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

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This is the 34th annual review of the application of atomic spectrometry to the chemical analysis of environmental samples. This Update refers to papers published approximately between August 2017 and June 2018 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]*. The review is not intended to be a comprehensive overview but selective with the aim of providing a critical insight into developments in instrumentation, methodologies and data handling that represent a significant advance in the use of atomic spectrometry in the environmental sciences.*

SUMMARY OF CONTENTS

1. **Introduction**

This review is intended to provide a critical insight into the most significant advances of atomic spectrometry as applied to the environmental sciences. Close to the beginning of each paragraph is an italicised word or phrase that highlights the subject of that particular paragraph. Regular readers will note that Owen Butler has stepped down as co-ordinator of this review after many years of diligently getting the review to press on schedule. He continues to write the section on the analysis of air and so we shall still benefit from his knowledge and experience.

In the field of air analysis, highlights within this review period included the fabrication of a new portable cascade impactor sampler that is also wearable and a portable $PM_{2.5}$ sampler that could be deployed in large numbers around wildfires. Coupling air sampling units to ICP-MS is of interest to those wishing to determine elemental species in near-real time. In a laboratory setting, a new air sampler that incorporated an XRF detector for time-resolved measurements performed well when challenged with test aerosols. Data generated during subsequent field trials agreed with those generated by conventional filter sampling and ICP-MS analysis. Improvements in the capabilities of aerosol mass spectrometers were noted as were developments in other complementary techniques such as combustion analysis and spectrophotometry for the measurement of diesel fume, silica and oxides of nitrogen.

In the field of water analysis, progress was made in multielemental and species-specific concentration methods, along with methods for the preconcentration of NPs and the elimination of the background contribution from dissolved elements before single particle counting. Researchers are starting to take advantage of the flexibility of ICP-MS/MS instrumentation to determine elements such as F previously undetectable or to replace radiochemical methods for radioisotope determinations. In addition, LA-ICP-MS is now being used to investigate concentrations of elements in ice cores at greater depth resolution than previously possible, a trend that will continue into the future once ice cores with older ice become available.

For the analysis of soils, there was no noticeable diminution in the research into sample preparation procedures in which analytes are extracted from solid matrices into mineral acids for subsequent determination by an atomic spectrometry technique. Nor was there any reduction in efforts to increase the concentration of analytes in such digests so that methods involving spectrometries such as FAAS could achieve meaningful LODs. The possibilities of SPE in which micro- or nano-particulate material was separated magnetically seemed particularly attractive, as this combined the advantages of high-efficiency phase separation with the high extraction efficiency of a dispersed extraction procedure. In addition, there was some interest in alternate procedures such as alkaline extraction and fusion. Reports on the applications of LIBS for direct solids analysis continued to grow in number though it is clear that calibration, and hence accuracy, remained a major challenge. Although X-ray spectrometry continued to be used widely, the relative maturity of some techniques was reflected in the fact that many reports concerned pure application and did not present advances in the measurement science. Interest in the applications of pXRFS was sustained, in particular for rapid screening purposes. Advances in MS were mainly focused on the need to remove or to correct for interferences as well as on isotope analyses.

Significant progress has been made in the development of appropriate matrix-matched RMs suitable for calibration and quality control in the elemental and isotopic analysis of geological materials. Another area of great activity is the application of *in situ* techniques, such as LA-ICP-MS, SIMS and μEDXRFS, to obtain elemental and isotopic information for geological materials at high spatial resolution. A notable number of contributions described analytical developments related to the dating of different minerals, especially the use of *in situ* techniques.

2 Air analysis

2.1 Review papers

A *review* (72 references) summarised[7] sampling and measuring techniques available for assessing occupational exposure to ultrafine particles. Krause *et al.*[8] (39 references) evaluated the utility of various analytical techniques such as sp-ICP-MS, TEM, SAXS, XRD, ion-beam techniques and Raman microscopy for the characterisation of Al, Al_2O_3 and TiO_2 NPs. Trends in the use of various analytical techniques for the characterisation of airborne particles were studied[9] (252 references) and a useful guide to the suitability of any given technique presented. Metcalf *et al.*[10] reviewed (191 references) the potential use in aerosol measurements of microfluidics, the science of handling small liquid volumes. Techniques designed to capture small sample masses from air samples, such as spot sampling and particle-into-solution sampling, were most amenable to subsequent measurements using microfluidics.

2.2 Sampling techniques

Developments in *particle sampling* included a low-flow rate cascade impactor[11]; a low-cost $PM_{2.5}$ sampler[12] and a mobile high-flow rate PM_4 sampler[13]. The portable cascade impactor ran at a nominal 2 L min^{-1} flow rate and employed 10 impaction stages to segregate particles in the size range from 60 nm to 9.6 µm. By removing the two lowest impaction plates, the sampler became wearable thereby making personal sampling of particles down to 170 nm size possible. A prototype compact battery-powered $PM_{2.5}$ filter sampler, designed for rapid deployment around wildfire incidents, enabled the generation of time-averaged smoke concentration data comparable in quality to those derived from larger US EPA reference air samplers. The low build cost, estimated to be ~1/20th of that of a reference sampler, made this device potentially suitable for large-scale deployment around bush-fires and in other campaigns where saturation monitoring may be required. Future work will aim at refining the ability to measure particle concentrations in real-time using an embedded low-cost optical sensor. Little is known about the levels of respirable (PM_4) crystalline silica in ambient air. A new mobile PM_4 sampler, operating at 50 L min^{-1}, used[13] porous foams to achieve the desired particle size cut. The battery power was sufficient to collect 30 m^3 air samples so allowing RCS to be quantified at levels below 1 µg m^{-3}.

Passive air samplers can be deployed in large numbers and in locations where the logistics and cost of operating pumped (powered) samplers become prohibitative. Canadian researchers developed[14] a new Hg^0 passive sampler for ambient air studies. Laboratory chamber studies were used to determine the nominal sampling uptake rate of 0.121 m^3 per day and to investigate the effect of temperature and wind speed on this uptake rate. In order to neutralise any corrosive effects on TD-AAS components caused by SO_2 liberated from the S-impregnated activated-carbon sorbent used, 0.15 g of Na_2CO_3 was added to each sample prior to combustion. A week-long field deployment was sufficient for ambient concentrations of 1-2 ng m^{-3} to be quantified. However, the development of passive samplers for the collection of particles is more challenging. When the University of North Carolina passive air sampler was deployed[15] in a working mine, the airborne mass concentrations measured were only 24-35% ($PM_{2.5}$) and 39-58% (PM_{10}) of those measured at the same time by pumped sampling onto filters.

Innovations in air sampling included[16] a radio-controlled quadcopter, equipped with a Au-coated quartz tube for sampling Hg emissions. The authors concluded that this new sampling platform could play a useful role in assessing emissions above remote landscapes or above point sources which are currently inadequately characterised. From the realms of science fiction, an EDB was coupled[17] to a mass spectrometer so that individual particles could be levitated in an electric field for predetermined time intervals prior to their transfer into the MS system. This novel EDB-MS system offered potential for future studies of atmospheric chemical reactions in laboratory chambers.

2.3 Reference materials and calibrants

A candidate *reference material* of a $PM_{2.5}$-like dust was prepared[18] by spiking a particle suspension with an aqueous solution containing Ca^{2+}, K^+, Mg^{2+}, Na^+ and NH_4^+ ions. Excess water was siphoned off, the solid residue subjected to shock freezing in liquid N_2 and any residual moisture removed by freeze drying. The resultant material resembled $PM_{2.5}$ dust physically and had similar leaching characteristics when analysed for ions. The authors concluded that this approach may be amenable for preparing other dusts containing, for example, metals or PAHs. A new aerosol generation system for the simultaneous production of up to 96 replicate air filter samples used[19] a flame atomiser to convert metal-containing liquid standards (Co, Cu, Ni, Pb and Zn) into metal oxide NPs. Upon dilution in air, the NPs were introduced into a sampling chamber containing 96 individual air samplers. Filters, prepared with elemental loadings of 5-100 μg per filter with a batch precision of <4%, were used in a laboratory proficiency testing programme. The production of certified reference filters is now planned. A sensitive scanning XRF system with a beam resolution of ~0.5 mm enabled[20] the spatial distribution of various elements across the surface of air filters to be examined. Application to commercially available Micromatter filter standards, widely used by XRFS laboratories that undertake air filter analysis, demonstrated that the distributions of elements were uniform to within 2%.

2.4 Sample preparation

A review (141 references) on new approaches in *microwave-assisted* digestions included[21] the following topics: digestions involving dilute acids; reactants such as O_2; UV-mediated reactions; high-pressure FIA digestions and microwave-initiated combustion procedures. The development of a new microwave method, using HNO_3 heated to 240 °C, for the dissolution of workplace air filter samples was reported[22, 23] in German with English abstracts. The first paper discussed the initial method development whilst the second paper described a collaborative trial involving a number of German laboratories to generate method precision data. For elements such as Cr, Fe, Mn and Ni, data between laboratories agreed well when the supplied reference dust samples were analysed. More variability in results was encountered in samples containing elements such as Sb and W where dissolution in only HNO_3 is not appropriate. A third paper detailing the findings of a second collaborative trial involving international participants is planned.

Although the measurement of the *bioaccessible* metal fraction of workplace aerosols is of interest from a health perspective, the lack of standardised methods and associated performance data has hampered progress until now. An interlaboratory study assessed[24] the performance of a procedure described in ISO 15202-2 which advocated leaching air filter samples into water at 37±2 °C for 60 minutes. Test welding fumes containing Cr, Fe, Mn, Mo and Ni were sent to 10 laboratories for analysis. The repeatability (within-laboratory precision on replicate filters) was satisfactory at 11-21% but reproducibility (between laboratory precision) was noticeably poorer at 19-53%. Further studies to understand the reason for such variations would be welcomed. The first use of DGT for assessing the biocharacteristics of airborne particulates involved[25] preparing polyacrylamide hydrogels embedded with Chelex 100 ion-exchange resin and immersing them in simulant dust suspensions for various time intervals. Upon removal, the probes were digested in a HNO_3-HCl (4+1) acid mixture using MAD and analysed by ICP-MS to determine the labile metal content released from these dusts. Simultants were prepared by suspending in water dust samples recovered from inside an air conditioning unit. The total metal contents were determined using a MAD that required HF to digest the siliceous matrix. Further development of this procedure will involve applying DGT to real air filter samples. In a continuation of work reviewed[1] last year, researchers in Scotland proposed[26] the use of a novel two-step sequential-extraction procedure to assess the biaccessibility of As, Cd, Cr, Cu, Fe, Mn, Pb and Zn in urban air particulate matter. A new artificial mucus fluid extractant was applied to samples followed by either the SBET or the stomach phase of the UBMG so enabling metal bioaccessibility fractions in both the upper airways and the stomach to be determined.

2.5 Instrumental analysis

2.5.1 Atomic absorption, emission and fluorescence spectrometry

In the determination of Pb in road dust by solid-sampling *high resolution continuum-source AAS*, either the use of the insensitive 261.418 nm line or a partial peak (pixel) integration of the more sensititive 283.306 nm line was required[27] to provide a method with a useful assaying range. The significant background affecting the absorption lines was attributed to molecular recombinations such as AlCl, SiO and SiS overlapping at 261.418 nm and SiS at 283.306 nm. A least-squares background protocol was required to correct for this. The results obtained from the determination of Pb in three CRMs (BCR-723 (road dust), IAEA SO-2 (soil) and NIST SRM 2586 (soil)) were in good agreement with the certified values.

Atmospheric Hg measurements are commonly carried out using the Tekran™ AFS instrument. An alternative software protocol for processing the raw *atomic fluorescence* signal output gave[28] an improvement in LOD of 31-88%.

Researchers at NIOSH are focused on developing new and interesting portable analytical techniques for the determination of *elemental species in workplace aerosols*. Recent work was summarised in the following three papers. In a procedure involving a prototype *rf*-GD-AES instrument, aerosols were preconcentrated[29] on a microelectrode tip. The achievable LOD was in the range 0.05 to 1 ng with a reproducibility of 5-28% when tested with 100 nm-sized particles containing C, Cd, Mn and Na. Zheng *et al.*[30] recorded emission intensities from the C I and C II atomic lines in their investigation of the spatial and temporal dynamics of a pulsed, electrical spark microplasma using black carbon particles. The results provided insights into the dynamics of the plasma and will be useful in future optimisation of this technique for elemental analysis of aerosols. A new multivariate PLS calibration approach for use with SES has been described[31]. In the analysis of a reference welding fume aerosol, the RMSEP obtained from the PLS model was 13% for Cr, 23% for Fe, 22.5% for Mn and 12% for Ni. In the LIBS analysis of filter samples for assessment of worker exposure to airborne CNTs, the Al and Fe impurities in the CNTs were measured[32] as surrogate markers because of the ubiquitous presence of C. Using a personal air sampler running at 1 L min^{-1} for 8 h, it was possible to achieve an elemental LOD of ~1 ng cm^{-2} on the filter. This was equivalent to an airborne LOD of ~8 ng m^{-3} and provided a CNT LOD in the workplace (~0.4 μg m^{-3}) below the NIOSH-recommended CNT exposure limit of 1 μg m^{-3}.

2.5.2 Mass spectrometry

2.5.2.1 Inductively coupled plasma mass spectrometry. The SMPS provides size distributions and concentrations of NPs in air with a temporal resolution of a few minutes or less. There is ongoing interest in the benefits of coupling the SMPS to ICP-MS systems for the generation of *real-time elemental data* so Swiss researchers provided[33] a practical guide, including video clips, to setting up such a system and its operation. Whereas radiochemical monitoring methods are slow and time consuming for the determination of radioactive ^{90}Sr released during nuclear power plants accidents, a ICP-MS/MS procedure for the determination of ^{90}Sr in airborne particles had[34] a run-time of only 10 minutes. Air was sampled through a $PM_{2.5}$ impactor to generate an aerosol containing only small particles. The aerosol was introduced into a gas-exchange device in which the air matrix was replaced by Ar. Isobaric interferences arising from $^{89}YH^+$, ^{90}Y and ^{90}Zr were eliminated through optimisation of the cell chemistry. The LOD of 3.6 x 10^{-4} ng m^{-3} was equivalent to 1.8 x 10^{-6} Bq cm^{-3}. It was acknowledged that the incomplete vaporisation or ionisation of larger particles within the plasma could be responsible for poor Sr recoveries, which were only 30-76% of those obtained using a more conventional filter sampling method. However, even with this bias, the authors concluded that this new approach merited consideration as a useful early warning tool. The online measurement of ambient aerosols by ICP-MS involved[35] sampling air through a cyclone at 30 L min^{-1} and depositing the resultant <250 nm sized particles into an impaction well which was continuously flushed with water. Nitric acid was then added downstream and the resultant suspension passed through a quartz photo-reactor for digestion. Further work was required to minimise system blanks and so take advantage of the inherent ICP-MS sensitivity.

Other *notable ICP-MS applications* have been described. In a procedure involving the tandem use of LA and LIBS for the characterisation of U particles in nuclear materials, simulants were prepared[36] by depositing reference U-containing particles on forensic double-sided tape. Rapid elemental profiling by LIBS enabled a 5 x 5 mm target area to be rastered in <50 minutes. When U-rich particles had been located, LA-ICP-MS was used for IRA. The determined $^{235}U/^{238}U$ ratios were within 10% of theoretical values for particles containing U at 0.01% (*m/m*). Suggested refinements included the use of MC-ICP-MS for more accurate and precise IRA. Determination of the $^{87}Sr/^{86}Sr$ isotopic ratio in particles trapped in snow can provide useful information on the source of atmospheric pollution in the Polar Regions. Accurate and precise IRA is however compromised because of the low analyte (particle) concentrations and the small quantity of snow available for analysis. A HEN MC-ICP-MS method made it possible to determine[37] the isotopic composition of sub-ng amounts of Sr in Antarctic snow. The method sensitivity was boosted through use of a HEN with membrane desolvation, a high ion transmission cone interface and 10^{12} Ω amplifiers instead of the standard 10^{11} Ω amplifiers. The $^{87}Sr/^{86}Sr$ ratio repeatability was <0.5% RSD for a test sample containing only 160 pg Sr. Procedural blanks were <3 pg. Pollution sources could be differentiated using only 30 g quantities of snow containing as little as 0.5-2 ng Sr. A HPLC-ICP-MS procedure for the simultaneous speciation of arsenate, chromate, molybdate and vanadate species in ash, cement and flue dust samples was considered[38] to be reliable, accurate (spike recoveries in the range 98-102%), precise (repeatability <3%) and fast (chromatographic separations in 10 minutes).

2.5.2.2 Other mass spectrometry techniques. *Secondary ion mass spectrometry* is a sensitive surface technique which has the capability for both spatial imaging and depth profiling. A review (143 references) highlighted[39] the advantages and limitations of its use in particle analysis, surveyed recent applications and suggested possible future developments.

Single particle aerosol mass spectrometry is an emerging technique for identifying the chemical composition, sizing and mixing state of individual aerosol particles so papers detailing instrumental performance are most welcome. A new commercially available SPAMS instrument had[40] an overall particle detection efficiency of 0.01-4.23% for PSL particles in the 200-2000 nm size range; 0.44-6.57% for NH_4NO_3 particles in the 300-1000 nm size range and 0.14-1.46% for NaCl particles also in the 300-1000 nm size range. Useful reference mass spectra were provided for 32 different particle types relevant for atmospheric aerosol studies such as NH_4NO_3 or diesel soot. A mass spectra dataset, generated during a single day of air sampling at a rural location near a tramline, was used as training data to test the capability of either fuzzy clustering or reference spectra deconvolution protocols for the classification of particles. Applications of SPAMS included the chemical interrogation of coal combustion particles[41] and urban aerosols[42]. In the former paper, comparative analytical data were generated using ICP-MS and TEM techniques and in the latter paper using aerosol MS. In a derivation of this technique, a new tool for the analysis of solid materials employed[43] LA to release particles from various powdered coal samples for subsequent analysis by SPAMS. Useful sample fingerprint data were thus generated for use in future source apportionment studies.

Other MS developments in the field of *nuclear safeguarding* included a PTR-MS method[44] for the determination of gas-phase CH_3I and the isotopic analysis of U-containing particles by either GD-TOF-MS[45] or LA-TOF-MS[46].

2.5.3 X-ray spectrometry

Collection of *aerosol particles* on greased quartz reflectors using a Dekati™ PM_{10} impactor for subsequent TXRF analysis was[47] feasible, avoided any intermediate sample preparation steps and gave LOD values of ~10 pg m^{-3} for medium Z elements (Fe to Sr). Key was development of an automated pipetting device to enable solution standards to be spotted on quartz reflectors for preparation of calibrants that were a realistic match for dust samples. Chinese researchers upgraded[48] their PIXE capability at the accelerator facility at the Beijing Normal University in order to improve the analysis of aerosol samples collected on either quartz or Teflon filters. Replacing the SDD with one with a higher sustainable counting rate minimised the potential for Si-K alpha count rate saturation when analysing quartz filters. As variations in the purge gas flow could have affected the attenuation of soft X-rays and degraded analytical precision, special attention was given to maintaining a constant and reproducible flow of the He purge gas and thereby improve the analysis of low Z elements. The improved LODs were 1-15 ng cm^{-2} for Teflon filter samples with a nominal 60 s data acquisition time and 3-30 ng cm^{-2} for quartz filter samples with a nominal 150 s data acquisition time. A new air analyser with good time resolution comprised[49] either a PM_{10} or $PM_{2.5}$ sampling inlet, a moving filter tape to collect particles as spot samples and an XRF detector. Innovative laboratory experiments involved the generation of simulant aerosols from nebulised elemental solutions, which were dried and split for three-way analysis. One split fed the XRF analyser (for elemental analysis), a second split fed a TEOM (for mass determination) and the third split fed a SMPS for particle sizing. Elemental and mass data were in agreement demonstrating the accuracy of XRF measurements. Data at three locations (downwind of a Ni refinery; at a heavily trafficked road site location; and at an urban location influenced by nearby metallurgical industries) correlated well with data generated using the EU-mandated reference ICP-MS method. The correlation plots for As, Ba, Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, Se, Sr, Ti, V and Zn had a median slope of 1.07 within a median R^2 value of 0.93. Differences in the results were attributed to a combination of factors which included spatial variation in air sampling inlets, elemental blanks in filter media and potential variability in the effectiveness of the mandated sample dissolution procedure for selected elements.

2.5.4 Other instrumental techniques

Thermal-optical analysis for the determination of carbonaceous content of atmospheric particles is well established but application of the methodology can vary from country to country. The development of the new consensus standard method EN 16909 is therefore welcome[50]. The method LOD for total carbon was 2 µg cm^{-2}. When filter loadings were above this LOD, the expanded MU of <25% met performance requirements set out in the EU air quality directive. A seven-wavelength analyser was used[51] in the new DRI model 2015 thermo-optical analyser to give better estimates of the contributions of brown carbon from biomass burning. The isolation of elemental C, the commonly used marker for diesel engine exhaust emissions, by thermal-optical analysis can be compromised by the presence of interfering organic carbon compounds that undergo pyrolysis during combustion. This so-called pyrolytic carbon artifact can then be misclassified as elemental C. Researchers in Sweden minimised[52] this effect by initially extracting ~60% of the organic C from filter samples using a 20 minute SCF procedure that involved supercritical CO_2 containing 10% (*v/v*) methanol at 60 °C and 350 bar. Workers in Finland found[53] that H_2SO_4 condensed on filter samples promoted the formation of pyrolytic carbon in the analysis of exhausts generated from heavy fuel oils used in marine engines. In the AVEC procedure proposed[54] as a new way of presenting organic and elemental C data from thermal-optical analyses, the accumulated carbon concentration was plotted against light attenuation. It was suggested that this plot could be used: to refine the determination of the organic and elemental C split point; to investigate the optical properties of particles collected on filters; or to spot the early evolution of pyrolytic C and/or elemental C during the inert combustion phase. Usefully, software written in R-code was supplied as supplementary material to the paper for other researchers to generate AVEC plots from their own data. Improvements in techniques for the analysis of carbonaceous particles included: a thermal-optical analyser coupled to a quadrupole mass spectrometer for enhanced $PM_{2.5}$ speciation capabilities[55]; better source apportionment by combining data from aerosol mass spectrometry with radiochemical C measurements[56]; and the compound-specific IRA of black carbon in source apportionment studies using HPLC-IRMS[57].

Although a feasibility study demonstrated[58] that direct-on-filter, field-portable FTIR analysis could quantify *respirable-size crystalline silica* in coal dust samples, a PLS regression protocol was required to deconvolute a spectral overlap from the kaolinite commonly present in such samples. A method for the determination of trace airborne concentrations of RCS employed[59] spot sampling to preconcentrate aerosols onto a small impaction target. The instrumental LOD was 8-55 ng and the resultant method LOQ 2-19 µg m^{-3} for a 12 L air sample. Analysis of certified RCS filter samples by a new QCL-based IR technique demonstrated[60] that an instrumental LOD of ~3 µg per filter was feasible. The potential for the development of a new compact hand-held aerosol analyser was therefore good.

New instrumental developments for *nitrogen oxide species* included[61] a new field-deployable method for the simultaneous, real-time measurement of the four most abundant N_2O isotopocules. Coupling of a trace-gas extractor unit with a QCLAS enabled autonomous operations at remote monitoring sites to be conducted at a sampling frequency of ~1 per hour with repeatabilities better than <0.17‰. A fully autonomous QCLAS was successfully deployed[62] on a tram in Zurich to provide city-scale NO_2 concentration maps at high spatio-temporal resolution. Initial laboratory tests at typical urban NO_2 air concentrations gave precisions of 0.23 ppb at one-second integrations and 0.03 ppb after 200 s averaging. Comparison of results with those obtained by reference CLD revealed a systematic NO_2 loss of ~10% to the internal walls so a calibration correction was required prior to deployment. In operational use, temperature-dependent drift within the optics was easily corrected by regular baseline measurements of NO_2-free air provided *via* a separate air sampling line equipped with a NO_2 scrubber unit. A new photometer design enabled[63] measurements of both NO_2 and NO to be made just a few seconds apart. The NO_2 species was measured directly by absorption at 405 nm. The NO species was converted to NO_2 by *in-situ* reaction with O_3 and then measured as NO_2. The folded tubular design enabled an effective optical path length of 2 m to be packaged within a compact size. The LOD was <1 ppb. Interestingly, the authors proposed a similar photometric approach for the measurement of other key atmospheric pollutants such as black carbon or SO_2 – so readers should watch this space!

3. Water Analysis

3.1 Sample preconcentration and extraction

Fewer *review papers* were published this year in comparison to previous years, perhaps reflecting the maturity of the methods currently used, and tended to be more specific– for example on the use[64] of functionalised nanomaterials for SPE prior to analysis by ICP-MS (190 references) or the continued use[65] of micro-extraction for speciation analysis of Se in various matrices including water (52 references). The endless quest to extract Cd from environmental matrices was extensively covered[66] (91 references).

The most significant advances in *analyte preconcentration for water analysis* are summarised in Tables 1–3.

3.2 Speciation and nanomaterial analysis

3.2.1 Elemental speciation.

Methods continue to be developed for the *speciation analysis of arsenic* in water samples. A two stage SPE method used[67] a silica column modified either with the strong anion exchange trimethyl aminopropyl functional group to retain As^V selectively or with silver chloride to retain both As^{III} and As^V. Organic As species such as DMA were not retained by either material and were quantified in the column eluent. The As^{III} concentration was calculated by subtracting the organic As and As^V concentrations from the total As concentration. The LODs for ICP-AES detection were 2.30, 1.48 and 2.51 µg L^{-1} for As^{III}, As^V and DMA, respectively. Recoveries from industrial waste waters were quantitative for all determinands. It should be noted that the authors assumed that DMA was the only organo-arsenic compound present. In a simplified IC-ICP-MS method[68] for the separation and detection of As^{III}, As^V and AB in ground and bottled waters, the analytes were eluted isocratically (50 mM $NaHCO_3$, 1.0 mL min^{-1}, 200 s) with baseline resolution from an IonPac® AS9-HC column (4 mm id x 250 mm long). The LODs were 6.2, 16.5 and 14.1 ng L^{-1} for AB, As^{III} and As^V, respectively. In the analysis of NMIJ CRM 7901-a (arsenobetaine reference standard) and UME CRM 1201 (spring water), the sum of the concentrations of the As species agreed with the certified total As concentration. Gilmartin and Gingrich[69] suggested that, as the US EPA drinking water control limit is relatively high at 10 µg L^{-1}, instrumentation more widely available than HPLC-ICP-MS would be suitable for analysis. They compared the sensitivity of HPLC coupled with UV or MS/MS detection with that of HPLC-ICP-MS. However, the standard HPLC conditions used (Hamilton PRP-X100 column plus a stepped buffer gradient) gave poor LODs of 454 (As^{III}) and 56.2 (As^{V}) µg L^{-1} for UV detection and 45.4 (As^{III}) and 56.2 (As^{V}) µg L^{-1} for single ion monitoring mode with MS detection. Only MS detection in MRM mode (LODs of 4.54 (As^{III}) and 5.62 (As^{V}) µg L^{-1}) or ICP-MS detection would be suitable for detecting As below the drinking water limit.

