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

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SUMMARY OF CONTENTS

*Abstract*

*Highlights in the field of air analysis included: a new focus on measuring micro and nano plastic particles in air, the development of hyphenated ICP-MS systems for in-situ sampling and measurement of airborne metallic particles and the reported use of wearable black carbon sensors for measuring exposure to diesel fumes within the workplace. Significant advancements in the analysis of waters have been made in developing novel resin materials and new protocols for existing commercially available resins, aimed at the determination and speciation of trace levels of metals and metalloids in water matrices. These developments have been validated for sample purification and pre-concentration. In addition to traditional column chemistry, on-line hyphenated techniques were employed to enhance speciation analysis, with optimized methods enabling faster analysis and facilitating a more holistic approach by allowing the simultaneous detection of multiple species or elements in a single run. Efforts have also been directed towards detecting particles in the micro- and nanometer range, broadening the analytical scope beyond the ionic fraction. This year, the focus shifted from natural and engineered nanoparticles towards the critical field of plastic pollution, with several innovative methodologies introduced. Furthermore, to achieve better precision and lower detection limits in the field of MS/MS, numerous studies explored the behaviour of gases and reactions within reaction cells, contributing to the refinement of these techniques. In the analysis of soils and plants, methods aimed at improving the efficiency of green solvents were again prominent. Developments in AES were largely driven by the desire to create small, low-*

*cost, low power consumption instrumentation suitable for field deployment. The study of NPs in soil and plants systems continued to be a focus for sp-ICP-MS. The past year has again seen a large volume of publications featuring LIBS, with particular interest in methods to enhance signal intensity and thereby improve limits of detection. Of interest in XRF was the development of in-house spectrometers for underwater mercury screening and in vivo plant analysis. Developments in geological analysis include new homogeneous natural and synthetic materials that have been developed as reference materials (RMs) in the analysis of geological samples by microanalytical techniques, such as LA-ICP-MS, LIBS and SIMS. Additional information on already existing RMs has been obtained for in situ isotope ratio determinations. Attention has been paid to sample preparation and purification methods able to shorten the analysis time and to improve the accuracy. Much attention has been paid to the use of LA-ICP-MS/MS as a means for removing spectral interferences in the case of in-situ localized isotopic analysis and dating of geological materials. The development of new chemometric models as well as software has continued to improve data quality. The use of artificial intelligence is growing and techniques such as machine learning have led to significant improvements in the quality of geochemical results.*

## 1 Introduction

This is the 40th annual review of the application of atomic spectrometry to the chemical analysis of environmental samples. This Update refers to papers published approximately between August 2023 and June 2024 and continues the series of Atomic Spectrometry Updates (ASUs) in Environmental Analysis[1] that should be read in conjunction with other related ASUs in the series, namely: clinical and biological materials, foods and beverages[2]; advances in atomic spectrometry and related techniques[3]; elemental speciation[4]; X-ray spectrometry[5]; and metals, chemicals and functional materials[6]. This review is not intended to be a comprehensive overview but selective with the aim of providing a critical insight into developments in instrumentation, methodologies and data handling that represent significant advances in the use of atomic spectrometry in the environmental sciences.

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

## 2 Air analysis

### 2.1 Review papers

The current knowledge of *microplastics* in road dust were discussed[7] (154 references), and methodologies for their sampling, preparation and analysis summarised. In the determination of the number and mass concentration of MP, use of the µ-Raman and TOF-SIMS techniques was recommended[8] (137 references) and the utility of atomic spectrometric techniques such as LIBS and XRF for identifying, classifying and tracing MP sources discussed[9] (120 references).

Measuring *engineered nanomaterials* was a subject reviewed in two complementary IUPAC technical reports. In report one[10] (115 references) suitable analytical techniques were presented and a useful listing of relevant (C)RMs tabulated. In report two[11] (227 references), which focused on real-world measurement applications, whilst the authors acknowledged the emergence of sp-ICP-MS as a valuable and practical measuring tool, they noted that further development of the underpinning metrological infrastructure was still required.

*Other review papers* of note published included: the analytical challenges and possibilities for the quantification of tyre-road wear particles[12] (113 references); the characterisation of total and speciated forms of Hg in natural gas and its condensates[13] (245 references); chronological developments in GSR detection techniques[14] (89 references); spectroscopic techniques for stable C isotope measurements in gases[15] (70 references); application of emerging LA spectroscopic techniques for stable gaseous isotope measurements[16] (46 references) and the utility of MS techniques such as aerosol MS, CIMS and PTR-MS in the study of atmospheric haze chemistry[17] (288 references).

## 2.2 Sampling techniques

To further exploit the sensitivity of the TXRF technique in measuring APM, researchers[18] developed a new 5 L min$^{-1}$ flow-rate cascade *impactor sampler* thus ensuring that particles were deposited efficiently onto sampling (target) carriers for illumination under the resultant X-ray beam so enabling airborne metals to be determined at low ng m$^{-3}$ concentrations following a short 30 min sampling interval. In a complementary endeavour, their development of a new spin-coating technique enabled a thin layer of adhesive grease to be applied to targets in a consistent and repeatable manner that facilitated the effective sampling of the required $PM_{10}$, $PM_{2.5}$ and $PM_1$ size fractions because particle bounce was now minimised. In the development of a new prototype impaction-based aerosol concentrator, the concentrating and focusing of APM onto target spots < 1.5 mm in diameter was achieved[19] using successive multiple smooth converging stages. The ability to concentrate particles >1000 nm in size, undertake potential spot analysis using laser-based techniques, and readily transport the device were considered advantageous. Useful chemical mass-to-size distribution data can be generated when wearable impactor samplers are deployed on workers for assessing occupational exposure to airborne metallic UFP but they can be cumbersome to prepare, so a new tutorial paper[20] on their practical use is most welcome.

Representative sampling of atmospheric *reactive mercury species* can be challenging due to their reactivity once sampled on media and because airborne concentrations are typically < ng m$^{-3}$. In further evaluating the performance of their air sampler assembly, for $Hg_P$ collection onto PTFE filters and GOM collection either onto cellulose ester membrane or onto nylon filters, Gustin and her team concluded[21] that new methodologies for the effective sampling of $Hg_P$ were still required.

### 2.3 Reference materials

Following a review[22](72 references) on the current status of *microplastic* RMs it was concluded that use of commercially produced RMs, which are typically spherical, homogenous and monodisperse in nature, was not ideal in supporting environmental measurements because real-world particles varied in size, morphology and chemical composition. The required physiochemical attributes to be considered when producing new RMs were thus outlined.

To support future nuclear safeguarding measurements, development of a new thermal sprayer device enabled new candidate *isotopic reference materials* particles to be produced[23] as exemplified by the preparation of new U/Th oxide materials with an average diameter of ~1 µm and a geometric SD of <1.15 µm and which contained $^{232}$Th concentrations between 1 ppm and 10% when ratioed to $^{238}$U. Starting materials were assayed by TIMS, the U/Th oxide particles were generated with a vibrating orifice aerosol generator with resultant certification using MC-ICP-MS following particle dissolution. As atmospheric $CO_2$ concentrations increase, with a corresponding shift towards a lighter isotopic composition similar to that of fossil fuels, there is a requirement for C isotopic measurements that are accurate, precise, and reproducible in supporting source apportionment studies and subsequent abatement interventions. It is therefore illuminating to read an informative tutorial paper that chartered the development since the 1950's of C isotopic RM[24] which included a description of a material derived from the calcified remains of Jurassic-era squids.

Procedural use of TOA is by nature operationally defined as codified in various standard methods but the application of such methods leads to variation in results when carbonaceous particles collected on air filter samples are analysed. The development of *RM filters that contain a traceable organic and elemental carbon content* is therefore desirable. Synthetic RM can be prepared by aerosolising solutions containing organics and carbon black suspensions, which once dried can simulate those organic and elemental carbon moieties in APM sampled onto filters. In order to generate an organic carbon simulant that better mimicked carbonaceous APM, use of a precursor organic solution mix that contained benzo[a]pyrene, benzoic acid, potassium hydrogen phthalate, sucrose and xylose was proposed.[25]

## 2.4 Sample preparation

*Methodologies for the extraction, isolation and purification* of NP from environmental matrices for subsequent assays using sp-ICP-MS assays were summarised[26] (69 references). Pyrohydrolysis is a useful approach for liberating halogen species from environmental matrices. Reported applications conducted over the past 30 years were tabulated[27] (147 references) and critically assessed against alternative approaches such as alkaline extractions or fusions and combustion-based methodologies such as the traditional Schöniger oxygen flask technique or the more recently developed microwave-induced approach.

In developing a new procedure for the *determination of metal isotopes* in digested APM that used a NOBIAS PA1® SPE cartridge to separate Cd, Cu, Ni, Pb and Zn from common matrix elements such as aluminum, iron, manganese and titanium prior to their separation using an AG MP-1M® AEC, the authors claimed[28] that their two-step approach was advantageous because high-sample throughput was possible and effective assays could be realised.

A method for the determination of *Pt NP in road dust* samples involved[29] sonication of samples in water, application of a centrifugal separation step with dilution and analysis using sp-ICP-MS. When applied to aliquots of BCR CRM 723 (*road dust*) it was determined that 12% of the certified Pt content was in a NP form. In road dust samples subsequently analysed, the Pt concentrations determined were 6.0-20.0 ng g$^{-1}$ of which 11-27% were in NP sizes of 15-75 nm.

