 10 min) of 0.5 g Supelco CRM SQC001 (metals in soil) with 9 mL of H_2SO_4 and 3 mL H_2O_2, however, gave relative measurement errors for As, Cd, Co, Cr, Cu, Ni and Pb of -13% (Cd) to +13% (Cr). The fact that values for As, Co, Cr, Cu, Ni and Pb from nine soil samples were less than half of those obtained for digestion with HF + $HClO_4$ further highlights that H_2SO_4 + H_2O_2 did not digest all soil types completely.

An example of an *element-specific extraction* was a method**[136]** for the determination of As in the field. The optimised slurry sampling process involved addition of 0.4 mL HF + 4 mL HNO_3 to 200 mg of soil, UA irradiation of the resultant mixture for 25 min, dilution with 6% HCl (*v/v*), addition of thiourea (40 g L^{-1}) and further irradiation for 10 min to obtain a homogenised slurry. This was introduced into the HG-DBD trap-AES system using a coupling method described previously[137]. The LOD was 0.18 mg kg^{-1}. The results (n = 5) for the analysis of Chinese CRMs GBW 07430, 07447 and 07449 (soils) of 18 ± 2, 10.7 ± 0.5 and 8.7 ± 0.6 mg kg^{-1}, respectively, agreed with the certified values of 20 ± 2, 10.3 ± 0.6 and 8.5 ± 0.8 mg kg^{-1}, respectively. It is noteworthy that the entire procedure was carried out in the field even though the use of HF clearly imposed limitations on transportation and handling on site .

The occurrence of high concentrations of naturally occurring NPs is a major obstacle in the *determination of engineered metal-NPs*, as is the lack of RMs. Philippe *et al.*[138] proposed colloidal extraction for the separation of anthropogenic TiO_2 NPs from naturally occurring particles, of which only a small fraction was colloidal in size. Background correction with Nb as a proxy for natural TiO_2 gave an ICP-MS LOD of *ca.* 10 µg g^{-1} TiO_2. The recoveries from four different soil types spiked at between 200 and 600 µg g^{-1} were 29.1% (sand) to 86.7% (clayey soil) but could be improved by repeating the extraction. A sonication-sedimentation procedure with a sedimentation time of 6 h and a sediment:water ratio of 2:5 was proposed**[139]** for the separation of Ti- and Zn-containing NPs from larger sediment particles in sediment, soil and road dust samples. For efficient separation in samples with TOC >5%, sonication times had to be increased from 20 to 30 min and temperatures from 15-25 to 25-35 °C. Method efficiency was assessed by spiking the samples with silver and gold NPs. Recoveries were 44 to 68% and 54 to 83%, respectively. The magnetic properties of zero-valent Fe were exploited[140] to separate the nanoscale engineered-particles widely used for soil and water decontamination from naturally occurring colloidal and dissolved Fe. Under optimised extraction conditions (2.5 mM tetrasodium pyrophosphate extractant, 30 min sonication), the LODs of the procedure based on UAE, magnetic separation and sp-ICP-MS were 43.1 nm and 50 µg g^{-1} for particle size and concentration, respectively. Six soil samples with OM contents of 7.0−64.6 g kg^{-1} were spiked with 50 or 100 nm-sized Fe NPs at concentrations of 50, 100 or 500 µg g^{-1}. The recoveries were 62.0 ± 10.8% to 96.1 ± 4.8% for number of particles and 70.6 ± 12.0% to 119 ± 18% for mass of Fe. The authors noted that although the method had potential for general application, care should be taken with unknown samples which might have high background levels of magnetic Fe.

An extraction procedure for the separation of *naturally occurring mercury NPs* from soils was based[141] on using tetrasodium pyrophosphate (10 mM) for the dispersion of soil particles and $Na_2S_2O_3$ and 2,3-dimercaptopropanesulfonate sodium salt (0.5 mM) for the chelation of Hg. The procedure involved shaking (200 rpm, 70 min), sonication (40 kHz, 15 min), agitation and sedimentation (2 h). Quantification was by sp-ICP-MS. The authors considered the very significant and frequently overlooked effect of ageing when assessing the efficiency of the extraction protocol and found no statistically significant difference between the recoveries of Hg from spiked samples that had been stored for either 24 h or 30 days.

Extraction methods for radionuclides continued to be developed. In the analysis of contaminated soil from the Fukushima Daiichi nuclear-power-plant, the concentration of the extracting acid influenced**[142]** the Cs isotope ratios determined by TIMS. Extraction with dilute (3 M) HNO_3 resulted in a statistically significant 3‰ higher $^{135}Cs/^{137}Cs$ average isotope ratio than extraction with concentrated acid. Alkali fusion was proposed**[143]** for sample dissolution in a procedure for the determination of Th and U. The optimised method utilised NaOH-Na_2O_2 fluxes in the fusion process, radiochemical separation of Th and U and analyses using ICP-MS and α-particle spectrometry. Relative measurement errors for U in five CRMs ranged from -39% for IAEA 385 (Irish Sea sediment) to -9% for IAEA 327 (soil from Moscow, Russia). The corresponding errors for Th ranged from -16% for IAEA-326 (soil from Kursk region, Russia) to -7% for IAEA-447 (soil from Hungary). Determination of ^{107}Pd at low levels (<2 ng kg^{-1}) was achieved**[144]** through a multistep separation process involving Pd retention on a Ni resin and determination with ICP-MS/MS. The method was applied to sediment from the cooling pond at Chernobyl.

The *bioaccessibility* of As, Cd, Cr, Pb and Sb in NIST SRMs 2710 (Montana soil), 2710a (Montana I soil) and 2711 (Montana II soil) and in BGS 102 (Ironstone soil) was determined**[145, 146]** with the continuous online leaching method (COLM) already employed in food studies. The US EPA, United States Pharmacopeia, and UBM simulated gastrointestinal fluids were used for extraction. Although there were no statistically significant differences in results from the online and batch extraction procedures, the COLM procedure significantly decreased extraction times from up to 5 h to 5-15 min. An appealing option for bioaccessibility studies when using online leaching was the possibility of determining Pb isotope ratios, thereby providing additional information on contamination sources.

New *methods for extraction from plants* included**[147]** MAE with dilute TMAH as a rapid method for the extraction of halogens. Under optimised extraction conditions (6 mL 100 mM TMAH, irradiation at 5 min and 240 °C) and ICP-MS analysis, there was no statistical difference between measured and certified concentrations for Br, Cl and I in NIST SRMs 1572 (citrus leaves) and 1547 (peach leaves). Two UAE procedures based on a HNO_3-H_2O_2 mixture as the extractant were proposed as greener alternatives to extractions with concentrated acid. In an optimised method, Iftikhar *et al.***[148]** used both FAAS and ICP-AES to determine essential and non-essential nutrients extracted from carrot, cauliflower, pumpkin and spinach by 0.5 M HNO_3-10% H_2O_2. Extraction efficiency was validated with NIST SRMs 1515 (apple leaves) and 1570a (spinach leaves) for which low relative measurement errors (<-5%) were obtained for all elements. In the method of Curti *et al.***[149]**, extraction with 7 M HNO_3-30% H_2O_2 yielded relative measurement errors of -18% (Zn) to +10% (P) when applied to the Chinese RM NCSZC7310 (maize). Low LODs (0.04-0.12 ng g^{-1}) were the attraction of a procedure**[150]** for the determination of Se species in rice that was based on enzyme extraction, ion-pairing RP chromatography and ICP-MS/MS analysis. When protease XIV extraction was used, the sum of the extracted species Se^{IV}, Se^{VI}, $SeCys_2$, SeMeCys and SeMet accounted for 93-109% of the total Se content of rice. Spike recoveries were 96-103% for all species except $SeCys_2$ for which the recovery was 66-77%. Already well established in sample preconcentration procedures, NADESs are gaining popularity for metal extraction because of their non-toxic nature. The efficiencies of nine NADESs selected by predictive modelling were assessed**[151]** for the extraction of Cu, Mn, Mo and Zn from barley grass. Optimum extraction efficiency was obtained when the water content of the solvents was >50%. The accuracy of the optimised method was tested using CRM ERM-CD281 (rye grass). The concentrations of Cu, Mn and Mo, as determined by ICP-MS, agreed with certified values but the Zn content was overestimated.

4.3.2 Analyte separation and preconcentration

Several reviews covered *separation and preconcentration techniques*. Methods for the extraction, preconcentration and analysis of a range of nanomaterials in natural waters, wastewaters, soils and sediments and biological samples were critically reviewed (291 references) by Jiang *et al.*[57]. The review (146 references) of Viana *et al.*[60] on extraction from waters, soils and sediments for metal speciation included techniques such as MAE, UAE, SPE, SPME and LPME. Jalili *et al.*[152] reviewed (113 references) supramolecular solvent-based microextraction techniques, primarily for the analysis of waters but also for the analysis of soils. The mesoporous silica sorbents summarised[153] in a review (113 references) included magnetic materials, materials functionalised with organic carbon and molecularly imprinted polymers. The selectivity and enrichment ability of sorbent materials such as carbon nanotubes, aerogels, covalent-organic frameworks and MOFs were considered[154] in a review (152 references) in the Chinese language. The sample matrices covered in a review (157 references) by Gumus and Soylak[59] on applications of MOF included waters, waste waters, soils and sediments, plants, fish and industrial effluent. Carbon-nitride frameworks were reviewed by Kang *et al.*[155] (132 references). The reviews of Andruch *et al.*[156] (85 references) and of Herce-Sesa *et al.*[157] (69 references), discussed DES in LLME procedures.

Numerous preconcentration procedures for specific analytes have been reported. 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 7 (LPE methods) and 8 (SPE methods).

Insert Tables 7 and 8

4.4 Instrumental analysis

4.4.1 Atomic absorption spectrometry

Although traditionally considered as a technique for measuring one element at a time, ETAAS can also be used for multielement analysis by incorporating either multiple HCLs or a CS. A review (154 references) on *advances in simultaneous or sequential multielement analysis by ETAAS* in the period 2000-2020 advocated[34] further development and greater use of HR-CS-ETAAS. A solid sampling HR-CS-ETAAS method for the determination of Cd, Fe and Ni in seeds used[158] 5 µg Pd + 3 µg Mg + 15 µL H_2O_2 as matrix modifier and aqueous standards for calibration. Cadmium was determined first at an atomisation temperature of 1600 °C and then the other elements were determined at 2500 °C. A background correction using the time:absorbance ratio was proposed[159] as a potential improvement over least squares background correction for overcoming spectral overlap in HR-CS-ETAAS. The advantage of this approach was that the nature of the spectral interference did not need to be known *a priori*. Application of this correction method improved results for Pb in NIST SRMs 1570a (spinach leaves) from 0.350 ± 0.130 to 0.241 ± 0.068 mg kg^{-1} (reference value 0.2 mg kg^{-1}). Although analyte oxide species are often the source of interference in CS-ETAAS, they can sometimes be used to advantage as demonstrated in a method[160] for the determination of Si based on molecular absorption by SiO. This was successfully applied to the analysis of solid sample suspensions, including two soil and two sediment CRMs.

Use of a novel *platinum-coated tungsten coil atom trap* improved[76] sensitivity for the determination of As by over an order of magnitude relative to conventional HG-AAS. The LOD was 0.016 µg L^{-1} for a trapping time of 90 s. Although primarily intended for use in (potable) water analysis, the method was tested with Supelco CRM 023 (sandy loam 7) for which the result of 375 ± 3.8 mg kg^{-1} agreed with the certified value of 380 ± 6.7 mg kg^{-1}.

A *single-point standard-addition method*[161] was proposed as an alternative to conventional external calibration in the ETAAS and ICP-AES determinations of trace elements in complex sample matrices. When silty soils BIM-1 and NES-1 from the Geo*PT* proficiency testing programme were analysed using the new method, the results for As, Cd, Pb, Sb, Se and Te agreed with the assigned values.

4.4.2 Atomic emission spectrometry

Research has continued in development of *miniaturised AES systems* with the ultimate goal of creating field-portable instruments. Different approaches have been taken for sample introduction and microplasma generation. Two methods optimised for the determination of As were based on HG-DBD-AES. Dried and powdered seaweed was digested[162] to generate arsine which was preconcentrated on the DBD's inner surface leading to improved sensitivity on ignition of the excitation plasma. The solution LOD was 0.2 μg L^{-1} and the method LOD 0.25 mg kg^{-1}. Results for Chinese CRMs GBW 08521 and 10023 (both laver bread) agreed with the certified values. In a method described in more detail in section 4.3.1 of this ASU, soil samples were introduced[136] into the HG-DBD-AES system as a slurry. Swiderski *et al.*[163] investigated hanging-drop-cathode APGD as an excitation source for AES. Incorporation of a Dove prism, to rotate the discharge image by 90°, and addition of 8% (*m/m*) formic acid together enhanced the intensity of analyte lines relative to background. Following optimisation by a DoE approach, results for INCT CRM TL-1 (tea leaves) were statistically in agreement with the certified values for Pb and Tl. The recovery of a Ag spike was 102%. Cai and Wang[79] took a different approach with the aim of eliminating the need for CVG reagents and pneumatic nebulisation. They used a solution anode GD not as an emission source but as a vapour generator for the determination of Cd and Hg by ICP-AES. Signal intensity was increased by almost a factor of 12 for Cd and of 90 for Hg. The result for Cd in Chinese CRM GBW 07312 (aquatic sediment) was 3737 ± 102 μg kg^{-1} (certified value 3935 ± 63 μg kg^{-1}). A solution cathode GD was also proposed[164] for VG in the determination of Hg by ICP-AES. Spike recoveries from samples of fish, human hair and soil were 92 - 104% and the LOD at 194.1 nm was 0.22 μg L^{-1}.

In *the determination of F in plant-based materials by solid sampling ETV-ICP-AES*, addition of H_2 to the carrier gas improved[165] LODs to 0.05-0.8 μg kg^{-1}, depending on the F emission line studied. Multivariate optimisation yielded: rf power 1.7 kW; Ar carrier gas flow 0.15 L min^{-1}; Ar bypass gas flow 0.2 L min^{-1} and H_2 reaction gas flow 3 mL min^{-1}. The analysis of 2 mg solid samples with a pyrolysis temperature of 200 °C and a vaporisation temperature of 2200 °C gave results for NIST SRMs 8432 (corn starch) and 8437 (hard spring wheat) that were not statistically different from information values according to Student's t-test at 95% confidence.

Environmental analysis was included in a review by Fontoura *et al.*[166] (95 references) of recent *advances in MIP-AES* for trace element determination. It was concluded that the technique could offer a lower-cost alternative to ICP-AES for some applications. A similar conclusion was reached by Proch and Niedzielski[167] who compared HPLC-MIP-AES and HPLC-ICP-AES for Fe speciation analysis in soil, sediment and plant samples. As expected, the LODs for the MIP approach were poorer – by roughly an order of magnitude – than those obtained with ICP-AES, but it was still possible to quantify Fe^{II} and Fe^{III} in some samples.