A series of *tetrabromobisphenol-A-based brominated fire retardants* were successfully determined[70] in river, tap and seawaters by HPLC-ICP-MS/MS. Using a binary gradient elution system of 0.1% (*v/v*) acetic acid added to methanol (eluent A) or water (eluent B), seven fire retardant derivatives of the tetrabromobisphenol molecule were separated on a 15 cm long standard bore C_{18} column. An instrumental LOD of 0.1 µg L^{-1} for ^{79}Br was achieved when ICP-MS/MS detection (H_2 reactant gas) was used. For real samples, a 200 mL filtered aliquot was adjusted to pH 4-5 with HCl and extracted three times with 100 mL dichloromethane. The combined extracts were dried and the residue dissolved in 1 mL of methanol:water (4+1) of which 50 µL was injected onto the column. This extraction procedure gave recoveries of 84% (tap water) to 105% (seawater) depending on the spike level, and a MDL of 0.7-1.0 ng L^{-1} dependent on the target analyte. This performance was sufficient to detect tetrabromobisphenol A in a seawater sample and tetrabromobisphenol A-bis(2-hydroxyethyl ether) in a tap water sample.

Manganese in the +2 and +7 oxidation states was successfully separated[71] on a column of C_8-bonded silica using a pH 7.5 aqueous mobile phase containing 1mM tetrabutylammonium hydroxide as an ion pairing agent and 0.36 mM EDTA as a complexing agent for Mn^{II}. Baseline resolution was achieved in <8.5 minutes when a flow rate of 1 mL min^{-1} was used. The ICP-MS LODs were 0.22 and 1.55 µg L^{-1} for Mn^{II} and Mn^{VII}, respectively. Although maintaining the stability of the sample could be difficult because Mn^{VII} converts to Mn^{II} slowly over time if present as the dominant form, this situation was actually unlikely for tap water samples. Results for the SCP Science ES-H-2 (ground water) and EU-H-3 (waste water) RMs were well within the expected ranges. The Mn^{II} concentrations in bottled, tap and artesian waters were successfully determined. In the opinion of this reviewer, this method is ripe for the use of SSID to correct for the redox interconversions that occur in the samples.

In a sequential extraction scheme for the *selective extraction of* Pt^{II} *and* Pt^{IV} *from river or tap water*, platinum ion associates were formed[72] in solution after reacting the chloro-anions of Pt with 5 mL of 5 × 10^{-3}M NaSCN and 5 mL of 1 × 10^{-3}M 1,3,3-trimethyl-2-[3-(1,3,3-trimethyl-1,3-dihydroindol-2-yliden)-propyl-1,3-dienyl]-3H-indolium chloride. These complexes were dispersed in the sample using DMF and then back extracted into 1 mL toluene before determination by ETAAS. Separation of the species occured because the ion associates of Pt^{II} formed easily and were extracted first whereas Pt^{IV} ion associates only formed after sonication (400 W) of the sample for 5 minutes. For a 25 mL water sample, the LOD was 0.3 µg L^{-1} Pt.

The LODs for *the determination of organolead, mercury and tin species by GC-ICP-MS* were improved[73] (for example to 0.1 pg L^{-1} for TML and to 12.6 pg L^{-1} for Hg^{2+}) by adopting large volume injections. This was made possible by removing high-boiling-point matrix components through use of a programmed-temperature vaporisation inlet packed with the Bondesil-ENV, 125 µm, styrene-divinylbenzene polymeric resin on which analytes were preconcentrated at the head of the column. The analytes in a 50 mL sample were propylated with sodium tetrapropylborate and extracted into 500 µL of hexane. Three 25 µL sequential injections were made. Good results were achieved for a GEOTRACES comparison sample when using external calibration and isotopically labelled internal standards. Results for river water samples agreed with those obtained using the standard GC-ICP-MS method already in use by the authors.

3.2.2 Characterisation and determination of nanomaterials.

Two *reviews* on sample pretreatment are worthy of note. One, in the Chinese language, reviewed[74] (66 references) the progress made in the detection of NPs in water samples. The other was more specific and reviewed[75] (66 references) the use of CPE before the spectrometric detection of NPs. Although not strictly within the scope of this Update, a review[76] of the sources, pathways, fate and ecotoxicology of NPs will be of interest to any environmental scientist and highlights why so much effort is put into their detection and quantification.

Although the instrumental settings for *single particle counting of nanoparticles by ICP-MS* seem to have been standardised, sample treatment has not. Dilution of samples to the concentration range of 1-25 x 10^4 particles per mL provided[77] linear and reproducible results. Centrifugal filtration and asymmetric FFF as pretreatment steps to eliminate the ionic fraction and to reduce the size LOD were considered unsuitable due to loss of finer material. Analysis of lake and tap water samples gave results below the instrumental LOD for total silver (value not reported) and below the size distribution LOD of 12-15 nm. When samples were spiked with 50 and 80 nm silver NPs at a concentration of 50×10^3 particles mL^{-1}, the measured particle sizes were 49 and 76 nm, respectively, and the particle number recoveries 84 and 135%, respectively. This suggested overestimation of the number concentration for the larger particles. The agreement of results with those obtained from TEM and asymmetric FFF analyses demonstrated that sp-ICP-MS was suitable as a first screening method for environmental samples. To enable the size characterisation of smaller (<60 nm) silver NPs, 10 mg of magnetic graphene oxide were added[78] to a 10 mL solution containing 2 µg L^{-1} Ag^+ and 0.05 µg L^{-1} of silver NPs for selective DME of the interfering Ag^+. After removal of the graphene oxide, the silver background decreased from around 500 cps to about 10 cps, thereby reducing significantly signal overlaps and improving discrimination of particle events above the background signal. Prior to extraction only particles above 60 nm could be distinguished but after removal of 98% of the Ag^+, particles down to 30 nm in diameter could easily be characterised. The method was tested on various river waters spiked with 0.25 µg L^{-1} Ag^+ and 50 ng L^{-1} silver NPs.

3.3 Instrumental analysis

3.3.1 Atomic absorption spectrometry.

By choosing resonance lines with wavelengths close together, it was possible[79] to determine Rh and Ru simultaneously in the *CS-ETAAS analysis* of water, ore and road dust samples. Best results were obtained by using the Rh 343.489 nm line and the adjacent secondary line of Ru at 343.674 nm. Under optimised pyrolysis and atomisation temperature conditions and by using three pixels per line for signal acquisition, the LODs were 1.0 and 1.9 µg L^{-1} for Rh and Ru, respectively. Analysis of SARM CRM 76 (Platinum ore) gave good recoveries (93 and 90% for Rh and Ru, respectively). For spiked river water samples, recoveries were 85 and 93% for Rh and Ru, respectively. Bromine could be determined[80] indirectly in bottled and tap water samples by adding 15 µL of a 10 g L^{-1} Tl modifier to the sample in the furnace and detecting the TlBr rotational line at 342.9815 nm. Silver nitrate was used as an additional modifier to precipitate and stabilise Br as AgBr so that a pyrolysis temperature of 400 °C could be used to eliminate concomitant element interferences. Optimum TlBr formation occurred at an "atomisation" temperature of 900 °C, giving a LOD for a 10 µL sample injection of 30 µg L^{-1}. Results for the analysis of the Sigma Aldrich QC 1060 (anions) RM gave results in agreement with the certified values and those for analysis of tap and bottled waters agreed well with results obtained using the authors' standard method (cathodic stripping chronopotentiometry).

In-furnace *preconcentration by repeat injection* has been rediscovered[81] for the determination of Tl in drinking waters by ETAAS. Using a 2 g L^{-1} ascorbic acid solution as a modifier and 10 drying (90-120 °C ramp) and pyrolysis (650 °C) steps before atomisation at 1400 °C, a LOD of 0.01 µg L^{-1} was obtained. Results for drinking waters compared well with those obtained using ICP-MS. Analysis of the Chinese water RMs GSB07-1978-2005 (206702, 206706, 206704) gave results within the certified values.

3.3.2 Vapour generation.

A method for *electrolytic hydride generation* for the determination of Se^{IV} in waters involved[82] reduction of Se^{IV} to SeH_2 using an L-cysteine-modified carbon paste electrode before detection by AFS. Using the modified electrode as the cathode (current density 200 mA cm^{-2}, 0.5M HCl as the catholyte solution) and a platinum anode (0.5M H_2SO_4 as the anolyte solution), Se^{IV} was selectively and quantitatively reduced to SeH_2 gas. At a sample flow rate of 3.5 mL min^{-1} the LOD was 0.065 µg L^{-1} and the dynamic range linear between 0.5 and 60 µg L^{-1}. Recoveries from spring water were 97% for a 10 µg L^{-1} spike and 93% for a 20 µg L^{-1} spike. The results obtained for unspiked samples were in good agreement with those obtained using the authors' standard HG-AFS method.

The use of *photochemical vapour generation with photocatalysts* is becoming more widespread to improve the effectiveness and speed of reaction. A nanoscale amine-functionalised titanium-metal organic framework (MIL-125) was used[83] to improve the generation efficiency for Se^{IV} and Se^{VI} in solution. After careful optimisation of the UV irradiation time, carrier gas, flow rate, pH and concentration of organic acid, a catalytic conversion efficiency of >80% was achieved resulting in an LOD of 0.3 ng mL^{-1} with ICP-AES detection. Analysis of the Chinese CRM GBW(E) 080395 (water) gave a result that fell just inside the range of certified values and the analysis of a water sample gave a value that agreed well with that obtained by ICP-MS analysis. When the internal walls of a microfluidic device were coated[84] with Au-coated TiO_2 NPs as photocatalyst, the PVG of inorganic As species occurred within 15 s at an irradiation wavelength of 365 nm and power density of 11 mW cm^{-1}. This meant that the device could be used as an interface between an HPLC column and an ICP-MS instrument for the determination of As^{III} and As^{V} in the eluent from the chromatographic column. Optimisation of the pH, formic acid concentration and pre-reduction step with 0.1% (*m/v*) $Na_2S_2O_4$ gave spike recoveries of >92% for both species even in the presence of high concentrations of coexisting ions. The LODs for the optimised method were 0.23 and 0.34 µg L^{-1} for As^{III} and As^{V}, respectively, and spike recoveries from industrial ground water were 93%. Analysis of the NIST SRM 1643e (trace elements in water), for which the total As concentration has a certified value of 60.45 ± 0.72 µg L^{-1}, gave a concentration of 55.83 ± 0.36 (n=3) µg L^{-1} for As^{V} .

3.3.3 Inductively coupled plasma atomic emission spectrometry.

Although popular for AAS analysis, *the use of DLLME with plasma instruments* is not particularly favoured due to the viscosity of the solvents used. Researchers in Spain employed[85] three of the most commonly used solvents in DLLME procedures (1-undecanol, the ionic liquid 1-butyl-3-methyl-imidazolium hexafluorophosphate and chloroform) to investigate the main problems experienced when coupling DLLME with ICP-AES. The first two solvents are very viscous and immiscible with water so simple dilution (1+1 or 1+0.5) with methanol improved their nebulisation and transport efficiency. Use of a FI manifold further improved analysis. Although chloroform can be directly introduced into the plasma, the authors recommended the use of FI with dilute HNO_3 or HCl as the carrier solutions. Under optimum conditions when using 1-undecanol or chloroform, recoveries from sea, tap and river waters were quantitative for a 100 µg L^{-1} multielement (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) spike. The LODs ranged from 0.7 (Ni) to 35 (Al) µg L^{-1}. The ionic liquid extractant gave a quantitative recovery only for Pb with a LOD of 5 µg L^{-1}. The authors concluded that with careful optimisation ICP-AES can be used with DLLME, thereby exploiting the multielement detection capability of this technique.

3.3.4 Inductively coupled plasma mass spectrometry.

A review (69 references) of *antimony isotope ratio analysis* covered[86] the use of MC-ICP-MS, as well as preconcentration, separation and sample introduction methods.

The high sensitivity and selectivity of ICP-MS/MS means it is often used for *single element determinations* in water. Gallium was determined[87] in natural water by ICP-MS/MS in both collision and reaction modes so that IDA could be used to quantify Ga accurately. Although the ^{71}Ga signal acquired in H_2 collision mode had no appreciable interference from MnO^+, the ^{69}Ga peak was significantly interfered by Ba^{2+} so NH_3 had to be used as a reaction gas to mass shift the analyte to *m/z* 86. Using a high efficiency nebuliser, the best LOD obtained was 0.02 ng L^{-1} for *m/z* 71 with H_2 as the collision gas. At *m/z* 86 the LOD was 0.28 ng L^{-1}. Analysis of the NWRI RMs TM 9.2 and TMDA 64.3 (waters) gave results in good agreement with the reference values. Analysis of a series of mineral and ground waters showed that measurements at both masses gave comparable results so the use of IDA could be an appropriate approach in future research. The addition of Ba to the carrier flow via a T-piece allowed[88] the determination of F by ICP-MS/MS as the $^{138}Ba^{19}F$ ion. The ions at *m/z* 157 were selected in the first quadrupole and interfering ions removed by collision with O_2 in the collision cell. The signal response in the second quadrupole at *m/z* 157 was proportional to the F concentration. The LOD was 0.043 mg L^{-1} for total F. The recovery for water samples spiked with 1 mg L^{-1} of F was 97 ± 4% (n=10). The reaction was rapid enough to allow the coupling of a chromatographic method for fluoride and fluoroacetate analysis to the ICP-MS instrument. The F response was independent of the compound being analysed so ICP-MS analysis would be suitable for the determination of other F-containing organic compounds. To determine ^{238}U directly in filtered acidified seawater, the two quadrupoles were set[89] at *m/z* 233 and 238, respectively. By using no reaction or collision gas in order to avoid signal attenuation, the formation of $^{232}Th^1H$ was reduced to negligible levels. Use of the $^{238}U/^{233}U$ ratio in the IDA gave best results for the IAEA-381 (seawater) interlaboratory comparison standard when samples were diluted 20 times. The LOD was 0.1 ng L^{-1}.

The high sensitivity of ICP-MS/MS means it is now being investigated for *the determination of radioisotopes* in water. By setting both quadrupoles to *m/*z 210 without any reaction or collision gas to avoid any loss of signal, it was possible[90] to determine ^{210}Pb in drinking water with an instrumental LOD of 314 fg L^{-1}, the equivalent of 0.9 Bq L^{-1}. However, this level was still well above the WHO control level of 100-200 mBq so a previously published CPE preconcentration method followed by back extraction of ^{210}Pb from a 390 mL sample was employed to lower the LOD to 15 fg L^{-1} (45 mBq L^{-1}). This had the added advantage of removing the polyatomic interferences from Bi, Er and Pt. The sample turnaround time of 4.5 h was a considerable improvement over the 3-6 days required for liquid scintillation counting.

Using ICP-MS/MS in single quadrupole mode with He as a collision gas, ^{226}Ra was determined[91] directly in ground water at levels down to 1 Bq L^{-1}. The method LOD could be reduced to 5 mBq L^{-1} by using standard radiometric sample preparation procedures (SPE and evaporation) to preconcentrate from 1 L samples. In comparison to analysis using α-spectrometry which has an acquisition time of 5 days per sample, sample throughput was much improved due to the ICP-MS/MS acquisition time of just 5 minutes per sample.

The *use of LA-ICP-MS* for the determination of Hg in water has been proposed[92]. Mercury was preconcentrated onto a printed gold electrode in the field using portable voltammetry. Use of a deposition voltage of 0.2 V ensured the electrodeposition of all inorganic and organic mercury species. In the laboratory the electrode was placed into a custom-made 15 cm^3 LA cell and was ablated with a 266 nm laser operating at a spot size of 160 µm, a pulse repetition rate of 20 *Hz* and sampling rate 35 µm s^{-1}. The method LOQ was 0.2 µg L^{-1}. The method was validated against the Chinese CRM GBW08603 (water). The concentrations in river waters were below the LOQ but spike recoveries at 0.5 and 10 µg L^{-1} were 98-101% even for effluent samples. The direct analysis of ice cores by LA-ICP-MS means that high temporal resolution data can be obtained. In the estimation of subannual variability in dust levels , a 2.85 m long section of the North GRIP ice core was cut[93] into 50 x 11 x 11 mm slices that could be placed into a custom cryocell in which the samples were ablated with a UV laser (200 µm spot size). The major elements Al, Ca, Fe, Mg and Na were detected by ICP-MS. An ice sample spiked with the NIST SRM 1648a (urban dust) was used to calibrate the procedure. The LODs were between 0.6 (Ca) and 48 (Na) µg L^{-1}. Analysis of a section of the core from 2691.20 m below the surface showed that a large drop in elemental concentrations occurred over only 10 mm (corresponding to approximately 1 year). This was at a point where other research had identified a switch between a climatic stadial (cold) to an interstadial (warm) period occurred demonstrating that high resolution elemental analysis can complement stable isotope and other high resolution analyses for this kind of sample.

Although MC-ICP-MS would usually be used for *isotope ratio analysis of natural waters*, a quadrupole ICP-MS method has been published[94] for the determination of Sr isotope ratios in mineral waters and wine. To separate Sr from the interfering Rb isotopes, Sr was coprecipitated out of solution by the slow addition of a 1M Na_2CO_3 solution. Following washing with the coprecipitation solution, the precipitate was redissolved in 0.5M HNO_3. The instrument was used in time-resolved analysis mode so that only one point per peak was used with an integration time of 0.05 s per isotope thereby increasing the scanning speed over a

120 s acquisition. A series of sample dilutions were analysed for their Sr isotopic composition to generate a plot in which the slope gave the isotope ratio in the sample. This allowed signal variations due to the plasma or sample dilution to be corrected. Mass bias was corrected for using the NIST SRM 987 (strontium carbonate isotopic standard). Analysis of an in-house standard gave a δ^{87}Sr value of −12.37 ± 0.66‰. It was possible to discriminate between 3 mineral waters using the measured δ^{87}Sr values. An improved metal-free low-volume distillation method was developed[95] to separate Br from Cl in water and seawater before determination of the Br isotope ratio by MC-ICP-MS. In the traditional method, Br^- is oxidised to Br_2 which is distilled into a KOH collector solution as BrO^- before reduction to Br^- by boiling with metallic zinc. Analysis of this final solution would have contaminated the instrument with high levels of Zn, so to avoid this, the authors oxidised the Br^- with HNO_3 added in the ratio of 1+4 HNO_3:sample up to a maximum sample volume of 8 mL. The sample was heated with a candle and the distillate collected in 1 mL 0.5 M NH_3 receiver solution for 10 minutes or until the receiver solution volume reached 1.5-3 mL. The Br collected was stable in this solution without the need for reduction to Br^-. Analysis of 15 aliquots of an in-house seawater standard gave a mean δ^{81}Br value of +0.06 ± 0.11‰ (1SD). This compared well with results from a chromatographic separation method. The determination of S isotopes by MC-ICP-MS is hampered by the $^{16}O^{16}O$ interference on ^{32}S. Although this can be prevented by using a desolvation system, the high affinity of S (as SO_4^{2-}) for the membranes used[96] results in a large signal loss (>90%) and memory effects. Addition of NaOH to the sample at a Na:S mole ratio of 2:1 resulted in the formation of Na_2SO_4, a molecule that is thermally stable and has little affinity for the desolvation membrane, thereby reducing memory effects and signal loss (<2%). At concentrations of 3 nM S in pore waters, this improved method gave accurate determinations of δ^{34}S and Δ^{33}S (2SD precisions of ±0.18 and ±0.10‰, respectively) when the results were compared to those obtained for the NIST SRM NASS-5 (seawater) by IRMS and for a mono-elemental RM by ICP-MS.

3.3.5 Laser induced breakdown spectroscopy.

The trend for coupling well-tested atomic spectroscopy sample introduction techniques to LIBS continues as demonstrated[97] by *the use of HG-LIBS* for the determination of As in waters. A standard GLS unit was coupled to a PTFE laser cell for the generation of an As-rich plasma. The As emission at 228.8 nm was measured using a fibre optic cable connected to an echelle type spectrometer. The presence of the hydride-forming elements Sb and Sn at concentrations above 50 mg L^{-1} caused a 60% reduction in the As signal. Although no LOD was given, As was detectable at concentrations above 10 µg mL^{-1}.

3.3.6 X-ray Fluorescence spectrometry.

As with LIBS analysis, *preconcentration* is required before XRFS elemental analysis of water samples is possible. Coprecipitation of Cd, Cr and Pb from water using a mix of NaOH and NaS as precipitating agents resulted[98] in an homogeneous thin film that could be analysed by EDXRFS. The LODs for 50 mL samples were 7.4 (Cr) to 29.6 (Cd) µg L^{-1}. Results for the analysis of waste water discharges compared well to those obtained by ICP-MS analysis. The direct determination of F in water by TXRFS was achieved[99] by depositing 5 µL of sample onto F- and O-free Si wafer supports in the absence of acidic internal standards thereby preventing formation of volatile HF during drying. The F K-line intensity was measurable at F concentrations >100 ng mL^{-1} in low-matrix waters such as tap water. Spike recoveries were good and within the range of 2-16 µg mL^{-1}.

4. Analysis of soils, plants and related materials

4.1 Review papers

Two *broad-based reviews* have appeared in the year covered by this Update. In one (107 references), on the analytical techniques used in paleotempestology studies of past tropical cyclones in the western North Atlantic Basin, the analysis of tree rings was discussed[100]. Most of the review was concerned with either the application of X-Ray spectrometry to the analysis of mineral cores or with the use of proxies, such as grain-size analysis and loss-on-ignition. The report for a long-term study of the transformation of PTEs in soil/water/sediment systems included[101] a review of sequential extraction procedures. The researchers also presented work aimed at improving the BCR methodology, in particular by the use of CF systems and sonication (to accelerate leaching).

Reviews on the *determination of individual elements* have also appeared. In one (121 references) of thiolated As in natural systems, the authors provided[102] an overview of formation mechanisms, reaction chemistry, speciation and analytical methodologies. Unsurprisingly, the reviewers concluded that future research needs to be devoted to determining the molecular structure of unknown thioarsenic compounds in various environmental samples. In reviewing (85 references) Sb measurements in environmental matrices, Maher *et al.* [103] reported that it was not possible to quantify organic Sb species in plants because of the oxidation of Sb^{III} to Sb^{V} and the formation of artefact Sb species. It was therefore thought that XAS should be considered for this analysis as it can discriminate between Sb^{III}, Sb^{V}, Sb minerals, oxides, and adsorbed Sb species. A review (46 references) covered[104] the application of NAA and ID-MS to the determination of metals and metalloids in dietary supplements. In addition, speciation studies in which separation techniques combined with element-specific detectors were considered.

Reviews on the *applications of several laser-based techniques* included a discussion by Bauer and Buckley[105] (52 references) of recent and novel applications of LIBS. Also discussed were calibration-free and indirect measurements, such as that of pH and humification in soil and heating value in coal. The analyses of agricultural materials, coal, minerals, and metals were included in the review as was the potential of spatial heterodyne spectroscopy to overcome, through the use of interferometers, the limitation of the small optical throughput of most spectrometers. Both LIBS and LIFS methods were considered[106] (36 references) suitable for measuring the degree of humification of soil organic matter in whole soils. In particular, LIFS could be used to probe the whole solid soil sample, thereby avoiding the need for chemical or physical treatments to separate organic matter from the mineral matrix. It was also concluded that the emerging application of LIBS to whole soils appeared promising due to its good sensitivity, selectivity, accuracy and precision. In a review by Busser *et al.*[107] (83 references) on elemental imaging by LIBS, particular attention was paid to the *in situ* elemental profiling and mapping of metals in biological materials, including plants. Advantages of this technique included minimal sample preparation, compatibility with optical microscopy and the simultaneous detection of low and high-Z elements. Advances in the applications of LA-ICP-MS are such that publications in just the past three years merited a review[108] (142 references). The authors highlighted the value of fast wash-out ablation cells and calibration strategies such as ink printing and dried-droplets for applications such as the mapping of elemental distributions in biological samples (including plant tissues), detection of NPs and protein and single cell analyses.

4.2. Reference materials

Various comparison studies have featured *soil, vegetation and sediment CRMs*. The NIST SRMs 2709a (San Joaquin soil) and 1515 (apple leaves) were included[109] in the suite of eight RMs used in an interlaboratory comparison of MC-ICP-MS methods for the determination of ^{25}Mg and ^{26}Mg isotopic abundances. It was concluded that all the materials were suitable for validation of ^{25}Mg and ^{26}Mg determinations in geochemical studies. The ^{129}I content of three environmental CRMs were determined[110] by AMS and TIMS. One of the materials, IAEA-375 (soil collected approximately 160 miles northeast of Chernobyl), is currently the only soil/sediment material with a certified ^{129}I activity but has not been available for purchase since 2010. The other two materials, NIST SRM 4354 (freshwater lake sediment) and NIST SRM 4357 (ocean sediment) have certified activities for a variety of radionuclides but not for ^{129}I. The discrepancy between the values measured by AMS and TIMS in this study and those published previously indicated that a more thorough ^{129}I assessment was needed, including measurements by other laboratories, before these two NIST SRMs will be useful in the determination of ^{129}I. The researchers concluded that there is an immediate need for CRMs with known ^{129}I concentrations. As the lack of CRMs was seen as the main problem in the QC of the determination of ^{237}Np in environmental samples, Benedik and Trdin[111] used a combination of three techniques (γ-ray spectrometry; α-particle spectrometry following separation of Np radioisotopes by ion-exchange or extraction chromatography; and pre-separation radiochemical NAA) to determine ^{237}Np in a variety of environmental materials, including CRMs, sediments and soils. The Ge concentrations for three Chinese soil CRMs (GBW 07401, GBW 07404 and GBW 07407) were revised[112] and a value proposed for the plant CRM ERM-CD281 (ryegrass).

4.3 Sample preparation

4.3.1 Sample preservation

Dry and wet preservation methods were studied[113] for the determination of Cd, Cr, Cu, Hg, Mn and Pb in indocalamus leaves by ICP-MS. The first method involved drying in hot air, the second boiling and sealing in a bag. Both methods decreased the concentrations of Cd, Cr, Mn and Pb, in indocalamus leaves but wet-preservation resulted in high concentrations of Cu and so was not recommended. Of two digestion methods (HNO_3-H_2O_2 and HNO_3-HF) used, the latter resulted in more complete digestion and so gave more accurate results. The accuracy of the method was validated by the analysis of two CRMs, NIST SRM 1547 (peach leaves) and GBW 08513 (tea leaves). The LOD was 0.003 ng L^{-1} to 0.516 ng mL^{-1} and the MDL 12-96 ng g^{-1}. The recoveries for both methods were 80-115%.

4.3.2 Sample dissolution and extraction

Reviews of aspects of sample preparation included that of Karak *et al.*[114] (222 references) which covered methods for the determination of micronutrients in tea leaves and in their hot water extracts. An *et al.* reviewed[115] (273 references) the use of "non-conventional" solvents in LPME and aqueous biphasic systems as the basis of rapid sample preparation methods. Examples of applications to the analysis of tea, medicinal plants and rice were included. Duborska and Bujdos[116] summarised the most widely used analytical and sample preparation methods for the determination of I in plant tissues and soils (62 references).