## 2.5 Instrumental analysis

### 2.5.1 Atomic absorption and emission spectrometries

The simultaneous determination of Pd and Rh in spent automotive catalysts without recourse to a preliminary chemical separation was undertaken using[30] a HR CS *atomic absorption* spectrometer. Extractions were performed in aqua regia at 108 °C for 4 h and the LOD was 0.19 mg kg$^{-1}$ for Pd when measurements were performed at the 360.955 nm atomic line and 0.19 mg kg$^{-1}$ for Rh when measured at the 361.251 nm line. The relative measurement error against certified for Pd and Rh in samples of BAM ERM® 504 (*platinum group elements in spend autocatalyst*) tested was -3.1 % and -12.1 % with RSDs of 10% and 7%, respectively. By calibrating[31] a real-time AA spectrometer using traceable GEM standards, prepared via the reduction of diluted NIST SRM 3133 (*Mercury (Hg) standard solution*) solutions, the calculated MU (k = 2) for subsequent air measurements undertaken ranged from ±8% at 40 ng m$^{-3}$ to ±92% at concentrations <5 ng m$^{-3}$ where contributions arising from instrumental noise and transient fluctuations in the trace Hg concentrations dominated.

Biomass feedstocks can contain large amounts of K and other ash-forming elements that lead to operational issues such as fouling, agglomeration and corrosion within industrial boilers. To gain a better understanding of the kinetics of elemental emissions when wood-based biofuels are combusted, an *ETV-ICP-OES* system was employed[32] as a micro furnace simulator thus enabling reproducible temperature-resolved emissions by Ca, Cl, K, Na, Mg, P and S to be interrogated. It was deduced that K was released between 700 and 1400 °C either as elemental K or as KOH because inspection of concurrent ICP emission spectra did not show the presence of possible counter ions such as Cl or S.

Application of laser and spark-based techniques for the analysis of air-related samples are summarised in Table 1.

**Table 1:** Selected applications of LIBS and SES for air related measurements

| **Analyte** | **Sample matrix** | **Study rationale** | **Technique** | **Findings** | **Reference** |
|---|---|---|---|---|---|
| APM | Air | Evaluation of a prototype field deployable system for the online analysis and classification of individual aerosol particles | LIBS | Portability demonstrated in field trials. Optimum sampling rate was 10 particles min$^{-1}$ and optimum concentration for analysis was 1 particle/cm$^3$. Mass LODs for K, Mg and Na were 70, 40 and 2 pg, respectively. Minimum detectable particle size was 300-800 nm | [33] |
| APM | Air | Evaluation of a prototype field deployable system for the online analysis and classification of aerosol particles | LIBS | Measurement of up to 20 elements at 10 min measurement intervals possible and major elements such as Al, Ca, Cl, Mg, P, S and Si detected in an Asian dust event | [34] |
| NP | Air | Evaluation of a measurement approach for the analysis of engineered NP | LIBS | Both online (direct aerosol sampling) and offline (analysis of NP collected on filters) measurement approaches tested using mono and bimetallic NP generated via electrical discharge plasma generators. Online detection threshold for particles tested was for a diameter of >60 nm and a number concentration of >10$^6$ cm$^3$ | [35] |

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| NP | Air | Evaluation of a measurement approach for the analysis of single NP | LIBS | Ultrafast ps pulses used to interrogate single optically trapped NP both qualitatively and quantitatively. LOD for Cu of 27 ag for single particles of 18 nm diameter | [36] |
| Various | GSR | Evaluation of a mobile on-site particle screening capability | LIBS | In-field methodology for forensic analysis demonstrated. LOD of 0.2 ng (Ba), 2.0 ng (Pb) and 2.0 ng (Sb) achieved. Particle classification accuracy of >98.8% demonstrated for datasets examined. Potential for reduced classification times using LIBS (min) *vs.* conventional laboratory-based SEM-EDS (h) | [37] |
| Various | Surfaces | Evaluation of a portable system to measure metallic particles sedimented from air on workplace surfaces | SES | Tape-lift sampling of dust from contaminated workplace surfaces for analysis with a spectrometer calibrated for Co, Cr, Fe and Mn using calibrants prepared by depositing known sample masses on Cu tape. LOD of 3-19 ng cm$^{-2}$ | [38] |

## 2.5.2 Mass spectrometry

### *2.5.2.1 Inductively coupled plasma mass spectrometry.*

The utility of various ICP-MS platforms such as hyphenated-ICP-MS systems, ICP-MS/MS, LA-ICP-MS and sp-ICP-MS in supporting the toxicological assessments of *metallic NP* exposures was reviewed[39] (121 references). Coupling a rotating disk diluter (RDD) to sp-ICP-MS enabled measurements of elemental composition, particle size and particle number concentration in aerosol samples.[40] In a proof-of-concept study using 40-100 nm sized Au NP, a number LOD of < 30 particles $L^{-1}$ was achieved, and matrix effects were deemed minimal because the correct particle number and size data was realised when $PM_{10}$ and road dust samples spiked with NP were analysed. The presence of ionic metal salts, confounders when testing NP samples by sp-ICP-MS, can result in the incorrect determination of particle size profiles but this interference can sometimes be alleviated by diluting samples. This was effective[41] in the analysis of simulated aerosol samples, wherein online sample dilution, achieved by coupling a RDD to the sp-ICP-MS instrument, decreased the ionic $Au^{3+}$ background signal in the determination of Au NPs. Use of alternative remedies, namely a fractionation approach, achieved by either coupling a differential mobility analyser (DMA) or a centrifugal particle mass analyser (CPMA) with a sp-ICP-MS instrument, were also effective by enabling better discrimination between NP and background ionic signals. To rank the respective performances of these remedies, the authors calculated a quantitative separation factor for each approach, defined as the signal ratio between the particle number (Au NPs) and the average of ionic background intensity ($Au^{3+}$) and demonstrated that this ratio decreased in the order DMA > RDD > CPMA.

Hyphenated GC-ICP-MS can be used to measure volatile elemental impurities in *gaseous samples* as demonstrated[42] in an application paper that summarised the methods for testing speciality gases such as diborane, phosphine and silanes used in the microelectronics industries. Here the ability to perform compound-independent calibrations, because often specific calibration standards are either unavailable or unstable, coupled with use of ICP-MS/MS to minimise isobaric interferences was advantageous. A custom-made TD unit coupled to ICP-MS/MS enabled[43] the successful determination of $Hg^0$ isotopes in air samples following collection and concentration on Au traps and subsequent desorption. The LOD was 0.01–0.03 pg, and calibration linearity up to 300 pg was achieved with analytical precision of $\leq 3.5\%$ in resultant isotopic measurements.

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

**Table 2:** Selected applications of ICP-MS for air related measurements

| Analyte | Sample matrix | Sample preparation/introduction | Technique | Rationale and Findings | Reference |
|---|---|---|---|---|---|
| C | Microplastics in facemasks | Suspension nebulisation | sp-ICP-MS | Size analysis of PS particles in range 1 – 6 µm performed with size LOD of ~400 nm. Results comparable with those obtained using DLS and SEM | [44] |
| C | Microplastics | LA | sp-ICP-MS | Method for sampling and introducing MPs captured on filters into plasma. Resultant $^{13}C^+$ signal was linear with absolute C mass over a 2-20 µm particle size range | [45] |
| C | Microplastics | Suspension nebulisation | sp-ICP-MS | Downward facing ICP system (gravity fed) for effective transportation of particles up to 90 µm. System tested using PS beads where particle diameter measurements of 2.93 ± 0.24 µm compared favourably with 2.97 ± 0.04 µm measurements derived using TEM | [46] |
| I | Air | Acid extraction/solution nebulisation | ICP-MS | Method for sampling and analysis of gaseous $^{129}I$ with sampling from air onto charcoal sorbent tube; acid extraction and clean-up followed by ICP-MS analysis. LOD of 2 mBq per sample achieved | [47] |

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| Pd, Pt and Rh | Automobile catalytic converters | MAE, solution nebulisation | ICP-TOF-MS | Method for high accuracy analysis of converter materials. Exact matching ID used for Pd and Pt assays and IS used for Rh assays. MU (K = 2) <1% achieved, representing a 2 to 3-fold improvement in Rh and Pd assays and 6-fold improvement in Pt assays performed previously using sequential ICP-MS | [48] |
| Pt | NP | Suspension nebulisation | sp-ICP-TOF-MS | Comparison exercise between 9 laboratories for mass, size and isotopic analysis of 40 ± 7 nm and 59 ± 8 nm Pt NP suspensions. Precision for mass equivalent spherical size measurements and mass measurements was <16% RSD (within laboratories) and <4% RSD (between laboratories). Particle number concentration testing precision was 53% RSD (between laboratories). Accurate isotope ratios determined for $^{194}$Pt/$^{195}$Pt with precisions <1% but >20% for low abundant isotopes ratio measurements. | [49] |
| Pu and U | Surface particles | On-line extraction/solution nebulisation | ICP-MS/MS | Evaluation of an on-line method for extracting and analysing Pu/U in particles collected on cotton swabs. Tested on extraction of simulant swab samples that contained 2 pg Pu and 20-200 ng U reference particles spikes. $CO_2$ /He used as a collision gas mix to minimise U isobaric | [50] |

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| | | | | interferences on Pu. The percent relative difference between measured isotope ratios and certified isotope ratios were < ± 5% except for $^{240}$Pu/$^{239}$Pu ratio measurements which were < +6.7%. | |
| Sr | $PM_{10}$ | Acid extraction/solution nebulisation | ICP-MS | Development of a single QICP-MS method to determine stable Sr isotopic signatures for potential $PM_{10}$ source apportionment studies. By optimising a Sr-Spec resin-based clean-up method and the ICP-MS operating conditions, $^{87}$Sr/$^{86}$Sr ratios were measured with an internal precision of *ca*. 0.2 % at concentrations of 0.5-2 µg $L^{-1}$ | [51] |
| Various | GSR | Suspension nebulisation | sp-ICP-MS | Use of sp-ICP-MS deemed superior to established SEM-EDS approach because more elements besides the usual Ba, Pb and Sb could be measured and so provide a better GSR classification profile | [52] |
| Various | $PM_{10}$ | On-line extraction, solution nebulisation | ICP-MS | Online SBET methodology developed. Simulant test samples prepared by depositing known masses of NIST SRM 2711a (Montana II soil) onto air filter samples which were then extracted and analysed. Measured bioaccessible Pb value relative to certified value was 105%. | [53] |