The determination of Pb by HG-MIP-AES was demonstrated[82] for the first time. The experimental conditions for the generation of plumbane were optimised and the effect of acid concentration on signal intensity studied. A relative measurement error of -9.3 ± 4.6% was achieved for duplicate analyses of the Embrapa soil RM Agro E2002a. To assess whether the high salt content of reagents typically used to estimate trace element mobility and availability in soils and sediments would preclude their analysis by MIP-AES, Serrano *et al.*[168] investigated the effects of $MgCl_2$, $CaCl_2$, acetic acid, Na_2EDTA, $NaNO_3$, NaOAc-acetic acid and $NH_2OH.HCl$ on emission intensities for 15 elements. Although atomic lines with $E_{upper\ level}$ values of <4 eV were generally enhanced relative to their intensity in 5% HNO_3, the remaining atomic and ionic lines were suppressed. Matrix effects were worse in reagents containing elements with low IPs, such as sodium. Either Rh or OH molecular emission was recommended for use as a IS. Krogstad and Zivanovic[169] carried out a more empirical comparison of MIP-AES, ICP-AES and ICP-MS for measurement of Ca, Cu, Fe, K, Mg, Mn, P, Zn in ammonium lactate extracts of soil. The lower-cost MIP technique was deemed suitable for monitoring of nutrient levels and fertilisation planning.

4.4.3 Atomic fluorescence spectrometry

The advantages and drawbacks of *CVG-AFS methods for Se speciation analysis* were discussed[170] in a review (60 references). A pre-requisite for the determination of total Se is reduction of Se^{VI} to Se^{IV} but this reaction can be slow. Approaches described for overcoming this limitation included conventional heating, microwave irradiation and exposure to UV light.

A microplasma-induced CV-AFS method for the rapid screening and quantification of Hg in fruit gave[171] results within 7% of those obtained by HG-AFS when applied to tomatoes, lemons and oranges. Whole fruit samples were punctured with a needle and the resulting juice droplet drawn into a stainless-steel capillary. A voltage was applied between the far end of the capillary and a tungsten electrode, and an argon microplasma generated in which Hg ions were converted to Hg^0 before being swept into an AFS detector. The LOD of 0.3-0.5 $\mu g\ L^{-1}$ depended on the type of juice analysed.

4.4.4 Inductively coupled plasma mass spectrometry

Recent advances in FFF-ICP-MS for characterisation of engineered NPs in environmental media were reviewed[38] (103 references). The advantages of asymmetrical flow FFF and hollow fibre flow FFF were discussed and examples of their application to soil and sediment provided.

A critical and comprehensive review of sp-ICP-MS (301 references) discussed[39] the evolution and principles of the technique, together with methods for the study of NPs in numerous sample matrices including soils and plants. Another review (159 references) focussed[172] specifically on metallic NPs in biological samples. Both sets of authors identified the paucity of properly validated standardised methods and the lack of suitable NP CRMs as major factors hampering progress in the field.

Such issues did not deter other researchers from proposing *sp-ICP-MS methods for determination of various types of nanoparticles*, some of which are discussed in more detail in section 4.3.1 of this ASU. These methods included: a procedure[140] for determining nanoscale zero-valent Fe in soil that involved UAE in 0.25 mM tetrasodium pyrophosphate followed by magnetic separation; a procedure[141] for determining nanoparticulate Hg in soil that employed

0.5 mM tetrasodium pyrophosphate + 0.5 mM sodium thiosulfate + 0.5 mM 2,3-dimercaptopropanesulfonate sodium salt + 0.01 mM sodium nitrate extractant; a procedure[173] for determining gold NPs in plants that featured enzymatic digestion with Macerozyme R-10; and a procedure[139] for determining gold, silver, titanium and zinc NPs in estuarine sediments, road dust and soil that was based on UAE in deionised water.

A *versatile, open-source Python-based data-processing-platform with interactive graphical user-interface* was developed[174] for processing ICP-MS data from the analysis of single particles or biological cells. The capabilities of the algorithm were demonstrated by determination of TiO_2 NPs in surface waters, microplastics in soil (using sp-LA-ICP-MS) and C in algal cells.

Holbrook *et al.*[175] developed *a sp-LA-ICP-TOF-MS procedure for the direct determination of nanoparticles in road-deposited sediment*. The method was first evaluated using model gold and silver NPs, then tested on extracts of the sediments and finally applied to solid sediment mounted on double-sided tape. Element signals were classified into three groups. Group 1 consisted of elements (*e.g.* Al) present in such abundance that it was impossible to distinguish single particles from the background, group 2 consisted mainly of the REEs and group 3 was the PGEs. Single particles could be distinguished in both groups 2 and 3.

Several new *metal-assisted PVG-ICP-MS methods* used a ‘sensitiser’ – typically a transition metal ion – to enhance the generation of volatile species. A procedure for the determination of Cd in rice used[176] a Fenton-like digestion and 20 mg L^{-1} Co^{2+} to improve the PVG yield. The LOD was 1.6 µg kg^{-1} and results for Chinese CRMs GBW 100351 and 100357 (both rice flour) were not significantly different from the certified values. The analysis of a 0.7 mL sample containing 10% formic acid, 300 mg L^{-1} Co^{2+} and 30 mM Cl^- enhanced[177] the photochemical reduction of Ge to give a LOD of 0.008 µg L^{-1}. Results for the two soil CRMs IGGE GSS-3a and GSS-5a were not significantly different from the certified values. Dong *et al.*[178] reported the first use of vanadium species as sensitisers in PVG. The addition of 40 mg L^{-1} V^{v} (in the form of VO_3^-) increased the response for both Te^{IV} and Te^{VI} up to 55-fold compared with direct solution nebulisation and 1.5-fold relative to Co^{2+}-assisted PVG. The LOD was 2.9 ng L^{-1} and accurate results were obtained for Te in the Chinese CRMs GBW 07303a and 07305a (both stream sediment). A method for the determination of Os used[179] 50 mg L^{-1} Fe^{2+} (or Fe^{3+}) as a sensitiser to achieve a LOD of 0.16 pg mL^{-1}. The method was validated by spike recovery because few CRMs certified for Os are available. Recoveries of 1 ng mL^{-1} Os added to water, sediment and fish protein samples were 94 -109%.

The *coupling of chromatographic separation with ICP-MS* remained of interest. Of particular note was a HPLC-ICP-MS method[180] for determination of inorganic As species in rice. A novel on-column species-specific internal-calibration-strategy was proposed to overcome challenges associated with ID, such as cost and non-availability of suitable isotopically enriched standards. A species-specific ID HPLC-ICP-MS method previously applied to other foodstuffs was shown[181] to be applicable to the Cr speciation analysis of rice. When 10 rice samples of different origin were analysed, no Cr^{VI} was detected. Indeed, a Cr^{VI} spike added to basmati rice was reduced to Cr^{III} within 2 h thereby confirming that Cr in rice is present solely as Cr^{III}. An HPLC-ICP-MS method was developed[182] and applied, together with LA-ICP-MS, to study Cr uptake in *Taraxacum officinale* (dandelion). Two methods for Se speciation analysis, one for rice[150] and the other for plant-based foods[183], were based on enzymatic extraction and RP IC-ICP-MS. A species-specific ID-GC-ICP-TOF-MS method was developed[184] for the determination of MeHg in canal sediment. The LOQ and precision for measurement of the ^{201}Hg/^{202}Hg isotope ratio were similar to those obtained by ID-GC-ICP-Q-MS and ID-GC-ICP-SF-MS. It was noted that the superior performance of ICP-TOF-MS previously observed with continuous liquid-sample-introduction was not achieved for analysis with transient signals.

Rapid data acquisition is important in the *elemental mapping of botanical tissues by LA-ICP-MS* in order to obtain high-resolution images in minimal time. Careful optimisation of the type of ablation cell, the mixing bulb and the inner diameter of the aerosol-transport tubing reduced[185] the single-pulse response for Hg and Se to 50 ± 2 and 61 ± 4 ms, respectively. This represented a 5-fold improvement over the standard instrument configuration and allowed mapping of a segment of mushroom tissue at up to 20 pixels s^{-1}. A simple calibration strategy based on aqueous standards deposited on filter paper was proposed[186] for the determination of Cu and Zn in tree rings. Even though most results were significantly different statistically from those obtained for the analysis of wood digests when normalised using ^{13}C as an IS, the method was nevertheless able to reveal trends in analyte concentrations.

Wider availability of instrumentation led to an increase in *publications featuring ICP-MS/MS*. A review (79 references) considered[37] articles published in the period January 2018 to July 2021 and included some featuring the analysis of soil or plant materials. A method for the Sr isotopic analysis of microsamples combined[187] a syringe-driven pump delivering a stable 20 μL min^{-1} microflow of sample with a high-efficiency sample introduction system, originally designed for the introduction of single cells, to compensate for the low uptake rate. Even though no chromatographic separation of Rb and Sr was undertaken, the ^{87}Sr/^{86}Sr ratio could be determined at ng g^{-1} concentrations in as little as 240 μL of sample. In a multielement method, N_2O was preferred[188] to O_2 in the ICP-MS/MS collision/reaction cell because it improved sensitivity and selectivity for the determination of "technologically critical elements" in sediments. A procedure for ultra-trace level quantification of ^{241}Am in soils involved[189] radiochemical separation followed by the introduction of 0.09 mL min^{-1} He containing 20% O_2 and 12 mL min^{-1} He reaction/collision gas mixture into the cell for determination of the isotope in mass-shift mode as AmO^+. The LOD was 0.017 fg g^{-1}. Results for the two soil CRMs IAEA Soil 6 and IAEA 375 were similar to values reported in the literature.

Several research groups have recommended different *collision/reaction cell gas combinations in the determination of Pu isotopes by ICP-MS/MS*. The aim was to eliminate the interferences from uranium hydrides. Zhang *et al.*[190] quantified Pu in soil by combining gas flows of 0.15 mL min^{-1} O_2/He and 12 mL min^{-1} He both to dissociate interfering polyatomic ions and to form PuO_2^+. In their measurement of Pu in lake sediments, Xu *et al.*[191] used 0.4 mL min^{-1} NH_3 to remove interferences by formation of adduct species such as $UH(NH_m)_n^+$. Bu *et al.*[192] also used NH_3 (30% NH_3 in 5 mL min^{-1} He) to eliminate UH^+ interference in the measurement of the ^{240}Pu/^{239}Pu ratio in soil and sediment. The LODs of all three methods were sub-fg.

Precise measurement of the ^{234}U/^{238}U and ^{235}U/^{238}U isotope ratios in Fukushima soil samples was facilitated[193] by an *improved sample preparation method for MC-ICP-MS analysis*. Of various combinations of resin tested for recovery of U, three sequential UTEVA™ columns provided the highest recovery and the smallest mass bias. Lead isotope analysis was performed[194] by a novel combination of plasma-induced CVG and MC-ICP-MS. Although mass-dependent fractionation of the Pb isotopes occurred, this was successfully corrected by a ^{205}Tl/^{203}Tl external normalisation combined with SSB. The method gave results for the two

USGS basalt RMs BCR-2 and BHVO-2 that were said to be in good agreement with GeoReM preferred values although no statistical comparison was actually reported. The method was applied to soil samples, mine waste and ore. A procedure for determining Cd isotopes involving MAE and resin purification gave[195] results similar to those reported by previous authors for a suite of soil, sediment and plant CRMs. Enrico *et al.*[30] made novel use of a direct mercury analyser as a rapid means of solid sample preparation. Mercury in the effluent from the instrument was trapped with >90% efficiency in a 5:1 *v/v* mixture of 10% HCl and BrCl and the solution then analysed by MC-ICP-MS. No significant isotopic fractionation was observed and δ^{199}Hg and δ^{202}Hg values for NIST SRM 1775a (pine needles) and NRCC MESS-2 (sediment) were similar to literature values.

A reminder of the need to choose *the correct IS for ICP-MS analysis* was provided by Alvarado *et al.*[196] who compared ^{6}Li, ^{45}Sc, ^{69}Ga, ^{89}Y, ^{103}Rh, ^{115}In, ^{159} Tb and ^{209}Bi for the determination of As in soil. Significant analytical bias occurred when the 'native' concentration of the nuclide selected as IS in the soil digest approached or exceeded the concentration added.

4.4.5 Laser-induced breakdown spectroscopy

Numerous *review articles* featuring soil and plant analysis have been published. Goncalves *et al.*[108] (83 references) provided a brief introduction to LIBS principles and instrumentation and described some recent applications featuring analysis of environmental samples, including soils and sediments. In their review (151 references) of articles published in the period 2010-2019, Zhang *et al.*[107] focussed on environmental applications, including the analysis of soils and sediments. The use of ANN-based chemometrics in LIBS was discussed by Li *et al.*[197]

(149 references). Wang *et al.*[198] highlighted (244 references) that measurement uncertainty and matrix effects were two major (and interlinked) factors hindering progress in LIBS analysis and proposed a useful research framework for improving quantification. Hu *et al.*[199] reviewed (137 references) calibration-free LIBS in which the measured concentration is derived from an algorithm rather than from the analysis of standards. Ren *et al.*[200] summarised (134 references) applications of LIBS in agriculture in the period 2017 to 2021 with particular reference to the detection of nutrients and PTEs in soils, fertilisers, waters and crops. Khan *et al.*[109] included the analysis of plants and plant-derived foodstuffs in their review (207 references) which also featured a useful comparison of the advantages and disadvantages of different types of LIBS analysis.

A novel *signal-enhancement strategy for LIBS analysis of soil* combined[201] APGD and cylindrical (plasma) confinement. The LODs of 2, 31, 21, 35, 49, 67, 43, 20 and 18 mg kg^{-1} for Ba, Cu, Eu, La, Lu, Ni, Ti, Y and Yb, respectively, were significantly better than the values (10, 133, 102, 175, 262, 356, 246, 158 and 105 mg kg^{-1}, respectively) achievable using conventional LIBS. An alternative approach involved[202] addition of 15% KI to soil samples to increase plasma temperature and electron density. The new technique of multidimensional plasma grating-induced breakdown spectroscopy also improved[203] emission intensities (*ca.* twofold relative to 1D plasma-grating induced breakdown spectroscopy). The LOD for the determination of Mn in soil at 403.17 nm was improved from 394 to 306 mg kg^{-1}.

Amongst *other advances in the analysis of soils by LIBS* was a combined atomic- and ionic-line algorithm[204] that improved spectral stability and therefore reduced uncertainty in calibration and a method[205] designed specifically for analysis of wet soils that could be used to estimate the sample moisture content and to correct for its influence on the ablation process. A procedure for the determination of Cr combined[206] the adaptive least absolute shrinkage and selection operator with support vector regression. Different amounts of $Cr(NO_3)_3$ were added to the Chinese soil CRM GBW 07403 in the method development but a linear response was obtained (R^2=0.998) only for Cr concentrations of 0.02 to 1.0 % which are far higher than the Cr concentrations typically found in soils.