The topic attracting most attention in the sample preparation of soils has been *acid extraction*. The best MAE procedure for the determination of multiple elements in organic soil amendments used[117] a mixture of 3 mL HNO_3, 1 mL HBF_4 and 2 mL H_2O for 150 mg of sample and was validated by the analysis of a CRM (Sigma-Aldrich sewage sludge CRM 029). In the comparison[118] of open-vessel digestion on a hot plate and closed-vessel MAE for the multi-elemental analysis of the organic-rich soil CRM BCR 700, the MAE procedure was faster and easier to use. In a method for the determination of Cd in soil micro-arthropods, a sample mass of 50-150 µg was digested[119] with 30 µL of a HNO_3-H_2O_2 (3+1) mixture at 105 °C for 3 h. Two analytical procedures based on the generation of volatile TBT derivatives, their separation by headspace SPME and subsequent determination using ICP-AES were developed[120] for the selective determination of trace TBT in the presence of other butyltins and inorganic tin in sediments without the use of chromatography. A microwave-assisted leaching of Sn compounds from the sediment using 25% *(v/v)* acetic acid was applied as sample pretreatment. The first method took advantage of TBT chloride releasing from the lecheate after adding 3M HCl. The analyte was subsequently obtained by headspace SPME using carboxen-poly(dimethylsiloxane). The second method involved the use of masking agents, namely EDTA and diphenylcarbazone, which formed stable chelates with MBT and

DBT, respectively, followed by the ethylation of TBT at pH 5 using sodium tetraethylborate. The methods were validated by the analysis of several CRMs, including NRCC marine sediments PACS-2 and SOPH-1, and BCR 646 (freshwater sediment).

The *acid digestion of plants* has attracted considerable attention. For the comparison of the digestion and spectroscopic determination methods used to measure B concentrations in maize shoots, increasing doses (0, 2.5, 5 and 10 mg kg^{-1} B) were applied[121] to soil and maize plants. Although the measured concentrations were dependent on the sample preparation and measurement procedures used, there were no statistically significant differences between the results obtained using dry ashing and MAD when the final determination was by ICP-AES. Therefore the ICP-AES measurement was considered compatible with both dry ashing and MAD and so was suggested as a suitable method to determine B contents of maize shoots. The effects of boiling time and acidity were studied[122] in the determination of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in aqueous herbal teas extracts by various acids including lemon juice Multivariate techniques such as redundancy and PCA were used. Metal release was not considerably affected by the boiling time whereas the acidity of the medium was generally positively correlated. The extraction efficiencies of the metals were classified as highly, moderately, and poorly extractable, with Cr showing largest variations. The optimised procedure for the extraction of Ca, Cu, Fe, Mg, Mn and Zn from cassava peel involved[123] extraction with dilute HNO_3, HCl and acetic acids assisted by ultrasound and microwave radiations. The accuracy was checked by the analysis of NIST SRM 1515 (apple leaves) and by comparison of the results with those obtained with a microwave-assisted total digestion method. A fast analytical method for the determination of Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn in foodstuff samples by ICP-AES involved[124] the use of ultrapure 50% (*v/v*) formic acid on a heating block. The recoveries for three NIST SRMs were 80.7-114% and the RSDs <20%. The LODs were 0.06 to 600 mg kg^{-1}. It was concluded that the formic acid procedure is a simple alternative to MAE and, as formic acid is not an oxidant, that it has potential as an extraction procedure for speciation analysis.

The *advantages of acid extraction* include speed, simplicity, low cost and use of diluted acid solutions in mild conditions (temperature and pressure). However, most extraction procedures are performed in batch mode and so are more laborious, time-consuming and susceptible to errors than procedures employing flow and flow-batch modes. A flow-batch system was developed[125] for the online determination of macro and micronutrients in dried plant leaves by ICP-AES with the aim of producing a fast screening procedure. The procedure was simple to operate, inexpensive, allowed online determination and could easily be applied in any routine analysis laboratory. The best efficiency extraction was achieved using 50 mg of dried spinach leaves, 10 mL of 8% (*v/v*) HCl and a 4 minute extraction time even though some elements (Cu, K, Mg, Mn and Na) could be extracted in as little as 30 s.

Standard protocols for the digestion of plant matrices do not generally involve the use of HF and so silica will remain in the solid phase after digestion. A study on the determination of Cu, Mn and Zn in herbs by FAAS showed[126] that *incomplete oxidation of carbon* was beneficial as the residual carbon blocked silica surfaces, and so prevented reabsorption of the metal ions. It was advised that particular attention should be paid to the presence of silicon in plant samples, including CRMs for which silicon contents are rarely given.

Selenium isotope variations have been proved to be a powerful tracer for redox processes and are therefore promising for the exploration of the species-dependent Se metabolism in plants. The analysis of plant tissues and growth medium (phytoagar) is particularly challenging and requires specific preparation and purification steps to ensure precise and valid Se isotope data. Validation tests on Se-free plant material and phytoagar doped with a RM of known Se isotope composition revealed[127] the high impact of organic residues on the accuracy of MC-ICP-MS measurements. Extraction using either a MAD procedure for plant tissue or a vacuum filtration method for phytoagar gave full Se recoveries and reduced organic residues to a minimum. Only the purification method with no detectable organic residues, HG and trapping, resulted in valid mass bias correction for plant samples with an average deviation to true $\delta^{82}Se/^{76}Se$ values of 0.2 ‰ and a reproducibility (2SD) of ± 0.2 ‰. For phytoagar, this test yielded a higher deviation of 1.1‰ from the true value and a reproducibility (2SD) of ± 0.1 ‰. The developed methods provided sufficient accuracy and precision to be considered a promising approach to resolve plant internal Se isotope fractionations, for which $\delta^{82}Se/^{76}Se$ values of +2.3 to +3.5 ‰ for selenate and +1.2 to +1.9 ‰ for selenite were obtained.

Understanding the translocation of *nanoparticles* into plants is challenging because qualitative and quantitative methods are still being developed and the comparability of results produced by different methods remains uncertain. A study on the uptake of TiO_2 NPs and larger BPs in rice plant (*Oryza sativa L.*) used[128] electron microscopy and sp-ICP-MS to analyse plant extracts. Two dissolution procedures were evaluated for their ability to dissolve particles without causing aggregation. An acid digestion procedure resulted in higher particle numbers and the detection of a broader range of particle sizes than an enzymatic digestion approach and so highlighted the need for development of robust plant digestion procedures for NP analysis. The ICP-AES total elemental analysis of plants exposed to TiO_2 NPs and BPs at 5 and 50 mg L^{-1} concentrations revealed that TiO_2 NPs penetrated into the plant root and resulted in higher Ti accumulation in above ground tissues than that produced by BPs.

Several procedures were developed with *extraction and digestion reagents other than acids*. A microwave-assisted wet partial-digestion method using H_2O_2 in a high-pressure system was developed[129] for the determination of Br, Cl and I in soils by ICP-MS. Sample masses of 50 and 25 mg containing 50 and 98% organic matter, respectively, were digested efficiently with just 5 mL of 50% H_2O_2 solution at a maximum temperature of 250 °C. The inaccurate results for I obtained at lower digestion temperatures were attributed to the formation of I_2 during nebulisation. The method was validated[130] by the comparison of the results with those obtained by pyrohydrolysis and by the analysis of NIST SRM 1632c (bituminous coal). The ICP-MS determination of I is prone to both memory effects and isobaric interferences. To support the study of ^{131}I deposition following the Fukushima Daiichi Nuclear Power Plant accident, a method of extraction with TMAH at 90 °C was developed[131]. Oxidation with $K_2S_2O_8$ released I from co-extracted organic matter. The addition of ammonium sulfite (0.01% (*m/v*)) overcame memory effects, and the use of LLE avoided both a matrix effect and isobaric interferences in the subsequent ICP-MS-MS analysis. The method was validated by the analysis of several CRMs and was applied to the determination of ^{129}I and $^{129}I/^{127}I$ ratios.

Residual carbon can be an issue in the determination of As because it can enhance ionisation in a plasma. By showing that the results of the determination of total As in the sub-critical water-3% (*v/v*) H_2O_2 extracts[132] of rice by ETAAS were, on average, not significantly different from those by ICP-MS, it was deduced that there was no carbon effect. Samples (200 mg) were extracted with 10 mL H_2O-H_2O_2 (9+1) at 200 °C and 25 bar. All As^{III} was converted to As^V so making speciation by AEC-ICP-MS easier as the inorganic As peak was moved away from the peaks of any As cations present in the void volume and also from the poorly resolved DMA peak. Three CRMs and two well-characterised rice flours (IMEP 107 and NIES 10a) were analysed and, although there was agreement regarding the total As concentration, there were problems with the results for the As species. The authors concluded that "total As in extracts can be quantified by ICP-MS without the use of a collision/reaction cell as the residual carbon doesn't cause any enhancement of the ICP-MS signals." However, the ionisation enhancement effect in question occurs in the plasma, and is not affected by gas-phase reactions inside the spectrometer.

A number of *methods involving sample fusion* were reported. Germanium exists at trace levels in the Earth's crust and is a powerful geochemical tracer of the Si cycle. A simple and reliable method for determining Ge contents in environmental samples used[112] the chemical preparation procedure developed for Si isotopes, as Ge and Si have very similar chemical properties. Powdered samples were fused with NaOH at 720 °C after initially drying at 105 °C and then calcinating at 250 °C rising to 450 °C. Advantages were: (a) efficient removal of the matrix and main interferences affecting Ge determinations by ICP-MS; (b) a low LOD of 6 ng L^{-1}; (c) relative repeatability of approximately 3% obtained on ^{74}Ge; (d) robustness and accuracy based on agreement within errors with the published Ge values for rock reference materials (BHVO-2, AGV-2 and BCR-2). The Ge values for the three soil CRMs GBW 07401, GBW 07404 and GBW 07407, were revised to 1.67 ± 0.09, 2.41 ± 0.18 and 1.89 ± 0.10 μg g^{-1}, respectively. In addition, a value of 70 ± 3 μg g^{-1} was proposed for the plant CRM ERM-CD281. This procedure should make it possible to use both Ge and Si as tracers of the Si biogeochemical cycle within a single measurement procedure. An alkali flux (K_2CO_3-MgO) was used[133] to fuse rocks, soils and sediments for the determination of total S and sulfate S by ICP-AES. The fused material was leached with water, acidified with perchloric acid and the $KClO_4$ precipitate removed by filtration. The emission line at 181.978 nm was used with nitrogen purging. Interference effects were investigated and the method validated by the analysis of seven CRMs. A method for the determination of actinides (Am, Np, Pu, Th and U) and ^{90}Sr in soils by ICP-MS was based[134] on fusion with $LiBO_2$-LiBr (98.5+1.5) followed by coprecipitation with $Ca_3(PO_4)_2$ by adding NH_4OH. The analytes were preconcentrated by SPE in an automated flow system connected directly to the spectrometer. The procedure was applied to the analysis of soils obtained in intercomparison exercises (IAEA-TEL-2012-03 and IAEA-TEL-2015-04) organised by the IAEA and to the analysis of the CRM IAEA 385 (Irish Sea sediment). A pretreatment method commencing with lithium metaborate fusion was developed[135] for the determination of Am, Cm and Pu isotopes in large environmental samples by α-spectrometry and ICP-MS. After fusion, the button was dissolved in a mixture of HNO_3 and HCl and polyethylene glycol (PEG-6000) added to flocculate and remove the gelatinous silica precipitate. For the subsequent co-precipitation step, $TiOCl_2$ solution was added and the pH of the sample raised to 12-13 with 10 M NaOH. The iron hydroxide precipitate that formed was removed by centrifugation and dissolved in concentrated HCl. A further co-precipitation with CeF_3 was carried out with dissolution in a mixture of HNO_3 and boric acid followed by preconcentration by SPE. The method was validated by analysis of 20 g of soil samples, spiked with known amounts of ^{241}Am and ^{239}Pu, as well as by the analysis of the IAEA CRMs 384 (Fangataufa Lagoon sediment) and 385 (Irish Sea sediment).

Developments in *sample treatment prior to extraction or dissolution* included[136] a study of sample storage and preparation procedures for characterisation of element fractionation in lichens by ICP-MS. Cryogenic freezing gave the best reproducibility for total extractable elemental concentrations over a period of several months but was inappropriate for sequential extraction procedures. For such procedures, either no sample preparation or drying in a desiccator gave the best extraction recoveries so the assumption that species stability can be ensured through cryopreservation and freeze-drying techniques needs to be revisited. Two IEC separation schemes for the selective and quantitative isolation of the REE group from accompanying elements were developed[137] because direct analyses by ICP-MS or INAA could be inaccurate for some REEs. After checking their performance with the aid of radioactive tracers, the schemes were further used for the determination of the REEs in CRMs. Comparison of these results with those obtained by ICP-MS and INAA analyses without preseparation revealed that, although the direct analyses provided reliable results for the majority of REEs, results for Sc, Yb and Tm were inaccurate. High performance IR quartz tubes were used[138] in dry-ashing devices as heating elements for the first time and were proposed for preparation of botanical samples with high levels of organic matter. A layer of gold was plated on the surface of the heating tube in order to reflect and focus IR light and enhance the effect of heating. The flow-through quartz ashing tube built in-house ensured oxygen penetrated the entire sample layer, thereby increasing the efficiency of ashing. In addition, the heating chamber had a very small volume so the size of the proposed device was only one-fifth of a traditional muffle furnace. The sample could be heated from room temperature to 900 °C in just 1 minute and for most kinds of samples, ashing was complete within 30 minutes. The procedure was validated by analysis of five Chinese CRMs. The procedure was further developed[139] (a) to allow the addition of O_3 to accelerate the carbonisation process, (b) to trap volatile elements in a cold trap and (c) to use ultrasound to accelerate dissolution of the ash. The so-called "volatile" elements As, Cd and Pb were determined accurately in three Chinese CRMs.

Three *pretreatment methods involving ferric hydroxide precipitation* were compared[140] for the determination of Pu in water-soluble and exchangeable (1M ammonium acetate) fractions of soils. The best method involved wet-ashing with HNO_3-H_2O_2 followed by $Fe(OH)_3$ coprecipitation. In the final stage of the procedure, the Pu was preconcentrated by multistep SPE. Using an SF instrument for analysis, the LOD for ^{239}Pu in a 100 g sample was 9 µBq kg^{-1} for the overall process. Recoveries of ^{242}Pu spikes from both water-soluble and exchangeable fractions were 70%.

4.3.3. Preconcentration procedures.

The numerous *preconcentration procedures* reported for specific analytes are summarised in Tables 4 and 5.

4.4 Instrumental analysis

In the following sections, *advances in methodology* in which the nature of the instrument or some feature of the instrument operation has been a key feature have been selected for inclusion under the appropriate headings. Sample handing and introduction procedures, such as CVG and LA, are included in the section appropriate to the spectrometric technique concerned.

4.4.1 Atomic absorption spectrometry.

Environmental contamination by metals resulting from cigarette smoking is a significant human health risk. Although a number of investigations have been performed on the detection of metals in cigarette tobacco, only very limited data have been reported for the determination of these metals in other parts of cigarettes. The contents of Cd, Cr, Cu, Ni and Pb in cigarette tobacco, smoke, ash and butts were quantified[141] using *HR-CS-ETAAS* with LODs of 0.020, 0.025, 0.010, 0.030 and 0.012 μg L^{-1} for Cd, Cr, Cu, Ni and Pb, respectively. The method was validated by the analysis of the Chinese CRM GBW 10052 (green tea) and by the recoveries of spikes. The results indicated that the majority of the PTEs (41 to 69%) remained in ash, with 10 to 28% condensed in butts and 7 to 23% released into the mainstream smoke. A simple, efficient and environmentally friendly method was proposed[142] for determination of Be in soil and sediment samples employing slurry sampling and HR-CS-ETAAS. The spectral effects originating from SiO species were identified and successfully corrected by means of a mathematical correction algorithm. The parameters optimised were particle size (<54 μm), glycerol concentration (stabilisation, 20% w/w), HNO_3 concentration (extraction, 0.1 – 10% w/w), ultrasonic agitation (slurry homogenisation, 1–5 minutes), chemical modifier concentration (0.5 g L^{-1} Rh + 25 g L^{-1} of citric acid) and pyrolysis and atomisation temperatures (1100 and 2700ºC, respectively). The LOD was 0.02 mg kg^{-1} and the characteristic mass was 1.3 pg. The method was validated by the analysis of two CRMs (NIST SRM 2702, inorganics in marine sediment, and IGI BIL-1, Baikal bottom silt) and by comparison of the results for 10 real samples obtained by this slurry sampling method with those determined by ICP-TOF-MS after MAE.

Other *applications of AAS* included[143] the determination of P by ETAAS in soil fractions. The procedure was validated by the analysis of CRMs BCR-141R (trace elements in calcerous loam soil) and NIST SRM 2710a (Montana soil) and by comparison of results with those obtained by spectrophotometry. A PVG system with sonication-assisted batch-type gas-liquid-separator was optimised[144] to improve the sensitivity, precision and accuracy of Ni determination by AAS. The inefficient nebuliser of the flame unit was replaced by a UV-assisted vapour generator and atomisation of the volatile species generated was achieved with a quartz tube atomiser. Parameters optimised included organic acid (formic acid) and concentration (6M), UV irradiation period (4 minutes), sonication period, carrier gas flow rate (2140 mL min^{-1}) and atomiser temperature (1000 ^{o}C). The LOD was 10 µg L^{-1}. The method was validated by spike recoveries (95-104%) and the analysis of a waste water CRM, EU-L-2.

Addition of Freon R12 (CCl_2F_2) as modifier gas in ETAAS had[145] a strong influence on pyrolysis and vaporisation temperatures and sensitivity. Although the Freon lowered the volatilisation temperature through creation of volatile fluorides and so allowed direct analysis of medicinal herbs without digestion, standard additions were still necessary because the Freon introduced variable matrix effects in the determination of As, Cd, Cr, Cu, Mn, Ni, Pb and Zn in medicinal herbs. Results for the analysis NIST SRMs 1515 (apple leaves) and 1574 (peach leaves) were in good agreement with the certified values.

4.4.2 Atomic emission spectrometry

Developments in sample introduction continued to receive attention. Although ICP-AES is widely used for routine trace multi-elemental analysis because of its robustness and low maintenance cost compared to those of ICP-MS, pneumatic nebulisation remains its Achilles' heel due to the poor (<15%) transport efficiency. A simple approach for enhancing sample transport efficiency of pneumatic nebulisation involves converting the sample aerosol into vapour prior to its introduction into the plasma without removing the solvent from the system. A 50-mL cyclonic spray chamber was modified[146] by insertion of an IR lamp heater at its centre. The 7-cm base of the torch was also heated with a rope heater made of ceramic beads to prevent condensation. When compared to the results obtained with an unmodified spray chamber, there were 2-5 and 2-7 fold gains in sensitivities and LODs, respectively, for 26 elements. The larger enhancements for ionic emission lines than for atomic emission lines was attributed to increased transport efficiency and the conversion of the aerosol to vapour, which significantly improved plasma excitation conditions. The more robust plasma allowed accurate multielement analysis of drinking water and soil digest samples to be performed using a simple external calibration without internal standardisation or matrix-matching.

The novel use of matrix-matched RMs made with gelatine made it possible[147] to determine Ca at concentrations of up to 1000 µg g^{-1} in the *LA-ICP-AES* determination of Ca, K and Na in tobacco plant stems and leaf petioles. Advantages of the system over LA-ICP-MS analysis included simultaneous detection, lower running costs, lower sensitivity to contamination and user-friendliness. Plant samples were mixed[148] with paraffin as a binder to provide better cohesion of the particles in the pellets as well as supply C to serve as IS (atomic line C I 193.027 nm) as a way to compensate for matrix effects and variations in the ablation process. The LODs were 0.4-1 and 20-600 mg kg^{-1} for metallic and metalloid elements (B, Ca, K, Mg, Mn and Zn) and non-metallic elements (P and S), respectively. The method was validated by the analysis of the four NIST plant SRMs. Sample preparation involved grinding the samples to $\leq$75 µm to have the same particle size as the SRMs, binder addition and mixing and pellet pressing. This direct solid analysis was considered less time-consuming and "more efficient" than wet sample digestion methods.

Reports on *modifications of the plasma conditions* included[149] a paper in Japanese in which the determination of trace-levels of Rb with cool plasma conditions (750 W and 0.95 mL min^{-1} carrier gas flow rate) was described. The low LOD of 0.005 mg kg^{-1} could be attributed to the effective suppression of spectral interference from argon emission lines when measuring the Rb emission line, thereby improving the S/N 20-fold. Matrix effects of Ca and K were still observed for the measurement of Rb by cool plasma ICP-AES, so approaches such as gravimetric standard addition incorporating IS correction were required to correct for these matrix effects in real samples. Results for the analysis of NMIJ CRMs 7502-a (white rice flour), 7505-a (tea leaf powder) and 7512-a (milk powder) were in good agreement with the certified values (2 to 9 mg kg^{-1}).

In comparison with FAAS, an *AES instrument with a MIP sustained in inexpensive N_2* had[150] similar linear dynamic ranges but significantly improved sensitivities. It also had short start and warmup times (~20 minutes). When used with a simple dry-ashing apparatus, it was a cost-effective alternative for trace element analysis. The Helios Rapid Ashing prototype reached 750 °C using a ceramic radiative heating element, and so gave sample decomposition in <5 minutes. It required inexpensive sample holder materials such as aluminium foil and quartz fibre pads. Samples were decomposed at 500 °C, and the analytes extracted into a 10% (*v/v*) HCl solution before analysis. The LODs were 2, 20, 30, 0.6, 2 and 5 µg L^{-1} for Ca, Fe, K, Mg, Na and Zn, respectively. The procedure was validated by the analysis of NIST SRM 1573a (tomato leaves) and by comparing the results to those obtained with an acid MAE procedure. The method was applied to the analysis of “challenging samples” such as cheese, butter, peanut butter, infant formula and biodiesel.

The possibility of *direct analysis of soils* by using a high-powered (5-15 kW) two-jet plasma AES was investigated[151] using certified RMs of black earth, grey desert and red soils. Calibration standards were prepared by mixing 100 mg of a suitable powdered CRM and 100 mg of a spectroscopic buffer (graphite powder containing 15% (*w/w*) NaCl) and an aerosol generated by a spark discharge between zirconium electrodes, which created blast waves that agitated the powder. The elements As, B, Cd, Cu, Hg, P and V could be determined after a 2-fold dilution with the spectroscopic buffer, whereas a 10-fold dilution was used for Be, Co, Cr, Ga, Nb, Pb and Zn. The strong matrix effects observed for red soil with its high Al and Fe concentrations led to overestimation of the Ni, Pb and Sn concentrations. Clear advantages of the technique over existing methods were the simple sample preparation process requiring no reagents except for the spectroscopic buffer, and the use of the same calibration samples in the analysis of different soils.

4.4.3 Atomic fluorescence spectrometry

Analytical methods for the *determination of MeHg* include many steps and require adaptation to different matrices. Two methods were validated[152] for MeHg determination in sediments and cyanobacteria and applied to the study of Hg methylation of planktonic organisms in water from a contaminated site in Brazil. The MeHg was extracted from cyanobacteria and microalgae, derivatised with tetraethylborate, trapped on Tenax and then thermally desorbed into a GC column coupled to a pyrolysis AFS detector. The results were linear over the range 0 to 400 pg MeHg spike recoveries were 93-129% and the LODs were 0.04 and 1 μg kg^{-1} for sediments and cyanobacteria, respectively. The procedure was validated by analysis of the CRMs BCR-580 (estuarine sediment) and NRCC DORM-3 (fish protein). In the analysis of cultures of cyanobacteria and microalgae isolated from water samples collected in an ancient Hg-contaminated gold mining area in Brazil, the production of MeHg was detected only in the culture of the microalga *Stichococcus* species (0.23% of total Hg). This indicated that this culture participated in the biotransformation of Hg. Both MeHg and inorganic Hg were determined[153] in rice and aquatic plants using a 40 minute procedure which consisted of extraction by closed-vessel MAE, derivatisation by ethylation and analysis by GC-pyrolysis-AFS. An alkaline (TMAH) extraction was deemed to be inferior to extraction with HNO_3 due to problems with blanks. The method was validated by the analysis of CRMs BCR-60 (aquatic plant), BCR-482 (lichen) and NCS ZC73027 (rice) that were spiked with MeHg. The sum of species concentrations was not significantly different from the certified values for total Hg. The LODs were 0.7-1 ng g^{-1}. Some samples were preconcentrated by evaporation of the hexane phase in which the species were derivatised.

4.4.4 Inductively coupled plasma mass spectrometry

An outstanding aspect of MICal, a straightforward matrix-matching strategy that may be considered a good *alternative to the traditional calibration methods* for analysing complex-matrix samples by ICP-MS, was[154] that it did not require any instrumental modifications. Only two calibration solutions were required. One was composed of sample solution and a standard solution (1+1) and the second of sample and a blank (1+1). The signal intensities of several isotopes of the same analyte in both solutions were monitored and the analytical signals from the first solution (x-axis), were plotted against those from the second solution (y-axis). The analyte concentrations in the sample were calculated from the slope of the plot and the concentration of the standard. Matrix-matching was easily achieved as both solutions contained the same amount of sample. As only two calibration solutions were required, accurate results could be obtained with relatively high sample throughput, especially when compared with that of standard addition. Results for Ba, Cd, Se, Sn and Zn in seven NIST SRMs were in good agreement with the certified values. In comparison to other calibration methods, the new method had the advantage that isobaric interferences could readily be identified and the signal arising from these excluded but the disadvantage of not being applicable to monoisotopic elements. However, another study from the same group of researchers described[155] a novel procedure that was indeed applicable to monoisotopic elements. It took advantage of the gas-phase chemistry available in ICP-MS/MS and, rather than employing several standard solutions and a single *m/z* ratio, the multispecies calibration used only one standard reference concentration and several chemical species of a monoisotopic element for calibration. Multiple oxide and ammonia species generated in the collision/reaction cell were used to determine As, Co and Mn in rice and liver samples. The LODs were 0.07, 0.03, and 0.07 μg L^{-1}, for As, Co and Mn, respectively. The results obtained for NIST SRMs 1573a (tomato leaves) and 1577b (bovine liver) were not significantly different from the certified values.

Developments in *sample introduction by CVG* included[156] a novel and sensitive LSDBD–CVG procedure developed for the measurement of Pb by ICP-MS. Dissolved Pb^{2+} was readily converted to volatile species by LSDBD-plasma-induced chemical processes in the presence of 5% (*v/v*) formic acid in a supporting electrolyte (0.01M HCl). The sample solution was converted to aerosol and simultaneously mixed with the discharge generated at the nozzle of a pneumatic nebuliser. This facilitated the CVG of Pb because of the enhanced interaction of sprayed analytes and the plasma. The LOD was 0.003 μg L^{-1} and the RSDs (n=5) were 2.1 and 1.7% for 0.03 and 1 μg L^{-1} Pb standards, respectively. In comparison with other CVG methods, the new procedure required no unstable reagents, had a rapid response, was easy to interface with FI and had a high tolerance for coexisting ions. The accuracy of the proposed method was demonstrated by analysis of several CRMs including plants and soils. The new procedure extended the number of elements accessible by plasma–CVG and provided an alternative efficient approach for the CVG of Pb.