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| Various | Tyre rubber | MAE, solution nebulisation | ICP-MS | Fingerprint assay using metal markers developed to aide future source apportionment studies. Data compiled for 25 metals from 60 different tyres sampled. Mean mass fraction (*m/m*) of Zn was 1.117% consistent with previously reported values of *ca*. 1% | [54] |

***2.5.2.2 Mass spectrometry techniques other than inductively coupled plasma mass spectrometry***:

Measurement of elemental isotopic signatures in APM can provide valuable insights into their respective emission sources but high quality *calibrants* are essential for accurate determinations. Korean researchers calibrated[55] EA-IRMS by analysing in-house isotopic standards prepared by blending mixtures of various USGS and IAEA RMs, which enabled reference values with uncertainties for C, N and S isotope ratios in KRISS CRM 109-02-004 (*urban particulate matter*) to be determined. Calibration of aerosol MS typically involves the analysis of a given mass of particles with a known size and number concentration but development of a new calibration approach, the heated Mo/Pt catalyst-based conversion technique, which uses nitric oxide (NO) and carbon dioxide ($CO_2$) gas-phase standards, enabled reactive N and TOC measurements to be made.[56] This new calibration approach was evaluated using dried particles composed of pure ammonium nitrate (AN), other ammonium salts, and nitrogen-containing organic species and it was determined that the nitrate ionisation efficiencies determined by either calibration approach agreed within experimental uncertainties of ±15%. Furthermore, it was demonstrated by using this new independent calibration protocol that the relative ionisation efficiency for the ammonium ion was essentially the same for different ammonium containing compounds (±9%), regardless of formula or the corresponding anion, thereby validating a major assumption inherent in aerosol MS calibrations.

### 2.5.3 X-ray spectrometry

Two of the many relevant topics discussed[57] (82 references) in a tutorial review on the applicability XRF for the *analysis of airborne particulate matter* were the selection of suitable sampling substrates and the implementation of appropriate calibration approaches. In the µSRXRF analysis[58] of the elemental composition of $PM_{2.5}$ collected on filters, only 5 mm diameter portions were required for testing. The LODs ranged from 0.04 to 36.6 ng $m^{-3}$ with analysis times of <360 s per sample. Calibrants were prepared by spiking filters with multi-element solutions over a 0-16 ng $mm^{-3}$ linear range with ICP-MS assays performed to verify the spiked values. Performance benchmarked against two other measurement approaches, a conventional approach where air filters were analysed by ICP-MS and the *in-situ* analysis using an air sampler device equipped with an embedded EDXRF analyser, yielded elemental correlations with slope values of 0.4-1.0 with $r^2$ values of 0.62-0.89 and slope values of 0.29-0.89 with $r^2$ values of 0.39-0.80, respectively. Such diversity demonstrates the challenge in objectively comparing the performance of different measurement platforms that operate on different principles. There is a growing concern regarding the potential toxicity of APM in subway air so new studies here are welcome. By employing XAFS it was determined[59] those airborne particles, arising from high-temperature wheel and track wear processes, contained $Fe_3O_4$, $\gamma$-$Fe_2O_3$ and $Cu^I$ species that were found to cause cellular damage when laboratory cell line studies were subsequently conducted.

### 2.5.4 Carbonaceous particle measurements

Tutorial reviews that summarised analytical approaches such as combustion, optical, microscopic and MS-based techniques for identifying and determining *black carbon* in environmental matrices (225 references),[60] and methodologies for characterising the mass, size and morphology of soot particles (600 references) [61] were published. The comparative testing[62] of different black carbon analyser systems, namely

AE33® and MA20® aethalometers, a multi-angle absorption photometer, a soot particle aerosol MS and an elemental carbon TOA analyser, undertaken by challenging them to laboratory generated soot particles, yielded median concentrations that were within 25% of each other. The generation of carbonaceous test aerosols within a laboratory setting for instrumental testing purposes is typically undertaken using a soot generator that runs on gaseous fuels such as propane, but resultant emissions may not fully mimic those emitted from real-world engines so operation[63] of a miniCAST® soot generator using diesel fuel enabled more realistic soot particles to be produced in the size range 18-39 nm.

The ability to distinguish between graphene, graphene oxide and reduced graphene oxide species in *workplace air* was possible when TOA assays were conducted[64] on filter samples collected from an advanced manufacturing facility. It was suggested that such measurements would complement other measurements undertaken by Raman and SEM in providing better worker exposure assessments. Wearable aethalometers are used to undertake black carbon measurements within ambient air settings, but their reported use[65] in harsher mine air environments was new. The ability to generate exposure data in real-time provided new insights into task-specific worker exposure dependencies that will aide future control intervention studies. The aethalometer-derived eBC measurements correlated well with those regulatory EC measurements, undertaken in parallel, with linear regression $r^2$ values of 0.911-0.999 but there was a between-method bias because regression slopes were 0.993-2.103. To reduce such bias in future studies, use of more appropriate mass absorption cross section values that are site-specific to correct eBC values was suggested. The authors also recommended installing an aerosol dilutor and an aerosol drier on the sampling inlet of the aethalometer if high fume concentrations and high RH are encountered in such underground work settings. End-of-working-shift air filter measurements conducted on-site with portable instrumentation offer the potential for exposure data to be generated more quickly than at present which involves sending samples to a laboratory for TOA analysis. The prompt return of such data could then allow swifter interventions to control emissions. In a proof-of-concept study, the analysis of air filter samples by portable NDIR yielded[66] LOD of 20, 37, and 46 μg $m^{-3}$ for elemental, organic and total C. Incorporating the spectrometer within an air sampling device equipped with a spoolable filter tape for a near continuous *in-situ* measurement capability was also proposed.

It is interesting to note developments in on-line *carbonaceous aerosol monitors*. The comparative testing[67] of a new prototype total C analyser, so-called FATCAT (fast thermal carbon totalizator), against a similar but commercially available TCA08® analyser demonstrated that non-volatile total C measurements were in agreement when challenged with either mature, fully graphitised soot (with an organic-to-total C ratio of < 0.1) or young, partially formed soot (with an organic-to-total C ratio of 0.6) that was denuded at 350 °C. The FATCAT instrument possessed a catalyst to convert CO or VOC, arising from sample heating, to $CO_2$, which if not fully oxidised would otherwise may go undetected. It was therefore concluded that this instrument was better suited for measuring a wider range of soot and organic APM than the TCA08 instrument, which did not possess such a catalyst and so could only measure those sampled carbonaceous APM species that convert fully to $CO_2$ upon heating. A prototype on-line monitor for the concurrent measurement of TOC and water-soluble organic carbon (WSOC) in both $PM_{2.5}$ and $PM_{2.5-10}$ was developed[68]. The $PM_{2.5}$ air sampling line consisted of a versatile aerosol concentration enrichment system connected to an aerosol-into-liquid-sampler, whereas the system for collecting the $PM_{2.5-10}$ fraction consisted of two tandem virtual impactors connected to a BioSampler™. An embedded Sievers M9 TOC analyser was then used to determine the TOC and WSOC contents of the particles.

## 3 Water Analysis

### 3.1 Reviews

*Sample preservation and preparation* are crucial steps for the accurate determination of concentrations in environmental samples. Given the significance of elements with multiple labile forms in the environment, a comprehensive overview[69](88 references) of this topic focussed on mercury. The authors concluded that preserving and transporting mercury samples, particularly from remote or resource-limited areas, poses significant challenges due to the need for different preservation methods and hazardous materials. While current methods emphasize rapid transportation to laboratories, SPE methods using specialized sorbents offer a promising alternative. These methods effectively preserved Hg species without altering their chemical forms and provide a safer, more cost-effective option for field-to-laboratory transport. They eliminated the need for expensive materials (*e.g.*, PTFE) or heavy, fragile containers (*e.g.*, glass) and did not require additional chemicals to stabilize the Hg species. However, further research was needed on the long-term storage of adsorbed Hg species, especially MeHg, to establish SPE as a reliable preservation method fully.

Another legacy pollutant is *lead contamination* with severe impacts on both the environment and human health. A comprehensive review[70](61 references) highlighted the importance of accurately determining Pb levels in different water sample types. The authors discussed the merits of various detection techniques and pointed to emerging technologies, such as precious metal nanotechnology (*e.g.*, nanoclusters), paper-based microfluidics, and new fluorescent molecular probes, that are making Pb detection more economical, portable, and rapid.

*Stable isotopes analysis* is a powerful tool to understand environmental processes. A comprehensive review[71](111 references) examined various spectroscopic techniques and their potential applications in environmental sciences. This article focused on six atomic spectroscopy methods (*i.e.*, AES, AAS, LEAFS, saturated absorption spectrometry, four-wave mixing spectrometry, and Doppler-free two-photon spectrometry), discussing both their fundamental principles and current limitations. While atomic spectrometry is commonly employed for determining the elemental composition, it generally falls short of MS in precision and accuracy for isotope analysis. However, atomic spectrometry offers notable advantages, including fewer interferences, easier correction, and the capability for rapid, *in situ*, and remote real-time isotope analysis, especially when combined with laser ablation.

## 3.2 Certified reference materials

A comprehensive investigation of RM was carried out[72] to assess their suitability for *the determination of $^{237}$Np in environmental samples*. This study summarized values obtained from the available literature, reporting certified and informative values for 25 RM (over 200 activity concentration data). The literature values (44 references) were further analysed by calculating statistical values (arithmetic mean). In addition, the activity concentration of the RM SRM JSAC-0471 (soil), issued by the Japan Society for Analytical Chemistry, was determined and reported for the first time.