The *influence of laser-spot size on the determination of Al, Ca, Cr, Fe, Mg, Mn, Ti and V in stream sediments by fibre-optic LIBS* was studied[207]. A change in lens-to-sample distance of as little as 1 mm resulted in a larger ablation crater, lower laser fluence and decreased analyte emission intensities. Under optimised conditions, results close to target values were obtained for a CRM from Tanmo Quality Inspection Technology Co., China.

Interest in *the analysis of plant materials by LIBS* is growing and it is welcome to see many authors including CRMs or comparisons with established techniques in their work. A single calibration model[208] based on matrix-matched RMs was applied to the DP-LIBS determination of Ca, Mg, Mn and P in soybean and sugar cane leaves. Results for the majority of samples were 100 ± 20% of ICP-AES target values. In the CF-LIBS analysis[209] of *Maerua oblongifolia*, a medicinal plant native to Pakistan, results for Al, Ca, Fe, K, Mg, Na and Sr were similar to those obtained by ICP-MS whereas Si was underestimated and Ba, Li, Rb and Zn were overestimated. Another CF-LIBS method was tested[210] using both plant and soil CRMs. Results for Al, Ca, Mg, N and Na in Chinese RMs NCSZC73014 (tea leaf) and NCSZC73012 (cabbage leaf) were generally within 80 to 120% of the certified values, provided the analyte concentration was normalised to that of a major element such as K.

4.4.6 X-ray spectrometry

Reviews on the *use of XRFS in soil and plant analysis* covered methods related to the *in situ* mapping and availability of P in soils[**119**] (106 references), advances in plant imaging[**211**] (172 references) and potential problems commonly encountered during forensic soil analysis[**212**] **(**46 references).

Improving the accuracy of XRFS analyses of dried plant samples through the modification of sample preparation methods such as sample:binder ratio and pelletising pressure was the aim of several XRFS studies. A sample mass of 20 mg per 5 mL dispersant and a particle size of 200-300 mesh improved[213] analytical performance in the determination of medium and high atomic number elements in tea powder by TXRFS. In the standardless WDXRFS analysis of the conifer species *Pinus nigra* and *Abies alba,* a wax binder ratio of 20% in the pellet preparation led[**214**] to a statistically significant underestimation of the concentrations of the light elements Al and Mg but an overestimation of those for Fe and Mn**.** Variations in pellet mass (1-5 g) and pressure (10 and 25 t) did not have a significant effect on the results. Orlic *et al.*[**215**] compared the performance of WDXRFS using a standardless calibration based on fundamental parameters (UniQuant) with external calibration using cellulose standards, prepared either with a wax binder or as a thin film. The accuracy, precision and LODs obtained with standard calibration using 20% wax binder were better than when either the thin layer or the semi-quantitative standardless methods were used. These last two methods overestimated most element concentrations with a marked drop in accuracy for light elements at concentrations of <50 mg kg^{-1}.

5 Analysis of geological materials

5.1 Reference materials and data quality

The annual Geostandards and Geoanalytical Research *bibliographic review* (over 600 references) provided**[216]** an overview of papers published in 2020 that contributed important data for geoanalytical RMs. A substantial number of the publications focused on newly developed RMs and analytical data for existing RMs obtained using improved methods. All the data referred to in this review have been entered into the GeoReM database that is freely available online (http://georem.mpch-mainz.gwdg.de).

Much of the current effort has been directed toward identifying natural minerals that are sufficiently homogeneous to act as *reference materials for microanalytical techniques*. Particularly prominent in this review period was the characterisation of new materials for isotope ratio determinations; these have been collated in Table 9. Although most of these materials are available from the authors, many do not exist in sufficient quantities to facilitate their widespread use and so in reality are little more than in-house QC materials.

Insert Table 9

An alternative strategy has been to characterise *well-known geological RMs* for additional elements and isotope systems not included in the original characterisation. These new data are summarised in Table 10. Many of these materials are powdered RMs that are quite widely available; it should be noted that after a hiatus of several years, the USGS will be selling many of their more popular geological RMs once again.

Insert Table 10

While RMs are an important cornerstone of method development and quality assurance, *proficiency testing* is another facet of good laboratory practice. Meisel *et al.*[217] reviewed (35 references) some lessons learnt from 25 years of the Geo*PT*, the highly successful proficiency-testing programme for the geochemical analysis of geological materials. The data submitted to Geo*PT* provided a valuable resource that allowed detailed comparison of different methods of sample preparation and measurement principles. Examples included in the discussion were the recurring problems with the dissolution of the refractory minerals zircon and chromite when only acid digestion is involved, and issues related to preparing samples for XRFS analysis.

In a commendable initiative to promote *a more efficient and transparent system for curating geochemical data*, a consortium of Australian research laboratories collaborated[218] to build a platform called AusGeochem to preserve, disseminate and collate geochronology and isotopic data. The cloud-based system is an open relational data platform designed to be a geosample registry, a geochemical data repository and a data analysis tool. The next stage is to create a global geochemical data network through coordination and collaboration among international geochemical providers *via* an EU-funded project called OneGeochemistry. At the very least, this will require global agreement on international standards, best practices and vocabularies.

5.2 Sample preparation, dissolution, separation and preconcentration

For whole rock determinations by acid digestion, *complete sample digestion* is essential for the accurate determination of trace element mass fractions in geological materials, as highlighted by Meisel *et al.*[217]. In recent years, NH_4HF_2 has been proposed as a “green” alternative to HF-based dissolutions but complete digestion can be time-consuming. Zhang et al.**[219]** designed and manufactured a PTFE digestion vessel with a lid that could be operated safely at 300 °C in a procedure to reduce the time for sample evaporation and redissolution in a NH_4HF_2 digestion. Microwave heating was employed at the redissolution stage to suppress formation of insoluble fluoride residues during the high-temperature evaporation stage. The optimised procedure reduced the time for sample evaporation and redissolution from 9 h to 21 min. Results were within ±10% of the reference values for 37 elements in seven rock RMs with a range of lithologies. To overcome the problem of insoluble fluorides formed during an HF digestion, Kagami and Yokoyama**[220]** adjusted the Ca-Al-Mg composition of the samples prior to digestion in a high-pressure system for the determination of 27 elements, including the HFSEs, by ICP-MS. Whereas mass fractions of Hf, Ti and Zr were determined by an ID method, all other elements were determined by an ID-IS procedure using solutions containing enriched spikes of ^{91}Zr-^{179}Hf or ^{113}In-^{203}Tl as ISs. One drawback of this method was the need to know the Al, Ca and Mg contents of the sample before analysis but the method was considered particularly beneficial for the analysis of valuable materials, such as samples returned from space missions, because of the wide range of elements that could be determined on as little as 0.50 mg of material. Alkaline fusion is an alternative approach to sample dissolution for silicate rocks. The sodium peroxide sintering method was adapted[221] successfully for the determination of B mass fractions and δ^{11}B by MC-ICP-MS. The sintering was carried out in glassy carbon crucibles in a muffle furnace at 490 °C for 30 min with a flux-to-sample ratio of 3+1. The elements were isolated by single-column ion-exchange chromatography using Amberlite 473 resin and aliquots were spiked with ^{10}B-enriched NIST SRM 952 for determining B mass fractions by ID. All solutions were analysed in 2% HNO_3. Advantages of this method were that it removed Na and Si from the sample matrix effectively and was capable of generating accurate B mass fraction and isotopic data within a day without the need for expensive laboratory equipment and reagents. A table of measured and published data for a range of geological RMs, seawater and coral demonstrated the accuracy and precision of the procedure.

Sample preparation procedures for the *precious metals and PGEs* continue to attract attention. Conventional procedures involve lead or nickel sulfide fire assays but a novel method for the determination of Au and the PGEs involved**[222]** bismuth fire assay combined with ICP-MS analysis. The bismuth bead produced from the fire assay at 1060 °C was cupellated for 30 min in a magnesia cupel at 850 °C before microwave digestion of the bismuth granule in 40% (*v/v*) *aqua regia*. The method accurately quantified Au, Ir, Pd, Pt and Rh and the volatile element Ru and was applied to a range of geological samples including chromite, black shale and polymetallic ores. The LODs were 0.002 (Rh) to 0.025 (Au) ng g^{-1}. Wu *et al.***[223]** developed a method for the determination of trace amounts of Ag in geological samples using extraction with inverse *aqua regia* and ICP-MS analysis. An online aerosol-dilution strategy involving dilution of a sample aerosol with argon prior to the plasma was adopted to reduce the amount of water and acid entering the plasma and thereby eliminate interferences from polyatomic Nb and Zr species. This helped to maintain the high temperature of the plasma while minimising the formation of oxides and other polyatomic ions. The method had a LOD of 0.2 μg g^{-1} and was applied to 68 geological RMs.

5.3 Instrumental analysis

5.3.1 Laser-induced breakdown spectroscopy

Laser-induced breakdown spectroscopy (LIBS) was described**[198]** as the "future superstar for chemical analysis". However, as indicated in various *reviews*, the technique has several major challenges to overcome before it can live up to this claim. Zhang *et al.*[107] (152 references) summarised progress of LIBS technology and its application to environmental monitoring between 2010 and 2019. The review included a helpful introduction to LIBS, signal enhancement techniques and chemometric methods and a discussion of progress in its application to soil, water and atmospheric monitoring. A review (245 references) aimed at LIBS researchers with a basic knowledge of the technique summarised**[198]** recent hardware improvements and advances in quantification. The impacts of signal uncertainty and matrix effects were explained and different strategies for improving LIBS quantification compared. Generally, there are two types of quantification model: one is based on calibration with RMs and the other type is calibration-free. A detailed overview**[199]** (137 references) of calibration-free LIBS covered the basic theory, together with improvements proposed to overcome non-stoichiometric ablation, self-absorption effects and the complexity of algorithms. Many of the existing problems blighting the practical application of calibration-free LIBS were discussed and future perspectives considered. Liu *et al.***[224]** (102 references) reviewed the application of LIBS to the analysis of coal over the last decade (2011-2020). Suitable LIBS instruments, pretreatment of samples, processing of spectral data and methods for coal analysis were assessed. Matrix effects were considered to be the main obstacle to the application of LIBS to the quantitative analysis of coal.

As highlighted in several of the reviews, problems in the use of LIBS are the extraction of useful information from complex LIBS data and the need to reduce interference effects such as background signals, noise and overlapping peaks. As a consequence, much effort has been devoted to *chemometric methods for handling LIBS data*. These included: a convolutional neural network model for the analysis of phosphate ore slurry**[225]**; a convolutional neural network model with a 2D algorithm for the determination of the lithology and major element compositions in rocks**[226]**; rapid LIBS multielement imaging combined with deep-learning theory for the classification of rocks**[227]**; and machine-learning algorithms to determine structural water in rocks**[228]**.

The ability of LIBS to detect virtually any element in the periodic table on-site with little or no sample preparation is very attractive to the mining industry. The *application of LIBS to ore prospecting and processing* included: evaluation of gold-bearing rocks in Canada**[229]**; determination of the total Fe content in Australian iron ores **[230]**; measurement of the chemical composition of Cu ores**[231]**; study of matrix effects in the analysis of coal**[232]**; identification of the major and accessory minerals in lithium-bearing pegmatites**[233]**; and quantification of six REEs in graphite pellets at the ppm level**[234]**.

Various strategies have been adopted for the *analysis of rock samples by LIBS*. In a novel method for the determination of F in geological samples, pure $SrCO_3$ was placed**[235]** orthogonally to the sample and ablated using an additional laser to provide sufficient Sr atoms for promoting the formation of SrF radicals. The SrF radical spectra have a stronger intensity and suffer from less interference than F atomic emission spectra so the ability of LIBS to detect F in rocks was enhanced. The LOD was 6.36 $\mu g\ g^{-1}$. Of great relevance was a study[236] on how best to quantify measurement limits when analysing geological materials using multivariate analysis modelling techniques. The aim was to provide a template for calculating LOQs based on multivariate LIBS regression models and to understand how this value was affected by factors such as instrumentation, method of outlier removal and different atmospheres (air, vacuum or simulated Martian conditions relevant to the ChemCam instrumentation). By studying the effect of the LOQ on model validation, it was demonstrated that the LOQ was an essential metric for a better understanding of model quality.

The *development of the LIBS technique* has benefitted greatly from its successful deployment in the SuperCam instrument on Mars. Compensation for spectral differences caused by varying distances between sample and sensor usually involve conventional spectral data processing but a new chemometrics model with powerful learning ability has been constructed[237] for this correction. The performance of the convolutional neural network designed in this project surpassed those of four alternative chemometric approaches, making it a promising methodology for geochemical sample identification in future space missions. Associated with the LIBS equipment in the SuperCam instrument suite was a microphone, which was used**[238]** to retrieve the physical properties of ablated targets by listening to the laser-induced acoustic signal. Sound data recorded during the LA of hematite, goethite and diamond showed a sharp increase in the amplitude of the acoustic signal during the first laser shots. Examination of the laser craters using Raman spectroscopy and SEM indicated that hematite and goethite had been transformed into magnetite and that diamond had been transformed into amorphous-like C. It was concluded that these transitions were the root cause of the increase in acoustic signal and that this behaviour occurred only for specific phases. This concept was further explored**[239]** by probing Fe-based and Ca-based minerals at a sampling distance of 2 m to test whether merging the acoustic signals with the LIBS spectra could improve the discrimination of spectrally similar minerals in a remote LIBS configuration. Once validated under Earth conditions, the approach was tested in a Mars-like atmosphere. From these preliminary experiments, it was concluded the implementation of this strategy in an open environment needed to be conducted with care and that instruments with a better S/N could improve the results obtained in a Mars-like atmosphere. A portable standoff LIBS instrument was designed**[240]** and constructed within three weeks to monitor changes in the composition of lava streams from an active volcano in the Canary Islands at a minimum of 20 m from the lava flow. This strategy was adopted after several drones carrying compact

LIBS instruments had crashed during low-level flights because of the hostile environmental conditions. In spite of there being only subtle spectral differences between samples but considerable signal variability induced by the wind, sufficient information could be extracted from the data using PCA for sample classification.