Although *PVG* is emerging as a promising analytical tool for Te determination thanks to its efficient matrix separation and simple procedure, the PVG generation efficiency has remained low. The sensitivity was[157] 15-fold better in the presence of ferric ions when using nano-TiO_2 as a photocatalyst in the reaction chamber compared to the conventional PVG response. The high photocatalytic performance of TiO_2 under short-wavelength UV irradiation (254 and 185 nm) provided equal and high PVG generation efficiencies for Te^{IV} and Te^{VI} in the presence of ferric ions. The LOD was 1.0 ng L^{-1}. The precision (n=7) for Te^{IV} was 2.3% (RSD) at 0.5 μg L^{-1}. The procedure was validated by the analysis of the Chinese stream sediment CRMs GBW07303a and GBW07305a. The method was considered to have potential for the highly sensitive determination of vapour-forming elements. In a novel sensitive approach for the determination of Cl by SF-ICP-MS using PVG for sample introduction, methyl chloride was generated[158] from different chlorine species in a flow-through photochemical reactor using a 1% solution of acetic acid containing 7.5 μg g^{-1} Cu^{2+}. The volatile product was directed by an argon carrier gas to a gas–liquid separator and introduced into the instrument. The sensitivity obtained for a flow rate of 1.7 mL min^{-1} and a

45 s irradiation time was 74-fold better than that of conventional nebulisation. Although limited by blanks, the LOD of 0.5 ng g^{-1} was suitable for quantitation at trace levels. The procedure was validated by the analysis of the NIST SRMs 1568b (rice flour) and 1571 (orchard leaves) and by spike recovery from three brands of bottled water.

New *separation techniques coupled with ICP-MS detection* included[159] an analytical procedure for $^{37}Cl/^{35}Cl$ analysis in perchlorate designed to be simpler than the method currently in use. Solutions containing less than 200 mg L^{-1} were preconcentrated by SPE and the perchlorate then separated from chloride by IC prior to analysis by MC-ICPMS. The accuracy of the method was validated by analysis of international perchlorate CRMs USGS-37 and USGS-38; analytical precision was better than ±0.4‰. In the analysis of enriched microbial cultures from a contaminated soil, the isotope enrichment factor $\varepsilon^{37}Cl$ of -13.3±1‰ was in the range reported previously for perchlorate biodegradation by pure microbial cultures. A method for the simultaneous detection of trace Zn dimethyldithiocarbamate and Zn ethylenebisdithiocarbamate by CE and ICP-MS involved[160] chelation of the compounds with *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid to form a macromolecular complex. The two chelates were separated by α-cyclodextrin-modified CE at a separation voltage of 15 kV for 12 minutes. The LODs were 2 and 3 ng mL^{-1} (as Zn) for Zn dimethyldithiocarbamate and Zn ethylenebisdithiocarbamate, respectively. The two compounds spiked into cabbage leaves were successfully extracted by UAE and determined with a RSD ($n = 5$) of $\leq 6\%$ and a recoveries of 95–107%. The careful separation, identification and characterisation of polymer-coated quantum dots in complex media such as soil solution is key for understanding their behaviour and to predicting accurately their fate in the environment. A synthesised CdSe/ZnS core/shell suspension, stable for at least six months, was characterised[161] for dimension, structure and elemental composition. The element-specific data obtained by ICP-MS after asymmetric FFF separation enabled the signal to be deconvoluted reliably. It was possible to determine quantum dot populations which interacted with the soil solution and so would be susceptible to either aggregation or dissolution. Analytical performance was evaluated by the analysis of CRM TM-25.4, batch 0914 (Lake Ontario water). The LODs were 0.01, 0.05, and 0.03 μg L^{-1} for Cd, Se and Zn, respectively, when using ICP-MS detection.

Reports on *the determination of isotopes with MC instruments* included[162] a new method developed for precise and accurate Mo isotope ratio measurements in plant materials. The Mo species in a 0.2M HF-0.5M HCl mixture were retained on AG® 1-X8 anion exchange resin while the matrix components were removed. The species were then eluted with dilute HNO_3. Use of an Apex-Q desolvating nebuliser and the addition of 0.04% EDTA solution enhanced sensitivity 10-12-fold. The drift in instrumental mass bias was corrected by normalisation to the response for an Pd IS added online. This led to an improvement in measurement precision for the $\delta^{X/95}$Mo values. The method was validated by the analysis of NIST SRM 1547 (peach leaves). The Mo isotope ratios could be determined in sample solutions with Mo concentrations as low as 10 ng g^{-1}. Application of the method to the determination of natural variations in the isotopic composition of Mo in different anatomical parts of plants showed for the first time that Mo isotope fractionation occurred during long-distance transport of Mo in plants. The magnitude of Mo isotope fractionation during translocation of Mo was different for different plant species. The authors considered the Mo isotope ratio data obtained by MC-ICP-MS could be used as a sensitive probe of processes controlling transport and distribution of Mo in plants. Heroin chemical signatures provide important information to law enforcement agencies. In the first report on the use of $^{87}Sr/^{86}Sr$ analysis of heroin for the profiling of samples from specific geographic regions, DeBord *et al.*[163] extracted Sr using MAE and, if necessary, preconcentrated it by SPE prior to analysis by MC-ICP-MS. South American and Mexican heroin samples are currently the most difficult to identify based on their organic compositions but were correctly classified 82 and 77% of the time, respectively, when Sr isotope ratios were used. In addition, a value for $^{87}Sr/^{86}Sr$ in the NIST SRM 1570a (spinach leaves) was reported for the first time. This was 0.70905 ± 0.00002 (95% confidence interval, n = 3).

Analyses with tandem MS instruments included[164] the determination of 12 trace elements (As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, V, and Zn) in the water decoction of MFH plants. A detailed discussion of potential interferences was presented and how they were overcome by reaction with oxygen. The percentage extractions, determined following MAD of the residue, were all ≤30%. The methods were validated by the analyses of NIST SRMs 1515 (apple leaves) and NIST 1547 (peach leaves). The LODs ranged from 0.1 (V) to 7 (Zn) μg kg^{-1}. In the determination of the toxic elements As, Cd, Hg and Pb in 50 common MFH plants by the same research group, samples were also prepared[165] by MAD with HNO_3-H_2O_2. A 400 μg L^{-1}

Au standard solution was added to all sample and standard solutions to eliminate a Hg memory effect, and Bi, Sc and Tb were used as internal standards. The results were validated by the analysis of NIST SRM 1515 (apple leaves) and by comparison of the results for three samples with those obtained by AAS. The LODs were 1, 1, 0.8 and 0.6 for As, Cd, Hg and Pb, respectively.

4.4.5 Other mass spectrometry techniques

A *new RIMS method* made it possible[166] to detect 1.5 x 10^9 atoms of ^{99}Tc per g of soil samples in what was claimed to be the first time that the 97, 98 and 99 isotopes had been measured simultaneously. The detection capability of the method was demonstrated by the measurement of 1.5×10^9 ^{99}Tc atoms per gram of dried sample when 8.8×10^{10} atoms of ^{97}Tc were used as tracer isotope.

Radiocaesium has been widely dispersed across the Earth due to nuclear operations since the first atmospheric nuclear weapons test in 1945. The strong affinity of Cs for particulates makes it a powerful tracer for a range of environmental processes but one of the principal challenges in the TIMS determination of ^{135}Cs/^{137}Cs isotope ratios is the elimination of Ba as an isobaric interference. A combination of double AMP-PAN separation and Sr-spec resin column purification was developed[167] to provide excellent separation of Cs from the alkali metals in a range of environmental sample types. An emission activator of glucose solution for the ionisation of Cs gave the optimal combination of a stable Cs^+ beam, minimal low-temperature polyatomic interferences and improved ionisation efficiency. The mass-spectrometric determination of low abundance ^{135}Cs and ^{137}Cs was compromised by the presence of the high abundance $^{133}Cs^+$ beam, which could be scattered and caused significant spectral interferences. In addition, minor polyatomic interferences needed to be taken into account when the $^{133}Cs^+$ intensity was large relative to those of $^{135}Cs^+$ and $^{137}Cs^+$. The method was evaluated by the analysis of samples and standards from regions affected by fallout from the Chernobyl (IAEA-330) and Fukushima nuclear accidents and was applied to the measurement of extremely low concentrations (^{137}Cs approximately 12 fg g^{-1}) in estuarine sediments from SW England.

A *new laser–SNMS* system combined[168] the high spatial and good mass resolution of a TOF-SIMS instrument with the element-selective process of resonant laser ionisation and so met all requirements for spatially resolved ultra-trace analysis of radionuclides. Low saturation laser powers of several mW confirmed an ideal overlap between the three laser foci and the sputtered neutral particle cloud. The apparatus delivered a decision threshold of 5×10^8 to 5×10^9 atoms. Further potential for optimisation of the technique was indicated by the estimated decision thresholds derived from efficiency measurements on U that were two orders of magnitude lower. Furthermore, it was believed that improvements in the overall efficiency would be possible by reducing the oxidised fraction through use of suitable reduction agents or carriers or by modifying the ion extraction. The first analytical measurements by the laser–SNMS system demonstrated that isobaric contaminations, whether from organic background or other interfering elemental or molecular species, could be efficiently suppressed. As a consequence, the SNMS system will be applied to the detection, visualisation and ultra-trace analysis of radionuclide-containing NPs in environmental samples with a strongly reduced or even no need for chemical preparation.

4.4.6 Laser induced breakdown spectrometry

There has been a very substantial increase in the number of papers describing developments in LIBS methodology for the analysis of plants and, in particular, soils. As LIBS becomes more widely used, it is not surprising that reviews of *aspects of this technique and its applications* have been presented. One (69 references) on the use of LIBS for food analysis contained[169] a useful tutorial introduction to the instrumentation and methodology as well as a survey of applications that included the analysis of plants. Although LIBS technology had many advantages, including minimal sample destruction, spatial resolution, multielement analysis of solids and potential for application in process analysis, challenges remained. These included issues in sample preparation, matrix effects, spectral pre-processing, model calibration and instrument development. In the determination of Cd, Cr^{VI} and Pb in plant materials, the greatest challenges were[170] calibration and LODs insufficient for monitoring the maximum residue limits drawn up by various governments. A combination of matrix-matched RMs, spiked sample materials and ISs as well as chemometrics was recommended for calibration. The LODs could be improved through appropriate choice of analyte emission line and signal enhancement.

Guezenoc *et al.*[171] demonstrated the *importance of variable selection* on the prediction ability of LIBS quantitative partial least squares (PLS) models. The spectral lines of K at 766.49 nm and 769.90 nm were considered in the framework of an agricultural soils analysis. Whereas univariate models had very poor correlations between the peak areas of the K lines and the related concentration values, a series of PLS models improved significantly the prediction ability. This gain was significant because the two spectral lines of K exhibited unusual profiles. A PLS model with only variables related to the edges of these lines had a significantly better predictive ability than another PLS model which included variables related to only the central parts of these lines. Other such studies included variable selection in the determination of Ba, Cr and Cu in soil[172], Cd and Pb in soil[173], Ba, Ca, Cr, Cu and Mg in soil[174], Al, Ca, Fe, K, Mg, and Na in soil[175] and Al, C, Ca, Fe, Mg and Mn in Chinese tea leaves[176]. It would appear that there is as yet no agreement about which is the best method.

Calibration of LIBS remains challenging because the methodology is highly matrix dependent. The different approaches taken to meet this challenge included the use of PLS regression for the determination of Cd in polluted fresh leafy vegetables[177], the use of matrix-matched calibration standards in the determination of Ca in biochar-based fertilisers made from peanut shells, eucalyptus residue and banana fibres[178] and the use of nonlinear multivariate calibration in the determination of Mg in soil[179].

Various reports on the measurement of Pb indicated the *matrix-dependency of LIBS*. In the determination of Pb in soils, best results were provided[180] by the combination of a multivariate calibration model based on three principal components and the use of the 3rd harmonic of a Nd:YAG laser. The LOD was 13 ppm. The concentration (40 ppm) determined for a soil sample agreed with that obtained by XRFS analysis. Calibration based on the intensity of a single line at 405.78 nm gave[181] acceptable results for the determination of Pb in soil contaminated with drilling fuel. The LIBS results for five samples were not statistically different from those obtained using ICP-AES. However, this method did not work[182] well in the determination of Pb in tea leaves. Best results were obtained using calibration by a multiple linear regression based on the intensities of (a) the Pb line at 405.78

nm, (b) the C line at 247.856 nm and (c) the sum of the Mg lines at 403.076, 403.307 and 403.449 nm. It was assumed in this study that the concentrations of C and Mg were constant across all samples. In addition, the concentrations of Pb were high at 0.3 to 3%. For the determination of Cd, Cr, Cu and Pb in soils, Chinese researchers employed[183] a portable instrument modified to contain the plasma and increase the intensity of the emitted light, which was collected by a multi-channel optical fibre. Calibration was by the standard additions method with non-linear curve-fitting. In a later study on the spatial distribution of Cr, Cu and Pb in soil, the same research group found[184] that calibration based on single spectral line intensities worked only for Cu and Pb. Results for Cr were more accurate when a calibration-free method was combined with the Saha equation. The Cr/Si concentration ratios correlated well with the total concentrations. Rehan *et al.*[185] compared this calibration-free method with both a calibration curve method using normalisation to the intensity of the K atom line at 404.72 nm and an integrated intensity ratio method for the determination of 15 elements in betel leaves. The normalised calibration curve method gave results in closest agreement with those obtained by ICP-AES. The LODs for Cu, Cu and Zn were 1, 4 and 6 ppm, respectively.

It is important to study the *effects of various operating parameters on LIBS analysis*. Peng *et al.*[186] investigated the role of laser wavelength in the determination of Cr in rice leaves. Calibration based on standardised normal variate transformation gave results for a 532 nm laser better than those obtained with a 1064 nm laser. In another study they found[187] that the emission line intensity was only higher for irradiation at 532 nm for elements such as C (atom line at 193.03 nm, 7.685 eV) and Si (atom line at 212.41 nm, 6.616 eV) with higher upper energy levels. The opposite was the case for elements such as Fe (atom line at 368.75 nm, 4.220 eV and Ti (atom line at 336.12 nm, 3.716 eV) with lower upper energy levels. Kim *et al.*[188] obtained a significant enhancement in emission intensities when argon was supplied to the soil sample surfaces. Other researchers investigated[189] not only the role of the surrounding gas but also its pressure. To detect Cs in soils from the vicinity of the Fukushima Nuclear Power Station, measurements were made with irradiation at 355 nm (Nd-YAG laser) and with nitrogen and helium as ambient gases at both atmospheric and low pressures. The emission spectra with 0.5 kPa nitrogen gave the best signal and an LOD of 0.3 ppm.

Chinese researchers investigated the *effects of long pulse lengths*. In one study, 500 µs pulses produced[190] a "quasi-stable" plasma in local thermal equilibrium. The peak intensities for Cr and Pb occurred at about 320-350 µs. The plasma temperature was calculated to be 6,612 K and the LODs for the analysis of soils were 40 and 35 ppm for Cr and Pb, respectively. In a second study, the pulse duration of 80 µs produced[191] a plasma temperature of 15,800 K and gave an improved LOD of 16 ppm for the determination of Cr in soil.

Improved detection capabilities can also be obtained with *double pulses*. To map the spatial distribution of Ag NPs, Ag and Cu in root tissues of *Vicia faba*, the initial plasma produced by a 266 nm Nd:YAG laser was reheated[192] by radiation from a second Nd:YAG laser operating in the fundamental mode of 1064 nm. The LODs were 3, 18 and 4 pg for the Ag NPs, Ag and Cu, respectively. Co-linear and orthogonal beam-convergence double-pulse configurations were compared[193] for the determination of Cl in plant materials. Suppression of interfering molecular bands in the latter configuration led to better sensitivity even though the S/N was slightly poorer.

Khumaeni *et al.* reported on two *metal-assisted procedures for the analysis of soils*. In the first[194], the soil was mixed with a coarse metal powder and irradiated with light from a CO_2 laser at 10.6 µm. The LODs for Cr, Hg and Pb in loam were 0.8, 0.7 and 15 mg kg^{-1}, respectively. In the second procedure[195], the powdered sample was packed into a cylindrical hole in an acrylic holder and covered by a stainless steel mesh (0.1 mm wires with 0.4 mm spaces). Using the same CO_2 laser system, the S/N was better than that obtained with direct irradiation of a pressed soil pellet. The LODs for Cu and Hg were 3 and 10 mg kg^{-1}, respectively.

The *application of portable LIBS* is becoming more common. Suspended particulate matter mobilised in a storm in an urban river was analysed[196] *in situ* by a handheld instrument in order to characterise the environmental impact of potentially hazardous elements. The spectra, analysed by PCA following outlier identification, made it possible to differentiate between monitoring sites. In addition, some of the discriminant variables allowed PTEs such as Cr, Cu, Ni, and Pb to be determined and their sources to be identified. The performance of a hand-held LIBS system was compared[197] with that of a laboratory-based instrument for the determination of Cu, Pb and Zn in soils. Both emission intensity and stability were significantly lower for the handheld device, but IS calibration improved the stability of data to 6% and, for heavily contaminated soils, the measurement errors were <12%. The LODs of the laboratory system were <10 mg kg^{-1}, though some sample preparation was needed to decrease the effects of moisture and soil porosity.

One of several reports dealing primarily with *applications of LIBS* was[198] on the performance of the ChemCam instrument mounted on the Curiosity Rover for the determination of H on the surface of Mars. The emission intensity signal at 656.6 nm was measured. To improve discrimination between various mineral phases in the Martian soil, 198 naturally occurring hydrous samples covering a broad range of bulk compositions were used to create more robust prediction models based on the data acquired under Mars conditions. All normalisation and data processing methods for quantifying H resulted in models with statistically indistinguishable prediction errors (accuracies) of ±1.5% (*w/w*) so application was limited to discrimination between phases with large differences in hydration such as chlorites (12%), smectites (15-20%) and gypsum (20%). The determination of Al, Ca, Fe, K, Mg, Mn, Na and Ti in 32 surface sediments collected from Cienfuegos Bay, Cuba, in 2011-2013 made[199] it possible to correlate a small number of anomalous results with external events. The signals for Ca, K and Mg in citrus plants correlated[200] with damage caused by the bacterial disease Huanglongbing. A simple calibration method sufficed[201] for quantifying Cu in tobacco leaves with an LOD of 8 µg g^{-1}. Multiple-linear regression was needed[202] for calibration in the determination of Cu and Pb in the traditional medicine *Ligusticum wallichii* with LODs of 6 and 16 µg g^{-1}, respectively. To characterise machta and green tea powder, the LIBS spectra between 230 and 880 nm were analysed.[203] Linear discriminant analysis based on four characteristic wavelengths (C I 247. 94 nm; Ca II 393. 45 nm; Fe II 766. 68 nm; Mg II 279. 60 nm) gave rapid identification of matcha produced by different manufacturers and of green tea powder made by different fixation methods. The LIBS results for Al, Ca, Cu, K, Mg and Mn in the leaf ionome of the black cottonwood poplar (*Populus trichocarpa*) were[204] in agreement with those obtained by NAA but that for Cl was not. It was concluded that LIBS could be used in large-scale field phenotyping projects as a fast, high-spatial-resolution technique to quantify relevant elements.

4.4.7 X-ray spectrometry

An example of *solid state validation of extraction procedures* was[205] the XANES analysis of a sequential extraction procedure for Se speciation in phosphate mine soils. The Se was incompletely removed during extractions. It was concluded that mineralogical and chemical characterisations should be undertaken prior to applying a sequential extraction procedure in order to identify extractable phases or mineral components that could influence the extraction efficiency.

The performance of silicone-coated silicon reflectors was superior[206] to that of reflectors coated with poly(vinyl alcohol) for the *TXRFS analysis of plant materials*. Digests (HNO_3-H_2O_2) of *Mentha longifolia L.* leaves collected from different cities in Saudi Arabia were applied to the reflectors and 15 elements quantified. A HNO_3-H_2O_2 digestion was also used[207] in the analysis of some teas and herbs. After mixing with Ga IS, 10 µL of the digest was transferred to a quartz glass reflector and evaporated to dryness on a hot plate. Thirteen elements were determined with LODs of 0.1-3 mg kg^{-1}. A new method of direct analysis of tree leaves was evaluated[208] as an approach to air quality monitoring. The leaves were prepared by a SMART STORE device that first compressed a leaf between two 75 µm thick organic foils, one of which was adhesive and metal free, and then cut out a 30 mm diameter disc. The disc was stuck to a reflector and inserted into the TXRF instrument. Results were compared with those obtained by microwave-assisted digestion and it was concluded that the non-destructive direct method allowed rapid screening of the leaf samples with acceptable LODs of 0.5-18 mg kg^{-1}.

The micro-*PIXE* determination of Ca, Fe and Zn in genetically modified and wild-type sorghum grains was compared[209] with ICP-AES analysis. Whereas no difference between the two types of grain was found from the ICP-AES analysis, the spatially resolved micro-PIXE data showed significantly lower levels of Zn in the bran layer of the transgenic grain than in the wild-type. The mineral accumulation during different developmental stages of *Blepharispermum subsessile,* an endangered medicinal plant from India, was followed[210] by

PIXE analysis. The results allowed researchers to formulate a medium to induce high-frequency regeneration of the plant species for its *ex situ* conservation.

In a paper in the Czech language with an English abstract, a reliable, fast, simple and low-cost analytical procedure based on *radionuclide XRFS* was proposed[211] to identify and determine PTEs in various antitussive preparations of synthetic and biological origin. Some materials (tablets, granules, plants) could be analysed directly without the need for matrix removal so errors in the analytical process were minimised. Other materials such as effervescent tablets and hard capsules were more problematic in that homogeneous incorporation of standards was not possible. In these cases, external matrices which gave similar background noise levels and had the same levels of PTEs concentrations were used to prepare well-defined tablets containing standard additions of PTEs for calibration. The LODs had low single-digit µg g^{-1} values. The procedure was considered suitable for routine use in QC laboratories.

A review (108 references) of the *applications of X-ray elemental mapping techniques* to elucidate the ecophysiology of hyperaccumulator plants covered[212] sample preparation methods and gave tutorial explanations of the basis of each technique and comparisons with non-X-ray techniques. The reviewers included a useful section entitled “cautionary notes about preparation of plant material for elemental microanalysis.” They concluded that characterising the cellular and tissue-level distribution of elements is challenging and that accurate X-ray analysis requires careful sample collection, preparation and selection of analytical conditions to avoid elemental redistribution, chemical changes or ultrastructural modification. The LODs of a new µXRFS instrument for *in vivo* elemental analysis in plants ranged[213] from 0.04 (Fe) to 0.20 ng mm^{-2} (Pb) and so were comparable to those obtained with second-generation synchrotron facilities using a freestanding film reference. The spot size was <14 µm for the Rh K alpha line (20.214 keV). Relative sensitivities were determined for elements from S to Pb using the freestanding film reference and a 13-element standard dried-droplet deposition. A 3D-printed sample holder was used for *in vivo* measurements. An instrument with an ellipsoidal capillary was applied[214] to the 2D mapping of Ca, Cu, Fe and K in a holly leaf. The theoretical calculations behind the design of the capillary, which produced a 176 µm spot size at a focal distance of 40 mm, were fully described. The S/N obtained was much superior to that obtained with a 200 μm pinhole for which no signal was observed. A new μXRF spectrometer with polycapillary microfocus X-ray beam excitation with a rhodium anode (50 kV, 1 mA) and a SDD was used[215] to study both the location of Ca, Cu, Fe, K, Mn, Pb, and Zn in germinating maize seeds and the mobilisation of Pb in rock biofilms. Other applications included a study of the effects of two Zn fertilisers on the leaf tissues of green beans (*Phaseolus vulgaris L.*)[216], a study of the Se toxicity and distribution of Ca, Cu, K, Mn and Na in cowpea plants[217], the characterisation of small Fe-Mn nodules in red clay soil[218] and a study of Fe and Zn distributions in wheat grown in untreated and Zn-enriched soil[219].

In a review (49 references) on the use of *pXRFS* for the characterisation of tropical soils, attention was drawn[220] to the various factors that can influence results such as soil moisture content, particle size distributions, spectral interferences, scanning through plastic bags used for sampling and the scanned area and penetration depth of X-rays. Some of these factors were further evaluated[221] in a follow-up study from the same research group. Whereas results for Fe_2O_3 and TiO_2 correlated with those obtained following H_2SO_4 digestion, those for SiO_2 and Al_2O_3 did not. It was considered that pXRFS had potential for use in some studies of tropical soils as it was faster, more economical and “greener” than traditional H_2SO_4 digestion. Although factors affecting pXRFS analysis such as object geometry, soil moisture content and soil heterogeneity are well documented, the effect of organic matter is poorly understood. Ravansari *et al.*[222] evaluated their hypothesis that pXRF concentration measurements would be attenuated in proportion to the fraction of organic matter present by conducting a series of laboratory experiments using an organic-free soil with known concentrations of 13 elements. Twenty incremental additions were made for each of three organic matter surrogates (cellulose, graphite powder, and confectioner's sugar) and concentrations of 13 elements measured as a function of the organic matter fractions. Plots of measured trace metal concentrations against organic matter fraction were generated for each organic matter surrogate and compared with theoretical response curves based on dilution of the soil with organic matter. Empirical correction functions subsequently developed to adjust pXRFS data for each of the 13 elements investigated were evaluated using four RMs with known organic matter content. The different response for each element highlighted the element-dependency of pXRFS analysis.

Although the *pXRFS determination of contaminants in soils* has the advantage of being rapid and convenient, problems of calibration need to be addressed. Soil pollution by metals and metalloids has rapidly become a major threat to food security with nearly all cultivated soils being at risk of metal accumulation. Measurements made by pXRFS under *in situ*, *ex situ* and sieved conditions were compared[223] with data obtained by ICP-MS analysis of digested soils. Whereas the results for Cu, Mn and Zn were closely correlated, there were no significant correlations for As, Ni and Pb. The uncertainties in the pXRFS measurements arising from soil heterogeneity, moisture and particle size accounted for 20% of the total variability. It was found that greenhouse soils could be contaminated by Cu and Zn attributed to anthropogenic activities. Analysis using pXRFS was considered to be promising as a rapid and nondestructive *in situ* technique for assessing the potential risks of PTEs at trace concentrations in greenhouse soils. As pXRFS instruments can investigate a considerably greater number of sampling points more rapidly than alternative methodologies, they are useful for rapid planning in a soil survey process. In the characterisation of metal contamination in soils from near an abandoned iron mine in South Korea, hot spot analysis and a proposed group classification method were employed[224] to map Cu contamination hot spots in a given study area and to support the development of soil sampling plans. The pXRFS data were validated by ICP-AES analyses. The relatively low accuracy of pXRFS data was a potential source of error so the hot spot analysis and group classification method were applied to each soil sampling phase, not only to identify the hot spot areas but also to identify results suspected to be in error.