## 3.3 Sample preconcentration

The most significant advances in analyte preconcentration for water analysis are summarised in Table 3 (solid-phase extraction) and Table 4 (liquid-phase extraction).

**Table 3.** Preconcentration methods using solid-phase extraction for the analysis of water.

| Analytes | Matrix | Technique | Substrate | Coating or modifier | LOD in µg L$^{-1}$ (unless stated otherwise) | Method validation | Reference |
|---|---|---|---|---|---|---|---|
| $As^{III}$ | Ground and tap water, food samples | ICP-MS | Metal organic framework | None | 0.554 ($As^{III}$) | Spike recovery (water, food samples) | [73] |

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|---|---|---|---|---|---|---|---|
| As, Cd, Pb | Groundwater | GFAAS | Magnesium oxide NPs | Chitosan | 0.008 (As), 0.006 (Cd), 0.012 (Pb) | Spike recovery (water) | 74 |
| As, Cu, Pb | Sea water | ICP-OES | Manganese oxide octahedral molecular sieve | None | 0.3 (As), 0.1 (Cu), 2.1 (Pb) | Spike recovery (sea water) | 75 |
| $As^{III}$, $As^{V}$, $Cr^{III}$, $Cr^{VI}$, $Se^{IV}$ and $Se^{VI}$ | Water and urine | ICP-MS | Polyamide porous monolith | Titanium oxide NPs | 0.004 ($As^{III}$), 0.0007 ($As^{V}$),<br>0.0109 ($Cr^{III}$), 0.0119 ($Cr^{VI}$), 0.0323 ($Se^{IV}$) and 0.0132 ($Se^{VI}$) | NRCC CASS-4 (nearshore seawater), and SLRS-5 (river water), NIST 1643f (fresh water), Seronorm L-2 (trace elements urine) and spike recovery (seawater, river water, agriculture waste, and human urine samples) | 76 |
| Au and AuNPs | River, lake, sea water | FAAS and GFAAS | Zirconium(IV) metal organic framework | mercaptosuccinic acid, formic acid | 650 femtomol L$^{-1}$ | Spike recovery (water) | 77 |
| Ba, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn | Waste water | ICP-OES | ZIF-67 | Activated carbon | 2.6 (Ba), 0.39 (Be), 1.5 (Cd), 1.3 (Cr), 1.2 (Cu), 9.8 (Fe), 5.1 (Hg), 0.82 (Mn), 9.9 (Ni), 21 (Pb), 0.81 (Zn) | ERM-CA713 (waste water)<br>Spike recovery (water) | 78 |
| Bi | Water, food, cosmetic samples | FAAS | $MgAl_2O_4$@$MoSe_2$ nanocomposite | None | 0.012 (Bi) | NCS ZC 73028 (rice), NCS ZC 73036 (green tea) | 79 |
| Cd | Lake water | FAAS | Manganese ferrite magnetic NPs | None | 1.3 (Cd) | Spike Recovery (lake water) | 80 |
| Cd | Sea water | SAGD OES | Graphene oxide | None | 0.003-0.2 (Cd) | Reference measurements via ICP-MS | 81 |
| Cd, Co, Ni | Spring, mineral, factory process waste water | FAAS | Magnetic *pinus pinea* cone powder | None | 2.3 (Cd), 19.3 Co, 12.5 (Ni) | UME CRM 1204 (elements in wastewater), Spike recovery (water) | 82 |
| Cd, Cu | Tap water, mineral water, drinking water, food samples | FAAS | Magnetic polystyrene-b-poly dimethyl siloxane block copolymer | None | 1.7 (Cd) 0.8 (Cu) | NIST SRM 1570a (spinach leaves), ERM BCR-032 (phosphate rock) Spike recovery (water, juice) | 83 |
| Cd, Cu, Pb | Drinking water | ICP-OES | Cellulose nanoparticles | Ethylenediaminetetraacetic acid-linked polyethyleneimine | 0.4 (Cd, Cu, Pb) | Spike recovery<br>(water) | 84 |
| $Cd^{II}$ and $Pb^{II}$ | Swimming pool water | GFAAS | Open-cell polyether-type polyurethane foam | None | 0.5 ($Pb^{II}$) and 0.02 ($Cd^{II}$) | Spike recovery (water) | 85 |
| Ce, Dy, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Tb, Y, and Yb | water | WDXRF | NH2-MIL-53 | *N,N*-bisphosphono(methyl) glycine | 0.4-4.7 | Spike recovery (water) | 86 |
| $Cr^{III}$ | Water | GFAAS | Several ion-imprinted polymers | None | 0.35-0.47 ($Cr^{III}$) | NIST SRM 1643e (surface water) | 87 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cr$^{III}$, Cr$^{VI}$, total Cr | Waste, tap, mineral water | FAAS | Multiwalled carbon nanotubes@CuAl$_2$O@SiO$_2$ | None | 6.2 (Cr$^{VI}$) | INCT-OBTL-5 (Oriental Basma tobacco leaves) and ECCC TMDA-64.3 (fortified water) | 88 |
| Cr$^{VI}$ | Water and sea water | TXRF and EDXRF | Graphene oxide | Tetraethylenepentamine | 0.053 (Cr$^{VI}$, EDXRF) and 0.0035(Cr$^{VI}$, TXRF) | Sigma Aldrich RMs QC1088 (Cr$^{VI}$ in water) and QC3016 (sea water) | 89 |
| Cu | Water, food samples, soil | FAAS | Fe$_3$O$_4$@SiO$_2$ | Creatine | 1.50 (Cu) | Spike recovery | 90 |
| Cu | Water, food samples | FAAS | BaTiO$_3$ | None | 1.6 (Cu) | ECCC TMDA-64.3 (water) | 91 |
| Cu$^{II}$ | Mineral and sea water | ICP-MS | Several ion-imprinted polymers | None | 0.0152 | Spike recovery (water) | 92 |
| Cu$^{II}$, Hg$^{II}$ Ni$^{II}$, Pb$^{II}$, Zn$^{II}$ | Water | ICP-OES | Cobalt ferrit nanoparticle | Deep eutectic solvent (choline chloride and p-aminophenol) | 0.544 (Cu), 1.33 (Hg),<br>1.12 (Ni), 0.622 (Pb), 0.962 (Zn) | SPS-WW2 Batch 108 (water) | 93 |
| Ga$^{III}$ and In$^{III}$ | Water, soil, electronic scrap | GFAAS | Fe$_3$O$_4$ particles | None | 0.02 (Ga$^{III}$) and 0.01 (In$^{III}$) | NIST SRM 2711 (soil), NCS DC 73319a (soil), ECCC TM-25.4 (water) and TMDA-62.2 (water) | 94 |
| P | Water and artificial seawater | EDXRF | Graphene oxide | Lanthanum oxide | 0.4 (P) | Spike Recovery (water) | 95 |
| Pb | Water | FAAS | Polysulfone fibres | Acrylic acid | 50 (Pb) | Spike recovery (water) | 96 |
| Pb$^{II}$ | Tap and mineral Water, lettuce | GFAAS | Cu-benzene-1,3,5-tricarboxylic acid@Fe$_3$O$_4$ | None | 0.026 | Spike recovery (water) | 97 |
| Pb$^{II}$ | Tap and waste water, food samples | FAAS | Zink oxide nanoflower | Ag | 8.52 (Pb$^{II}$) | GBW07424 (soil) and GBW07425 (soil) and spike recovery | 98 |
| Pd | Sea water and river water | FAAS | Dicobalt orthosilicate NPs | Mordant red 3 | 0.14 (Pd) | Spike recovery (water) | 99 |
| Sb$^{III}$ and Sb$^{V}$ | Tap, river, lake, underground water and acid mine drainage | ICP-MS | Reduced graphene oxide | Fe$_3$O$_4$ | 0.006 (Sb$^{III}$) | GBW(E)080545<br>(Standard Solution of Sb)<br>Spike recovery (water) | 100 |
| U | Tap, river, sea water | WDXRF | Fe$_3$O$_4$@COF | 1,3,5-triformyl-phloroglycerol and terephthalohydrazide | 0.04 (U) | NRCC CASS-6 (near shore sea water), GBW07311 (stream sediment) | 101 |
| V$^{V}$ and V$^{IV}$ | Sea water | ICP-MS | chelex-100 resin | none | 0.87 nanomol kg$^{-1}$ (V$^{V}$) and 0.47 nanomol kg$^{-1}$ (V$^{IV}$) | NRCC NASS-7 (sea water) | 102 |