An exciting development in recent years has been the potential afforded by *the integration of LIBS data with data obtained by complementary techniques* such as LA-ICP-MS. This was demonstrated**[241]** in the elemental imaging of a uranium ore sample prepared as a thin section. A preliminary view of the elemental distribution on a large area was obtained by LIBS and then a detailed survey of selected areas was performed using LA-ICP-MS. Specially-developed software allowed the imaging data from the two techniques to be merged so that detailed structures (from ICP-MS) could be superimposed on the overall sample image obtained by LIBS. Using this approach, structures responsible for migration of elements in the uranium ore could be identified. Several combined LA-ICP-MS/LIBS instruments are now commercially available, making it possible to acquire simultaneously both spatially resolved data for elements such as C, F, H, O and N and conventional MS data. This configuration provides a wider elemental coverage and greater dynamic range than either instrument alone and we expect to see more reports of its use in geological applications before too long. A novel procedure**[242]** for the analysis of volcanic brines involved freezing the fluids before analysis by LA-ICP-MS/LIBS. Liquid RMs were prepared by adding elements of interest at known but varying concentrations to a natural brine sample taken from a volcanic crater lake. Differences in ablation yield were accounted for by adding Li as an IS and all samples were run as line scans rather than point analyses to prevent the samples thawing. Data for Al, Ca, Cl, Fe, K, Li, Mg, Na and S in volcanic brine determined by cryo-LIBS and cryo-ICP-QMS in collision cell mode were within 10% of the values obtained by solution ICP-AES. The only exception was the determination of Fe by LIBS for which the difference was 17%. The attraction of the cryo-analytical method was the ease of sample preparation and the potential for determining major and trace elements simultaneously. However, care needs to be taken to ensure homogeneity of the frozen brines.

5.3.2 Dating techniques

Improvements in *sample preparation procedures for dating techniques* included**[243]** a method for separating and concentrating zircons from mafic rocks that combined physical separation with chemical dissolution. This was more efficient than conventional density and magnetic-separation methods, particularly for medium- to fine-grained mafic rocks in which zircons were rare, small in size and commonly associated with ferromagnetic minerals. Overall, there was a 15- to 1000-fold increase in the zircon yield so analytically viable amounts of zircon for U-Pb geochronology could be recovered from relatively small samples (<1 kg). Li *et al.***[244]** developed a new H_2SO_4-Na_2CrO_4 method for digesting black shales for Re-Os dating. The initial Re blank of the Na_2CrO_4 reagent was greatly reduced by purification with acetone and the overall procedural blanks of <1 pg for Os and 1-2 pg for Re were an order of magnitude lower than those in the widely-used H_2SO_4-CrO_3 digestion method.

There has been much research activity focused on the *U-Pb dating of accessory minerals other than zircon* by microanalytical techniques. Minerals investigated included: apatite**[245]** by LA-ICP-MS/MS, carbonates**[246]** by LA-MS-ICP-MS, cassiterite**[247]** by LA-SF-ICP-MS, garnet**[248]** by SIMS, ilmenite**[249]** by LA-ICP-MS, rutile**[250]** by LA-ICP-MS, scheelite**[251]** by LA-SF-ICP-MS, titanite**[250, 252]** by LA-ICP-MS and SIMS, vesuvianite**[253]** by LA-SF-ICP-MS, wolframite**[254]** by LA-ICP-MS and xenotime**[255]** by APT. The continued development of U-Pb dating methods to a wide range of minerals is fundamental in increasing the number of geochronological tools available for unravelling geological processes.

In a review of detrital *zircon U-Pb data,* Powerman *et al.*[256] noted various obstacles in making use of the growing volume of available data and proposed guidelines for publishing detrital zircon geochronology data. They designed a new software tool called Dezirteer, which could rapidly process and analyse large amounts of detrital zircon analyses (10^2-10^5) in batches and prepare tables and images ready for publication. In a new statistical approach for improving the regression of low-count U-Pb geochronology data, Davis *et al.*[257] took LA-ICP-MS line-scan data from samples with low-U mass fractions and regressed them as count rates in a 3D space rather than as ratios on a 2D plot. They demonstrated that the maximum-likelihood estimation for the best-fit mixing surface in a 3D signal-count-space gave accurate results consistent with geological and synthetic data. They observed that this approach did not replace commonly-used programs such as Isoplot but allowed optimal interpretation of LA-ICP-MS data for samples with low U contents. Lin *et al.*[258] assessed factors affecting downhole fractionation in zircon crystals during the rapid LA-MC-ICP-MS acquisition of U-Pb data at high spatial resolution (≤10 µm spot). Two analytical modes using various combinations of FCs and ion counters were employed to cover a wide range of U and Pb mass fractions in the study of three zircon RMs. By correcting for downhole fractionation using Iolite software, U-Pb ages with an accuracy of <1% and a precision of <0.5% could be obtained. A problem encountered in LA-ICP-MS analysis is that the laser focus can vary during routine operation with both manual and automatic focusing systems. Huang *et al.*[250] demonstrated that a 30 µm variation of laser focus led to a systematic shift of 4-6% in ^{206}Pb/^{238}U ratios when ablating zircon RMs. They suggested that poor focusing could explain the relatively poor reproducibility of U-Pb dating by LA-ICP-MS when compared with SIMS analysis.

There has been increasing interest in *in situ Rb-Sr dating* using LA coupled to either MS/MS or MC-ICP-MS instruments. Rösel and Zack**[259]** presented a procedure to measure, calculate and validate Rb-Sr ages from individual laser spots on detrital micas. The Sr isotopic composition was measured in mass-shift mode using N_2O as the reaction gas and Mica-Mg as the primary RM. Data reduction was undertaken using a script written by the authors for Iolite. The procedure was validated using various mica samples of known ages; the Rb-Sr ages determined were not significantly different from the respective reference values. A nanopowder pellet called Mica-Fe was proposed as a secondary RM for Rb-Sr geochronology. In a study of LA-ICP-MS/MS applied to the Rb-Sr dating of celadonite to decipher alteration conditions after accretion of oceanic crust, methyl fluoride was employed**[260]** as the reaction gas and the $^{87}Rb/^{86}Sr$ ratios calibrated using several of the MPI-DING glass RMs. Bevan *et al.***[261]** demonstrated the capabilities of a prototype "tribrid" MS system coupled to a UV LA system for *in situ* Rb-Sr dating. The instrument consisted of a quadrupole mass filter and collision cell coupled to a MC-ICP-MS system to provide enhanced ion transmission and simultaneous collection of all Sr isotopes. These features improved the precision on the $^{87}Sr/^{86}Sr$ ratio by a factor of *ca.* 25 compared to that of a quadrupole ICP-MS/MS instrument operated under the same conditions with SF_6 as the reaction gas. The importance of mass filtering before the collision cell for *in situ* Sr ratio measurements was highlighted; without this feature, the measured $^{87}Sr/^{86}Sr$ ratios were inaccurate. No corrections for atomic or polyatomic isobaric interferences were necessary when only ions of *m/z* 82 - 92 were allowed to enter the collision cell. The greatest benefits of the improved precision occurred for relatively young samples with low $^{87}Rb/^{86}Sr$ (<30) contents and so offered new opportunities in geochronological studies. Subsequently, replacement of the quadrupole mass filter in this prototype instrument with a new precell mass filter resulted**[262]** in an improvement in abundance sensitivity of more than an order-of-magnitude. This new setup was capable of producing a stable and flat transmission window between *m/z* 82 and 94, a vital prerequisite for *in situ* LA-MC-ICP-MS/MS Rb-Sr dating.

In studies of *other geochronometers,* a fully automated system was developed**[263]** for *in situ* measurements of K-Ar ages. The automated prototype consisted of a laser system, an optical spectrometer, a vacuum line, a noble gas mass spectrometer and control software and was designed to date many samples at low cost and with a precision suitable for applications in exploration geology. The K content was quantified by LIBS and Ar in gases produced by the laser was measured by noble gas MS. The system was capable of performing 100 K-Ar analyses within 24 h with uncertainties typically below 5% (1 RSD). Data were reported for different reference minerals including biotite, glauconite, phlogopite, sanidine and tektites. In contrast to K-Ar dating, ^{40}Ar/^{39}Ar dating requires samples to be irradiated in order to produce sufficient ^{39}Ar from ^{39}K for accurate age determination while minimising the production of ^{40}Ar and ^{36}Ar. Zhang *et al.***[264]** discussed recent advances in analytical technology and the optimisation of irradiation parameters for Ar-Ar dating. A new approach**[265]** to U/Th dating using fs LA-SF-ICP-MS enabled small archaeological carbonate specimens (shells) with low U contents (ng g^{-1}) to be dated. After optimising the LA coupling to improve the U and Th transmission in the mass spectrometer, image processing was performed to identify contaminated and leached areas at the mm scale and to determine a correction for any detrital material incorporated within the shell structure. Measured ages were consistent with those determined by luminescence methods and with the ages of speleothems dated by conventional solution U/Th techniques. In order to resolve the problem of isobaric interferences of ^{176}Lu and ^{176}Yb on ^{176}Hf in the Lu-Hf geochronology of garnets, apatites and xenotime, Simpson *et al.*[266] proposed a LA-ICP-MS/MS method with NH_3 as the cell gas. The resulting age uncertainties were as low as *ca.* 0.5% (95% CI). Although not as precise as the Lu-Hf ages obtained following chemical separation, the rapid analysis combined with high spatial resolution afforded by this technique offered the opportunity for cost-effective reconnaissance campaigns in complex terrains that record many phases of metamorphism.

5.3.3 Inductively coupled plasma mass spectrometry

A tutorial review (136 references) on *isotopic measurements* by ICP-MS covered[267] the use of enriched stable isotopes and the measurement of natural variations in elemental isotopic composition. These two fields of study are often treated separately in the literature even though they share many fundamental principles. The review concentrated on the similarities between both fields and provided detailed information on terminology, mass bias, interferences, measurement precision and RMs. Another review article (129 references) focused[268] on challenges and new developments in the measurement of Ca isotope ratios by ICP-MS, SIMS and TIMS. Advancements in purification techniques and the application of collision-cell technology were highlighted together with the need to adopt common RMs to confirm data quality, aid inter-laboratory comparisons, assist method development and improve the usefulness of published Ca isotope datasets.

The considerable research effort focussed on *isotope ratio determinations by MC-ICP-MS* and other techniques is reflected in Table 11. Because the range of elemental isotope ratios now being measured in geological materials is so diverse, this table is provided as a starting point for readers to explore the systems of most relevance to them. In general, it is difficult to discern any major breakthroughs, as many of the studies provided modest improvements to existing separation procedures or analytical protocols.

Insert Table 11

A case study investigated[269] instrumental conditions that govern *oxide formation in MC-ICP-MS* and how different oxide formation rates affect the measurement error of Nd isotope ratios. The several instrumental setups investigated included wet and dry plasmas, different sample introduction methods, the addition of N_2 and various sampler and skimmer cone geometries. The oxide-induced isotopic offsets were mostly associated with the introduction system and cone geometry. A qualitative model was developed to predict the expected isotopic offsets and recommendations were given on how to reduce measurement errors in the determination of Nd isotopic ratios by MC-ICP-MS.

For over 20 years, LA-ICP-MS has been the technique of choice for quantifying the *elemental composition of fluid inclusions*. However, the resultant short transient signals are difficult to sample representatively with single collector ICP-MS instruments. Laurent *et al.*[270] demonstrated that this issue could be overcome by reducing quadrupole settling times significantly through use of a fast-scanning quadrupole mass spectrometer. This allowed faster cycling through a given element list and therefore better resolution of the signals. Short quadrupole settling times of 0.2 ms allowed the analysis of smaller inclusions (down to 4 µm) than usually targeted to be made for more elements (up to 52 in this study) without impeding the basic instrument performance.

Multielement imaging by LA-ICP-MS for geological and other applications continues to be a study area with significant growth. Tanaka *et al.*[271] improved the spatial resolution of fs LA-ICP-MS images by combining a newly designed small-volume ablation cell (internal volume 4 mL) and in-torch mixing of Ar make-up gas to provide a shorter washout time. In addition, they employed a "shaving ablation" protocol in which the distance between line profiles was smaller than the size of the laser pit. Although this research was conducted on biological samples, the authors felt it could be adapted for geochemical applications. A new, open-source, stand-alone software called Ilaps[272] was written in Python and designed for processing LA-ICP-MS data for bulk analysis and imaging. It was planned that future versions of this software would be capable of processing data from other techniques such as LIBS, thereby facilitating the intercomparison of results. In order to obtain a signal of short duration for element imaging using LA-ICP-TOF-MS, Neff *et al.*[273] designed a parallel flow ablation cell to speed up aerosol washout. The two-volume LA cell was based on a tube cell design and included a recess in the cover for an improved gas flow pattern at the ablation site. At a LA sampling frequency of ≥1000 Hz, the system was capable of acquiring a 1 megapixel image in less than 20 min, thereby increasing the sample throughput significantly.

The benefits of the reduction in various polyatomic interferences obtained when using *ICP-MS/MS* in geological applications have been highlighted in several contributions. Klein *et al.*[188] developed an ICP-MS/MS method for the determination of technologically critical elements such as Ga, Ge, In, Nb, Sc, Ta, Te and REEs in sediment digests using N_2O rather than O_2 as the reaction gas to eliminate spectral interferences selectively. The LODs were between 0.00023 $\mu g\ L^{-1}$ (Eu) and 0.13 $\mu g\ L^{-1}$ (Te) and, except for Te, the results for RMs were within ±20% of certificate values. In contrast, O_2 was employed[274] as the reaction gas in an ICP-MS/MS procedure to determine REEs in uranium ore samples. Specific chemical separation procedures were established to remove the uranium matrix before measurement and all the REEs were measured as REE oxides in a mass-shift approach. The method was validated using GSJ RMs JA-2 (andesite), JB-2 (basalt), JR-2 (rhyolite) and USGS RM BCR-2 (Columbia River basalt). The significant suppression of polyatomic interferences resulted in LODs of <1 pg mL^{-1} for all REEs. Lindahl *et al.*[**275**] observed large irregular biases during repeated measurements of U isotopic ratios using two identical ICP-MS/MS instruments. The source of these variations was drift in the mass calibration of the two mass filters which was more pronounced for heavier isotopes. Considerable improvement in the precision and accuracy of U isotope ratios was achieved by optimising the hardware settings for the mass filter peak resolution. This resulted in a precision of 0.07% RSD for long-term measurements of $^{235}U/^{238}U$. An investigation by Bolea-Fernandez *et al.*[**276**] on whether the ISs used in mass-shift approaches should also be subjected to a mass-shift or could simply be monitored on-mass revealed differences in the behaviour of atomic ions compared to reaction product ions. However, it was found that these differences could always be attributed to insufficient time for stabilisation within the reaction cell.

Examples of *laser ablation split stream analysis* applied to geological materials included[**277**] the simultaneous determination of S isotope ratios and the trace element composition of several sulfides and sulfates. Although the smaller sample volume introduced into the quadrupole ICP-MS detector in the LASS setup resulted in lower sensitivity and poorer LODs for trace element determinations than for when LA-ICP-MS was used alone, the measurement precision and accuracy for the S isotope ratios by MC-ICP-MS were not compromised. Obtaining data for both S isotope ratios and element concentrations provided the ability to identify relationships between individual pyrite minerals and their formation histories. Simultaneous determination of Sm-Nd isotope ratios and trace element compositions together with U-Pb ages of titanite were achieved**[278]** by splitting the aerosol from a LA system into two gas streams. One line was connected to a MC-ICP-MS instrument for Sm-Nd isotope analysis while the other was used for trace element analysis and U-Pb dating by SF-ICP-MS. Addition of water vapour to the gas stream after the LA cell improved the MC-ICP-MS sensitivity for Nd by 40% and thereby improved the precision of the Sm-Nd isotopic data. The simultaneous acquisition of these geochemical parameters yielded detailed age information based on complicated mineral growth zoning.