Few studies have previously used pXRFS to evaluate *metal and metalloid concentrations in vegetation* which are of critical importance for establishing the toxicity or deficiency of essential elements in plants or for investigating harmful elements extracted from the soil. A pXRF spectrometer was used[225] to scan 228 organic material samples (thatch, deciduous leaves, grasses, tree bark, and herbaceous plants) from smelter-impacted areas of Romania to demonstrate the application of pXRFS to the determination of element concentrations in vegetation. Samples were analysed as received from the field (moist), after drying at 70 ^{o}C, or after drying and milling to <2 mm size. After calibration with the reference 316 calibration alloy, the NIST SRMs 1515 (apple leaves) and 1547 (peach leaves) were analysed and correction factors for Ca, Fe, K, Mn, Pb, Sr and Zn calculated. Although the best agreement for Cd, Cu, Fe and Pb was obtained for the dried and ground samples, even under field moist conditions pXRFS could reasonably be used for the determination of Zn. This approach was considered useful as a quick assessment of element concentrations in vegetation.

The *application of pXRFS in cultural heritage studies* (works of art and archaeological artefacts) is considered[5] in full in our companion XRFS ASU.

5 Analysis of geological materials

5.1 Reference materials and data quality

Well-characterised RMs are crucial in geochemical analysis, both for method development and in order to obtain precise and accurate results for unknown samples, since they can serve as calibrants and QC materials. This section focuses on newly developed RMs and the further characterisation of established RMs to provide additional information on their elemental and isotopic compositions.

Renewed interest in REE mass fractions in coal and its by-products prompted a study[226] to evaluate the *consensus values for current and historical coal RMs*. Two RMs, NIST SRM 1632a (historical bituminous coal) and USGS SBC-1 (Pennsylvania shale), were analysed by ICP-MS after lithium metaborate digestion. A major finding was that the published Tm concentration in NIST SRM 1632a (0.39 mg kg^{-1}) could not be reproduced using modern analytical techniques and was likely to be too high. A revised value of 0.16 mg kg^{-1} Tm was recommended.

Reference material data sheets typically provide information on the uncertainty associated with each elemental reference value, together with a *minimum recommended mass of material* to be taken for chemical analysis. However, Rostron and Ramsey[227] demonstrated that this minimum recommended mass of material may not be appropriate if beam techniques such as pXRFS are employed, because of the elemental heterogeneity of the small test portion masses sampled. When three IAG silicate RMs SdAR L2, M2, and H1 (metalliferous sediments) were analysed by pXRFS, the test portion masses were mainly significantly below the recommended minimum mass of 0.2 g at beam sizes of 8 and 3 mm. Elements with the highest uncertainty due to heterogeneity appeared to be those associated with either an accessory mineral (*e.g.* Zr in zircon) or low test portion mass (associated with low Z). Revised uncertainties on the reference values of these RMs were calculated using pXRFS data.

Knowledge of the *heterogeneity of geological RMs* is essential in the assessment of measurements by microanalytical techniques. Thus, the homogeneity of RM AuRM2, originally developed and certified for the bulk analysis of refined gold, was evaluated[228] for its suitability as a RM for the microanalysis of native gold by LA-ICP-MS. Elements considered to be homogeneous in AuRM2 on the basis of a measurement repeatability of <10% RSD included Al, Cu, Fe, Mg, Ni, Pb, Pt, Rh, Sb, Se, Sn, Ti and Zn for a 3.4 μg test portion mass; other elements (As, Bi, Mn, Pd and Te) had repeatabilities of between 10 and 20% RSD. These heterogeneities were considered to be negligible compared with the range of chemical signatures observed in native gold. Thus RM AuRM2 was shown to be sufficiently homogenous for its intended purpose. A new synthetic chalcogenic glass was proposed[229] as a RM for the determination of trace elements in base metal sulfides by LA-ICP-MS. Approximately 10 g of homogenous glass doped with relatively high concentrations (~100 μg g^{-1}) of PGEs, chalcogens (As, Bi, Sb, Se and Te) and transition metals was produced by melting a mixture of powders in a sealed silica ampoule at close to 1000 °C and then quenching over a total period of 30 h. The trace element homogeneity of the resulting glass material was verified by LA-ICP-MS and the absolute concentrations determined by solution ICP-MS and LA-ICP-MS. Although most of the doped elements were homogeneously distributed at 100 μg g^{-1}, the concentrations of Mo, Re and W (~10 μg g^{-1}) had to be lower to prevent the formation of phases that would concentrate these elements and so make their distribution heterogeneous. Weber *et al.*[230] investigated the micro-homogeneity of Sr isotopes in several carbonate and phosphate RMs to evaluate their suitability for microanalytical analysis. All materials were analysed by LA-MC-ICP-MS using two different LA systems (ns and fs lasers). Strontium isotope data for the same RMs obtained by solution MC-ICP-MS after column chemistry agreed within analytical uncertainty with data in the literature. A comparison with solution data showed that both LA systems provided reliable $^{87}Sr/^{86}Sr$ as well as $^{84}Sr/^{86}Sr$ ratios for the RMs with low REE contents (JCt-1, JCp-1 and MACS-3). The accuracy of these data, together with their homogeneity on a μg-scale, made them suitable for use as matrix-matched microanalytical RMs. However, RMs with a significant REE mass fraction (USGS MACS-1, MAPS-4 and MAPS-5) yielded biased Sr ratios, indicating that some REE interferences may compromise these data. The polycrystalline, hydrothermal Diamantina Monazite (Espinhaço Range, SE Brazil), notable for its low Th and U content, was investigated[231] as a potential RM for *in situ* matrix-matched U-Pb geochronology and Sm-Nd isotope geochemistry. Previous work had indicated that differences between the Th compositions of monazite RMs (usually containing high amounts of Th) and those of samples introduced bias to the data obtained. The analytical data sets reported indicated that crystal fragments of Diamantina monazite were homogeneous with respect to both their major and trace element content and their isotopic composition (U-Pb, Sm-Nd and O); BSE images and compositional maps showed no evidence of crystallographic zoning.

Santos *et al.*[232] described a new potential *zircon reference material* named BB zircon from Sri Lanka for use in LA-ICP-MS U-Pb geochronology and Hf isotope geochemistry. They investigated 20 megacrysts by ID-TIMS, LA-ICP-MS and SIMS. The BB zircon was considered to be a suitable RM for both U-Pb and Lu-Hf isotope systems as long as analyses targeted pristine cathode-luminescence-dark grain domains. The within-grain REE composition appeared to be homogeneous but this needed to be confirmed by further analyses before the zircon could be considered also as a RM for *in situ* REE determinations. Results from SIMS analysis on the within- and between-grain homogeneity were promising enough to consider BB zircon as a possible calibrant for $\delta^{18}O$ determinations by SIMS. Zircon OG1/OGC from the Owens Gully Diorite of the Pilbara Craton was found[233] to be an ideal QC material for Hf isotope determinations in ancient zircons by LA-MC-ICP-MS. In addition, these zircons were considered to be particularly suitable for LA techniques such as concurrent Pb-Hf isotope determination or LASS in which U-Pb age and Hf isotope data are obtained during a single ablation. Another study presented[234] (U-Th)/He data on the Penglai zircon which occurs as megacrysts in basalts in northern Hainan Province, China. A weighted mean age of 4.06 ± 0.35 Ma (2SD) was derived from measurements on 18 fragments of four zircon megacrysts using single-crystal laser fusion He determinations and an U-Th ID method. The Penglai zircon was considered a suitable RM for (U-Th)/He isotope geochronology on the grounds of the unlimited quantity of material, large grain size, mostly weak broad zoning, rapid cooling and homogenous (U-Th)/He ages. The trace element homogeneity of the zircon GJ-1 was evaluated[235] from the micro- to atomic-scale using cathode luminescence imaging along with quantitative crystallographic orientation, LA-ICP-

MS and atom probe tomography analyses. The results showed that GJ-1 was structurally and chemically homogeneous at all scales and had no mineral inclusions. Significant abundances of Hf, P, Y, Yb and U indicated that the gem quality GJ-1 reference zircon, commonly used for U-Th-Pb and Lu-Hf-isotopic studies, would also be suitable for microanalytical trace element analysis. To improve the accuracy of Ti-in-zircon determinations for temperature estimates of crystallisation conditions, a new suite of zircon RMs for Ti was presented[236]. It was based on two well-characterised zircons (zircons 91500 and GZ7) for which LA-ICP-MS and SIMS data revealed sufficient homogeneity with respect to Ti/Si for them to be used as primary calibration materials. Recommended Ti concentrations based on ID-ICP-MS measurements were derived for these zircons. In addition, 16 other zircon RMs were characterised with Ti concentrations anchored to the new ID values established in this study, thereby enabling comparisons of Ti-in-zircon datasets whenever data for these secondary RMs are reported.

Efforts to determine *isotope ratio data for well-known international geological RMs* continued. He *et al.*[237] reported stable Ca isotopic compositions for 10 geological RMs relative to NIST SRM 915a (calcium carbonate) and its replacement NIST SRM 915b, ranging in composition from peridotite to sandstone. By applying a ^{43}Ca–^{48}Ca double-spike technique, δ^{44}Ca/^{42}Ca and ε^{40}Ca/^{44}Ca were measured simultaneously by TIMS with a precision of ±0.03‰ and ±1.0, respectively (n≥8). The comprehensive compilation of Ca isotopic compositions provided for these geological RMs should enhance future interlaboratory comparisons of Ca isotopic measurements. In a similar study[238], high-precision Ca isotope ratios of 35 geological RMs of varying compositions, including MPI-DING glasses and RMs supplied by GSJ and USGS, were determined by TIMS using a ^{42}Ca–^{43}Ca double spike protocol. It was observed that the δ^{44}Ca/^{40}Ca values of ultramafic rocks were positively correlated with their MgO contents and negatively correlated with their CaO contents. This was interpreted as indicating possible Ca isotopic fractionation during partial melting of mantle peridotites. An interlaboratory comparison between five laboratories yielded[109] δ^{25}Mg and δ^{26}Mg values for eight widely available RMs, including solids (limestone, soil, dolomite, vegetation) and waters (river, spring water and brine), representative of a wide range of Earth-surface materials from low-temperature environments. The data from the different laboratories agreed well despite differences in sample preparation, sample size, instrumentation and measurement procedures. Recommended δ^{25}Mg and δ^{26}Mg values proposed for these RMs were based on the results of this study and published values. The use of these RMs as QC materials was advocated given the small interlaboratory variability for all the RMs (≤0.17‰ for δ^{26}Mg) and the fact that they cover a wide range of sample matrices. Zhang *et al.*[239] evaluated the homogeneity of geological RM USGS BIR-1a (basalt) with respect to its Re-Os isotope composition. Over an 18-month period, 63 measurements were made using Carius tube digestion with and without HF desilicification prior to measurement by NTIMS and ICP-MS. From the results obtained for Re (0.691 ± 0.022 ng g^{-1}, 2SD) and Os (0.343 ± 0.089 ng g^{-1}, 2SD) mass fractions and ^{187}Os/^{188}Os isotope ratio (0.13371 ± 0.00092, 2SD) at the 0.2–1.0 g test portion level, the authors concluded that BIR-1a was more homogeneous than previously thought. Consequently, they recommended it as a suitable RM for method validation, QC and interlaboratory comparisons of Re-Os isotopic measurements of mafic geological samples when using test portions >0.4 g.

The Institute of Geology, Chinese Academy of Geological Sciences, Beijing produced[240] and certified GSB 04-3258-2015, a *new isotope reference solution* for the calibration of ^{143}Nd/^{144}Nd isotope ratio measurements. A certified reference value of 0.512438 (combined expanded ($k = 2$) uncertainty of 5×10^{-6}) was obtained from an interlaboratory comparison of data from 11 participating laboratories using MC-TIMS or MC-ICP-MS. A new Japanese Pb isotope standard solution with natural isotopic abundances, NMIJ CRM 3681, was characterised[241] using EDTA titrimetry as the primary measurement method. The ^{208}Pb/^{204}Pb ratio in the ^{208}Pb-^{204}Pb double spike, used for the correction of mass discrimination in MC-ICP-MS measurement of the Pb ratios, was determined with an uncertainty of <0.006%. Consequently, the Pb isotope ratios of this new solution not only have combined standard uncertainties smaller than those in NIST SRM 981 (common Pb isotopic standard) but are also SI traceable.

Two *new mica reference materials*, USGS57 (biotite) and USGS58 (muscovite), were developed[242] to replace the NBS 30 biotite RM for δ^{2}H measurements, as supplies of this previously widely used material are now exhausted. Their δ^{2}H values were determined in six laboratories using either glassy carbon-based or chromium-based online conversion to H_2 prior to measurement. The results were confirmed by off-line conversion. These isotopically homogenous, hydrous mineral RMs cover typical ranges of δ^{2}H that occur in materials of crustal and mantle origin, and so enable users to construct a two point calibration. Five new biotite RMs (UNIL_B1 to B5) were calibrated[243] for ^{18}O/^{16}O measurements by SIMS against

NBS-28 (quartz). Their δ^{18}O compositions were expressed relative to VSMOW. Repeated SIMS analyses on <20 µm spots had a measurement repeatability of 0.3‰ (2SD). Different crystallographic orientations had no effect on the results.

5.2 Sample preparation, dissolution, separation and preconcentration

Digestion methods for challenging geological sample matrices have been improved by different approaches. A simplified method for the determination of ferrous Fe mass fraction in silicate rocks included[244] a Schlenk line to expel air to prevent oxidation during sample digestion and titration with $KMnO_4$. Closed-vessel acid digestion under an argon atmosphere proved to be a cost-effective method for the digestion of 21 geological RMs with a range of compositions. This environmentally friendly procedure gave only moderately accurate but highly precise data. The reported LOD of 0.35% for FeO was based on 3SD of seven measurements of the procedural blank. Bokhari and Meisel[245] optimised the sodium peroxide sintering procedure for the complete digestion of rock samples containing refractory minerals such as zircon and chromite prior to analysis by ICP-MS. For zircon- and chromite-rich geological materials, the optimum ratio of sample to Na_2O_2 was 1:6. Recommended decomposition times for samples with and without refractory phases were 120 and 30-45 minutes, respectively. Mathur *et al.*[246] compared two published dissolution procedures for the determination of Sn isotopes in cassiterite by MC-ICP-MS: (i) reduction to Sn metal with KCN at 800 °C followed by dissolution in HCl; and (ii) reduction to a Sn solution with HI at 100 °C. The KCN method consistently gave yields of >70% Sn and appeared not to fractionate the Sn isotopes over a 2 h period. In contrast, the yield for the HI method was <5% due to Sn volatilisation and a large degree of fractionation of the Sn isotopes occurred. Unsurprisingly, this methodology was not recommended.

O'Hara *et al.*[247] evaluated reaction conditions for the decomposition of a range of solid inorganic matrices (glass, quartz, zircon, soil and pitchblende ore) using *molten ammonium bifluoride (ABF)* in sealed fluoropolymer vials. Use of the optimum ABF:sample mass ratio, which was dependent on the sample matrix, gave decomposition of the sample (except for zircon) in just 1 h at 230 °C. Recoveries for 19 elements were assessed by the ICP-AES and ICP-MS analyses of digests of NIST soil SRMs 2709, 2710 and 2711 and three IAEA pitchblende RMs. Sample decomposition was effectively complete and loss through volatilisation did not occur. It was noted that the analytical precision for the NIST soils may have been degraded as only 50 mg was taken while the certified minimum test portion is 250 mg. Although this method was designed to provide a solution for ICP-AES and ICP-MS analyses, it would also be possible to prepare the sample as a solid for analysis by techniques such as LA-ICP-MS, LIBS, and XRFS. Further work by Grate *et al.*[248] demonstrated the feasibility of preparing a solid suitable for LA-ICP-MS analyses from the product of the reaction between a low grade uranium ore and molten ABF in sealed PFA fluoropolymer vials at 230 °C. Single-element standard solution spikes included in the molten salt reaction were evenly distributed in the pressed powder pellets prepared from the new solids. The inclusion of a ^{235}U spike improved the precision of the ^{238}U determinations dramatically from 17% to 0.1%. The incorporation of internal standards in this manner opened up the possibility of using analytical methodologies such as standard addition and ID and the preparation of matrix-matched solid RMs for LA-based methods.

In spite of the improved detection capabilities of modern ICP-MS instruments, c*hemical separation and preconcentration* are sometimes required to determine elements present at very low concentrations. A procedure to determine 37 minor and trace elements mass fractions in ultramafic rocks involved[249] addition of Tm, HF-$HClO_4$ digestion and coprecipitation with $Mg(OH)_2$ and $Fe(OH)_3$. Analysis of four ultramafic RMs demonstrated that the HR-ICP-MS analysis of a simple dilution of the acid digest produced accurate data for elements down to mass fractions of 0.1 μg g^{-1}. The coprecipitation method extended the detection capabilities and provided reliable data for REEs, HFSEs, Pb, Th, U and some of the transition elements (Sc, Ti and V). Elements such as Ba, Co, Cr, Cs, Cu, Ga, Li, Mn, Ni, Rb, Sr and Zn were not fully coprecipitated and so could not be determined by this method. Data from two separate analyses (the coprecipitation method and direct digestion of the sample) provided a comprehensive dataset for trace elements at very low concentrations. A separation procedure for the determination of Ge in environmental samples was adapted[112] from one developed for Si isotopes because of the similar chemical properties of these two elements. After sample digestion with a solid NaOH flux, the solutions were purified by cation-exchange column chemistry before measurement of ^{74}Ge by ICP-MS. Method accuracy was difficult to evaluate because of the paucity of certified Ge data but was estimated to be *ca.* 5% with a precision of 3%. The procedure had the advantage that Si isotopes and Ge mass fractions could be measured, with care, using the same separation procedure. This would be a great asset in the interpretation of the Si cycle in which these elements are complementary tracers.

Many examples of studies devoted to *improving the efficiency of separation and purification techniques prior to isotope ratio measurements* are given in Table 6. A fully automated, low-pressure chromatographic system enabled[250] the unattended processing of one sediment digest every 2 h for the separation of Nd, Pb and Sr in a single-stage extraction step using DGA resin columns. The procedure was validated using Chinese RM GBW-07313 (marine sediment) as a matrix-matched CRM as well as samples spiked with NIST SRMs 987 (Pb isotopes) and 981 (Sr isotopes) and GSJ JNdi-1 (Nd isotopes). Recoveries of >90% were achieved for all elements together with low procedural blanks (0.57, 0.03 and 0.07 $\mu g\ L^{-1}$ for Nd, Pb and Sr, respectively). The DGA resin could be used for the separation of more than 10 sediment digests without significant carry-over or memory effects. However, the overlap of Pb and Sr elution peaks limited the yields for both elements. Yuan *et al.*[251] increased the speed of elution from ion-exchange columns by pressurising the columns with high-purity N_2. For the separation of Cu isotopes on AGMP-1 resin, the time was reduced from 12 to 4.5 h using a flow of 20 $mL\ min^{-1}$ N_2 while still achieving a recovery of >99.9%. An effective separation of Nd from Sr was also achieved within 10 h for the USGS RM AGV-2 (andesite). The isotope ratios obtained by MC-ICP-MS were within ±2SD of the reference values.

New sample preparation procedures for making powder pellets for LA-ICP-MS included[252] a ABF digestion procedure that produced ultrafine powders with a typical grain size $d_{80} < 8.5$ µm. The excellent cohesion and homogeneity of the resulting pressed powder pellets made them suitable for LA microanalysis without the addition of a binder, which would otherwise have diluted the sample. The results for six rock RMs covering a wide range of sample types agreed to within 10% with recommended values for most of the 10 major and 35 trace elements determined. The precision was <5% (1 SD) for most major elements and <10% for most trace elements. Compared to other methods of sample preparation for bulk analysis by LA-ICP-MS, the ABF digestion method enabled complete dissolution of refractory minerals in 3 h with limited loss of volatile elements such as Pb and Zn. At the same time the risk of contamination, which can be a problem when preparing ultrafine powders by grinding, was minimised. Additional benefits included the potential to add an IS, reduced matrix effects because of the relatively uniform grain morphology and the ability to prepare matrix-matched calibrations. Bao *et al.*[253] developed a method of preparing nanoparticulate pressed powder pellets from natural sulfide minerals of pyrite, chalcopyrite and sphalerite for *in situ* Pb and S isotope analyses. Powders with grain sizes of ~75 µm were mixed with traces of galena before wet-milling to a grain size of d_{50} <2.5 µm. The resulting material had excellent cohesion making it suitable for pressing without a binder. Homogeneity of the Pb and S isotope ratios was demonstrated by multiple spot analyses by LA-MC-ICP-MS. External precisions were <0.026% for ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb and <0.057% for ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb (2RSD). The precision for ^{34}S/^{32}S (2SD) was <0.41%.

An alternative approach for bulk analysis by LA-ICP-MS is the preparation of *fused beads*. In a fusion procedure developed[254] for the analysis of U ore concentrates and uraniferous ores with low silica contents, highly pure synthetic enstatite ($MgSiO_3$) was added to ~1.5 mg of sample powder in the proportion of 9+1 (enstatite + sample) to improve the fusion properties of these materials. The blended mixture was fused on an iridium strip resistance heater in an argon-purged chamber to form glass beads. The total preparation time was typically <10 minutes. Data for the REEs determined by LA-ICP-MS on glass beads prepared from a variety of samples, including eight geological RMs and three uranium CRMs, agreed well with published values. Although this procedure was designed to support nuclear forensic investigations, its speed of preparation, small sample mass requirement and suitability for microbeam analysis could be extended to other geochemical materials with inherently low silica levels, such as manganese nodules and polymetallic ores.

In a noteworthy study, gloves were examined[255] as potential *sources of contamination during sample preparation* of geological and biological samples for trace element and Zn isotopic analyses. Fifteen different nitrile, latex, neoprene and vinyl gloves from major suppliers were tested by exposing the gloves for 40 h to dilute acid (20 ml of 0.4M HNO_3 + 0.05M HF) to mimic the effects of leaching by acid fumes when handling samples in the laboratory. Several elements were released into the acid in significant amounts, *e.g.* up to 17 mg of Zn, 200 µg of Mg and 10-60 µg of Fe, Sr, Ti and Zr. Vinyl gloves released the lowest amounts of the elements other than In and Sn. The easy transfer of most elements from the gloves by simple contact with a pipette tip was particularly true for Zn so would potentially bias data for not only trace element content but also for isotopic composition. A single contact between glove and labware released on average ~6 ng Zn so the δ^{66}Zn value could be shifted significantly when the total amount of Zn processed through the procedure was <500 ng.

5.3 Instrumental analysis

5.3.1 Review papers.

An authoritative review[256] (452 references) of *key analytical advances relevant to the characterisation of geological and environmental materials* since 2014 covered a wide range of techniques, including TIMS, ICP-MS, SIMS, accelerator-based methods, focused ion beam techniques, INAA, XRFS and electron backscatter diffraction. Many of the newer applications provided analysis at increasingly finer resolution, e.g. LA-ICP-MS, atom probe tomography, nanoscale SIMS and micro-XRFS. A summary of new developments in the preparation and characterisation of rock, microanalytical and isotopic RMs also highlighted recent changes and revisions to relevant ISO guidelines. A review[257] (187 references) of advances in the study of ore mineralogy also focussed on the explosion of new micro- and nano-analytical techniques that are rapidly transforming research in this field. These included LA-ICP-MS, focussed ion beam SEM, high-angle annular dark field scanning TEM, electron back-scatter diffraction, synchrotron XRFS mapping, automated mineral analysis, nanoSIMS, atom probe tomography, radioisotope geochronology using ore minerals and *in situ* non-traditional stable isotope analyses. A combination of microbeam technologies provided information on different types and levels of quantification and offered insights into ore-forming processes and the sequence of alteration and mineralisation events in complex ore systems. An overview[258] (74 references) of procedures for the analysis of meteorites proposed a combination of non-destructive techniques for obtaining elemental as well as molecular and structural data without destroying such unique samples. The analytical scheme involved techniques such as LIBS and XRFS for elemental characterisation. A novel instrument collected EDXRFS, Raman and SEM data from the same spot areas. The removal of isobaric interferences using ICP-MS/MS has attracted increasing interest in the geochemical community and a tutorial review (110 references) by Bolea-Fernandez *et al.*[259] will be of interest to anyone new to this technique. It included a compilation of elemental and isotopic applications to a wide range of sample types.

In the field of *isotope ratio determinations*, Meng and Hu[260] (72 references) reviewed the history of Ge isotope analysis, methods for sample digestion and purification, MS measurements and the notation and RMs used for Ge isotopes. The section devoted to MC-ICP-MS measurements discussed different sample introduction systems, methods for minimising interferences and alternative approaches to mass bias corrections. Isotope ratio determinations of B by different MS techniques were discussed by Aggarwal and You[261] (188 references). They described B isotope variations that occur in the environment and advances in analytical methodologies for B extraction and purification. The capabilities, advantages and limitations of different mass spectrometric techniques, including ICP-MS, LA-ICP-MS, SIMS and TIMS were compared. Current and future applications, inter-laboratory comparisons and RMs were also discussed.

5.3.2 Dating techniques.

Several *improved correction procedures for U-Pb zircon dating by LA-ICP-MS* were published recently. Sliwinski *et al.*[262] demonstrated how the accuracy of U-Pb age determinations of young (Cenozoic) zircons in particular could be influenced by the degree of lattice damage, caused by radioactive decay of Th and U, which would result in different ablation rates throughout the analysis. By measuring a number of zircon RMs under well-constrained conditions, they derived a regression-based, multistandard correction for the amount of α-particle dose accumulated by a zircon. Their novel data reduction scheme developed for use with the Iolite data reduction software decreased systematic biases in age determinations and improved reproducibility. An assessment[263] of the downhole fractionation characteristics of three zircon RMs (Plešovice, Temora-2, zircon 91500) demonstrated that the fractionation behaviour was non-linear. Consequently, correction models based on these RMs had variable influence on the accuracy of the Pb/U ratios for unknown zircons. Different pre-treatment protocols were applied to assess their relative effects on the zircon ablation characteristics. Results indicated that annealing reduced the magnitude of U-Pb mass fractionation in most cases. A robust downhole correction method was proposed based on characterising the downhole fractionation behaviour in different RMs and correcting data for unknown samples using the RM that behaved most similarly during ablation. The relationship between zircon radiation dose and the amount of U-Pb fractionation was also investigated by Thompson *et al.*[264] who came to the same conclusion that the choice of calibration RM was a critical factor in obtaining accurate U-Pb ages by LA-ICP-MS. Correction factors were derived from plots of zircon RM U-Pb ages against apparent radiation doses calculated from Th and U concentrations. Another, hitherto unrecognised, source of uncertainty in LA-ICP-MS U-Pb ages was variations in the amount of atmospheric air absorbed on sample surfaces. Most of the absorbed air was removed by placing sample mounts in a desiccator and as a result the U-Pb ages showed no variation across the laser cell. Air in the laser cell was monitored by measuring the ArO^+ signal at *m/z* 56.