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

| Analytes | Matrix | Technique | Method | Reagents | LOD in $\mu$g L$^{-1}$ (unless stated otherwise) | Method validation | Reference |
|---|---|---|---|---|---|---|---|
| AgNPs and TiNPs | Tap water | ICP-MS | Surfactant assisted DLLME | Triton X-114 and 1,2-dichloroethane | 55.5 nm (TiNPs) and 14.1 nm (AgNPs) | Spike recovery (reference particles in water) | [103] |
| Ag, Cu, Pd, Pt, | Tap, river, sea water | ICP-OES | DLLME | 1-butyl-2-diphenylphosphino-3-methylimidazolium hexafluorophosphate and methanol | 0.2 (Ag), .0.4 (Cu), 2 (Pd), 1 (Pt) | ISC Science RM CRM-DW1 (drinking water) spike recovery (water) | [104] |
| As, Cd, Pb, Hg | Water and food samples | GFAAS | DLLME | *l*-Menthol and salicylic acid | 0.0088 (As), 0.0084 (Cd), 0.0076 (Pb), 0.0043 (Hg) | Spike recovery (water) | [105] |
| $\delta^{13}$C in chlorinated phenols | Ultrapure and river water | GC-IRMS | DLLME | Acetone, tetrachloroethylene and acetic anhydride | Limit of precise isotope analysis: 100-200 | Spike recovery (different reference standards) | [106] |
| Cd | Sea, river, tap, mineral water and food samples | FAAS | DLLME | Ethanol and choline chloride/4-bromophenol | 0.9 (Cd) | Spike recovery (water) | [107] |
| Cd, Co, Cu, Mn, Ni and Pb | Water | ICP-OES | LLME | benzethonium chloride and dihexyl sulfosuccinate | 0.04 (Cd), 0.5 (Co), 0.2 (Cu), 0.1 (Mn) 0.1 (Ni) and 1.0 (Pb) | SPS-SW2 (Surface water) | [108] |
| Co | Drinking water | FAAS | spray-assisted fine droplet formation LPME | Ethyl-2-(((7-hydroxy-2-oxo4-phenyl-2H-chromen-8-yl)methylene)amino)-3-(4-hydroxyphenyl) propanoate and chloroform | 2.2 | Spike recovery (water) | [109] |
| Cr$^{VI}$ | River water | GFAAS | Single phase LLE | Water, ethanol and amyl alcohol | 0.05 | NIST SRM 1643e (surface water) | [110] |
| Cr$^{VI}$ | Surface water and wastewater | FAAS | LLME | 1-(2-(Quinolin-8-yloxy)ethyl)pyrrolidinium Chloride, $NH_4PF_6$, water | 0.0055 | Spike recovery (water) | [111] |
| Cr$^{VI}$ | Sea, tap, well, wastewater | TXRF | LLME | Cetyltrimethylammonium bromide and chloroform | 0.9 | Spike recovery (water) | [112] |
| Hg | Sea water | Direct Mercury Analyser | Vortex-assisted LLME | Ammonium pyrrolidine dithiocarbamate and hexane | 0.0082 | NRCC NASS-7 (sea water), SLEW-3 and ERM BCR-505 (both estuarine water). | [113] |
| V | Water and food samples | FAAS | Vortex-assisted LLME | [ChCl/p-cresol] $[FeCl_4]$ and bis(acetylpivalylmethane)ethylenediimine | 0.3 | NIST SRM 1643f (trace elements in water) and NIST SRM 1570a (spinach leaves) | [114] |

### 3.4 Speciation

The development of many protocols for column-based chemistry, as shown in tables 3 and 4, underline the importance of species-specific metal determinations in evaluating the condition of aquatic systems. A common approach for such analysis is HPLC coupled with a suitable detector. Utilizing HPLC-ICP-MS, a method[115] was developed to *simultaneously speciate five Pb, Hg and V species*, of environmental concern: $Pb^{II}$, TML, $Hg^{II}$, MeHg, and $V^{V}$. To reach lower LODs the authors incorporated an on-line SPE step with a synthesized novel nanomaterial sorbent consisting of silica-coated magnetic particles and graphene oxide functionalized with methylthiosalicilate (M@GO-TS). The magnetic NPs were easily retained within a microcolumn or knotted reactor using an external magnetic field during adsorption and elution. Separation on a C18 HPLC column was achieved by a two-phase gradient method (thiourea/$H_3PO_4$ and TBAOH/$H_3PO_4$). Using ICP-MS, allowed the parallel detection of all three metals without requiring complete resolution. The method achieved low LODs: 5 ng $L^{-1}$ for TML, 20 ng $L^{-1}$ for MeHg, and 2 ng $L^{-1}$ for $V^{V}$, with RSDs of around 5%. The method was validated using the NRCC CRM TMDA 64.3 (fortified lake water) and was successfully applied to real-world samples, including seawater and human urine, demonstrating its potential for routine environmental monitoring and biomonitoring applications.

A similar *SPE-HPLC-ICP-MS method for tin and lead species* was developed[116] for TMT, TET, TBT, TPhT, TML, TEL, and $Pb^{II}$. As above, a nanomaterial composed of GO and silicon dioxide (GO@SiO2) was used for on-line SPE enrichment with subsequent species separation using a C18 HPLC column and sodium dodecylbenzenesulfonate as the eluent. The optimized method achieved LODs of 0.004 ng $L^{-1}$ for TMT, 0.002 ng $L^{-1}$ for TET, 0.007 ng $L^{-1}$ for TBT, 0.008 ng $L^{-1}$ for TPhT, 0.005 ng $L^{-1}$ for TML, 0.006 ng $L^{-1}$ for TEL, and 0.004 ng $L^{-1}$ for $Pb^{II}$. The method was validated by diluting and spiking a seawater matrix, satisfactory recoveries between 90% and 104% were obtained, with RSDs ranging from 1% to 5%. The total runtime of approximately 17 minutes per sample supports high-throughput analysis, and the low LODs in the pg $L^{-1}$ range make it suitable for analysing large environmental sample sets.

The authors applied their method to investigate the occurrence of Sn and Pb species in the coastal seawater of Hangzhou Bay and reported the presence of these species in some samples.

Antimony, a toxic metalloid whose occurrence is significantly influenced by human activities, such as mining, is classified as a priority pollutant with regulated limits in drinking water. To effectively *monitor the presence of Sb species ($Sb^{III}$ and $Sb^{V}$) in drinking water*, a fast and reliable method was developed[117] using frontal chromatography coupled with ICP-MS (FC-ICP-MS). The method employed a strong cation-exchange resin and diluted $HNO_3$ (0.1, 0.5 or 1 M) as the eluent to achieve a separation where $Sb^{III}$ interacts with the resin while $Sb^{V}$ does not. This approach was validated using spiked drinking water samples, as no suitable RM were available. The method demonstrated good recoveries; however, the authors noted that when there was a high ratio between the two species (*ca.* 100:1), the concentration of the less abundant species might be overestimated. Despite this, the authors concluded that this issue is unlikely to be significant in natural surface waters. The optimised method achieved low LODs of 0.9 ng $L^{-1}$ for $Sb^{III}$ and 0.4 ng $L^{-1}$ for $Sb^{V}$, and high-throughput (3 min per sample).

To reduce the risks from *handling Hg species in the environment and in laboratory settings* a $Me_2Hg$ generator that produced[118] high-purity $Me_2Hg$ stock solutions on demand by reacting methylcobalamin with $Hg^{2+}$ under optimized conditions has been developed. The system was designed so that freshly formed $Me_2Hg$ was volatilized and diffused into an outer buffer solution. The authors then used this high-purity $Me_2Hg$ as standard to develop a purge-and-trap GC-CV-AFS method for $Me_2Hg$ determination in water samples. In this method, nitrogen gas was used as a purge, with a gold trap that captured $Hg^0$ followed by a Tenax® trap that captured the other Hg species. Thermal desorption with Ar as a carrier gas was performed at 500 °C to liberate $Hg^0$ prior to AFS detection. The other Hg species were desorbed at 200 °C and then separated and detected by GC-AFS. The method was validated through spike recovery experiments (spike levels: 0.05, 0.2, 1 ng $L^{-1}$), achieving recoveries of 93% to 102% for $Me_2Hg$ in water samples, with RSDs of 4% to 6%.

### 3.5 Nano- and micromaterials

In recent decades, awareness and concern about *small-scale particles in aquatic environments* has significantly increased. While metal-based particles have been studied for a long time, attention has now shifted to investigating nano- and microplastics and their impact on aquatic ecosystems. Detecting carbon-based NPs is challenging, so Pirade *et al.* developed[119] an indirect spICP-MS method using gelatin-coated gold NPs to measure the number concentration of plastic nanoparticles. The gold NPs conjugate with the target plastic particles, enabling the measurement of the plastic particle number concentration by detecting the presence of Au. Using this method they successfully detected 390 nm diameter polystyrene particles in both tap and canal water. Hendriks and Mitrano[120] introduced a direct method for detecting polystyrene microparticles (PS-MP) by measuring the $^{12}$C signal by spICP-MS, even in the presence of up to 20 mg L$^{-1}$ DOC in freshwater. Their approach utilised the multi-elemental capability of ICP-TOF-MS to differentiate PS-MP from other carbon sources, such as algae (by using their multi-elemental fingerprint), achieving a size detection limit of 1.56 µm. A microdroplet generator (MDG) for calibration purposes was used[121] together with spICP-TOF-MS to enable the direct detection of 3.4 µm PS-MP in seawater via the $^{12}$C signal. Vonderach *et al.* aligned[122] their MDG with a custom-built ICP-TOF-MS with a downward-pointing plasma using the force of gravity to improve particle transport efficiency when detecting 3 µm polystyrene particles using the $^{12}$C signal. An optimised[123] ICP-MS method for detecting PS-MP in river water, utilized the $^{13}$C signal and achieved a size LOD of approximately 1 µm. To avoid false positive events from other OM *e.g.* algae, they developed a premeasurement acid digestion procedure. A common challenge with all these methods for the microplastic detection is the inability to differentiate between plastic types. To address this, a comprehensive approach[124] was developed that combined optofluidic force induction with Raman spectroscopy and ICP-TOF-MS, enabling detailed particle characterization.

In addition to determining the size of plastic particles, the investigation of *the 'Trojan horse' effect* is another important field of research. For example, Patidar *et al.*[125]

studied microplastics as vectors for metals in rivers, using ED-XRF to detect several elements. They found that microplastics were contaminated with various metals, posing potential risks to aquatic species that ingest the microplastics. A study on the potential of nanoplastics to carry[126] toxic tin species was conducted, demonstrating that these particles served as vectors for the remobilization of TBT from sediments. This was particularly concerning because these NPs exhibited higher mobility than sediment particles. A study by Baalousha's research group[127] explored the use of fingerprint elements to track the fate of released nanoplastics in the environment. Additionally, two studies[128, 129] investigated microplastics as carriers for NPs, including iron, copper, and zinc oxide NPs. Both confirmed that the adsorption of NPs onto microplastics took place and suggested that this may lead to harmful effects on aquatic ecosystems.