5.3.4 Secondary ion mass spectrometry

As in previous years, several contributions focused on *high-precision isotope ratio measurements on various minerals*. These included: improved precision for δ^{37}Cl measurements on apatite**[279]** using a FC fitted with a 10^{12} Ω amplifier to collect ^{37}Cl; δ^{94}Zr measurements on zircon**[280]** with an external precision (2SD) of 0.04-0.7‰; improved precision for U-Pb dating of zircons[281] in U-series disequilibrium; Li isotope ratios in garnet**[282]** using specially-developed glass RMs prepared from either natural garnets or oxide and silicate powders; and Pb-Pb and U-Pb dating of Zr-rich minerals**[283]** at sub-µm spatial resolution.

A set of 27 synthetic glasses covering a broad compositional range with respect to six major oxides (Al, Ca, Fe, Mg, Si and Ti) was developed**[284]** to study *instrumental mass fractionation* (IMF) in O isotope measurements. Data from a single continuous SIMS session confirmed that the chemical composition strongly influenced O isotope matrix effects in silicate glasses and that the cation-oxygen bond strength had a strong influence on the IMF value. An empirical model based on the correlation of six major element oxides with the IMF was proposed as the most reliable of the models examined when correcting for such matrix effects in silicate glasses. Another study reported**[285]** that IMF caused $\delta^{18}O$ values in aragonite to increase linearly with increasing Ca content by about 3.4‰. The use of multiple aragonite RMs with compositions that bracket that of the unknown sample was recommended for accurate correction of the O isotopic measurements. A natural aragonite crystal (VS001/1-A) was evaluated as a potential new SIMS RM. Taracsak *et al.*[286] characterised matrix effects found in the S isotope analysis of silcate glasses by SIMS. They made more than 600 S isotope measurements on nine different glasses which contained 500-3400 µg g^{-1} S with a wide compositional range, including mafic glasses, rhyolite and phonolite. The finding of significant composition-dependent IMF effects in measured S isotope ratios was in stark contrast to previous studies that had assumed or shown these effects to be negligible for S isotope ratio measurements by SIMS. Calibration with multiple well-characterised RMs with a wide compositional range was recommended.

5.3.5 Other techniques

A cutting-edge review by Otter *et al.*[287] (89 references) provided a thorough overview of nanoscale chemical imaging by *Photo-induced Force Microscopy (PiFM)*. This non-destructive technique combines the advantages of atomic force microscopy with IR spectroscopy providing simultaneous acquisition of 3D topographic data with molecular chemical information at high spatial (*ca.* 5 nm) and spectral (*ca.* 1 cm^{-1}) resolution. The aim of the review was to introduce this new analytical development to a broader geochemical audience by covering the fundamentals of the technique and presenting its first application to geochemical samples (zoned zircons, high-pressure experimental phases and mother-of-pearl). It was demonstrated that PiFM imaging enabled nanoscale phase identification and complemented nanoscale imaging and elemental characterisation using other geochemical methods such as NanoSIMS, SEM/TEM and APT.

The effectiveness of *atom probe tomography* (APT) was tested**[288]** for nanoscale characterisation of hydrous phyllosilicate minerals, which are likely to be major constituents of material bought back to Earth by extra-terrestrial missions. Application of this technique to a terrestrial analogue (lizardite) showed that the technique had better resolution than more established imaging techniques so it was possible it to detect previously unobservable nanominerals and nanostructures within phyllosilicates. It was concluded that APT could be a key tool in the analysis of planetary samples. For example, new SiO-rich nanophases were revealed that provided new insights into the nature of the fluid and reaction pathways. The study also demonstrated that APT could be applied more broadly to other hydrous mineralogies. Cappelli *et al.***[289]** investigated the problems of atom loss and inaccurate estimates of stoichiometric composition when applying laser-assisted APT to garnet and spinel. By studying oxygen quantification and issues related to uneven ion desorption and variation in charge state ratios, a better understanding was obtained of how measured and true mineral stoichiometries diverged due to the influence of mineral properties and crystal structure on the atom probe field evaporation process.

A new method for the determination of $\delta^{13}C$ and $\delta^{18}O$ in carbonates featured**[290]** a *fibre-coupled laser-diode device* emitting 30 W at 880 nm. The carbonate was decomposed to CO_2 which was collected under a controlled atmosphere for offline analysis. A comparison of isotopic data for carbonate zones analysed both by classical methods (micro-drilling followed by acid digestion) and the new laser calcination method gave correlation coefficients of 0.99 for $\delta^{13}C$ and 0.96 for $\delta^{18}O$ for a range of different mineralogies and isotopic compositions. As well as decreasing the overall analytical time considerably by reducing the number of preparation steps, the new procedure offered the possibility of performing spatially resolved analysis at the mm scale. Fibre-coupled diode lasers are very compact compared to other laser systems so an exciting prospect was that they could be paired with field-deployable CRDS/IRIS optical-mass spectrometers for on-site measurements.

The *technique of XRFS* has been applied to the analysis of geological materials for many decades, particularly for the determination of major and minor elements. Modern XRFS instruments are capable of measuring the halogen elements, so a review**291** (154 references) on the application of XRFS to the determination of Br, Cl, F and I in geological materials was timely. Core scanning systems with a variety of sensors have the potential for automating many aspects of core logging and thereby provide detailed and continuous core data and imaging at an early stage in the processing of data from geological cores. This process was assisted**292** by the availability of new software, called Corascope, which merged the outputs from optical line-scan imaging and X-ray radiography with downhole elemental composition to reconstruct the complete sedimentary record from cores scanned in short sections.

The *μXRFS technique* is rapidly becoming a familiar tool for characterising geological matrices. Sample sizes ranging from thin sections to hand specimens can be analysed and information collected over the whole sample surface to provide chemical, textural and mineralogical information. An application to the quantitative mapping of minerals in a drill core from a gold deposit demonstrated**293** that μXRFS maps could provide information on mineralogy, mineral abundances and mineralogical textures not visible with the naked eye. Fast mineralogical and elemental mapping of ore samples from a PGE deposit by LIBS were validated**294** by μXRFS. Presentations at recent conferences (*e.g*. Geoanalysis 2022) have confirmed that there is a desire to capture both mineralogical and chemical compositions of geological materials through the integrated use of a variety of modern geoanalytical tools such as core scanners, μXRFS and LIBS. Maybe the day when mineralogists and analytical geochemists work together in the same laboratory and speak the same technical language is not far away?

6 Glossary of abbreviations

1D	one dimensional
2D	two dimensional
3D	three dimensional
AAS	atomic absorption spectrometry
AAE	absorption Ångström exponent
AB	arsenobetaine
AEC	anion exchange chromatography
AES	atomic emission spectrometry
AFS	atomic fluorescence spectrometry
AMS	accelerator mass spectrometry
ANN	artificial neural network
APDC	ammonium pyrrolidine dithiocarbamate
APGD	atmospheric pressure glow discharge
APM	atmospheric particulate matter
APS	aerodynamic particle sizer
APT	atom probe tomography
ASU	Atomic Spectrometry Update
ASV	anodic stripping voltammetry
BCR	Community Bureau of Reference (of the Commission of the European Communities)
BGS	British Geological Survey
C_{18}	octadecyl bonded silica

CC	collision cell
CE	capillary electrophoresis
CEC	cation exchange chromatography
CEN	European Committee for Standardisation
CF	continuous flow
CI	confidence interval
COLM	continuous online leaching method
CPC	condensation particle counter
CPE	cloud point extraction
CRDS	cavity ring-down spectroscopy
CRM	certified reference material
CS	continuum source
CV	cold vapour
CVG	chemical vapour generation
Cys	cysteine
DBD	dielectric barrier discharge
DCM	dichloromethane
DES	deep eutectic solvent
DGA	diglycolamide
DGT	diffusive gradient in thin films
DLLME	dispersive liquid liquid microextraction
DMA	dimethylarsonic acid
DoE	design of experiments
DOM	dissolved organic matter
DP	double pulse
DPM	diesel particulate matter
EC	elemental carbon
EDS	energy dispersive (X-ray) spectrometry

EDXRFS	energy dispersive X-ray fluorescence spectrometry
ELPI	electrical low-pressure impactor
EPMA	electron probe microanalysis
ERM	European reference material
ETAAS	electrothermal atomic absorption spectrometry
EtHg	ethylmercury
ETV	electrothermal vapourisation
FAAS	flame atomic absorption spectrometry
FC	Faraday cup
FFF	field flow fractionation
FI	flow injection
FT	Fourier transform
FTIR	Fourier transform infrared
GC	gas chromatography
GD	glow discharge
Gd-DOTA	gadoterate
GEM	gaseous elemental mercury
GO	graphene oxide
GSJ	Geological Society of Japan
HCL	hollow cathode lamp
HERFD	high energy resolution fluorescence detected
HFSE	high field strength element
HG	Hydride generation
HPLC	high performance liquid chromatography
HR	high resolution
IAEA	International Atomic Energy Authority
IAPSO	International Association for the Physical Sciences of the Oceans
IC	ion chromatography
ICP	inductively coupled plasma
ICR	ion cyclotron resonance

ID	isotope dilution
IDA	isotope dilution analysis
IGGE	Institute of Geophysical and Geochemical Prospecting, People's Republic of China
IHSS	International Humic Substances Society
IL	ionic liquid
IMF	instrumental mass fractionation
INCT	Institute of Nuclear Chemistry and Technology (Poland)
IP	ionisation potential
IPGP	Institut de Physique du Globe de Paris
IR	infra red
IRIS	interface region imaging spectrograph
IRMM	Institute for Reference Materials and Measurements
IS	internal standard
JMC	Johnson Matthey Company
JRC	Joint Research Centre (European Commission, Belgium)
LA	laser ablation
LASS	laser ablation split stream
LC	liquid chromatography
LDSA	lung deposited surface area
LGC	Laboratory of the Government Chemist (U.K.)
LIBS	laser-induced breakdown spectroscopy
LLE	liquid liquid extraction
LLME	liquid liquid microextraction
LOD	limit of detection
LOQ	limit of quantification
LPE	liquid phase extraction
LPME	liquid phase microextraction
MAC	mass absorption cross section
MAD	microwave-assisted digestion

MAE	microwave-assisted extraction
MC	multicollector
MDA	mineral dust aerosol
MeHg	methyl mercury
MIP	microwave induced plasma
MOF	metal organic framework
MPI	Max Planck Institute
MRI	magnetic resonance imaging
MS	mass spectrometry
MS/MS	tandem mass spectrometry
μXRFS	micro X-ray fluorescence spectrometry
NACIS	National Analysis Centre of Iron and Steel, China
NADES	natural deep eutectic solvent
NBS	National Bureau of Standards
NCRM	National Research Centre for Certified Reference Materials, China
NIOSH	National Institute of Occupational Safety and Health
NIST	National Institute of Standards and Technology
NP	nanoparticle
NRCC	National Research Council of Canada
NRCG	National Research Centre of Geoanalysis, Beijing
NTIMS	negative thermal ionisation mass spectrometry
NWRI	National Water Research Institute
OC	organic carbon
OM	organic matter
OPC	optical particle counter
PCA	principal component analysis
PCR	principal component regression
PFA	perfluoroalkyl

PGE	platinum group element
phHg	phenyl mercury
PiFM	photo-induced force microscopy
PM	particulate matter
PM_1	particulate matter (with an aerodynamic diameter of up to 1.0 µm)
$PM_{2.5}$	particulate matter (with an aerodynamic diameter of up to 2.5 µm)
PM_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)
PP	polypropylene
ppm	part per million
PTE	potentially toxic element
PTFE	polytetrafluoroethylene
PVG	photochemical vapour generation
pXRF	portable X-ray fluorescence
QC	quality control
QMS	quadrupole mass spectrometry
RCS	respirable crystalline silica
RDD	rotating disc dilutor
REE	rare earth element
rf	radio frequency
RM	reference material
RP	reversed phase
rpm	revolutions per minute
RSD	relative standard deviation
SAX	strong anion exchange
SD	standard deviation
SE	standard error
SEM	scanning electron microscopy

SF	sector field
SIBS	spark-induced breakdown spectroscopy
SIMS	secondary ion mass spectrometry
SMPS	scanning mobility particle sizer
S/N	signal-to-noise ratio
sp	single particle
SPE	solid phase extraction
SPME	solid-phase microextraction
SR	synchrotron radiation
SRM	standard reference material
SSA	single scattering albedo
SSB	sample standard bracketing
TC	total carbon
TEL	tetraethyl lead
TEM	transmission electron microscopy
THF	tetrahydrofuran
TIMS	thermal ionisation mass spectrometry
TMAH	tetramethylammonium hydroxide
TML	tetramethyl lead
TOA	thermal optical analysis
TOC	total organic carbon
TODGA	N,N,N′,N′-tetraoctyl diglycolamide
TOF	time-of-flight
TSP	total suspended particle
TXRF	total reflection X-ray fluorescence
TXRFS	total reflection X-ray fluorescence spectrometry
UA	ultrasound-assisted
UAE	ultrasound-assisted extraction
US EPA	United States Environmental Protection Agency

USGS	United States Geological Survey
UTEVA	uranium and tetravalent actinides
UV	ultraviolet
UV-VIS	ultraviolet-visible
VA	vortex-assisted
VCDT	Vienna-Cañon Diablo Troilite
VG	vapour generation
VOC	volatile organic carbon
VPDB	Vienna Peedee Belemnite
VSMOW	Vienna Standard Mean Ocean Water
WDXRFS	wavelength-dispersive X-ray fluorescence spectrometry
WHO	World Health Organisation
XANES	X-ray absorption near edge structure
XRD	X-ray diffraction
XRF	X-ray fluorescence
XRFS	X-ray fluorescence spectrometry

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Table 1. Developments in LIBS and SIBS for APM measurements