One of the continuing debates in U-Pb dating of zircons is on the relative merits of *zircon pretreatment*. A study of microstructural and U-Pb systematics compared[265] the behaviour of a 3500 Ma zircon which received either no pretreatment (pristine grains) or treatment by CA or TA. Hyper-spectral cathode luminescence and Raman spectroscopy were used for structural characterisation of the zircon grains and LA-ICP-MS for determination of trace element and U-Pb isotopic compositions. The effect of pretreatment was specific to individual samples and controlled by the microstructure of the original zircon grains. It was recommended that, rather than applying a standard pretreatment regime, a subset of pristine grains together with TA- and CA-treated grains be characterised by cathode luminescence imaging and Raman spectroscopy to determine the most suitable areas for reliable age determinations. It was emphasised that zircon RMs should be treated under the same conditions as samples of unknown composition. Guitreau *et al.*[266] used data from LA-ICP-MS line-scans together with information on internal textures as revealed by BSE and cathode luminescence images to identify zones of well-preserved U-Pb isotope systematics within complex zircon crystals. Data from different zones were used to construct discordia lines and obtain age information related to crystallisation and metamorphism within a single zircon crystal. A workflow for dating minerals *in situ* without extracting the minerals from the host rock combined[267] automated phase mapping by SEM/EDXRF with LA-ICP-MS. This approach was applicable to standard grain mounts, polished thin sections and hand specimens and did not require extensive manual mineral separation. The automated phase mapping provided rapid information on the chemical and mineralogical composition of the samples at high spatial resolution. The stage coordinates were converted to a file format readable by the LA system thereby locating the datable minerals in much shorter time than possible by conventional sample preparation procedures. This approach was applied to igneous, metamorphic and sedimentary samples. The high throughput was particularly advantageous for sedimentary provenance studies and could be applied to other accessory minerals such as apatite, monazite, rutile and titanite.

The use of *multiple ion counters* for U-Pb dating of zircons by LA-MC-ICP-MS made[268] it possible to date zircons with a ^{238}U signal of <0.5 mV with improved spatial resolution. The ^{202}Hg, ^{204}(Pb + Hg), ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{232}Th and ^{238}U isotope signals were measured simultaneously on only ion counters unlike previous studies that had used both ion counters and FCs. Tiny zircons and grains with small cores or narrow zonation could be analysed since three laser pulses (beam diameters 5 µm) consumed <5 ng of zircon. A precision of <1% (2SD) for ^{206}Pb/^{238}U ages was achieved at a spatial resolution of 5.8-7.4 µm diameter and <3 µm depth.

The *application of U-Pb geochronology to minerals other than zircon* is often limited by the matrix dependence of analysis combined with the paucity of matrix-matched RMs. Burn *et al.*[269] developed a novel approach to U-Th-Pb dating of allanite involving LA-ICP-MS measurement and data reduction using non-matrix-matched external calibration with the Plešovice zircon. Matrix-dependent downhole fractionation during LA was empirically quantified and corrected. The results obtained by this procedure on three allanite RMs had analytical precisions equal to those achieved by ion probe and LA-ICP-MS rastering. This calibration procedure could be employed for other non-matrix-matched pairs of a RM and a sample of unknown composition. An improved protocol for U-Th-Pb dating of xenotime by EPMA was developed[270] using the monazite RM Moacyr for which a TIMS age is known. The similar crystal and chemical properties of xenotime and monazite, along with the negligible initial Pb content, made it possible to apply monazite EPMA methodologies to xenotime. It was assumed that measurements would not be affected by the fact that the LREEs rather than the HREEs were dominant. The proposed protocol achieved analytical uncertainties of <10% for Pb, Th and U measurements in xenotime. Ages obtained for co-existing xenotime and monazite were consistent with previously published data. Matrix effects in the SHRIMP U-Pb-Th analysis of xenotime can be significant because of the wide natural range of U and REE contents in this mineral, so Cross and Williams[271] developed a matrix correction technique that required the concurrent analysis of three xenotime RMs with concordant U–Pb–Th compositions and different U and ΣREE concentrations. A least squares methodology was used to derive correction coefficients that related the SHRIMP matrix effects to the U and ΣREE concentrations. Calibrations using $^{206}Pb^+/^{270}(UO_2)^+$ and $^{208}Pb^+/^{248}(ThO)^+$ were crucial to the success of this technique. A LA-ICP-MS procedure[272] for the *in situ* dating of cassiterite, the main ore mineral in tin deposits, used ^{208}Pb instead of ^{204}Pb as a proxy for common Pb. The rationale behind this was that: (i) ^{208}Pb is much more abundant and does not suffer from interference by ^{204}Hg and (ii) cassiterite often has an extremely low Th concentration and so ^{208}Pb could be assumed to be mostly of non-radiogenic origin. The analytical procedure did not rely on an independently dated matrix-matched cassiterite RM but instead utilised NIST SRM 612 (synthetic silica glass) for calibration and a cassiterite from Russia (SPG) as a secondary RM. For each analytical session, a correction factor was determined from the difference between the Pb-Pb isochron date of the SPG cassiterite, accepted as a "true" age, and the biased U-Pb age resulting from the use of NIST SRM 612. The correction factor was then applied to correct the ^{238}U/^{206}Pb ratios for unknown samples.

Hornblende from the Lone Grove Pluton in Texas has acted as an irradiation RM in *^{40}Ar/^{39}Ar studies* for many years. Blackburn *et al.*[273] evaluated an apparent age bias between the U-Pb and ^{40}Ar/^{39}Ar geochronology systems using ID-TIMS to date zircons and titanites from the same rock from which the hornblende RM HB3gr was derived. The mean Th-corrected U-Pb date of the zircons was ~7 Ma older than the dates derived from K-Ar or ^{40}Ar/^{39}Ar measurements. Analysis of single titanite grains yielded dates ~6 Ma younger than the zircon age, indicating that the sample had experienced protracted cooling after initial crystallisation at 1090 Ma. Reconstruction of the cooling history suggested strongly that RM HB3gr was not an acceptable material for intersystem comparisons. It was also thought that any future use of this RM in ^{40}Ar/^{39}Ar studies should take into consideration the effects of Ar-loss through volume diffusion. Ellis *et al.*[274] were able to analyse a single sanidine grain by splitting large crystals into up to four fragments. One split was used to perform high-precision ^{40}Ar/^{39}Ar dating. The other splits were used to determine: (i) major element concentrations by EPMA; (ii) trace element concentrations (in the sanidine and melt inclusions) and Pb isotope compositions by LA-ICP-MS; and (iii) Sr isotope analysis by TIMS. Although ^{40}Ar/^{39}Ar is one of the best chronometers for dating extra-terrestrial bodies, the method relies on neutron irradiation of the samples. A discussion of potential solutions for making *in situ* extra-terrestrial ^{40}Ar/^{39}Ar measurements included[275] the challenges and feasibility of deploying a passive neutron source to planetary surfaces. Requirements for generating and shielding neutrons were described, as well as sample analysis and limitations such as mass, power and cost.

A recent study demonstrated[276] that *cosmogenic ^{38}Ar exposure dating of Ca-rich minerals* could be a valuable new dating tool and provided the first terrestrial cosmochrons using the ^{38}Ar isotope system. Previous application of this dating technique to terrestrial samples had been considered impracticable because of the high atmospheric ^{38}Ar background on Earth. A new generation MC noble gas mass spectrometer enabled very precise analyses of cosmogenic ^{36}Ar and ^{38}Ar abundances in irradiated terrestrial pyroxene and apatite from Australia to be made. The ^{38}Ar/^{36}Ar ratios could be measured with a precision of ±0.30% (1SD). The measured exposure age overlapped, within uncertainty, with the known ^{40}Ar/^{39}Ar eruption age of the sampling site. It was concluded that cosmogenic ^{38}Ar exposure dating on irradiated Ca-rich but Cl-free terrestrial minerals was potentially a valuable addition to the range of tools for dating cosmogenic exposure and examining geological surface processes on timescales of a few Ma.

5.3.3 Atomic absorption and atomic emission spectrometry.

The practicality of using *high-resolution ETAAS with a continuous spectrum source* to determine Pd in acid digests of platinum sulfide ores without further sample treatment was explored[277]. Results in agreement with those from extraction and separation procedures conventionally used with AAS could be obtained by measuring Pd at 244.791 nm and correcting for spectral overlap from the Fe line at 244.77 nm.

Makonnen *et al.*[278] investigated the characteristics of an *Ar-N_2-H_2 mixed gas plasma* for the analysis of geological and environmental materials by ICP-AES. When 3.7% (*v/v*) N_2 was added to the plasma gas and 1.1% (*v/v*) H_2 to the sheath gas around the Ar nebuliser gas flow, the sensitivity for 26 elements increased by factors of between 1 and 4. Measurement of the Mg^{II}/Mg^{I} ratio demonstrated that the mixed gas plasma was significantly more robust than a conventional Ar plasma. The LODs for the mixed gas plasma were similar to those obtained with an Ar plasma. Quantitative multielement analyses of eight RMs (till, lake and stream sediments, Zn-Pb-Ag sulfide ore) demonstrated the superior analytical performance of the mixed-gas plasma for complex sample matrices without the need for an IS or matrix-matched calibration.

5.3.4 Laser induced breakdown spectroscopy.

Obtaining quantitative information on the *composition of geological materials by LIBS* is challenging because of complex matrix effects that arise from the variability in sample matrices. Lepore *et al.*[279] evaluated the accuracy of univariate minor element predictions as a function of the composition of the major element matrices of the samples. From the analyses of five matrices with very different major element compositions, they concluded that prior knowledge of the sample matrix, use of normalisation and the availability of a persistent peak without spectral interference from nearby major elements were the key requirements for an accurate univariate calibration of minor elements. The uncertainty of the predicted concentrations could increase by more than an order of magnitude if the calibration matrix differed greatly from the sample matrix. In an innovative method of sample preparation for LIBS measurements of Al, Cr, Fe, Mg, Mn and Ni in nickeliferous minerals, a slurry was prepared[280] and mixed with an IS and a 10% *w/v* solution of polyvinyl alcohol. After 2 h at 50 °C, the samples were immobilised in the polyvinyl alcohol film and could be analysed by LIBS. Compared to the analysis of pressed pellets, the slurries were more homogeneous and produced less noisy LIBS spectra.

The challenges of *quantifying precious metals in geological samples by LIBS* have been explored. In the determination of Au in rock powders and drill cores, Rifai *et al.*[281] established calibration curves using 44 compressed powder RMs of various chemical compositions with Au concentrations ranging between 0 and 1000 µg g^{-1}. Principal component analysis revealed that the iron concentration accounted for about 83% of the variance in the spectra. The two different calibrations adopted for Si-rich samples (<5% Fe) and for Fe-rich samples (>13% Fe) had LODs of 0.8 and 1.5 µg g^{-1}, respectively. Normalisation with respect to the integrated spectrum intensity or to the spectral background close to the Au line improved the regression fit of the calibrations. The technique was applied to the analysis of fine and granular Si-rich uncompressed ore powders and to the mapping of bulk drill cores to demonstrate that Au could be detected in mineral samples at levels relevant for the mining industry. However, issues related to calibration and sample preparation remained to be solved. Diaz *et al.*[282] evaluated the performance of LIBS on pressed pellets of ore samples from a gold mine and surrogate samples doped with Ag and Au solutions. They achieved LODs of ~1 µg g^{-1} for Ag and Au in the surrogate samples and 0.4 - 2.3 µg g^{-1} for Ag for the ore samples. However, because of the discrete nature of Au particles, it was not possible to detect Au in the pelletised ore samples or reach the target LOD of 1 µg g^{-1} for mining samples. The authors demonstrated that an alternative approach, developed for aerosol analysis (conditional analysis), could be applied to ore samples. More than 100 gold-containing particles needed to be sampled, so >10^5 laser pulses across a pellet were required. Under these conditions, Au could be measured at concentrations as low as 1 µg g^{-1} even in ore samples.

Cáceres *et al.*[283] presented an *imaging methodology based on LIBS* to obtain the first megapixel images of large geological samples such as corals and speleothems and to provide resolution at the µg g^{-1} scale. Images of Mg, Na and Sr distributions were normalised to the Ca content. The instrumentation consisted of an optical microscope, a LIBS laser injection line, a standard optical-imaging apparatus and a 3D motorised platform for sample positioning. Compositional variations in marine mollusc shells were assessed[284] by elemental mapping using an automated LIBS system to acquire Mg/Ca intensity ratios of whole shell sections with a spatial resolution of ~90 µm and acquisition speed of 20,000 spectra per hour. This approach, which can be extended to other elements relevant to environmental studies, was regarded as a time- and cost-effective alternative to other methods, such as LA-ICP-MS, for deriving elemental distribution maps. Moncayo *et al.*[285] reported a methodology based on hyperspectral image analysis coupled to PCA for processing large raw data sets of LIBS spectra without spectral pre-processing or any prior knowledge of the sample composition. It was shown to be a powerful tool capable of identifying mineral phases and providing a deeper understanding of the sample, such as highlighting very delicate ion substitution in a mineral lattice.

5.3.5 Inductively coupled plasma mass spectrometry

5.3.5.1 ***Trace element determinations by solution-based ICP-MS.*** Methods for correcting for *spectral and non-spectral interferences in ICP-MS* have been investigated. Yokoyama *et al.*[286] examined the influence of non-spectral matrix effects on the determination of 22 trace elements (Ba, Cs, Nd, Pb, Rb, REEs, Sr, Th, U and Y) in rock samples by quadrupole ICP-MS. They developed a new ID-IS method using a mixture of ^{113}In- and ^{203}Tl-enriched spikes to correct for mass-dependent sensitivity variations. When combined with corrections for oxide and hydroxide interferences, good agreement (±10%) with abundances reported in previous studies was achieved for eight GSJ rock RMs of varying composition. For the andesitic and basaltic rocks (JA-2, JB-2 and JB-3) the agreement was better than ±5%. To overcome[287] Hf and Ta oxide interferences in the determination of trace amounts of Au in geological samples by ICP-MS, a combination of an aerosol dilution technique, in which Ar was added to the sample aerosol prior to the ICP, and addition of a CH_4 plasma modifier to the nebuliser Ar gas flow was employed. Adding 3 mL min^{-1} CH_4 increased the Au S/N by a factor of about 10 and resulted in a LOQ (10SD) of 0.014 ng g^{-1} Au. In an evaluation of the method using 39 soil, sediment and rock RMs, the levels of Au determined were consistent with the reference values, even though the Au was present at <1 ng g^{-1} in 11 of the geological RMs.

5.3.5.2 ***Trace element determinations by laser ablation ICP-MS.*** The potential added value of ultrafast lasers was evaluated[288] in a topical review (168 references) on the use of *fs lasers in LA-ICP-MS* for elemental and isotopic analysis over the last 15 years. Benefits included greatly reduced chemical fractionation effects, negating the need for matrix-matrixed RMs. In addition, independence of laser–matter interactions from the optical properties of the target material provided efficient ablation of optically transparent materials like quartz. Apart from the fact that there are geochemical applications for which fs lasers do not confer any key advantage, e.g. zircon U-Pb geochronology, one of the important limitations is still the high price of fs LA systems compared to that of ns excimer systems.

In order to evaluate *long term precision and accuracy*, a new Matlab-based software called "LA-MINE" was developed[289] to extract automatically RM data from large LA-ICP-MS datasets obtained over a 5-year period under a wide range of ablation and tuning conditions. This program required no user input and years of data could be processed within a few hours. Detailed consideration of data quality for Al, B, Ba, Fe, Li, Mg, Mn, Na, P, Pb, Rb, REE, Sr, Th, U, Y and Zn in 10 commonly analysed RMs highlighted where care needed to be taken, the relative effects of mass fractionation, and errors in the reported values of some elements in certain RMs. Recommendations for the improvement of data quality included the role of diatomic gas in the laser cell, the selection of appropriate RMs in calculating fractionation factors and choice of transport tubing material.

Several studies focused on *improvements in multielemental imaging* using LA-ICP-MS. A novel cylindrical ablation cell, with a 70 mm diameter was developed[290] specifically for this type of application. Based on the two-volume cell strategy, the major innovation of the new cell design was that the sampling tube was coaxial with the laser beam and fixed to the laser assembly, thereby enabling the sampling point to be positioned constantly over the ablation spot. A viscous film was used to seal the junction between the lower and upper parts of the cell. The figures of merit were assessed by monitoring the transient signal of ^{238}U from ablated NIST SRM 610 (soda lime glass). The washout time was 210 ms. This cell could be fitted on the stage of standard LA systems. Improvements in cell design, in particular to achieve faster washout times, have made it possible[291] to realise the benefits of combining LA with ICP-TOF-MS. A multielemental image of an area of 1 x 2 mm of a polished thin section of the mineral sphalerite (ZnS) was obtained at a spatial resolution of 5 µm in 80 minutes. The approach of Fox *et al.*[292] was to use numerical methods to improve the spatial resolution of elemental maps. They demonstrated that sub-spot size resolution could be achieved through linear inversion methods. As multiple LA spots may sample the same location, the area sampled in an analysis was divided into pixels and the measured concentration defined as the average concentration of the pixels sampled by a spot. A system of linear equations used information from multiple overlapping spots to infer sub-spot size variations in element concentrations. Examples from magmatic ascent speeds and (U-Th)/He noble gas thermochronometry were used to demonstrate the utility of this approach. A novel tool called Monocle was devised[293] for extracting quantitative elemental and isotope data from LA-ICP-MS maps. Histograms and density or probability plots of the element concentrations or isotope ratios contained within the area under a size- and shape-adjustable "virtual" loupe were displayed as the loupe was moved across the map. This tool was an add-on to the commercial Iolite data reduction program and it was expected that this approach to post-data acquisition analysis of images would increase the productivity of LA-ICP-MS facilities.

In the development of a protocol[294] for *in situ LA-ICP-MS analysis of fluid inclusions* to determine concentrations of I in addition to those of Br and Cl, potential RMs (scapolite Sca17, Durango apatite, USGS GSE-1G and GSD-1G) were first characterised. Although low in I content, only Sca17 was a suitable RM for all three halogens. The method was then verified by analysis of synthetic inclusions with known Br, Cl and I concentrations before applying the triple-halogen analysis to natural inclusions. Results from the study of fluid inclusions from three geological settings revealed very significant differences in I/Cl ratios whereas the Br/Cl ratios from the different settings were indistinguishable. The ability to determine I concentrations in addition to those of Br and Cl opened up new possibilities for studying the source and migration of crustal fluids. Three significant sources of contamination highlighted[295] in a practical guide to the LA-ICP-MS analysis of fluid inclusions were: the quality of the carrier gas; the material and cleanliness of ablation cell, tubing material and cones; and contamination of the sample surface during its preparation. A strategy for minimising contributions from these sources and optimising quantification of fluid inclusion data close to the LOD was advocated. Jian *et al.*[296] used a freezing cell in the UV-fs-LA-ICP-MS analysis of CO_2-rich fluid inclusions from a quartz vein-style Au-Mo deposit from central China. Transforming gaseous and liquid CO_2 into the solid state by freezing reduced the internal pressure of the fluid inclusions significantly. The frozen state was maintained during ablation because the fs laser pulses transferred a minimal amount of heat. Consequently, the transient signals were more stable than those from the ns-LA-ICP-MS analysis of such inclusions at room temperature and improved the analytical performance.

In the determination of *REE mass fractions* in olivine by LA-ICP-MS, large spot sizes of 160 µm and laser repetition rates of 30 Hz were used[297] to produce pit depths of ~165 µm and to ablate ~500 µg of material in order to maximise the REE signals. Typical LODs were 0.2-0.4 ng g^{-1} with biases of between 5 and 10%. The method was therefore suitable for studies of REE concentrations in olivines which could be as low as the ng g^{-1} level. In a study of the isobaric interferences that are a constant problem at many REE isotope masses, REE abundances were determined[298] in both low ($m/\Delta m = 300$) and medium ($m/\Delta m = 2500$) resolution modes by LA-SF-ICP-MS. The results obtained in medium resolution mode were significantly more accurate and precise, particularly for RMs with low REE contents. A list of preferred masses that are least susceptible to isobaric interferences was given.

5.3.5.3 ***Isotope ratio determinations by ICP-MS.*** Judging by the number of published papers, the *measurement of isotope ratios* by MC-ICP-MS and other ICP-MS techniques continues to be a fruitful area of research in analytical geochemistry. Many of these publications record relatively modest improvements in methodologies, such as the modification of an existing column chemistry protocol or alternative detector configurations. These are summarised in Table 6 and deal exclusively with solution sample introduction into the instrumentation concerned.

Measurement of Sr isotope ratios by LA-ICP-MS continues to attract interest for a variety of geological applications. The advantages of using LA-MC-ICP-MS for determining $^{87}Sr/^{86}Sr$ ratios in speleothems included[299] rapid data acquisition, higher spatial resolution, larger sample throughput and the absence of chemical treatment. The minimum Sr concentration required for reliable $^{87}Sr/^{86}Sr$ ratios was 300 µg g^{-1} but the best results were obtained when Sr concentrations exceeded 1000 µg g^{-1}. Line-scans provided better precision than spot analysis. Although a fs LA system provided a more stable signal than a ns laser, and therefore more precise measurements, its use for samples with low Sr contents (<1400 µg g^{-1}) was not recommended because of the lower signal intensities which led to less precise results. Another study compared[300] the characteristics of ns and fs LA-ICP-MS systems for *in situ* Sr isotope measurements in transparent minerals such as feldspars. The results indicated that the fs LA rates were more consistent than those for the ns laser system and provided higher sensitivities at similar energy settings. Addition of N_2 to the axial channel of the ICP suppressed the Kr and Rb signal intensities and the interferences from polyatomic and doubly charged ions such as $CaAr^+$, Ca_2^+, Er^{2+} and Yb^{2+}. Although the sensitivity for Sr was also suppressed by the addition of N_2, this effect was less than for the other elements so the S/N was enhanced and the accuracy of the $^{84}Sr/^{86}Sr$ ratio measurements in particular improved. Samples with a Rb/Sr ratio of <0.5 could be analysed with an accuracy of <0.0002 for $^{87}Sr/^{86}Sr$. Strontium isotope ratios were determined[301] in basaltic glasses with Rb/Sr ratios <0.14 by LA-MC-ICP-MS using seven FCs to collect signals at *m/z* 82 to 88. The isobaric interference of ^{87}Rb on ^{87}Sr was corrected by the peak stripping method and instrumental mass fractionation on $^{87}Sr/^{86}Sr$ corrected using an exponential law. A linear correlation between the residual analytical bias on $^{87}Sr/^{86}Sr$ and the measured raw $^{87}Rb/^{86}Sr$ ratio was observed. Three USGS basaltic glasses with different Rb/Sr ratios were analysed to establish this relationship for each analytical run; the residual analytical biases on the $^{87}Sr/^{86}Sr$ ratios of the unknowns were then corrected by applying this linear relationship. The final $^{87}Sr/^{86}Sr$ ratios were accurate to ±100 ppm.

In situ measurements of Pb by LA-ICP-MS have been investigated extensively. A ns LA-MC-ICP-MS method was developed[302] for high precision Pb and Sr isotope ratio determinations in archaeological glasses. Inaccurate data were obtained when glass RMs with basaltic matrices were used to correct for mass bias. Matrix-matched RMs were therefore regarded as indispensable. Four Corning soda-lime silicate glass RMs, mimicking the composition of archaeological glasses, were characterised for their Pb and Sr isotope compositions by solution and LA-MC-ICP-MS. Interferences from doubly charged REE ions affecting the Sr isotope ratios were circumvented by operating the instrument at higher mass resolution. The most accurate Pb isotope ratio results were obtained by correcting for instrumental mass discrimination with the exponential law, using Tl (introduced by pneumatic nebulisation) as an isotopic IS and Corning D glass as the bracketing isotopic calibrator. The *in situ* measurement[303] of "common" Pb isotope ratios in silicate glasses and minerals using a 193 nm excimer LA system coupled to a double-focusing single-collector ICP-MS instrument was evaluated as a possible alternative to MC-ICP-MS. Lead isotope ratios were corrected for mass bias relative to NIST SRM 610 (trace elements in glass). It was recommended that unknowns and bracketing RMs should be analysed at identical spot sizes and to use spot sizes ≥25 µm. Analysis of a range of NIST, MPI-DING and USGS RM glasses identified analytical artifacts that were attributed to non-spectral matrix effects. The precision (2SD) of the Pb isotopic measurements was similar to that obtained in previous studies. However, the authors doubted that further improvement in the precision of measurement of the $^{20X}Pb/^{206}Pb$ and $^{20X}Pb/^{204}Pb$ ratios for materials with high (>5 $\mu g\ g^{-1}$) Pb concentrations could be achieved with this approach and that, consequently, LA-MC-ICP-MS remained the preferred analytical technique.

Bauer and Horstwood[304] assessed suitable methods for the *combined determination of Lu-Hf and U-Pb isotope signatures* in zircons by solution and LA-MC-ICP-MS. By reducing the pit volume during LA and taking consecutive U-Pb and Lu-Hf isotopic measurements, they demonstrated that acceptable uncertainty levels could be achieved at a spot size of 25 µm and a pit depth of 18 µm. This corresponded to ablation of ~40 ng of zircon. The possibility of reducing the LA pit depth to 10 µm was demonstrated by decreasing the integration time for Hf analysis without seriously compromising the uncertainty. The method had the potential to yield geologically meaningful results from complex finely-zoned zircons. The LASS technique is an alternative approach that enables simultaneous collection of data from different isotope systems, such as U-Pb and Lu-Hf, on separate ICP-MS instruments. However, it has been noted[305] that the full benefits of such simultaneous datasets are often not exploited as laboratories usually process each dataset separately. New features were developed within the data reduction software Iolite to load, synchronise and visualise concurrently two or more datasets acquired simultaneously. The utility of this new data reduction facility in Iolite was demonstrated in case studies to image U-Pb and Lu-Hf isotope distributions in zircon and U-Pb and Sm-Nd isotope compositions in monazite.

One of the first *LA-MC-ICP-MS carbon isotope* studies of natural minerals has been reported[306]. The new method, which used an Excimer LA system coupled to an MC-ICP-MS instrument, adopted a SSB method using magmatic calcites as bracketing RMs to correct for instrumental mass bias. The method was validated using a suite of magmatic and hydrothermal calcites with $\delta^{13}C$ values ranging from -6.9 to 1.48‰ previously determined by IRMS. An analytical precision of ≤0.25‰ was achieved for homogenous magmatic calcites. The mean values obtained in the LA-MC-ICP-MS analyses of calcites and corals (aragonite) agreed within uncertainties with those determined by IRMS on bulk samples.