The combination of *fractionation and speciation approaches* commonly relies on multiple techniques, *e.g.* $AF_4$ and HPLC but to streamline the process and eliminate the need for costly and complex hyphenated methods prior to speciation, a procedure based[130] on membrane filtration was developed. This approach utilized a PVDF membrane for the offline fractionation of ionic Se species and Se NPs. The sample volume was first reduced from 1 L to 1 mL, achieving an EF of 1000. The NP fraction was then digested and directly analysed by ICP-MS, while the ionic fraction was analysed via HPLC-ICP-MS. Separation of Se species was performed using an anion-exchange column with $NH_4HCO_3$ as the eluent. The method was validated through spike recovery experiments to assess each step of the process. The optimized method was successfully applied to various spiked sample types, including tap water, groundwater, spring water, artificial lake water, and river water, demonstrating its effectiveness. The LOD was 1.8 ng $L^{-1}$ for Se NPs.

## 3.6 Instrumental analysis

**3.6.1 Atomic Absorption spectrometry.** High-resolution CS-AAS offers a sensitive method for *determining F concentrations* by measuring *in situ* generated fluorine-containing molecular surrogates *e.g.*, BaF, GaF rather than fluorine directly. However, this technique currently only enables the determination of fluorine species as a sum parameter. In the case of CS-AAS, the most commonly used parameter is EOF, which represents the extractable organic fluorine fraction. To address[131] this limitation and provide a more comprehensive assessment of organic fluorine species, a study was conducted using both HPLC-ESI-MS/MS and HR-CS-GFAAS. Samples were taken from Berlin rivers impacted by sewage treatment effluents. The study targeted 24 specific PFASs using HPLC-ESI-MS/MS, while the EOF sum parameter was measured via HR-CS-GFAAS. Before AAS measurement, the inorganic fluorine was removed and the organic fluorine was pre-concentrated using a SPE step, enabling PFAS detection in the ng $L^{-1}$ range. The method's accuracy was validated using the EC CRM ION-96.4 (water from the Grand River, Ontario) and an in-house QC standard solution, as no EOF RMs were available. The study revealed that targeted analysis accounted for a maximum of 14% of the EOF total, underlining the need for complementary approaches. Further, the authors showed that the organic fluorine concentration was strongly influenced by inputs from wastewater treatment plants that were potential point sources. This study highlights that multiple techniques are essential for a comprehensive assessment and interpretation of the organic fluorine burden in the aquatic environment.

*Thallium in Brazilian river waters was determined*[132] using a newly developed solid sampling HR-CS-GFAAS method that employed chromatographic filter paper for analyte enrichment and purification. This was achieved by placing the paper in a vial containing 9 mL of pH-adjusted sample together with EDTA. The paper was then directly analysed using the solid sampling HR-CS-GFAAS method. The LOD was 0.018 μg $L^{-1}$. The results from this fast and simple method demonstrated good agreement with comparative measurements using ICP-MS.

**3.6.2 Vapour generation.** Hydride generation remains one of the most common techniques for the determination of vapour-forming elements due to its excellent matrix separation capabilities and improved instrument sensitivity. To maximize the amount of information obtained by CVG AFS in a short time, a setup was developed[133] to simultaneously measure four elements (As, Bi, Hg and Sb) in coastal seawater. In many CF HG systems with a hydrogen diffusion flame atomizer, the $H_2$ required to sustain the flame is produced by the reaction of potassium borohydride under acidic conditions. This procedure has the drawback that the reaction conditions needed to generate the volatile derivatives cannot be decoupled from the need to ensure an adequate supply of $H_2$ for the flame. To address this issue, the authors developed an electrochemical $H_2$ generator, that allowed independent optimization of the spectrometer flame, enabling the simultaneous measurement of the four elements. The custom $H_2$ generator was connected to a specialized four-channel AFS system equipped with four hollow cathode lamps (HCLs), a photomultiplier as a detector, and an Ar-$H_2$ flame atomizer. With this setup, LODs of 0.015 µg $L^{-1}$ for As, 0.005 µg $L^{-1}$ for Bi, 0.001 µg $L^{-1}$ for Hg and 0.010 µg $L^{-1}$ for Sb were achieved, along with RSDs ranging from 1% to 4%. Additionally, when a KBr/HCl mixture was tested for the preservation of coastal seawater samples, the concentration of all four elements remained stable in the µg $L^{-1}$ range for at least 15 days. The method was validated against spiked seawater samples and was successfully applied to seawater samples collected from Xiamen Bay in Southeast China.

The precise *determination of ultra-trace levels of chromium in seawater* is challenging but essential. To address this[134], a USN-DBD-VG system was developed and interfaced with an ICP-MS instrument. This allowed the detection of total Cr with a LOD of 4 ng $L^{-1}$, using only 40 µL of sample. The system combined a commercially available USN with a custom-built DBD reactor, coupled at a 90° angle to the USN. Various parameters, including spray distance, carrier gas flow, and pH of the solution, were optimized to enhance performance and reduce matrix effects. The method was validated against two seawater CRMs: the Chinese RM BWB2511–2016 (5 metals in natural seawater) and the NRCC CRM NASS-7 (seawater), which were in good agreement. Spike experiments demonstrated that the method maintained high accuracy (89 % - 107 %) even in the presence of high matrix concentrations. The optimized method was successfully applied to seawater samples from Qingdao and Weihai, both located in Shandong, China.

For the *highly precise Hg isotopic ratio measurements* at low concentrations, a method[135] was developed using a cold vapor generator-MC-ICP-MS equipped with $10^{13}$ Ω FC amplifiers and a high-transmission Jet interface. The authors tested changing the cone setup (standard versus Jet), plasma conditions (wet versus dry), and FC amplifier types ($10^{11}$ Ω versus $10^{13}$ Ω). For data evaluation under wet plasma conditions, a combined fractionation correction approach was utilized, incorporating both the Russell law, an internal correction approach using NIST SRM 997 (isotopic standard for thallium), and an SSB approach against the NIST SRM 3133 (mercury (Hg) standard solution) as external correction. Under dry plasma conditions, only the external correction method was applied. The study found that the optimal setup involved using Jet cones, dry plasma conditions, and all four available $10^{13}$ Ω amplifiers. This instrumental setup allowed for precise Hg isotopic ratio analysis at significantly lower concentrations in water samples (0.25 μg $L^{-1}$) that were comparable to those previously reported at 10 μg $L^{-1}$.

A *single-vial sample preparation method for determining* $Hg^{2+}$ *in water* was developed[136] and evaluated to minimize errors during sample preparation. This method involved binding $Hg^{2+}$ in the sample with MNPs modified with L-cystine after the addition of an acetate buffer. The NPs were isolated using a magnet and desorbed with an HCl solution before analysis by CV-AAS. The reducing agent (sodium borohydride) was introduced together with an argon gas stream directly into the vial. Under optimized parameters, the method LOD was 0.4 μg $L^{-1}$ with an effective EF of 24, offered a fast and straightforward approach for determining Hg in the sub-μg $L^{-1}$ range.

To *enhance the LOD for As determination*, synergistic enhancement effects with antimony and cadmium were investigated[137] using PVG coupled with ICP-MS. The highest sensitivity was obtained by mixing the sample with 10% *v/v* acetic acid, 5.0 mg $L^{-1}$ $Sb^{III}$, and 20.0 mg $L^{-1}$ $Cd^{II}$, achieving a LOD of 2.1 ng $L^{-1}$, which represented a 50-fold improvement compared to that obtained with pneumatic nebulisation. The method was validated by spike recovery from various (tap, lake, and river water) water samples and Chinese CRMs GBW07303a and GBW07305a (sediment), with relative measurement errors between -4% and +8%.

**3.6.3 Inductively coupled plasma mass spectrometry.** ICP-MS instruments equipped with triple quadrupole-based mass separators are currently among the most versatile systems for interference removal using gases in CRCs. The *use of different cell gases and their reactions with analytes in the CRC* is still under active investigation. One promising gas is nitric oxide (NO), although its reactions with elements in the CRC are not yet fully understood. So, a study[138] was conducted on the applicability of NO in the determination of 50 different elements, with a particular focus on $^{239}$Pu for nuclear forensic applications. This involved experimental work and complementary theoretical (density functional theory) calculations of reaction enthalpies. The primary reaction product observed across the elements was $MO^+$, which aligned well with the predicted $MO^+$ reactivity from the theoretical models. Besides showing that NO is a suitable gas for the determination of Pu in challenging matrices, this study demonstrated that theoretical predictions of reactivity can effectively guide method development for the removal of isobaric and polyatomic interferences, offering valuable insights for a range of practical applications. A second study investigated[139] a broad range of elements (48 in total, with a focus on Pu) using different reaction gases ($CO_2$, $N_2O$, and $O_2$) and examined the influence of ion kinetic energy and cell gas flow rate on the reactions. In the ICP-MS/MS system used, these parameters correspond to the octupole voltage ($V_{Oct}$) and the cell gas pressure. The authors demonstrated that by selecting the appropriate energy and gas flow rates one could effectively remove isobaric interferences and cluster ions. These studies highlighted the significant potential and ongoing need for research to fully exploit triple quadrupole technology because by removing more and more interferences in the CRC, sample preparation can be drastically simplified.

The *capabilities of the triple quadrupole mass separator for water analysis* were demonstrated[140] in a river water study where three different CRC gases (He, $H_2$, $O_2$) were evaluated in the determination of 68 elements within a single ICP-MS/MS run. To validate and optimize the method, the authors used a wide range of water (C)RMs encompassing various water matrices and concentrations, alongside spike experiments. The BEC and the sensitivity were assessed for all investigated elements alongside monitoring for known isobaric interferences. With the optimized method, 68 out of 71 tested elements were accurately determined (excluding Au, I and Zr). The resultant best-practice method was further tested on samples from 12 different German rivers, confirming its suitability as a monitoring tool.