Analyte	Matrix	Study Aim	Technique	Findings	Reference
Ag-coated glass particles Ti particles	Test spherical particles	Development of a direct reading particle sizer and elemental analyser for large inhalable particles	LIBS	Prototype instrument was able to provide accurate sp measurements of aerodynamic diameter over 25-125 μm range using a TOF calculation in a laboratory setting using spherical particles. Successful integration of LIBS without compromising TOF measurements. Future work to include determining LIBS detection efficiencies and testing in the field with non-spherical and polydisperse aerosols	295
Fe, Ni, Ti	Air filter samples of exhaust gas from a boiler operation	Investigation into the use of a double-pulse LIBS procedure to enhance emission intensity	LIBS	Combination of 355 and 1064 nm laser wavelengths provided the best enhancement effect. The intensity of emission lines by a double-pulse laser was *ca*. 10x that of a single -pulse laser.	296
Various	Air Filter Samples from Antarctica	Rapid elemental APM characterisation on filters in remote locations	LIBS	New approach enabled the elemental composition of APM sampled onto filters to be determined rapidly. Undertaken with minimal sample preparation and preparation in field conditions at remote locations without recourse to use of complex equipment.	297
Various	Test aerosols	Evaluation of the	SIBS	Machine-learning models seemed to have	298

	generated using nebulised elemental standards	performance of a prototype SIBS instrument		better predicative accuracy and lower LODs than conventional univariate calibrations. The least absolute shrinkage and selector operator model performed best with $R^2 > 0.8$ achieved and LODs of 0.04-0.17 µg m^{-3} determined at a flow rate of 15 L min^{-1} with a sampling duration of 30 min.	
Various	Test aerosols generated using nebulised elemental standards	Evaluation of the performance of a prototype SIBS instrument	SIBS	LODs between 0.05 and 0.81 µg m^{-3} determined for elements such as Co, Cr, Cu, Fe, Ni and Zn at a flow rate of 15 L min^{-1} with a sampling duration of 30 min. Spectral overlaps, matrix effects and instrumental sensitivity issues currently hinder measurement of other elements of interest such as As, Cd, Hg, Pb, Sb and Se.	299

Table 2. Application of ICP-MS for APM measurements

Analyte	Matrix	Sample preparation	Technique	Findings	Reference
Fe, Ni	Air filter Samples	Microwave-assisted digestion as per EN 14902	ICP-MS/MS	H_2 collision gas (Fe) and H_2 + $NH_{3\ gas}$ (Ni) mediated mass-shift cell-chemistry optimised for improved Fe and Ni measurements in supporting future air quality and potential source apportionment measurements.	300
Fe, Ti	NPs emitted from coal-fired power stations	Extracted from particle emission control devices *e.g.,* bag filtration	sp-ICP-MS	Mass of NPs that escape chimney stacks determined to be low. Fe and Ti were the most abundant elements in those NPs released at a rate of up to 1.9 x 10^{18} and 1.6 x 10^{18} particles h^{-1}. Other metals release in NPs included Pb and Zn.	301
Sr	Atmospheric particles (PM_{10})	Acid digested	ICP-MS/MS	CH_3F-mediated mass-shift cell-chemistry optimised for improved Sr^{87}/Sr^{86} measurements. No need for prior Rb/Sr separation.	187
Various	Gunshot residue particles	Inside of shooters' gloves rinsed with a detergent/water	sp-ICP-TOF-MS	Rinsing method useful to extract small particles where extraction via tape-lift or adhesive stubs was inadequate. Elemental profiling of < 100 nm particles possible. Complemented existing SEM-EDS methods.	302
Various	Nanoscale mineral dust	Melting snow	sp-ICP-TOF-MS	Median MDA composition largely equated to	303

	aerosol (MDA) in snow			known crustal elemental abundance ratios. Particle size and composition of MDAs were effectively measured in wet deposition samples but there was a greater uncertainty in measuring the particle number.	

Table 3. Application of X-ray techniques for APM measurements

Analyte	Matrix	Study Aim	Technique	Findings	Reference
As	Ambient air particles (TSP and $PM_{2.5}$ fractions)	As speciation study	SR-XRFS SR-XANES	The As^{III}:As^{V} ratio determined in TSP was = 82:18 Total As determined in TSP was 2.7 ± 0.7 ng m^{-3} Total As determined in $PM_{2.5}$ was 1.6 ± 0.6 ng m^{-3}	304
As, Cr, Se	Coal fly ash	Solubility/toxicity study	SR-XANES LC-ICP-MS	Soluble hence mobile fractions that contained As^{V}, Cr^{VI} and Se^{IV} species determined and various treatment to render them immobile recommended.	305
Cr, Zn	Fine ($PM_{2.5}$) and coarse ($PM_{10-2.5}$) aerosol fractions	Cr and Zn speciation study	EDXRF SR-XANES	Cr_2O_3 and $Cr_2(SO_4)_3$ dominant species found in both fractions. Zn_2SiO_4 and $ZnSO_4$ found in both fractions. $ZnCl_2$ found only in coarse fraction. ZnC_2O_4 found only in fine fraction. Origin of Cr and Zn species suspected to be from local anthropogenic sources such as combustion sources and/or resuspended road dust.	306
Fe	Antarctic aerosol samples	Fe speciation and oxidation study to understand better factors affecting Fe solubility and bioavailability in the	SR-XRFS SR-XANES	Fe mineral-phase contained mostly hematite and biotite. Fe^{II} content in particles ranged between 60% (summer) and 71% (winter).	307

		surface ocean			
Fe	Urban aerosols	Fe speciation study	SR- HERFD-XANES	Better resolution with HERFD-XANES over conventional XANES for improved Fe species identification.	308
Mg	Aeolian dust originating from semi-arid regions of Asian continent transported by westerly winds to Japan (KOSA dust)	Mg speciation study	SR-XANES	Mg mostly found in phyllosilicates rather than carbonate minerals suggesting that the contribution of Mg to neutralisation reactions in the atmosphere may be lower than previously expected.	309
Ni	PM_{10} aerosol fraction	Identification and sources of Ni-containing emissions in an industrialised location	Near real-time *in situ* XRFS	Hourly air samples analysed with concentrations up to 2480 ng m^{-3} determined. Dominant emissions sources identified were a Ni refinery (90%) and a steel-mill (10%).	310
Ti	Size fractionated aerosol particles	Ti speciation study	SR - XANES	Several different Ti species determined in particles including anatase, ilmenite, rutile and titanite suggesting that the photochemical reactivity of Ti in aerosols, as determined in laboratory simulation studies, may be over-estimated because only TiO_2 is employed as a model species.	311
Various	$PM_{2.5}$ and PM_{10} aerosol fractions in an urban environment	Identification and sources apportionment of the elemental fraction of APM	Near real-time *in situ* XRFS	Thirteen sources of elements identified including:biomass burning (7.2%); construction (4.3%); dust (22.1%); heavy-vehicles (17%); industry (3.3%); light-	312

				vehicles (5.4%); railways (6.6%); wind-blown dusts (9.5%) sea-salt (5.4%) and sulfates (15.4%).	
Various	$PM_{2.5}$ and PM_{10} aerosol fractions in an urban environment	Intercomparison of online (XRFS) and offline filter measurements (ICP-MS)	Near real-time *in situ* XRFS ICP-MS	Highly correlated (R^2 >0.8) for major elements such as Al, Ba, Ca, Fe, K, Mn, Pb, Ti and Zn. However, differences of 10-40% noted for some elements. Suggested variables here could include: distance between respective $PM_{2.5}$ sampling inlets; spectral overlaps in XRFS measurements; filter digestion efficiencies and sample-to-sample variation in element contents in blank filters.	313

Table 4. Preconcentration methods using solid-phase extraction for the analysis of water

Analytes	Matrix	Substrate	Coating or modifier	Detector	Method LOD in µg L^{-1} (unless stated otherwise)	Validation	Reference
Ag, Cd, Pd, Re, Zn	Fresh water and seawater	AmberChrom® 1-X8 resin		ICP-MS/MS	0.11 (Re) to 19 (Zn) ng L^{-1}	NRCC CRMs SLRS-6 (River water), CASS-6 (near shore seawater) and NASS 7 (seawater)	314
Am, Pu, Sr, U	Lake water, seawater, urine	DGA branched resin and Sr resin both 50-100 µm	N, N, N′ , N′ -Tetra-2-ethylhexyldiglycolamide (DGA resin) and (4,4′ (5′)-di-t-butylcyclohexano 18-crown-6 in 1-octanol (Sr resin)	ICP-MS/MS	0.56 (^{239}Pu) to 1.75 (^{90}Sr) pg L^{-1}	Spike recover and IAEA proficiency scheme water samples	315
As^{V}	Water	SAX disk filter	Quaternary ammonium groups	LA-ICP-MS	0.028	Spike recovery	316
As^{III}, As^{V}, DMA, AB	Water, seawater, and urine	Graphene oxide	Fe_2O_3 and [1,5-bis(2-pyridyl)3-sulfophenylmethylene] thiocarbonohydrazide (from a previous paper)	HPLC-ICP-MS	0.2 (As^{V}) to 3.8 (AB) ng L^{-1}	NRCC CRMs TMDA 64.3 (Fortified Lake Water) and CASS 6 (near shore seawater)	317
As	Water and seawater	Gold NPs (at 350 °C)		HG-AAS	6.5 pg mL^{-1}	NRCC CRMs AQUA-1 (Drinking water), NASS-5	318

						(Seawater) and IRMM CRM ERM-CA713 (Waster water)	
As, Bi, Sb	Fresh, sear, waste and ground waters	Cellulose fibres	Trapping of hydrides on Ag NPs	ICP-MS	1 (Bi) to 15 (As) ng L^{-1}	Spike recovery	319
Bi, Cr, Pb, Zn	Water	Fe_3O_4 NPs coated with SiO_2	A Zr^{IV} metal organic framework with tetrakis(4-carboxyphenyl)-porphyrin (MPCN-224)	ICP-MS	0.9 (Bi) to 11.4 (Zn) ng L^{-1}	Chinese Ministry of Environmental Protection CRMs GSB 07-3186-2014 (200934) (water quality standard) and BY400143 (B2003113) (Environmental Water)	320
Cd	Tap, mineral and lake waters, and physiological solution		A Zr^{IV} metal organic framework with terephthalic acid (UiO-66)	FAAS with Ni furnace in the flame	0.03	Spike recovery	321
Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb	Wastewater	Silica gel	V_2O_5	FAAS	8.4 (Cd) to 50.6 (Cu)	Spike recovery	322
Cd, Co, Ni	Waste, sea, tap and reservoir waters		A thiol-functionalised covalent organic framework of 1,3,5-triformylphloroglucinol (Tp) and 2,5-divinyl-p-phenylenediamine	ICP-MS	0.1 (Cd) to 1.46 (Co)	Beijing Weiye Research Institute of Metrology	323

						and Technology CRM GBW08608 (metal elements in water) and spike recovery	
Cd, Cu, Ni	Eye drops, serum and tap, mineral and spring waters	Silica gel	N-N'-Bis(5-methoxsalicylidene)-2-hydroxy-1,3-propanediamine	ICP-AES	28 (Cd) to 62 (Cu) ng L^{-1}	Spike recovery and a multi-elemental ICP grade standard as an unknown	324
Cd, Cu, Pb	Sea and stream waters, pepper, black cabbage, eggplant, tomato	Melon peel biochar	$CoFe_2O_4$	FAAS	0.41 (Cu) to 3.16 (Pb)	Spike recovery	325
Cd, Pb, Te, and Sb	Drinking water	(3-Aminopropyl)triethoxysilane (multi ion imprinted polymer)	APDC	ICP-AES	0.037 (Sb) to 0.93 (Te)	Spike recovery and comparison with ICP-MS reference method results	326
Cr^{III}, Cr^{VI}	Spring water and sewage wastewater	Chelate resin (Lewatit TP207) and anion exchange resin (Lewatit MP68)		LIBS	88 (Cr^{III}) to 270 (Cr^{VI})	Spike recovery and comparison with ICP-AES results	327
Cr^{III}	Tap water	Styrene and 4-vinylpyridine	1,10-Phenanthroline	ETAAS	0.35 ng	Spike recovery	328

	and green tea	ion imprinted polymers			ml^{-1}	and NIST SRM 1643e (Trace elements in water)	
C,r Cu, Ni, Pb	Aqueous solutions, bottled water	Glass	GO	LIBS	14 (Pb) to 15 (other analytes)	Spike recovery	329
^{135}Cs, ^{137}Cs	Seawater	Ammonium molybdophosphate adsorption		ICP-MS/MS	15 fg L^{-1}	IAEA CRM IAEA-443 (Irish seawater) and comparison with TIMS analysis	330
Cu	Water	Activated carbon	Ion-imprinted polymer with N-methoxymethyl melamine and ethylendinitrilo tetraacetic acid, disodium salt	FAAS	0.038	NIST SRM 1643e(Trace elements in water) and ERML-CA021e (soft drinking water)	331
Hg	Water	Carbon fibre	(3-Mercaptopropyl)trimethoxysilane	ICP-MS	2 ng L^{-1}	Spike recovery	332
Hg, MeHg, EtHg, PhHg	Lake water and fish	Fe_3O_4 NPs	Polymer of 2,4,6-triformylphloroglucinol and methacrylic anhydride modified with 1,2-ethanedithiol	HPLC-ICP-MS	0.43 (Hg) to 1.1 (PhHg) ng L^{-1}	Spike recovery and NRCC CRM DORM-2 (dog fish)	333
Hg, MeHg	Lake and ground waters	Ultrasint® PA11 or PA12 3D printer powder	3-Mercaptopropyl-functionalized silica gel	ICP-MS	0.02 (MeHg) and 0.08 (Hg) ng L^{-1}	IRMM CRM ERM CA615 (ground water)	334
In	Drinking water	Silica gel	Covalently immobilised azolium groups	ETAAS	5.5 ng L^{-1}	Spike recovery	335

Mn^{II} , Mn^{VI}	tap water, ice tea, an energy drink, mineral water, Sprite	$ZnFe_2O_4$ nanotubes (selective adsorption Mn^{VII})	1-Phenyl-3-methyl-4-benzoyl-5-pyrazone and 1-undecanol (SFOD selective extraction of Mn^{II})	ETAAS	0.005 (Mn^{II}) and 0.007 (Mn^{VII})	Chinese RM GSBZ 50019-90 (Fe and Mn water quality standard) and spike recovery	336
εNd ($^{143}Nd/^{144}Nd$)	Seawater	Fe hydroxide coprecipitation	DGA Resin®	MC-ICP-MS	No LOD reported. The blank was 2pg from 3L of sample	Comparison with TIMS results	337
Pb	River water	Calcium alginate beads		FAAS	2	Spike recovery and comparison with ICP-MS results	338
Pd	Estuarine water	Presep® PolyChelate chelating resin		ICP-MS	0.010 ng kg^{-1}	Spike recovery	339
Pd	Seawater	Biorad AG® 1-X8 anion exchange resin		ICP-MS	0.060 pmol L^{-1}	Spike recovery	340
^{226}Ra (system also evaluated for Cd, Co, Cu, Pb, U and Zn)	Fresh, sea and fracking waters	Biorad AG® 50 W-X8 cation exchange resin, Nobias Chelate-PA1 and Eichrom Sr spec resin in series on a lab on a valve.		ICP-MS/MS	4.3 ± 0.1 mBq L^{-1} (1.75 fg L^{-1})	Spike recovery and NRCC CRM CASS 6 (near shore seawater)	341
REEs	Water and atmospheric particulate extracts and digests	SiO_2 coated Fe_3O_4 NPs	Phytic acid	ICP-MS	0.002 (Lu) to 1.1 (Nd) ng L^{-1}	Spike recovery	342
Tl^{I} and Tl^{III}	tap, spring,	Graphene-Fe_3O_4 composite	Aliquat 336	ETAAS	0.01	NIST SRM	343

	river, sea and bottled waters					1640a (Trace Elements in Natural Water), Environment Canada CRMs TMRain-04 (Simulated rainwater), TM-23.4 (fortified lake water), TM-25.4 (low level fortified lake water) and SPS RM SW2 (surface water)	