5.3.6 Thermal ionisation mass spectrometry.

Factors affecting the *accuracy and precision of Nd isotope ratio determinations by TIMS* were assessed in recent studies. A four step acquisition scheme was developed[307] to correct systematically for drift in collector efficiencies and amplifier gains. This scheme was based on monitoring the Nd isotope ratios dynamically and involved the use of four different magnet settings per cycle. It was assumed that Nd mass fractionation followed an exponential law when calculating dynamic ratios. Data from over 60 runs of the GSJ RM JNdi-1 (Nd oxide) analysed over a period of 1.5 years on three different instruments were used to determine figures of merit for the four step method. Two chromatographic separation schemes were also evaluated. It was advised that caution should be exercised when using fine Ln-spec resin (25-50 μm) for the chromatographic separation of Nd. The criteria and corrections developed in this study could also be applied to other isotopic systems. In a case study[308] of 1.48 Ga alkaline rocks from Khariar, India, the effect of various methods of data acquisition, fractionation correction and normalisation on the accuracy of ^{142}Nd/^{144}Nd determinations was investigated. A power-normalised exponential law was the most appropriate method to correct for mass fractionation after data acquisition in a multi-dynamic mode. Contradictory results from two previous studies of the same outcrops arose from the use of different Nd RMs (*e.g.* LaJolla Nd, JNdi-1, Ames Nd and many in-house RMs). It was proposed that a single and homogeneous terrestrial RM, such as JNdi-1, should be used for all studies of silicate differentiation in the early evolution of the Earth employing ^{142}Nd as a tracer.

The influence of low recovery rates from column separation procedures on *calcium isotope measurements by double spike TIMS* was investigated[309]. Three RMs, (a seawater and two basalts) were processed through a PTFE micro-column containing Bio-Rad AG MP-50 resin. The eluant was divided into five aliquots containing approximately 20% of the total Ca content. After correction using the ^{42}Ca–^{43}Ca double spike technique with exponential law, the δ^{44}Ca /^{40}Ca of the individual aliquots or "subcuts" showed limited variation and were consistent within uncertainties with the results from full recovery. On the basis of this, a "peak cut" procedure was proposed in which the double spike was added to the sample and equilibrated prior to column separation and only the middle part of the Ca eluate was collected to obtain a pure Ca fraction. In this way isobaric interferences from elements like K and Sr were effectively eliminated. This was particularly important for samples with low CaO contents. Mondal and Chakrabarti[310] proposed a novel sample loading method and protocol for Ca stable isotope ratio measurements by double spike TIMS. An external reproducibility for δ^{44}Ca/^{40}Ca of <0.1‰ for different sample matrices (seawater, carbonates and silicates) using a ^{43}Ca–^{48}Ca double spike was achieved, together with the simultaneous measurement of δ^{44}Ca/^{42}Ca. A sample loading technique employing a combination of Re and Ta filaments and a Ta_2O_5 activator provided an external reproducibility for δ^{44}Ca/^{40}Ca of better than 0.08‰

and was therefore preferred to the other two loading protocols tested for which the external reproducibility for $\delta^{44}Ca/^{40}Ca$ ranged from ±0.16 to 0.26‰.

A protocol for *microscale $^{87}Sr/^{86}Sr$ isotope ratios determinations* by TIMS combined[311] high-performance mechanical microsampling and high-precision TIMS measurements. A slurry prepared from a milled sample was collected with a micropipette and transferred to a Class 1000 clean room for digestion and purification. One of the most critical aspects of the TIMS determinations was the loading procedure of the very small samples onto single Re filaments. Measurements in dynamic mode were preferred over static mode because of the better long-term reproducibility. Although more time-consuming, this TIMS method gave more accurate and precise data than *in situ* LA-MC-ICP-MS analysis.

Further developments in *high-precision isotope ratio determinations by TIMS* are included in Table 6.

5.3.7 Secondary ion mass spectrometry.

The use of *SIMS for the determination of C and H concentrations and isotope compositions in silicate samples* relevant to geochemistry and cosmochemistry was reviewed[312] (65 references). Current instrumentation was summarised, problems arising from calibration procedures highlighted and performance characteristics, such as lateral and depth resolution, and LODs were considered.

There is an increasing need for *matrix-matched RMs for SIMS analysis* just as for other microbeam techniques. Ramsey and Wiedenbeck[313] proposed a method for quantifying the heterogeneity of candidate RMs at the pg scale. They illustrated their approach by measuring the oxygen isotope ratio of four quartz samples by SIMS using a large number (~100) of closely spaced duplicated readings. Measurement repeatability was extracted from the total variability using ANOVA statistics. The use of a sub-area of the test material was preferable to using a piece of unrelated homogenous silicate glass for estimating and correcting instrumental drift. Three approaches for estimating measurement repeatability were compared and a strategy proposed for predicting the number of measurements on individual fragments of a material required to achieve a specified target uncertainty. A study of two baddeleyite megacrysts, Phalaborwa S0045 and Mogok S0069, as potential RMs for oxygen isotope analysis by SIMS showed[314] repeated analysis of a number of fragments made it possible to measure the O isotopes with precisions (*e.g.* ±0.2 to ±0.25‰ per spot, 2SD) similar to those obtained in the analysis of zircons. Metamictisation, lattice orientation and chemical composition played no significant role in instrumental mass fractionation. Fourteen glass RMs comprising nine synthetic basaltic glasses, four natural basaltic glasses and one natural rhyolitic glass were characterised[315] for the measurement of volatile elements C, Cl, F, H, P and S by SIMS. The elemental concentrations were designed to cover the range of data for volatile elements reported in previous studies. Although limited quantities of the synthetic glasses were prepared, the natural glasses were available to other laboratories on request.

Matrix effects on instrumental mass fractionation of O isotopes in olivine measured by SIMS were investigated[316] over the entire olivine Fe-Mg solid-solution series. The matrix effects were reproducible between different SIMS instruments and between different analytical sessions. A model curve, developed to correct measurements on olivine samples with intermediate chemical composition for instrumental mass fractionation, achieved a precision and accuracy of ~0.4‰ for δ^{18}O at the 10-25 µm scale. Similarly, Sliwinski *et al.*[317] explored the effects of cation composition on instrumental mass fractionation in the SIMS determination of δ^{13}C and δ^{18}O in carbonates of the magnesite–siderite solid-solution series ($MgCO_3$–$FeCO_3$). A suite of 12 new RMs was developed for calibration purposes. The calibration curves of both isotope systems were non-linear and mass bias was consistently most sensitive to changes in composition near the iron-free end member, with deviations up to 4.5‰ for δ^{13}C and 14‰ for δ^{18}O with increasing Fe content. The cause of variability in the calibration curve shape was not well understood. This study demonstrated the importance of having available a sufficient number of well-characterised RMs so that potential complexities of curvature could be adequately delineated.

Carr *et al.*[318] evaluated possible *effects of crystal orientation* on measurements of U-Pb and O isotopic compositions in cassiterite (SnO_2) by SIMS. Previous studies had shown large effects of crystal orientation on SIMS analyses of rutile, which is isostructural with cassiterite. However, for cassiterite none of the key measurement parameters such as Pb/UO, UO_2/UO or ^{18}O/^{16}O ratios showed any dependence on crystallographic orientation. The contrasting behaviour of cassiterite and rutile provided new insights into the mechanisms involved when such effects are observed in SIMS.

Ishida *et al.*[319] developed an *in situ* method for the *simultaneous determination of C and N isotope ratios in organic matter by SIMS* with a spatial resolution of ~12 μm. Four molecular ions ($^{12}C_2^-$, $^{12}C^{13}C^-$, $^{12}C^{14}N^-$ and $^{12}C^{15}N^-$) were measured simultaneously using a new detector geometry and aperture settings. They evaluated the homogeneity of $\delta^{15}N$ values in potential anthracite RMs, for which $\delta^{13}C$ compositions were known to be homogeneous. The analytical precisions for $\delta^{13}C$ and $\delta^{15}N$ in RM UWLA-1 anthracite were 0.16 and 0.56‰ (2SD), respectively.

5.3.8 Accelerator mass spectrometry.

An investigation of the optimum conditions for coupling LA with AMS for the *spatially resolved analysis of radiocarbon* (^{14}C) in carbonates[320] involved first finding a suitable laser source for the ablation of carbonates for high conversion of $CaCO_3$ to gaseous C. Of the three lasers tested (Nd:YAG, 266 nm; Nd:YAG, 213 nm; and ArF excimer, 193 nm), the ArF excimer laser, with a C gas conversion efficiency of 70±4%, was most suitable for online ^{14}C analysis using LA-AMS. Special attention was paid to the design and washout behaviour of the LA-AMS cell so that the characteristics of the gas transported from the cell were compatible with the requirements of the AMS high vacuum ion source, which demanded low carrier gas flow rates. The use of different capillaries to interface the LA cell with the ion source of the AMS system showed that the gas flow rates applied in LA-AMS were more than a factor of five higher than for regular ^{14}C AMS gas measurements, resulting in reduced ionisation efficiencies. As a result of this study and with the aim of making LA-AMS a routine technique for online ^{14}C analysis of carbonate samples, an improved LA-AMS setup was under development to combine higher C gas production with optimised gas transport in order to gain higher ionisation efficiencies.

5.3.9 X-ray spectrometry.

Over the last 30 years, *portable XRFS instruments* have grown to be one of the key techniques for geochemical analysis in the field, particularly for mining and environmental applications. A valuable review (177 references) traced[321] the development of pXRFS, its current potential and limitations and offered advice on how to make the most of this technology while ensuring data quality and avoiding common pitfalls. A recent case study of the application of pXRFS in mineral exploration was[322] the analysis of carbonate minerals containing infilled hydrothermal veins. Suitable matrix-matched (in-house) RMs were selected to assess instrumental performance before establishing strict QA/QC procedures and developing linear calibration equations for carbonate-related elements. The lack of CRMs with suitable levels of trace elements made it impossible to make reliable corrections so the development of commercially available CRMs from carbonate-hosted mineral deposits was recommended. Results from this study indicated that pXRFS used in a qualitative manner was able to identify veins with multiple generations of carbonate infill and to define areas for further characterisation by laboratory techniques.

Alov and Sharanov[323] proposed a novel procedure for the rapid *analysis of Cu-Zn ores by TXRFS*. Several non-aqueous high-viscosity liquids were tested and ethylene glycol selected to prepare suspensions of the powdered ore. A Ni IS was added and the suspension treated with ultrasonic radiation (to destroy ore agglomerates) and homogenised before a sub-sample was taken with a micropipette. The suspensions were stable long enough (~2 minutes) for representative samples to be taken. This procedure made it possible to determine the elemental composition of solid ore samples rapidly because sample digestion was not necessary.

Advances in μ-EDXRFS mapping have opened up new opportunities for rapid analysis. Mineral distribution maps of thin sections of plutonic rocks were acquired[324] by applying a classification algorithm called spectral angle mapper. This physically-based spectral classification determined the spectral similarity between two spectra by matching pixels to reference spectra. The results obtained were in accordance with results from automated mineralogy obtained by other techniques and demonstrated that μ-EDXRFS mapping was a suitable method for providing fast overviews of chemical, mineralogical and textural information with little sample preparation effort and short acquisition times. The so-called Maia Mapper[325] was an automated laboratory μXRF mapping system for elemental imaging of drill core sections. It consisted of a Maia detector system, engineered several years ago for EDXRF and elemental imaging, a high brightness metal jet X-ray source from Excillum, a polycapillary lens and a sample scanning stage that took standard drill-core sections. The Maia Mapper was capable of high definition XRFS mapping of mineral samples across 500 mm at a spatial resolution of about 32 μm. The sensitivity was sufficient to capture fine details of trace element indicators and precious metal phases in mineralised veins.

A *comparison of PIXE and XRFS techniques* was conducted[326] to assess the best approach for the determination of major elements and some minor elements in heterogeneous lake sediments. Any discrepancies between the two techniques were mainly related to the texture of the sediments and the intrinsic features of PIXE and XRFS. It was recommended that to get the best accuracy by either technique, a linking powder should be added to the sediments to fill the voids and increase the fluorescence intensities and that replicate measurements should be made. Although appropriate, neither suggestion could be considered novel. Similar sample preparation procedures have been described previously and it should be common practice, especially when analysing inhomogeneous samples, to perform repeat analyses.

5.3.10 Other spectrometric techniques.

O*ff-axis integrated cavity output spectroscopy*, presented[327] as a new methodology for measuring the H isotope composition in hydrous minerals, actually took laser absorption spectroscopy methods widely used to measure the isotopic compositions of waters and applied them to the analysis of solid hydrous materials. Water was extracted from minerals in a high-temperature quartz column and transported to the analyser in a stream of dry air carrier gas. Detailed documentation of the hardware operation and data processing were provided together with recommendations for overcoming redox interferences in the analysis of biotite and other Fe-bearing minerals. The system was capable of determining δD in waters liberated from phyllosilicate and hydrous sulfate minerals with volumes as low as 0.25 μL. The average precision was 1.1‰ and the accuracy was within 1.5‰ of values obtained by IRMS.

6. Glossary of terms

2D	two dimensional
3D	three dimensional
AAS	atomic absorption spectrometry
AB	arsenobetaine
ABF	ammonium bifluoride
AEC	anion exchange chromatography
AES	atomic emission spectrometry
AFS	atomic fluorescence spectrometry
AMS	accelerator mass spectrometry
amu	atomic mass unit
ANOVA	analysis of variance
APDC	ammonium pyrrolidine dithiocarbamate
ASU	Atomic Spectrometry Update
AVEC	attenuation versus evolved carbon
BCR	Community Bureau of Reference (EU)
BP	bulk particle
BSE	back-scattered electron
C_{18}	octadecyl bonded silica
CA	chemical abrasion
CE	capillary electrophoresis
CF	continuous flow
CLD	chemiluminescence detection
CNT	carbon nanotube
CPE	cloud point extraction
cps	counts per second
CRM	certified reference material
CS	continuum source
CT	computed tomography
CV	cold vapour
CVG	chemical vapour generation
DBT	dibutyltin
DDC	diethyldithiocarbamate
DES	deep eutectic solvent

DGA	diglycolamide
DGT	diffusive gradient in thin films
DLLME	dispersive liquid liquid microextraction
DMA	dimethylarsenic
DME	dispersive microextraction
DMF	dimethylformamide
DOC	dissolved organic carbon
DRI	Desert Research Institute (USA)
EDB	electrodynamic balance
EDTA	ethylenediaminetetraacetic acid
EDXRFS	energy dispersive X-ray fluorescence spectrometry
EN	European Committee for Standardisation
EPMA	electron probe microanalysis
ERM	Environmental Resources Management
ETAAS	electrothermal atomic absorption spectrometry
EtHg	ethylmercury
ETV	electrothermal vaporisation
EU	European Union
FAAS	flame atomic absorption spectrometry
FC	Faraday cup
FFF	field flow fractionation
FI	flow injection
FIA	flow injection analysis
fs	femtosecond
FTIR	Fourier transform infrared
GC	gas chromatography
GD	glow discharge
GLS	gas liquid separator
GRIP	Greenland Ice Core Project
GSJ	Geological Survey of Japan
HEN	high efficiency nebuliser
HFSE	high field strength element
HG	hydride generation
HPS	High-Purity Standards

HPLC	high performance liquid chromatography
HR	high resolution
HREE	heavy rare earth element
IAEA	International Atomic Energy Agency
IAG	International Association of Geoanalysts
IC	ion chromatography
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma atomic emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
ICP-MS/MS	inductively coupled plasma tandem mass spectrometry
id	internal diameter
ID	isotope dilution
IDA	isotope dilution analysis
IEC	ion exchange chromatography
IGI	Institute of Geochemistry, Irkutsk (Russia)
IMEP	International Measurement Evaluation Programme
INAA	instrumental neutron activation analysis
INCT	Institute of Nuclear Chemistry and Technology (Poland)
IR	infrared
IRA	isotope ratio analysis
IRMM	Institute for Reference Materials and Measurements (EU)
IRMS	isotope ratio mass spectrometry
IS	internal standard
ISBN	international standard book number
ISM	incremental sampling methodology
ISO	International Organization for Standardisation
LA	laser ablation
LASS	laser ablation split stream
LGC	Laboratory of the Government Chemist (UK)
LIBS	laser induced breakdown spectroscopy
LIFS	laser induced fluorescence spectrometry
LLE	liquid-liquid extraction
LLME	liquid-liquid microextraction
LOD	limit of detection

LOQ	limit of quantification
LPME	liquid phase microextraction
LREE	light rare earth element
LSDBD	liquid spray dielectric barrier discharge
MAD	microwave assisted digestion
MAE	microwave assisted extraction
MBT	monobutyltin
MC	multicollector
MDL	method detection limit
MeHg	methyl mercury
MFH	medicine food homology
MIL	magnetic ionic liquid
MIO	magnetic iron oxide
MIP	microwave induced plasma
MLLE	micro liquid-liquid extraction
MMA	monomethylarsenic
MP	microwave plasma
MPI	Max Planck Institute (Germany)
MRM	multi reaction monitoring
MS	mass spectrometry
MS/MS	tandem mass spectrometry
MSPE	magnetic solid phase extraction
MU	measurement uncertainty
MWCNT	multiwalled carbon nanotube
m/z	mass to charge ratio
NAA	neutron activation analysis
NBS	National Bureau of Standards (USA)
NCS	National Analysis Center for Iron and Steel (China)
Nd:YAG	neodymium doped: yttrium aluminium garnet
NIES	National Institute for Environmental Studies (Japan)
NIOSH	National Institute of Occupational Safety and Health (USA)
NIR	near infrared
NIST	National Institute of Standards and Technology (USA)
NMIJ	National Metrology Institute of Japan

NP	nanoparticle
NRCC	National Research Council Canada
NRCCRM	National Research Centre for Certified Reference Materials (China)
ns	nanosecond
NTIMS	negative thermal ionisation mass spectrometry
NWRI	National Water Research Institute (Canada)
PAH	polyaromatic hydrocarbon
PCA	principal component analysis
PFA	perfluoroalkoxy alkanes
PGE	platinum group element
PhHg	phenylmercury
PIXE	particle-induced X-ray emission
PLS	partial least squares
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)
ppm	parts per million
PSL	polystyrene latex
PTE	potentially toxic element
PTFE	poly(tetrafluorethylene)
PTR	proton transfer reaction
PVG	photochemical vapour generation
pXRF	portable X-ray fluorescence
pXRFS	portable X-ray fluorescence spectrometry
QA	quality assurance
QC	quality control
QCL	quantum cascade laser
QCLAS	quantum cascade laser absorption spectrometry
RCS	respirable crystalline silica
REE	rare earth element
RIMS	resonance ionisation mass spectrometry
RM	reference material
RMSEP	route mean square error of prediction
RSD	relative standard deviation

SARM	South African Reference Material
SAXS	small angle X-ray scattering
SBET	simplified bioaccessibility extraction test
SBME	solvent bar micro-extraction
SCF	supercritical fluid
SD	standard deviation
SDD	silicon drift detector
SDS	sodium dodecyl sulfate
SEM	scanning electron microscopy
SES	spark emission spectroscopy
SF	sector field
SFOD	solidification of a floating organic droplet
SHRIMP	sensitive high resolution ion microprobe
SI	système international d'unités
SIMS	secondary ion mass spectrometry
SLME	solid liquid microextraction
SMPS	scanning mobility particle sizer
S/N	signal-to-noise ratio
SNMS	sputtered neutral mass spectrometry
sp	single particle
SPAMS	single particle aerosol mass spectrometry
SPE	solid phase extraction
SPME	solid phase microextraction
SPS	Spectrapure Standards
SRM	standard reference material
SSB	sample-standard bracketing
SSME	supramolecular solvent microextraction
SSID	species specific isotope dilution
SSME	supramolecular solvent microextraction
TA	thermal annealing
TBT	tributyl tin
TD	thermal desorption
TEM	transmission electron microscopy
TEOM	tapered element oscillating microbalance

TIMS	thermal ionisation mass spectrometry
TMAH	tetramethylammonium hydroxide
TML	tetramethyllead
TOF	time-of-flight
TXRF	total-reflection X-ray fluorescence
TXRFS	total-reflection X-ray fluorescence spectrometry
UA	ultrasound-assisted
UAE	ultrasound-assisted extraction
UBMG	unified bioaccessibility method (gastric fluid only)
USGS	United States Geological Survey
US EPA	United States Environmental Protection Agency
USN	ultrasonic nebuliser
UME	National Metrology Institute of Turkey
UV	ultraviolet
VG	vapour generation
VSMOW	Vienna Standard Mean Ocean Water
WHO	World Health Organisation
XANES	X-ray absorption near-edge structure
XAS	X-ray absorption spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
XRFS	X-ray fluorescence spectrometry
Z	atomic number

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Table 1. Preconcentration methods using solid phase extraction in the analysis of water

Analytes	Matrix	Substrate	Coating or modifier	Detector	LOD (in µg L^{-1}) unless stated otherwise	Validation	Reference
Ag NPs	Environmental waters	chitosan	Fe_3O_4 NPs	ICP-MS	0.016 for 31 nm particles	Spike recovery	328
Ag, Au, Pd	Water, ore, automobile catalyst	graphene oxide and $MnFe_2O_4$ NPs	2-mercaptobenzothiazole	ICP-AES	0.045 (Au) to 0.076 (Ag)	Spike recovery (for water samples)	329
Ag, Pt	Seawater	Dowex® 1×8	none	ICP-SF-MS	0.02 (Pt) to 0.20 (Ag) pM kg^{-1}	Spike recovery from internal Geotraces QA samples; ID	330
As^{III}	Water	Cellulose fibers coated with amorphous silica	(3-mercaptopropyl)-trimethoxysilane	XRFS	0.045 ng mL^{-1}	Spike recovery and IRMM CRM BCR-610 (ground water)	331
As, Cu, Pb, Se	Water	graphene oxide NPs	CeO_2	EDXRFS	0.07 (As^{v}, Pb^{II}) to 0.17 (Cu^{II}) ng mL^{-1}	Spike recovery and IRMM CRM BCR-610 (ground water)	332
As^{v}, Cr^{III}	Water	graphene oxide	alumina	EDXRFS	0.02 (As) and 0.11 (Cr) ng mL^{-1}	Spike recovery and NIST SRM 1640a (Natural Water)	333
As, Cr, Hg, Sb, Sn, V	Water	ethyl methacrylate and 2-diethylaminoethyl methacrylate	1,3-propanesultone	ICP-MS	1.0 (As) to 3.7 (Sn) ng L^{-1}	Chinese CRMs GSBZ3175-94, GSB07-1187-2000, GSB07-3171-2014, GSB07-1376-2001, GSB07-3173-2014, BWZ6705-2016, (all environmental water)	334

Bi, Cu, Ni, Pb, Se, Tl, Zn	Water	Fe_3O_4 NPs	*Insitu* MnO_2 coating	TXRFS	0.19 (Pb) to 0.73 (Se)	IRMM CRM BCR-610 (ground water)	335
Cd, Cu, Fe, Mn, Ni, Pb, Zn	Seawater	Nobias PA-1 resin	EDTA and iminodiacetic acid coordination groups	ICP-MS/MS	62.2 (Pb) pg L^{-1} to 1.76 (Ni) ng L^{-1}	NRCC CRM NASS-6 (seawater)	336
Cd, Co, Cu, Fe, Ni, Pb, Zn	Seawater	Presep® PolyChelate resin	carboxymethylated pentaethylenehexamine	ICP-SF-MS	0.6 (Pb) to 58.6 (Ni) pM	Internal Geotraces QA samples; spike recovery; IDA	337
Cr^{III}	Industrial and river waters	MWCNTs	L-arginine	FAAS	0.7 ng mL^{-1}	NIST SRM 1640a (Natural Water)	338
Cu, Fe, Pb, Zn	Drinking, tap and seawaters	silica gel	diethyldithiophosphate	FAAS	0.45 (Zn) to 1.17 (Pb)	NIST SRM 1643e (Trace Elements in Water); spike recovery	339
Cr^{VI}	Water	graphene oxide	3-aminopropyltriethoxysilane	EDXRF	0.17 ng mL^{-1}	Spike recovery	340
CH_3Hg^+	Water	CNTs	Fe_3O_4 NPs	GC-AFS	5.4 pg mL^{-1}	Spike recovery	341
Hg^{2+}, CH_3Hg^+	Water	graphene oxide	thiourea	HPLC-ICP-MS	3.8 (Hg^{2+}) to 1.3 (CH_3Hg^+) ng L^{-1}	Spike recovery	342
Hg^{2+}, CH_3Hg^+ and $PhHg^+$	Tap, environmental and waste waters	SiO_2 and Fe_3O_4 NPs	gamma-mercaptopropyltrimethoxysilane	HPLC-ICP-MS	0.67 (CH_3Hg^+) to 0.74 (Hg^{2+}) ng L^{-1}	Spike recovery	343
REEs	Water, seawater, sediments	TiO_2 NPs coated with Fe_3O_4	di(2-ethylhexyl)phosphoric acid	ICP-MS	0.01 (Tm) to 0.12 (Nd) ng L^{-1}	Chinese CRM GBW07301a (stream sediment); Spike recovery (water)	344
REEs and Al, As, Co, Cr, Cu, Fe, Ga, Mn, Ni, Pb Se, Sb,	River and seawaters	$Mg(OH)_2$ precipitate	triethylamine	ICP-MS	0.01 (Ho) to 72 (Al) ng L^{-1}	NRCC CRMs CASS-4 (near shore seawater) and SLEW-3 (Estuarine water)	345

Sn, V, Zn							
^{90}Sr	River water and reactor coolant	Sr-resin 20–50 μm and Dowex® 50Wx8 100–200 mesh		ICP-MS	14.5 Bq L^{-1} (2.9 pg L^{-1}).	IAEA water standard for proficiency testing (II) and spike recovery	[346]
^{99}Tc	Water	TRU® resin (50-100 mm) and AG®MP-1M resin		ICP-MS	0.4 pg L^{-1}	Samples spiked with Re as a recovery tracer	[347]

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

Analytes	Matrix	Method	Reagents	Detector	LOD in μg L^{-1} (unless stated otherwise)	Method validation	Reference
As^{III}	Water and soil	SSME	decanoic acid, tetrahydrofuran and APDC	ETAAS	0.2 ng mL^{-1}	Spike recovery	[348]
Cd	Seawater	SBME	trioctylmethylammonium chloride (Aliquat® 336), kerosene, dodecan-1-ol	ETAAS	0.04 nM	IRMM CRM BCR-403 (Seawater)	[349]
Cd, Cu	Tap, river and seawaters	CPE	Triton X-114, 4-phenyl-3-thiosemicarbazide	FAAS	0.2 (Cd) and 0.5 (Cu)	NRCC CRMs SLRS-5 (River water) and SPS RM SW2 Batch 127 (surface water)	[350]
Cd, Pb	Water, soil, rice and tea	DLLME	2-amino-3-sulfhydrylpropanoic acid, tetrafluoroborate and 1-butyl-3-methylimidazolium tetrafluoroborate	ETAAS	0.2 (Cd) and 0.7 (Pb) ng L^{-1}	NIST SRM 1643e	[351]
Fe^{3+} and total Fe	Tap, spring and river waters	DLLME	4,5-dihydroxy-1,3-benzenedisulfonic acid and cetyl pyridinium chloride	FAAS	5.6	HPS CRM-TMDW (Trace metals in drinking water)	[352]
Hg^{2+}, CH_3Hg^+ and EtHg	Water	DLLME	2-mercaptoethanol and 1-hexyl-3-methylimidazolium hexafluorophosphate	HPLC-CV-AFS	1.5 (Hg^{2+}, CH_3Hg^+) to 3.0 (EtHg) ng L^{-1}	Spike recovery	[353]
REEs	Simulated water	LLE	N, N, N', N'-tetraoctyl diglycolamide, EDTA, petroleum ether	ICP-AES	0.04 (Nd) to 0.5 (Ho) ng mL^{-1}	Spike recovery	[354]
REEs, Zn	Water, urine and serum	CPE	Triton X-114 and 1,10-phenanthroline	MP-AES	0.3 (Zn) to 1.0 (Tb)	Spike recovery	[355]