An automated[141] *preconcentration method for determining Pu by ICP-MS/MS* in the presence of uranium was developed. This method enabled the detection of Pu in seawater samples of up to 1 L. The procedure used the TK200 resin to isolate Pu from the acidified sample. The sample was treated with $NH_2OH{\cdot}HCl$ and $NaNO_2$, to adjust the valence of Pu, and loaded onto the column at a flow rate of up to 15 mL min$^{-1}$. The Pu was then eluted in 2 mL 0.5 mol L$^{-1}$ HCl and 0.1 mol L$^{-1}$ HF mixture, achieving and maintaining a recovery rate of 65%. While most of the uranium interference was removed during the isolation process, any remaining signal was effectively eliminated by use of $O_2$ in mass shift mode. A LOD of 2.32 µBq L$^{-1}$ was achieved and the method was validated using the RM IAEA-443 (Irish Sea water), yielding satisfactory results for both the Pu recovery and the $^{239}$Pu/$^{240}$Pu isotope ratio. This optimized method was applied to glacier samples, with measured Pu concentrations ranging from 6 µBq L$^{-1}$ to 23 µBq L$^{-1}$.

One of the challenges of spICP-MS is accurately *determining NPs in the presence of the ionic form* of the same element. To address this, 3D-printed scavengers were developed[142] that selectively retained ionic Ag but allowed AgNPs to pass through. The scavenger, which could be inserted into a standard syringe, was a 5 mm high and 16.5 mm diameter cylinder, cast from a 1 + 9 mixture of PS and an ion-exchange material, with a production cost of approximately 0.25 € per unit. The Ag NPs remained intact during the process, while the removal rate of ionic Ag exceeded 98%. Additionally, if needed, the ionic Ag could be desorbed with over 99% efficiency with sodium thiosulfate for subsequent analysis. The method was validated with water samples spiked with both ionic Ag and 30 nm and 50 nm Ag NPs. The results demonstrated that removing the ionic fraction improved the precision when determining both the size and number of nanoparticles. This optimized method was successfully applied to analyse both Ag fractions in ultra-pure water and spring water.

A $^{110}$Cd-$^{111}$Cd double-spike method for *Cd isotopic measurement by MC-ICP-MS* in sea water samples was developed[143]. One of the most critical steps for accurate isotopic ratio determination is the removal of the matrix, as matrix elements often introduce interferences that can hinder precise measurement. Given the high ionic load of seawater, a two-column separation process was optimized. The first column, Chelex® 100 resin, separated major seawater constituents such as sodium and magnesium from the Cd, while the second AG-MP-1M resin-filled column, eliminated residual sodium and magnesium, as well as isobaric interferences from elements like zinc, indium, and tin. The recovery for Cd from the first column was 98.3% ± 3.5%, and from the second column was 97% ±

3%. The method was validated with NIST SRM 3108 (cadmium (Cd) standard solution) spiked into synthetic sea water. The optimized method yielded $\delta^{114}$Cd/$^{110}$Cd values ranging from -0.01‰ to 0.02‰, which are consistent with reference values. Analysis of three deep-water samples resulted in $\delta^{114}$Cd/$^{110}$Cd values between 0.35‰ and 1.05‰.

The typically low concentrations make *precise isotopic ratio determination by MC-ICP-MS of Sb in surface waters* challenging. To address this, a new preparation method was developed that combined preconcentration and matrix separation to enable accurate ratio measurements. The procedure included[144] a digestion step designed to remove DOM, oxidise metals to a single high-valence state, and eliminate other interfering ions. This study highlighted the effectiveness of a BrCl based digestion procedure, which achieved recovery rates for Sb above 95%. After digestion, the Sb$^{V}$ present was reduced to Sb$^{III}$. For preconcentration and purification, the digested and reduced sample was loaded onto a thiol resin column. Elements, such as Sn, were washed from the resin with 2.5 M HCl. The Sb was eluted from the column using 6 M HCl, and $H_2O_2$ was subsequently added to the eluate. The solution was then heated in a closed vessel for 4 hours before being evaporated to near dryness and being redissolved into 3 M HCl + 0.5% (w/v) KI–ascorbic acid. The method was tested and optimized using NIST SRM 3102a (standard solution antimony), achieving sufficient precision for the entire procedure. The optimized method was successfully applied to various water sample types.

**3.6.4 X-ray Fluorescence spectrometry.** There is a need for cost-effective and rapid elemental speciation methods to assess the potential (eco)toxicological relevance of elements. WD-XRF can address *elemental speciation by utilizing valence-to-core (VtC) electronic transitions*. In this study[145], the authors used the As K$\beta_{2,5}$ fluorescence line to quantify As$^{III}$ and As$^{V}$ in drinking water after preconcentration onto an alumina pellet. The As K$\alpha_{1,2}$ analytical lines were employed for total As determination. The LOD was 0.23 µg L$^{-1}$ for total As and 50 µg L$^{-1}$ for the As species. Validation was performed using spiked water samples with varying concentrations and species ratios. This study demonstrated the potential of WD-XRF for direct speciation without extensive sample preparation (pre-concentration onto activated alumina, drying of the adsorbent, and press pellet) offering a fast and precise method for As speciation that requires further work to achieve realistic LODs for real samples.

To enable *fast and sensitive detection of U in water samples*, a direct preconcentration method[146] based on TXRF quartz sample holders functionalized with 3-amidoxytriethoxysilane was developed. The functionalization process involved cleaning and oxidizing the quartz sample holder surfaces by heating to 80 °C in a $H_2SO_4/H_2O_2$ (3:1) solution for 30 min, followed by rinsing. A 1 µL drop of the 3-amidoxytriethoxysilane solution was then deposited on the sample holder and dried. The prepared sample holders were dipped into a fixed volume of the sample solution and were subsequently rinsed with water to remove U from the non-functionalized areas. The method was validated by spike recoveries, achieving recoveries of 99% - 102%, and a LOD of 1 µg $L^{-1}$. This optimized method was applied to determine U concentrations in various water types, including groundwater, river water, and seawater.

Rare earth elements are widely used, and their release into water bodies due to mining and other human activities has become a concern. Therefore, efficient methods[86] for the preconcentration, storage, and *determination of REEs in water samples* are much needed. For this purpose, a resin based on N,N-bisphosphono(methyl)glycine-modified MIL-53(Al) was developed. This resin exhibited high selectivity towards REEs, enabling their separation from water and allowing storage of the samples as SPE discs. The separation process involved adding a small portion of the prepared resin to the sample, stirring for 5 min, filtering, drying, and then storing or analysing the sample, resulting in a fast and straightforward measurement procedure. The researchers demonstrated that the REE concentrations on the discs remained stable for at least six months. The XRF method was optimized for the simultaneous determination of 15 REEs (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y and Yb) achieving LODs between 0.4 µg $L^{-1}$ and 4.7 µg $L^{-1}$. Spike recoveries for the investigated elements ranged from 80% to 125%. The method's suitability was demonstrated by preparing on-site, water samples from the Gawu and Jinsha Rivers in China, as well as drinking and tap water samples. Another study focused[147] on the determination of lanthanides using TXRF. For this purpose, a CPE method was developed and optimized. The CPE utilized a mixture of N,N,N′,N′-tetra-octyl-diglycolamide, room-temperature IL and Triton X-114, which demonstrated selectivity towards lanthanides at pH 4 and exhibited high robustness against matrix interferences. The procedure was validated and optimized by spiking three RMs: NRCC

NASS-7 (sea water) and SLRS-6 (river water), and NIST SRM 1640a (natural water). For the investigated elements (Dy, Eu, Gd, Ho, La, Lu, Nd, Sm, Tb, Tm) recoveries of 98% - 99% were achieved across the different matrices.

# 4 Analysis of soils, plants and related materials

## 4.1 Review papers

Several reviews focussed on *the determination of certain elements*. Liu *et al.*[148] (140 references) summarised methods for measuring Pu isotopes in a variety of environmental samples, whilst Dowell *et al.*[149] (112 references) focussed specifically on Pu in soil. Thallium was the element of interest for Shi *et al.*[150] (205 references) whilst Sager and Wiche[151] (340 references) provided a comprehensive overview of the measurement and geochemistry of REE. De Almeida *et al.*[152] (69 references) discussed analytical approaches for the determination of Sr isotopes and proposed a standard protocol for application of $^{87}$Sr/$^{86}$Sr ratios in wine provenance studies.

*The analysis of traditional Chinese medicines* has proved a popular topic. Guo *et al.*[153] (110 references) reviewed the sources, effects, measurement, and risks of PTEs in medicines of marine origin, including marine plants. They recommended that improved quality systems be developed to ensure product safety. Two further reviews discussed research progress in the speciation analysis of As[154] (79 references) in animal- and plant-derived medicines, and of Hg[155] (73 references) in medicinal herbs.

Also of potential interest to ASU readers is a review[156] (133 references) on *research progress in nano-scale SIMS in soil science*. This technique can be used to study the behaviour and distribution of trace elements and is particularly suited to investigation of the interactions between PTE and soil components.

## 4.2 Reference materials

An evaluation[72] of *the $^{237}$Np activity concentrations reported in literature for a suite of 25 SRMs and CRMs* – including sediment, soil, seawater, airborne particulates, and plants – concluded that data obtained by ICP-MS were more accurate than those from radiometric techniques or AMS. A lack of soil CRMs containing low levels of $^{237}$Np was noted, so this nuclide was measured for the first time in CRM JSAC 0471, a soil from the area affected by the 2011 Fukushima Daiichi Nuclear Power Plant accident. The indicative value obtained was $5.8 \pm 0.5 \times 10^{-5}$ Bq kg$^{-1}$.