Table 5. 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
Ag^{I}	Water and soil	CPE	Citric acid and Triton™ X-100	FAAS	0.04	Spike recovery and comparison with spectrophotometry data	344
Ag_2S NPs	Water	CPE	Bis(p-sulfonatophenyl) phenylphosphane dehydrate dipotassium salt, $Na_2S_2O_3$, Triton™ X-114 and glycerol	sp-ICP-MS	Size LOD 22 nm, particle number LOD $5x10^4$ particles L^{-1}	Spike recovery	345
Al	Tap and river waters, rock, soil	CPE	3,4,5-Trihydroxybenzoic acid, Triton™ X-114 and back extraction into HNO_3	ICP-AES	0.31	Spike recovery and NIST SRM 1643f (trace elements in water)	346
Be	Seawater, air filters	DLLME	Dioctylsulfosuccinate, acetylacetone and chloroform	ETAAS	10 fg mL^{-1}	Spike recovery and NIST SRMs 1640 and 1640a (trace elements in natural water)	347
Cd	Drinking, tap and ground waters	CPE	Pyridyl-azo-naphthol and Triton™ X-114	HR-CS-ETAAS	1.3	Spike recovery	348
Cd, Fe, Pb	Drinking water	CPE	2,6-Diamino-4-phenyl-1,3,5-triazine and 3-amino-7-dimethylamino-2-methylphenazine, and	FAAS	5 (Pb) to 25 (Fe)	Spike recovery	349

			Triton™ X-114				
Co, Cu, Ni	Water, blood, urine	CPE	(E)-2-(2,4-Dihydroxybenzylidene)-N-phenylhydrazine-1-carbothioamide (DHBPHC) and Triton™ X-114	FAAS	0.34 (Co) to 0.94 (Ni)	Spike recovery	350
Cr^{VI}	Natural and waste waters	Deep eutectic solvent microextraction	Hexanoic acid and Tetrabutylammonium bromide	ETAAS	5 ng L^{-1}	Spike recovery	351
Fe^{III}	Water, food	DLLME	4,5-Dihydroxy-1,3-benzendisulfonic acid, 1-hexadecyl-3-methylimidazolium bromide, back extract in decanoic acid in tetrahydrofuran	FAAS	1.0	Spike recovery	352
Pd	Water	CPE	2-(5-Bromo-4-methyl-2-pyridylazo)-5-dimethylaminoaniline and Triton™ X-114	ETAAS	0.05	Spike recovery	353
REEs	Ground water, mining water run off	DLLME	2-(5-Bromo-2-pyridylazo)-5(diethylamino)-phenol, ethanol and a 1:1 mix of carbon tetrachloride and trichlorethylene	EDXRFS	1.1 (U) to 10.5 (Eu)	Spike recovery	354
Se^{IV}	Tap, river and well waters, food	LLME	(3,4-Dihydroxyphenyl)-3,5,7-trihydroxychromen-4-one (quercetin), menthol and lauric acid	HG-AAS	0.25 ng L^{-1}	Spike recovery (water samples) and NIST SRMs 1567a (wheat flour) and 1548a	355

						(typical diet)	
Zn	Tap water	DLLME	Dithiazone, choline chloride and dodecanol	FAAS	0.09	Spike recovery	356

Table 6. Methods for photochemical vapour generation in the analysis of water

Analyte	Matrix	Vapour generation reagents	Detector	LOD	validation	Reference
As	Lake and river waters, sediments	Acetic acid, formic acid and Fe_3O_4 NPs, 60 s irradiation time	ICP-MS	0.01 µg L^{-1},	spike recovery (water) and against Chinese CRMs GBW07303 and GBW07305 (both stream sediment)	357
Bi	Drinking and tap waters	Fe_3O_4 NPs as a SPE adsorbent and photocatalyst, acetic acid and formic acid. Online photochemical reactor.	AFS	0.07 µg L^{-1}	spike recovery	358
Br, BrO_3	Water	Cu^{2+} catalyst and acetic acid. Flow through UV reactor with a 14 s irradiation time	ICP-MS	0.01 µg L^{-1}	no validation, proof of concept on artificial samples	359
Br, Cl	Bottled and sea waters	Copper acetate, 58 s irradiation time	SF-ICP-MS	0.03 (Br) and 3 (Cl) µg L^{-1}	spike recovery	360
Hg	Water	Ivy root extract in ethanol, 30 s irradiation time	AFS	0.03 µg L^{-1}	spike recovery	361
Ru	Well, spring, contaminated and sea waters	Cd and Co catalyst with formic acid, 31 s irradiation time	ICP-MS	20 pg L^{-1}	spike recovery	362
Ru, Os	Water	Cd and Co photocatalyst and	ICP-MS	0.5 (Os) and 5 (Ru) ng L^{-1}	spike recovery	363

		formic acid, 45 s irradiation time				
Se^{IV}, Se^{VI}	Mineral and river waters	Cd ion photocatalysis and acetic acid, irradiation time not directly reported	HPLC-AFS	0.16 (Se^{IV}) and 0.21 (Se^{VI}) ug L^{-1}	spike recovery and analysis of Chinese RMs GBW(E)080395 (Se in simulated water) BWB2261-2016 (water quality Se standard)	364

Table 7. Preconcentration methods involving liquid-phase microextraction used in the analysis of soils, plants and related materials

Analyte(s)	Matrix	Method	Reagent(s)	Technique	LOD (µg L^{-1}, unless otherwise stated)	Validation	Reference
Ag	Water, sand	CPE	2,4-dimethyl pentane-3-one, $NaNO_3$ salting out agent, Triton X-114	FAAS	0.05	Spike recover (water samples)	365
Ag	Water, soil	CPE	Vitamin C, KNO_3 salting out agent, TritonX-100	FAAS	0.035	Spike recovery (water samples)	344
As	Honey, rice, water	VA LLME	DES benzyl triphenylphosphonium chloride and ethylene glycol, ethylenediamine-N,N'-disuccinic acid chelating agent	HG-AAS	6.5 ng L^{-1}	NIST SRM 1568a (rice flour) and 1643e (simulated fresh water), spike recovery (water, waste water samples)	366
Cu	Olive leaves	Sieve-linked double syringe LLME	[2-(((E)-2-(((E)-2-hydroxybenzylidene) amino) benzylidene) amino)], DCM	FAAS	1.5	Spike recovery (olive leaf extract)	367
Fe	Apple, human milk, rice, water	In-syringe supramolecular DLLME	Tiron (4,5-dihydroxy-1,3-benzendisulfonic acid) complexing agent; 1-hexadecyl-3-methylimidazolium bromide IL; extraction in reverse micelles of decanoic acid in THF	FAAS	1.04	Spike recovery (water samples)	352
Pb	Water, soil	LLE	Switchable hydrophilicity solvent N, N-dimethylcyclohexylamine-HAc; Dithizone complexing Agent; Triton X-114	ICP-AES	0.07	Spike recovery, Chinese CRM GBW (E) 080393(simulated water)	368

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

Analyte(s)	Matrix	Substrate	Substrate coating	Technique	LOD (µg L^{-1}, unless otherwise stated)	Validation	Reference
Ag, Au	Oak leaves, sunflower, tobacco, water	Fe_3O_4 magnetic mesoporous silica	Cetyltrimethyl ammonium bromide	FAAS	0.4 Ag, 0.7 Au	Spike recovery (oak leaves, sunflower, tobacco, water)	369
Cu as 1- (2-pyridylazo) - 2-naphthol ligand	Eggplant, garlic, water	Fe_3O_4@XAD-16		FAAS	10.2	NRCC HR-1 (river sediment), Environment Canada RM TMDA 53.3 (fortified lake water)	370
Hg	Beverages, biological samples, plants, seafood, water	GO/ thiosemicarbazide		EDXRFS; TXRFS	TXRFS: 2.1 pg mL^{-1} for liquids 1.8 ng g^{-1} for solids EDXRSF: 60 pg mL^{-1} for liquid and 73 ng g^{-1} for solid samples	Spiked recovery (water, apple juice, beer, wine); JRC ERM-CA615 (groundwater), CA713 (waste water), BB186 (Pig kidney); Sigma-Aldrich QC3163 (seawater); Consortium MODAS LGC Standards M-3 HerTis (herring tissue), M-4 CormTis (cormorant tissue), M-5 CodTis (cod tissue); NRCC Tort-2 (lobster); INCT-OBTL-5 (tobacco leaves); NACIS NCSZC73033 (scallion), 73032 (celery), 73013 (spinach)	371
Pb	Water, cooked meats, fish	Tergitol@SiO_2@Fe_3O_4 magnetic nano-material		FAAS	0.07	INCT-TL-1-(tea leaves); NIST SRM-1643e (trace elements in water)	372
Pb	Garlic, kefir, tea, tobacco,	$MgCo_2O_4$		FAAS	0.39	Spike recovery (garlic, kefir, tea, tobacco, tuna);	373

	tuna					NWRI TMDA-64.3 water; INCT-OBTL-5 (tobacco leaves)	

Table 9. New geological reference materials for isotope measurements

Isotopes	Matrix	Technique	RM name	RM or other validation	Reference
C, O	Carbonate of Jurassic age	IRMS	SHP2L	NBS 18 (carbonatite) and NBS 19 (limestone; normalised to VPDB	374
Cu	Chalcopyrite	LA-MC-ICP-MS	TC1725	Ratios expressed relative to NIST SRM 976 (Cu metal)	375
Fe, S	Iron sulfides	LA-MC-ICP-MS	Synthetic pyrite and chalcopyrite RMs using plasma-activated sintering	S ratios normalised to VCDT	376
Fe, S	Iron sulfides	SIMS, LA-MC-ICP-MS	JC-Po (pyrrhotite), JC-Pn (pentlandite)	Fe ratios by LA-ICP-MS normalised to IRMM-014 (Fe metal), and S ratios by SIMS to VCDT	377
Hf, O and U-Pb	Zircon	SIMS, LA-MC-ICP-MS, IRMS, TIMS	Zircon ZS	Zircon RMs TEMORA, 91500, Tanz, GJ-1	378
Nd and U-Pb	Apatite	LA-ICP-MS, LA-MC-ICP-MS	Sumé-570 apatite	U-Pb ages: zircons 91500 and Mud Tank. Range of RMs used to assess accuracy of Nd ratios.	379
Nd, Sr and U-Pb	Apatite	ID-TIMS, LA-ICP-MS	MRC-1 and BRZ-1	Apatite RMs MAD, Durango, McClure	380
O	Calcite	IRMS, SIMS	NJUCal-1	Normalised to VPDB	381
O, Zr and U-Pb	Zircon	LA-ICP-MS, LA-MC-ICP-MS, SIMS, ID-TIMS, IRMS	Tanz zircon megacrysts	Zircon RMs: 91500, GJ-1, Plešovice, M257 and Jilin	382
O, Zr and U-Pb	Zircon	ID-TIMS, SIMS, LA-ICP-MS, IRMS	Jilin	Zircon RMs: Plešovice Qinghu, GJ-1	383
O	O^{17}- enriched sodium sulfate	pyrolysis	Sulf-A, Sulf-B, Sulf-C	Nitrate RM USGS35	23
O	Apatite	SIMS, IRMS	MGMH#133648, MGMH#128441A, MZ-TH, ES-MM	SARM 32 (phosphate rock). Ratios expressed relative to VSMOW	384
Os, Re	Chalcopyrite	MC-ICP-MS.	XTC chalcopyrite (with low	NIST Henderson molybdenite RM 8599, NRCG	385

		NTIMS	Re mass fraction)	CRMs HLP (molybdenite), JDC (molybdenite), JCBY (Cu-Ni sulfide)	
S	Sulfide and sulfates	LA-MC-ICP-MS	Synthetic pyrite, chalcopyrite, sphalerite, galena, arsenopyrite, barite, and gypsum RMs	Targets synthesised from sulfide or sulfate NP powders mixed with epoxy resin. S ratios normalised to VCDT	386
S	Chalcopyrite	LA-MC-ICP-MS, IRMS	TC1725	IAEA-S-2 and IAEA-S-3 (Ag_2S powders from IAEA). S ratios normalised to VCDT	387
Si	Si powder	MC-ICP-MS	GBW04503	Blends of synthetic isotopically-enriched Si solutions	388
U-Pb	Scheelite	LA-SF-ICP-MS	Scheelite WX27	Wolframite YGX	251
U-Th	Zircon	SIMS, LA-ICP-MS, LA-MC-ICP-MS	SS14-28	Overall isochron with data from three different analytical techniques	389
Zr	Solution	MC-ICP-MS	ZIRC-1 (NRC)	IPGP-Zr and USGS RMs BHVO-2 (basalt) and AGV-2 (andesite)	390

Table 10. New data for existing geological reference materials

Determinand	Matrix	Technique	RM or other validation	Comments	Reference
B and δ^{11}B	Geological RMs	MC-ICP-MS	δ^{11}B values normalised to NIST SRM 950 (B isotope solution)	δ^{11}B values for 18 geological RMs reported	391
B, Hf, Li, Mg, Nd, O, Pb, Si, Sr isotopes, Fe^{2+}/ΣFe	Andesite glass RMs	SIMS, LA-MC-ICP-MS, EPMA, TIMS, colorimetric	Cross-checking of data from different techniques and labs	Expansion of available data for andesite glass RMs ARM-1, ARM-2 and ARM-3	392
δ ^{44}Ca/^{40}Ca	Geological RMs	TIMS	IAPSO seawater and NIST SRM 915a (Ca carbonate)	34 Chinese geological RMs	127
δ^{114}Cd/^{110}Cd	Geological and environmental RMs	MC-ICP-MS	Cd ratio normalised to NIST SRM 3108 (Cd isotope solution)	Cd isotope ratios reported for 34 RMs	130
Cr isotopes	Geological RMs	MC-ICP-MS	Cr ratios normalised to NIST SRM 979 (Cr isotope solution)	Cr isotope ratios reported for 18 existing RMs for the first time	393
Cu, Pb and Zn isotopes	Geological and biological RMs	MC-ICP-MS	Normalisation to Cu ERM-AE647 (Cu), NIST SRM 981 (Pb) and IRMM-3702 (Zn)	Cu, Pb and Zn isotope data for 23 geological RMs	394
Li isotopes	Geological RMs	MC-ICP-MS	Lithium carbonate RMs IRMM-016 and NIST SRM 8545, 8 geological RMs and seawater	New δ^{7}Li data reported for 10 geological RMs	124
Nd-Sm	Allanite	LA-ICP-MS, LA-MC-ICP-MS	*In situ* data consistent within uncertainty with solution methods	Daibosatsu and LE40010 suitable as RMs for allanite Nd-Sm microanalysis	395
Re, PGEs and ^{187}Os/^{188}Os	Organic-rich geological RMs	N-TIMS, MC-ICP-MS	RM 8505 (crude oil), RM 8505 (asphdiene)	New data for USGS RMs: SBC-1 (marine shale), SGR-1b (oil shale), SCo-2 (marine shale), ShTX-1 and ShCX-1 (calcareous organic-rich shales)	396
Si isotopes	Quartz and zircon	SIMS	NIST 8546 (previously NBS-28) quartz RM and NIST 610 (glass).	Quartz RMs: Qinghu-Qtz and Glass-Qtz. Zircon RMs: Qinghu-Zir and Penglai-Zir. Test materials found to be more homogeneous in Si isotopes than NIST	397