Table 3. Preconcentration methods using combined solid and liquid phase extraction in the analysis of water

Analytes	Matrix	Method	Substrate	Reagents	Detector	LOD	Method validation	Reference
Cr^{III}	Potable and seawaters	CPE	graphene oxide	Triton X-45	ETAAS	5 ng L^{-1}	NIST SRM 1640a (water), SPS RM SW2 batch 125, NRCC CRM CASS 6 (seawater), IRMM CRM ERM-CAO11b (Hard drinking water)	[356]
Se^{IV}	Rain, tap, river and seawaters	Micro dispersive SPE	nanosilica	1-dodecyl-3-methylimidazolium bromide, APDC, ethyl acetate/Triton X-114	ETAAS	1.1 ng L^{-1}	NIST SRM 1643e (trace elements in water)	[357]
V	Water and beer	CPE	graphene oxide	Triton X-114	ETAAS	0.02 µg L^{-1}	NIST SRM 1640a (Water), NRCC CRM NASS 6 (near coastal seawater), IRMM CRM ERM-CAO11b (Hard drinking water)	[358]

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

Analyte	Sample matrix	Method	Reagents(s)	Detector	LOD (μg L^{-1})	CRMs or other validation	Reference
As^{III}, As^{V}	Soil, water	UAE-SSME	decanoic acid, tetrahydrofuran, APDC	ETAAS	0.2 for both species	Dust CRM (no details given); spike recovery	[348]
Cd, Cu, Pb	Coastal seawater, surrogate digestive fluids, soil leachates		APDC, toluene, nitric acid	ICP-AES	0.002 for Cd, 0.001 for Cu, 0.006 for Pb	spike recovery	[359]
Cd, Pb	Soil, water, rice, tea	UA-DLLME	2-amino-3-sulfhydrylpropanoic acid (l-cysteine), tetrafluoroborate ion, 1-butyl-3-methylimidazolium tetrafluoroborate	ETAAS	0.0002 for Cu, 0.0007 for Pb	NIST SRM 1643e (trace elements in water); spike recovery	[351]
Co	Water, spinach, black and green tea, tomato sauce		DDC, methanol, carbon tetrachloride	FAAS	7	GSJ CRM JSL1 (Toyama clay slate); spike recovery	[360]
Cu	Edible oils	DLLME	Chitosan, hydrochloric acid, water	ICP-AES	2	spike recovery	[361]
Mn	Basil herb, spinach, dill, and	DE-LLE	choline chloride (vitamin B4) and tartaric, oxalic, or citric acids	ICP-AES	0.5 – 1.0	NIST SRM 1573a (tomato leaves); spike recovery	[362]

	cucumber barks						
Pd	Soil, water	UA-MLLE	Na DDC, octanol	FAAS	0.9	spike recovery	[363]
Se^{IV}, Se^{VI}	Rice	MIL-DLLE	2,3-diaminonaphthalene, 1-butyl-3-methylimidazolium tetrachloroferrate	ETAAS	0.02 for both species	NRCCRM CRMs GBW 10010 (rice), 10043 (Liaoning rice), and 10045 (Hunan rice); spike recovery	[364]

Table 5. Preconcentration methods involving SPE used in the analysis of soils, plants and related materials

Analyte	Matrix	Substrate	Substrate coating/modifying agent or analyte complexing agent	Detector	LOD (µg L^{-1} unless stated otherwise)	CRMs or other validation	Reference
Ag, Au, Pd, Pt	Waste water, seawater, road dust	graphene oxide, MIO NP, silica	polypyrrole-polythiophene	FAAS	0.1 - 1	Zidarovo-PMZrZ (206 BG 326) (polymetallic gold ore); spike recovery	365
As^{III}	Rice plants and ash tap, well and mineral water	MWCNTs	DDC	ETAAS	0.008	spike recovery	366
Cd	Tobacco leaves, cigarettes, pipe tobacco	Dowex 50W-X8		ICP-MS	0.001	NRCC CRM DORM-2 (dogfish muscle)	367
Cd, Co, Cu	Molasses, rice, water	silica gel	2-[N,N-bis(salicylaldimine)] aminoethyl amine	FAAS	0.5 for Cd, 1 for Co 0.6 for Cu	INCT CRM CTA-VTL-2 (Virginia tobacco leaves), LGC CRM NWTM-15.2 (water), comparison with an ICP-MS method; spike recovery	368
Cd, Fe, Mn, Pb, Zn	White and wild rice	oxidized MWCNTs	bathophenanthroline	FAAS	0.1 – 0.4	NCS CRMs DC73349 (bush branches and leaves) and ZC73029 (rice); spike recovery	369
Ce, Th	Bastnaesite ore	Amberlite XAD-16	anoxybacillus flavithermus	ICP-AES	0.4 for Ce, 0.1 for Th	IAEA CRM Soil-7	370

Cu	Tomato, shallot, green papaya, carrot, eggplant, garlic, yard long bean, chili pepper, lime green papaya salad	MIO chitosan-graphene NPs		ICP-AES	0.01	Comparison with another method; spike recovery	371
Cu species	Corn flour, cassava root flour, oregano leaves, cumin, wine	bamboo fiber	bathocuproine	FAAS	0.5	NIST SRM 1573a (tomato leaves); spike recovery	372
Cu	Plants, water	MIO NPs	SDS, 1-(2-pyridylazo)-2-naphthol	FAAS	0.6	HPS CRM TMDW-500 (drinking water), NIST SRMs 1570a (spinach leaves) and 1573a (tomato leaves); spike recovery	373
Cu, Pb	Poppy seeds,chamomile, water	MIO-MoS_2 nanocomposite		FAAS	2 for Cu, 3 for Pb	NCS CRMs DC73349 (bush branches and leaves), SPS-WW2 (waste water level 2), TMDA-53.3 (environmental water); spike recovery	374
Cu, Pb	Cigarettes, hair	MIO MWCNTs	Chromotrope FB	FAAS	4 for Cu, 12 for Pb	NCS CRM DC73349 (bush branches and leaves); spike recovery	375

Pb	Water, synthetic seawater, serum physiological solution, chocolate powder, Gingko biloba	Pb-imprinted poly(methacrylic acid)	1-(2-pyridylazo)-2-naphthol	FAAS	0.5	NRCC CRM MESS-3 (marine sediment); spike recovery	376
Pb	Water, chocolate powder, Ginkgo biloba	$SiO_2/Al_2O_3/SnO_2$ ternary oxide		FAAS	2	NRCC CRM MESS-3 (marine sediment); spike recovery	377
Pb	Industrial effluent, sludge, black tea, spinach leaves, green beans	silica	penicillium chrysogenum	FAAS	7	BCR CRM701 (lake sediment); comparison with another method (ICP-AES); spike recovery	378
Pd	Soil	MIO NP SDS 2-(5-bromo-2-pyridylazo)-5-diethyl aminophenol	5-amino-1,10-phenanthroline	FAAS	0.1	spike recovery	379
REEs	River water, lake water, seawater and	MIO-TiO_2 NP di(2-ethylhexyl)phosphoric acid		ICP-MS	0.0001 for Nd, 0.00001 for Tm	NRCCRM GBW07301a (stream sediment), spike recovery	344

	sediment						
REEs	Tea leaves, water	TiO_2 nanofibres		ICP-MS	0.0006 for La, 0.0001 for Lu	NRCCRM CRM GBW 07605 (tea leaves); spike recovery	380
Sb^{III}, Sb^{V}	Tea leaves, tea infusion	TiO_2 nanofibres	DLLME	ETV-ICP-MS	0.00002 for both species	NRCCRM CRM GBW 07605 (tea leaves)	381
Sb^{III}, Sb^{V}	Soil, tuna, rice, spinach, black tea, mixed fruit juice, iced tea	polystyrene oleic acid imidazole	DDC for Sb^{III}	ETAAS	0.006 for Sb^{III}, no LOD given for Sb^{V}	NRCC CRM SLRS-5 (river water); spike recovery	382
Tl^{I}, Tl^{III}	Soil, green cabbage	Al_2O_3	oxine, diethylenetriaminepentaacetic acid	ICP-MS	0.04 for Tl^{I}, 0.2 for Tl^{III}	IAG CRMs OU-6 (Penrhyn Slate), AMH-1(Mount Hood andesite), GBPG-1 (garnet-biotite plagiogneiss); NIST SRM 2711 (Montana soil); NRCC CRM GBW07405 (soil)	383
Th, U	Soil, sediment, phosphogypsum	UTEVA resin		ICP-MS	0.7 ng kg^{-1} for Th, 0.1 for U,	IAEA CRM 375 (soil); BCR CRM 320 R (sediment); MatControl RM CSN-CIEMAT 2008 (phosphogypsum)	384

Table 6. Methods used in the determination of isotope ratios in geological materials using solution ICP-MS or TIMS

Analyte	Matrix	Sample treatment	Technique	Analysis and figures of merit	Reference
Ag	Geological RMs, Ag ores	Digestion with HF–HNO_3 in Teflon beakers on a hot plate, further steps involving HNO_3 and HCl, final solution in 0.5M HCl. Two-column purification procedure involving anion-exchange resin AG1-X8 and cation exchange resin AG50W-X8. Mean Ag recovery obtained was 96.5 ± 2.5% (2SD, n ≥ 5).	MC-ICP-MS	Mass discrimination and instrument drift corrected by a combination of internal normalisation with Pd and SSB. Ag and Pd isotopes monitored using 6 FCs equipped with 10^{11} Ω resistors. External reproducibility for $^{109}Ag/^{107}Ag$ varied between ±0.006 and ±0.009‰ (n ≥10).	[385]
B	Rock RMs	Low temperature sample dissolution in mixture of HF, HNO_3 and 2% mannitol. Subsequent steps included refluxing with HCl at 65 °C overnight. Two-step chromatography: (i) Bio-Rad AG 50W-X8 to separate B and Li from silicate matrix; (ii) B purification on IRA 743 ion-exchange resin, followed by modified B micro-sublimation technique. Recoveries were almost 100% and blanks <0.8 ng B.	MC-ICP-MS	Sample introduction *via* dual quartz spray chamber with the commercial PFA-ST nebuliser. Concentrations of B adjusted to 10 ng mL^{-1}, yielding a ^{11}B intensity of 0.4–0.5 V. Mass bias correction performed by SSB. Long-term precisions for $\delta^{11}B$ (5 ng of B) better than ±0.35‰ (2SD).	[386]
Ba, Sr	Rock RMs	Rock powders digested with HNO_3–HF, refluxed with HCl, residue dissolved in *aqua regia* to oxidise all iron to Fe^{3+}; final solution in 6M HCl. Purification of Ba and Sr from same aliquot using a three-step column chemistry with AG1X8, Eichrom Sr resin and AG50W X8. Procedural blanks 340±70 pg Ba and <30±5 pg Sr.	TIMS	Ba and Sr isotope data for 3 geological RMs by TIMS in multi-dynamic mode on 9 FCs. Samples split into two aliquots: Sr fraction loaded onto single Re filaments using $TaCl_5$ as activator, Ba fraction loaded onto Re double filaments. External reproducibility (2SD) was 19 ppm for $^{84}Sr/^{86}Sr$, 2 ppm for $^{87}Sr/^{86}Sr$ and 4 ppm for $^{135}Ba/^{136}Ba$.	[387]
Ce	Rock RMs	Digestion with HF–HNO_3, with further steps involving HCl, boric acid and HNO_3; final solution in 3M HNO_3. Two-step chromatographic procedure: (i) bulk REE separated on Eichrom TRU resin; (ii) Ce purified on Eichrom Ln columns using $KBrO_3$ to oxidise Ce to Ce^{4+}. A thin layer of Eichrom pre-filter	TIMS	Multi-static acquisition routine, with 10^{11} Ω amplifiers connected to all FCs except the centre cup which had a 10^{10} Ω amplifier for collection of the large ^{140}CeO ion beam. Calculation of Ce isotope ratios involved subtraction of the contribution from the ^{140}CeO tail on the ^{136}CeO and ^{138}CeO signals	[388]

		resin on top of the Eichrom Ln resin prevented the Ln resin from floating when 10M HNO_3 was added to the column.		by exponential interpolation. Simultaneous correction for mass fractionation and isobaric ^{X}Ce^{18}O – $^{X+2}$Ce^{16}O interferences was performed off-line using ^{136}Ce/^{142}Ce= 0.01688. Reproducibility was 20–40 ppm (2SD).	
Cr	Geological RMs, rocks, soils, sediments	Silicate samples digested with HF–HNO_3 on hotplate. After repeated heating and sonication, further steps involved treatment with *aqua regia* and final solution in 2M HNO_3 mixed with H_2O_2. The digestion procedure was modified for other matrices. Improved three-step purification scheme: (i) cation (AG50W-X8) and anion (AG1-X8) columns in series to eliminate Ca, Fe, Ti and V; (ii) anion-exchange on AG1-X8 to separate Cr from Ti and V; (iii) purification of Cr on AG1-X8. Recovery 80-99% and blank <1 ng Cr.	MC-ICP-MS	Measurements performed in medium or high-resolution mode on 7 FCs equipped with 10^{11} Ω amplifiers in static mode. Interferences of ^{50}Ti and ^{50}V on ^{50}Cr, and ^{54}Fe on ^{54}Cr were monitored *via* ^{49}Ti, ^{51}V, and ^{56}Fe. A ^{50}Cr–^{54}Cr double spike was used to correct for isotope fractionation from chemical separation and instrumental mass bias. Long-term precision was 0.06‰ (2SD).	389
Fe	Rock RMs	Rock powders digested with HF–HNO_3 on hotplate. After repeated heating and sonication with HNO_3 and then 8M HCl, final solution prepared in 8.2M HCl mixed with 0.01% *v/v* H_2O_2. Recoveries >99%, procedural blank <7 ng Fe. Chemical separation by ion-exchange chromatography on AG MP-1M.	MC-ICP-MS	All 16 FCs fitted with 10^{11} Ω resistors. ^{61}Ni–^{60}N double spike method of correcting for mass fractionation preferred to SSB, using high mass resolution to eliminate polyatomic interferences. Precisions of <0.04‰ (2SD) for δ^{56}Fe and <0.06‰ (2SD) for δ^{57}Fe were obtained for IRMM-014 (iron wire).	390
Ir	Standard solutions	Standard solutions sourced commercially or prepared from Ir bromide and metallic Ir powder. All solutions spiked with Tl (NIST SRM 997) and Re (NIST SRM 989) isotopic standards.	MC-ICP-MS	Isotope measurements on FCs in static mode. State-of-the-art regression model used to correct for mass bias. New NRCC Ir CRM IRIS-1 proposed as delta zero standard for Ir isotope ratio measurements.	391
K	Geological RMs, rocks,	Procedure was applied to wide range of sample types, including silicate and evaporate minerals,	MC-ICP-MS	Instrument run in high resolution mode and cold plasma conditions (500–600 W) to	392

	silicate minerals, evaporites	seawater, and hair and plant RMs. Wide range of digestion procedures employed depending on matrix. Final solution in 0.2% HNO_3. Separation of K from other matrix cations using a Dionex IC system fitted with a CS-16 cation-exchange column and methanesulfonic acid as the eluent.		suppress Ar ionisation. Instrumental mass bias correction via SSB with NIST SRM 999b (KCl). Total range of ^{41}K/^{39}K ratios in the materials analysed was *ca.* 2.6‰; long-term external reproducibility was 0.17‰ (2σ, N=108).	
Li	Rock RMs	Li fraction collected from the first column further purified by IC on AG 50W-X8 cation-exchange resin. Yields of Li were almost 100% and blanks <5 pg Li.	MC-ICP-MS	Sample introduction *via* desolvation system. Mass bias correction performed by SSB. Long-term precision for δ^{7}Li (1 ng of Li) better than ±0.27‰ (2SD).	[386]
Li, Mg	Seawater, river water, sediment, foraminifera and rock RMs	Wide range of digestion procedures employed depending on matrix. Final solutions in 0.7M HCl. Ion-exchange chromatography on AGMP-50 for quantitative separation of Li and Mg from all matrices in a single-step elution with HCl. The Li and Mg cuts were dried down, refluxed with HNO_3, dried down and then taken up in HNO_3 for analysis.	MC-ICP-MS	Different sample introduction systems used for Li and Mg isotope ratio measurements. A concentration-matched SSB technique was applied to correct for instrumental drift and mass bias using NIST SRMs L-SVEC and DSM-3 for Li and Mg, respectively. Long-term precisions (2σ) were ±0.39 and ±0.07‰ for δ^{7}Li and δ^{26}Mg, respectively.	[393]
Mg, Ti	Ca-Al-rich inclusions in meteorites, rock RMs, olivine minerals	Silicate samples digested with HF–HNO_3; further steps involved treatment with *aqua regia* and final solution in 7M HNO_3. Series of discrete IC steps with novel sample pre-treatment procedures developed for the separation of very small amounts of Mg (~5 µg) and Ti (0.7-1 µg) from samples containing high amounts of Al, Ca, Fe and Mg. Recoveries >99.9% for Mg and >97% for Ti.	MC-ICP-MS	Instrument run in high-resolution mode and SSB used to correct for instrumental mass bias. Procedures consume significantly less material than previous methods and represented a 6 to 10-fold improvement in precision. Mass-dependent compositions determined with a precision better than 60 ppm amu^{-1} for Mg and Ti.	[394]
Nd	Rock RMs	Samples digested with HF–HNO_3 on a hotplate. Final solution in 3M HNO_3 loaded onto TODGA resin column. Nd eluted with 1.2M HCl. Blanks of 30-70 pg Nd were negligible relative to Nd content of samples.	MC-ICP-MS	Nine FCs employed; ^{140}Ce monitored to correct interference of ^{142}Ce on ^{142}Nd, and ^{147}Sm for interference correction of ^{144}Nd, ^{148}Nd and ^{150}Nd. Internal precisions were *ca.* 15×10^{-6} for ^{142}Nd/^{144}Nd, 2×10^{-6} for	[395]

				^{145}Nd/^{144}Nd, 3×10^{-6} for ^{148}Nd/^{144}Nd and 4×10^{-6} for ^{150}Nd/^{144}Nd.	
Nd	Basalt and carbonate RMs	After digestion, Nd was separated and purified on 3 columns: (i) TRU resin (Eichrom) to remove matrix elements; (ii) Ln resin (Eichrom) to separate Nd from other REEs; (iii) purification on Bio-Rad AG50W-X12. Recovery was 92% and blank 1 pg Nd.	TIMS	New total evaporation normalisation TIMS technique applied. Signals monitored on 9 FC (10^{11} Ω resistors) in static multi-collection mode. Isotope fractionation corrected by internal normalisation using exponential law and ^{146}Nd/^{144}Nd = 0.7219. Samples as small as 0.5 ng Nd were analysed with precisions better than 100 ppm (2RSD)	396
Pd	Chondrites, meteorites, terrestrial rocks	A ^{106}Pd-^{110}Pd double-spike was added to sample powders in porcelain crucibles prior to digestion via NiS fire assay; NiS beads dissolved in HCl. Purification using AG1-X8 anion-exchange resin; Pd eluted in 11M HCl with a recovery of *ca.* 96%. .	MC-ICP-MS	Ion beams at ^{102}Pd, ^{103}Rh, ^{104}Pd, ^{105}Pd, ^{106}Pd, ^{107}Ag, ^{108}Pd, ^{109}Ag, and ^{110}Pd were simultaneously collected on FCs (10^{11} Ω resistors). Double spike correction for instrumental mass fractionation. External reproducibility of ±0.032‰ on δ^{106}Pd demonstrated for the Allende chondrite.	397
Pt	Fe meteorites	Samples digested with HNO_3–HCl and refluxed on a hot plate for 48 h at 100 °C; final solution in HCl. A complex two stage separation scheme utilised the strong anion resin AG1-X8. Firstly, Pt was separated from matrix elements including Fe and Ni; Pd also isolated at this stage. In the second stage, Ir was reduced with ascorbic acid and eluted from the column before Pt collection. Yields were typically 50–70%, with blanks of 0.1-0.3 ng Pt.	MC-ICP-MS	Measurements in low-resolution mode with all Pt isotopes collected simultaneously, along with ^{188}Os^{+} and ^{200}Hg^{+} to correct for isobaric interferences, and ^{191}Ir^{+} to assess tailing of Ir onto Pt isotopes. SBB was used for the correction of instrumental mass bias by applying the exponential law. Precisions of 0.73 for ε^{192}Pt, 0.15 for ε^{194}Pt and 0.09 for ε^{196}Pt (2SD).	398
Se	Basalt and shale RMs	Rock powders mixed with ^{74}Se-^{77}Se double spike solution before dissolution in reverse *aqua regia* (3+1 HNO_3–HCl) in a high-pressure asher. Purification using two-step ion-exchange chromatography (Eichrom AG 1-X8 anion resin	MC-ICP-MS	Combination of double spike and HG sample introduction. Methane added to Ar carrier gas to increase Se signal and supress background. Se and potential interferences monitored on 9 FCs equipped with 10^{11} Ω resistors.	399

		and AG 50W-X8 resin).		Reproducibility was <0.10‰ (2σ) for δ^{82} Se /^{76}Se for a sample mass of 15 ng Se and 0.20‰ (2σ) for lower quantities down to 5 ng Se.	
Si	Geological RMs, meteorites (S and Fe-rich samples)	Geological RMs and meteorite powders dissolved using a NaOH fusion method. Final solution pH carefully controlled to avoid precipitation of Fe hydroxide. Purification by cation-exchange chromatography on Bio-Rad 50W-X8. Samples and RMs were doped with S to a fixed S/Si ratio to minimise differences in instrumental mass fractionation.	MC-ICP-MS	Instrument in medium resolution mode with a resolving power of about 4000. Simultaneous measurements of ^{28}Si, ^{29}Si and ^{30}Si. Instrumental mass bias and drift corrected using SSB with NBS 28 (Si and O isotopes in silica sand) as the bracketing calibrator.	400
Sn	Geological RMs	^{117}Sn-^{122}Sn double-spike added prior to digestion. Rock powders dissolved by HF–HNO_3 method with final solution in 0.4M HCl. Purification of Sn by three-stage ion-exchange chromatography on BioRad AGI-X8. Recovery was 100±5%; blanks of 0.70±0.64 ng (2SD) were negligible compared to Sn content of samples.	MC-ICP-MS	Simultaneous measurements of Sn, and potentially interfering Cd, Sb and Te isotopes on 9 FCs. Mass fractionation corrected by SSB and double-spike technique. Reproducibility for δ^{124}Sn better than 0.06‰ (2SD).	401
Sn	Cassiterite, stannite, tin metal, tin bronze	Cassiterite reduced to Sn metal and stannite to Sn bronze by adding KCN and Cu powder, respectively, in a muffle furnace at 1000 °C. Metal beads were dissolved in HCl–H_2O_2 and diluted before analysis. The bronze solutions were purified by column chemistry with the TRU-Spec resin; recoveries were 100±4%.	MC-ICP-MS	Isotopic measurements on 9 FCs equipped with eight 10^{11} Ω and one 10^{10} Ω resistors. Comparison of three different mass bias corrections. Combined analytical uncertainty (2s) of replicate dissolutions of bronze RMs (BAM 211, IARM-91D) was between 0.01 and 0.06‰ depending on the isotope ratio.	402
Sn	Geological RMs	^{117}Sn–^{122}Sn double-spike added to rock powders prior to digestion in HF–HNO in closed Teflon beakers on a hotplate at 120°C. Final solution in 0.5M HCl for anion-exchange chemistry. Chemical separation of Sn using Eichrom TRU	MC-ICP-MS	Simultaneous measurement of ^{116}Sn, ^{117}Sn, ^{118}Sn, ^{119}Sn, ^{120}Sn, ^{121}Sb, ^{122}Sn, ^{123}Sb and ^{124}Sn in a single cycle using FCs equipped with 10^{11} Ω resistors. Mass fractionation corrected by double-spike approach. External	403

		resin gave variable yields of between 13 and 66% for geological RMs.		reproducibility of ±0.065‰ (2SD) on $\delta^{122}Sn/^{118}Sn$ for two rock RMs.	
Te	Chondrites, geological RMs	After the addition of a ^{125}Te-^{128}Te double spike, all samples except Mn nodules were digested in a series of dissolution steps involving HF, HNO_3, *aqua regia* and HCl; Mn nodules were dissolved in HCl. After separation by anion-exchange on AG1-X8 resin, Te was further purified in two additional steps using AG1-X8 resin. Yields were ~55% and blanks were ≤11 pg Te. .	MC-ICP-MS	Simultaneous measurements on FCs were performed at masses 125 (^{125}Te), 126 (^{126}Te, ^{126}Xe), 128 (^{128}Te, ^{128}Xe), 129 (^{129}Xe), 130 (^{130}Te, ^{130}Xe, ^{130}Ba) and 135 (^{135}Ba). Background and interference corrections were applied. The ^{125}Te-^{128}Te double-spike methodology provided a long-term reproducibility (2SD) of 0.064‰ for $\delta^{130}Te/^{125}Te$ in an Alpha Aesar Te metal standard solution.	404
W	Geological RMs	After addition of a ^{180}W-^{183}W double spike, samples were digested in HF–HNO_3; further steps involved treatment with HCl and H_2O_2. Separation involved cation-exchange chromatography on Bio-Rad AG50W-X8 resin followed by purification of the W fraction on Bio-Rad AG1-X8 resin. Organics were destroyed with conc HNO_3+H_2O_2 before Eichrom TEVA resin was used to separate W from the remaining Hf, Ti and Zr. Yields for W were typically 60 to 95% and blanks *ca.* 50 pg.	MC-ICP-MS	Measurements in low resolution mode on FCs with 10^{11} Ω resistors. Simultaneous measurements of $^{177}Hf^+$, $^{181}Ta^+$ and $^{188}Os^+$ were used to correct for isobaric interferences from $^{180}Hf^+$, $^{180}Ta^+$, $^{184}Os^+$ and $^{186}Os^+$, respectively, by applying published relative isotope abundance data. After correction for mass-dependent fractionation using the double spike approach, results were expressed relative to NIST SRM 3163. External reproducibility of $\delta^{186}W/^{184}W$ in natural samples was ±0.018‰.	405