				8546	
Si and Zr isotopes	Zircons	LA-MC-ICP-MS	Si ratios normalised to NIST NBS28. Zr ratios normalised to IPGP-Zr	Zircon RMs SA01 and SA02	398
U isotopes	U ore concentrates	MC-ICP-MS, ICP-MS, SIMS, AMS, TIMS	Various validation strategies depending on analytical technique	13 labs reported data on CRMs from 3 NRCC (UCLO-1, UCHI-1 and UPER-1)	399
U-Pb ages	Apatites	ID-TIMS	Derived from 3D linear regressions	Reference ages for Durango and Wilberforce apatite RMs	400
U-Th-Pb ages	Allanite	LA-ICP-MS, LA-MC-ICP-MS	U-Th-Pb ages consistent within uncertainty with literature and ID-TIMS values	Allenite LE40010 suitable as RM for U-Pb dating and CAP[b] for Th-Pb dating	395
Zn isotopes	Zn metal, sphalerite	fs LA-MC-ICP-MS, MC-ICP-MS, EPMA	δ^{66}Zn normalised to JMC-Lyon	Zn metal RMs NIST SRM 683 and NBS 123 suitable as RMs for *in situ* Zn ratio measurements; matrix effects between sphalerite and Zn-rich minerals discussed	401

Table 11. Methods used for the determination of isotope ratios in geological materials.

Isotope	Matrix	Separation and purification	Technique	RMs and figures of merit	Ref
B	Marine carbonates	Modified microsublimation technique using droplet (<70 µL) of carbonate or RM solution	MC-ICP-MS	Method validated with 3 ERM boric acid RMs, NIST RM 8301 (foram) and a carbonate RM. δ^{11}B long-term reproducibility for NIST 8301 was 14.48 ± 0.18‰ (2SD, n=11) for B masses of 2.5 and 5 ng	402
C	Carbonates	Not applicable	fs LA-MC-ICP-MS	δ^{13}C reported relative to VPDB and compared with bulk values determined by IRMS for calcite, dolomite, magnesite and siderite samples. External reproducibility <0.45‰ (2SD)	403
Ca	Geological materials	Chemical purification using DGA resin followed by separation from Sr on Sr Spec resin	CC-MC-ICP-MS	Normalised to NIST SRM 915b ($CaCO_3$). 100 ng Ca sufficient to obtain precision of <100 ppm (2SD) for δ^{44}Ca/^{40}Ca. Validation using 9 rock RMs with a range of compositions	404
Ca	Carbonates, seawater	Automated IC with methanesulfonic acid as the eluent	MC-ICP-MS	Precision of 0.14‰ (2σ, n=56) for δ^{44}Ca/^{40}Ca. Data reported relative to IAPSO seawater RM.	405
Ca, Fe	Geological materials	Matrix removal on single TODGA resin column	MC-ICP-MS, TIMS	Procedure validated with USGS RMs AGV-2 andesite), BCR-2 (basalt) and BHVO-2 (basalt)	406
Cd, Zn	Marine carbonates	Different chemical cleaning methods assessed. Cd and Zn purified by double-pass AEC on AG-MP1 resin	MC-ICP-MS	Cd data reported relative to NIST SRM 3108 (Cd solution) and Zn data normalised to JMC Lyon-Zn. Precision (2SE) <0.05‰ for δ^{114}Cd and <0.02‰ for δ^{66}Zn	407
Cu	Geological materials	Separation protocol with 2 columns in tandem: (i) Cu-selective resin (Cu separation from matrix elements); (ii) AG50W-X12 resin to purify Cu	MC-ICP-MS	δ^{65}Cu long-term precision <0.07‰ (2SD). Protocol validated with 7 USGS RMs and 5 Chinese RMs (GBW series)	408,
Cu, Fe, Mo, Ni, Zn	Geological materials	Multi-step ion-exchange procedure for purification of selected metals from one sample aliquot	MC-ICP-MS	5 USGS RMs: basalts (BCR-2, BHVO-2), Fe-Mn nodules (Nod-A1, Nod-P1) and organic-rich shale (SGR-1) for validation.	409
Eu	Geological	Two step CEC on AG50WX-8 resin with 2-	MC-ICP-MS	Procedure validated using a range of USGS	410

	materials	hydroxyiosbutyric acid eluent for complete separation of Gd from Eu		and GSJ rock RMs. Mass bias correction using ^{147}Sm-^{149}Sm or ^{147}Sm-^{154}Sm provided the most accurate and precise Eu ratios	
Fe	Geological materials	Modified AEC procedure on AG1-X8 resin with two passes to purify Fe further	MC-ICP-MS	With double-spiking technique, long-term precision and accuracy <0.02‰ (2SD) for δ^{56}Fe. 5 USGS rock RMs for validation	411
Fe	Fe-dominated minerals	Samples mounted in epoxy resin	LA-MC-ICP-MS	Non-matrix-matched calibration achieved by Introduction of water vapour mixed with N_2after LA cell. δ^{56}Fe reported relative to IRMM-014 (iron wire). Precision and accuracy <0.10‰ (2SD)	412
Fe	Fe-rich minerals	No column chromatography; digested samples measured after dilution with 2% HNO_3. Comparison with δ^{56}Fe data obtained after column chromatography	MC-ICP-MS	δ^{56}Fe reported relative to IRMM-014 (iron wire). Long-term reproducibility for δ^{56}Fe <0.05‰ (2SD, n=123) on pyrite. USGS and IGGE rock RMs used to assess accuracy	413
Hf-Lu	Columbite-group minerals	Chemical separation of Hf from Ta using 2-column procedure: (i) Ln Spec resin to separate Hf, Lu and Ta from matrix; (ii) AEC on AG1-X8 resin to separate Hf from Ta	MC-ICP-MS and LA-MC-ICP-MS	Normalisation to ^{178}Hf/^{177}Hf = 1.4672 using exponential law in preference to ^{179}Hf/^{177}Hf = 0.7325 for LA technique	414
K	Geological RMs	Single column CEC with AG50-X8, K recovered with 0.5 M HNO_3 eluent	MC-ICP-MS	Precision of *ca.* 0.08‰ (2SD) for ^{41}K/^{39}K on NIST SRM 3141a (K solution) using cold plasma technique. Procedure validated using NIST SRM 999c (KCl powder) and six USGS RMs	415
K	Geological materials, seawater	Two-stage column separation by CEC on AG50W-X12 resin followed by purification on AG50W-X8 resin	MC-ICP-MS	External reproducibility for ^{41}K/^{39}K of <0.10‰ (2SD) for K solutions of 1 ppm or greater. Five USGS rock RMs used to assess accuracy and data normalised to NIST SRM 3141a (K solution)	416
K	Geological and biological RMs	Two-stage column separation required for geological materials: CEC on AG50W-X12 followed by purification on AG50W-X8 resin	CC-MC-ICP-MS	Long-term reproducibility for ^{41}K/^{39}K of <0.07‰ (2SD, n=12). Wide range of RM types to evaluate performance	417
K	Geological RMs	K separated from matrix elements by CEC on	CC-MC-ICP-	Intermediate precision for ^{41}K/^{39}K of	418

		AG50W-X8 resin using the same elution protocol twice	MS	<0.05‰ (2SD). Data reported relative to NIST SRM 3141a (K solution). 9 RMs including 4 USGS rocks to evaluate accuracy	
K, Mg	Geological materials	Single column CEC procedure on AG50W-X8 with 0.5 M HNO_3 (K) and 1.0 M HNO_3 (Mg) as eluents	MC-ICP-MS	Procedure validated using six USGS RMs.	419
Li	Geological materials	2-column separation using cation-exchange resin AG50W-X8	SF-ICP-MS	Measurement uncertainty (U; k=2) 1.2‰ on RM IRMM-016 (Li carbonate) and δ^{7}Li values for 19 silicate RMs reported	420
Mg	Geological materials	Mg purification by single-column CEC using AG 50W-X12 resin in micro-column with 4.0 mm internal diameter	MC-ICP-MS	Procedure validated using a range of USGS rock RMs. Long-term precision <0.06‰ for δ^{26}Mg	421
Mg	Silicate rocks	Not applicable	fs LA-MC-ICP-MS	Data reported relative to DSM-3 (Mg solution, Cambridge University). Validation using USGS and DING glass RMs. Long-term precision (2SD) for δ^{26}Mg was 0.10‰	422
Mg	Low-Mg rocks	Three-step chromatographic procedure using a single column containing AG50W-X8 resin	MC-ICP-MS	Long-term reproducibility for δ^{26}Mg was 0.06‰. Validation using six felsic rock RMs with MgO contents from 0.05 to 0.96 wt%.	423
Mo	Low-Mo rocks	Three column purification procedure using Muromac®1X8(similar to AG1-X8) anion and AG50W-X8 cation resins	MC-ICP-MS	δ^{98}Mo/^{95}Mo external precision <0.06‰ (2SD). Data normalised to NIST SRM 3134 (Mo solution). Data for 43 RMs reported	424
Nd	Geological materials	Nd purification using single column containing Eichrom TODGA resin	MC-ICP-MS	SSB with Eu as IS. Method validated using three pure Nd standards and 7 geological RMs. Reproducibility for δ^{146}Nd/^{144}Nd <0.030‰ (2SD)	425
Nd	Fe-rich silicates	Single column diglycolamide-based extraction chromatography using DGA resin to isolate Nd in presence of high levels of Fe	MC-ICP-MS	No significant difference in ^{143}Nd/^{144}Nd precision for two iron-rich RMs (from CRPG France) compared to $5x10^{-6}$ <2SE<10^{-5} for GSJ RM JNdi-1 (Nd isotope solution)	426
Nd	Silicate rocks	Modified CEC method to separate REEs using AG50W-X8 resin followed by Nd purification on AG50W-X4 resin with 2-methylactic acid eluent	TIMS	Precision of ±2-5 ppm for ^{142}Nd/^{144}Nd for BHVO-2 (basalt)	427

Nd	Foraminifera	Rigorous cleaning protocol prior to dissolution and ion-exchange chromatography on Sr, TRU and LN resins to purify Nd	TIMS	External reproducibility for ^{143}Nd/^{144}Nd of <90 ppm (2RSD) for 100 pg Nd loads	428
Ni	Geological materials	Three-step column chemistry: (i) CEC on AG50W-X8 resin; (ii) AEC on AG1-X8 resin; (iii) purification of Ni from Co, Cu and Zn using AG1-X8 resin	MC-ICP-MS	^{60}Ni/^{58}Ni in 20 geological RMs measured to validate method. Precision of 0.006-0.084‰ (2SD) for samples containing 100-200 ng Ni	429
Pt	Iron meteorites	Single-column AEC on AG1-X8 resin; Pt eluted with 13.5 M HNO_3	MC-ICP-MS	RM IRMM-010 Pt and NIST SRM 129c (high-sulfur steel) doped with RM IRMM-010 (PtS) prior to digestion to mimic S and Pt content of iron meteorites. Typical between-run precision for δ^{198}Pt was 0.06‰ (2SD)	430
Rb	Silicate rocks	Two column procedure: sample purified in two passes on AG50W-X12 followed by removal of residual K on Sr-Spec resin.	MC-ICP-MS	Data reported relative to NIST SRM 984 (Rb isotopes). Long-term precision <0.05‰ (2SD) for δ^{87}Rb	129
S	Sulfates and sulfides	SO_2 from offline combustion trapped in aqueous $BaCl_2$ and precipitated as $BaSO_4$ after oxidation with H_2O_2	EA/IRMS	IAEA and NIST RMs for validation. Long-term reproducibility and accuracy of δ^{34}S similar to those by direct EA/IRMS	431
Sb	Sb minerals	Not applicable	fs LA-MC-ICP-MS	Long-term reproducibility <0.045‰ for *in situ* δ^{123}Sb values, normalised to NIST SRM 3102a (Sb solution)	432
Sr	Geological materials	3-step column procedure using Eichrom Sr resin to: (i) remove Fe; (ii) separate Sr from matrix elements; and (iii) purify Sr	TIMS	Multidynamic method with fractionation drift correction yielded precisions of 29 ppm for ^{84}Sr/^{86}Sr and 5 ppm for ^{87}Sr/^{86}Sr	433
Sr	Limestones	Samples subjected to acetic acid extraction before online Sr separation based on CEC with 1M HNO_3 as eluent in the presence of 3.8 mM 18-crown-6	HPLC-MC-ICP-MS	Method validated using NIST SRM 987 (Sr carbonate) and JCp-1 (*Porites* coral) RM from GSJ	434
U	Carbonates, seawater, U mill tailings	Column chemistry based on AG1-X8 or UTEVA resins to separate U from other actinides	MC-ICP-MS	Estimated LOD for ^{236}U/^{238}U of 2×10^{-10} using new SEM method with retarding potential quadrupole lens. Precision ±4% for 5 fg ^{236}U at a ^{236}U/^{238}U of 1×10^{-8}	106

V	Marine carbonates	Fe coprecipitation plus AEC on AG1-X8 to remove Fe before 4-step chromatographic procedure to separate V from matrix elements	MC-ICP-MS	Long-term precision <0.14‰ (2SD) for δ^{51}V. Validated using in-house V isotope solution USTC-V and USGS RM COQ-1 (carbonatite)	435
Zn	Geological materials	Zn purification with two column AEC method using Eichrom AG1-X8.	MC-ICP-MS	Long-term reproducibility <0.025‰ (2SD) for δ^{66}Zn/^{64}Zn, normalised to JMC-Lyon. Method validated with IRMM-3702 (Zn isotope solution), and basalt RMs from the USGS and GSJ	436
Zn	Zn-rich minerals	No column chromatography; digested samples diluted in 2% HNO_3 prior to analysis. Comparison with Zn isotope data obtained after column chromatography.	MC-ICP-MS	SSB with Cu IS. Long-term precision (2SD, n=42) of <0.03‰ for δ^{66}Zn and <0.05‰ δ^{67}Zn	437