Improvements to analyte separation procedures prior to analysis by MC-ICP-MS have facilitated the measurement of *new isotopic data for a variety of RMs*. These included:

- a single-column separation[157] for Cd that allowed determination of $\delta^{114/110}\mathrm{Cd}_{\mathrm{NIST\ SRM\ 3018}}$ in IGGE GSS-1a (soil) and GSD-4a (stream sediment);
- a single column separation[158] for Zn that provided $\delta^{66}$Zn and $\delta^{68}$Zn values in GSS-11 and GSS-13 (both soils) and GSS-33 (sediment);
- a single column separation[159] for K that gave $\delta^{41}$K values for the CRMs BCR 679 (white cabbage) and IGGE GSV-2 (bush twin leaf), GSB-2a (wheat), GSB-3 (corn), and GSB-6a (spinach);
- a single column separation[160] for Cu, Fe and Zn that gave $\delta^{56}$Fe, $\delta^{65}$Cu and $\delta^{66}$Zn values in GBW10055 (whole soybean) and GBW(E)100199 (pumpkin);
- a two-stage (cation-exchange followed by anion-exchange) procedure[161] for V that produced $\delta^{51}$V results for three sediments, one loess, and three soils; and
- a two-stage (both anion-exchange) procedure[162] for Zn that provided the first $\delta^{66}$Zn values for 20 Chinese reference soils.

## 4.3 Sample preparation

### 4.3.1 Sample dissolution and extraction

*Reviews on digestion and extraction methods* included that of Oliveira *et al.*[27] (147 references) on pyrohydrolysis methods for the determination of halogens. Experimental parameters reviewed included sample mass, organic matter content, absorbing solutions, additives to improve method accuracy, and LODs. System automation and compatibility with techniques including IC, AES, ICP-MS, and XRD were also discussed. Sequential extraction methods for the determination of metal(loids) in plants were compared by Jahangir *et al.*[163] (188 references). Difficulties in the extraction of Gd and Cr phosphates and oxalates in the appropriate stages by designated extractants such as 2% acetic acid or 0.06 M HCl were highlighted. A review[148] (140 references) of methods for the determination of Pu covered pretreatment procedures, such as ashing, acid digestion and fusion, separation and purification methods, including LLE and SPE, as well as LODs of MS detection techniques such as TIMS, AMS, ICP-MS and SIMS in environmental matrices. Uses and environmental levels of Pu were also reviewed, and the establishment of a Pu database for environmental monitoring of the radionuclide proposed.

A 'new generation' *microwave applicator for high pressure flow digestion* was developed by Hallwirth *et al.*[164]. The digestor was composed of a microwave-heated applicator which housed a 2 mm internal diameter, coiled, pressurised, digestion tube, the geometry of which was optimised using computer simulation to achieve uniform heating. The digestion coil and all fittings were made of PFA, thus allowing the use of all acids including HF. The volume capacity of 22 mL and digestion temperature of 230 ℃, were reported to be an improvement on those of similar systems that operated at ambient pressure. The accuracy of the method was evaluated by the analysis of NIST SRM 1547 (peach leaves), IAEA-A-13 (freeze dried animal blood), and BCR CRM 185R (bovine liver). Digestion was performed with a 5 mL mixture of 6 M $HNO_3$ and 3 M HCl, 500 W microwave power, 40 bar pressure and a carrier flow rate of 5 mL $min^{-1}$. Relative measurement errors in analyte concentrations, determined by ICP-AES and ICP-MS, were within ± 10% for Al, As, B, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Rb, Sr, and Zn, but for Cd in BCR-185R and Fe in SRM 1547 ranged from -14% to +21% (t-distribution, $p < 0.05$). Residual carbon concentrations in these digests were <50 mg $L^{-1}$. Direct coupling of the system with ICP-MS was also being explored.

In *methods for extraction of PTE from soils*, the optimisation of DESs continues to be explored. The extraction efficiency of choline chloride with oxalic acid (1 + 2 mol/mol) was found to be superior[165] to combinations of choline chloride with ethylene glycol, 1,2-propanediol, xylitol, malic acid, or citric acid. Under optimised conditions (0.1 g sample, 1 g solvent, 40 min UAE, T = 80 ℃), no significant difference was observed between concentrations of target analytes Al, Be, Ca, Co, Cr, Cu, Mn, P, Pb, V and Zn in 24 soil RMs, following extraction with the DES, and certified values, as determined by ICP-AES, or between concentrations determined in real soil samples following digestion with HCl-$HNO_3$-HF-$HClO_4$ and following extraction with the less toxic DESs (student t-test, 95% CI). A mandelic acid dimer was proposed[166] for the extraction of Cd and Cu. The optimised procedure involved preparation of the dimer by heating 100 mg of the solid at 120 °C for 30 min in an ‘antifreezing/ anti-boiling bath’, followed by the addition of 0.2 g of soil and 10 mg of sodium diethyldithiocarbamate complexing agent. After microwave irradiation (3 min, 150 W), the mixture was vortexed (750 μL, 5% v/v $HNO_3$), centrifuged (6 min, 7000 rpm) and analysed (FAAS). The LODs were 0.16 and 0.17 mg $kg^{-1}$ for Cd and Cu, respectively. Spike recoveries were 88-93% for Cu and 93-97% for Cd (10 and 25 mg $kg^{-1}$ additions). The relative measurement error for Cu in BCR CRM-142R (light sandy soil) was < 5%. For Cd, the method LOQ of 0.5 mg $kg^{-1}$ was above both the certified content in the CRM and median soil background levels (EA 2007) for Cd, preventing verification of accuracy and limiting the application of this method to contaminated soils. Extraction of bioavailable As with 0.5 M $NaHCO_3$ is a common procedure, however, the high concentration of dissolved solids prevents analysis of the extractant with ICP-MS. In a quest for ICP-MS compatible extractants, Mishra *et al.*[167] compared 0.5 M $NaHCO_3$ to 0.1 N and 0.5 N $H_3PO_4$, 0.05 M and 0.25 M $H_2SO_4$, 0.1, 0.5, 1.0 and 1.5 M $HNO_3$, and 0.01 M $CaCl_2$ for the estimation of bioavailable As in 201 paddy field soils in West Bengal, India. Highest correlation was observed between 0.5 N $NaHCO_3$-extractable As and 1.5 N $HNO_3$-extractable As ($r = 0.47$ and $r = 0.64$ in case of grain and straw, respectively, significant at the 0.01 level), making this last extractant a potential alternative that is more compatible with ICP-MS.

In *microwave-assisted extraction methods for PTE in plants*, 216 modifications were studied[168] in the optimisation of a tunnel-type microwave digestion method for simultaneous determination of 18 elements by ICP-AES. Optimum conditions were found to be a sample size of 0.5 g, sequential addition of 4 mL $HNO_3$, 1.5 mL $H_2O_2$, 1 mL HCl, and 0.05 mL HF, and a three-stage vessel heating procedure with an initial rate of 2.76 K $min^{-1}$, maximum T of 180 °C and hold time of 15 min. Relative measurement errors in concentrations of Al, B, Ba, Ca, Cu, Fe, K, Na, Mg, Mn, Ni, P, Rb, Si, Sr, Ti, V, and Zn in Russian CRMs GSO 8921-2007/SO KOOMET 0065-2009-RU EC-1 (*Elodea canadensis*), GSO 8922-2007/SO KOOMET 0066-2008-RU (Gr-1) (grass mixtures), GSO 8923-2007/SO KOOMET 0067-2008-RU BL-1 (birch leaf), and GSO 11961-2022. PSN-1 (*Pinus sibirica* needles) were within ±10%, indicating wide-ranging suitability of the method with regard to species and elements.

Methods involving *digestion with heating blocks*, included a technical note[169] on a closed-vessel, convective heated aluminium block digestion system for the preparation of plant samples. The block was housed inside an insulated heating chamber thus ensuring that surfaces did not reach high temperatures for operator safety. Digestion vessels were composed of 45 mL quartz tubes and PTFE vessel lids with built-in safety disks designed for 28 bar maximum pressure, attached via a PVC connector. Experimental parameters in the 24-slot heater were optimised at 250 mg sample mass, 2.0 mL $HNO_3$, 1.5 mL of $H_2O_2$ and a block temperature of 240 °C, corresponding to a liquid phase temperature of 190 °C. Sample digestion required about 50 min including cooling step. No significant differences (unpaired t-test, 95% CI) were found between the certified values and concentrations of macronutrients Ca, K, Mg, P, and S and micronutrients B, Cu, Fe, Mn and Zn in plant standard reference materials NIST RMs 1547 (peach leaves), 1515 (apple leaves), and 1570a (spinach leaves) as determined by ICP-AES, indicating the closed-vessel digestion block method can provide a fast, safer, alternative to open-vessel acid digestion. Periera *et al.*[170] optimized a heating block digestion method by applying fractional factorial design. Vessels and lids were composed of PTFE, optimum parameters were found to be a digestion mixture composed of 1.38 mL $HNO_3$, 1 mL $H_2O_2$ and 2.62 mL deionized water, a heating temperature of 180 ºC and digestion time of 120 min. In the quantification of 14 PTE in medicinal herbs by ICP-AES, LODs ranged from 0.06 (Cd) to 1.9 (P) mg $kg^{-1}$. Accuracy was validated with CENA-USP CRM Agro C1003a (tomato leaves), CRM-Agro C1005a (sugar cane leaves) and CNACIS NCS DC 73351 (tea) with relative measurement errors of -17% to +18%.

In the *determinations of trace levels of Si in plants by ICP-MS*, Arslan *et al.*[171] found that hexafluorosilicates, formed in HF-based digestions, were highly volatile, resulting in losses when digestates were heated to eliminate HF and other acids. To overcome this, the authors developed a closed-vessel block digestion for plant samples based on two steps: an initial digestion of 0.1 g of sample with 4 mL $HNO_3$ and 1 mL HCl for 5 h at 140 ℃ with subsequent evaporation to incipient dryness, followed by a second step with 0.5 mL $HNO_3$ and 0.5 mL HF at 130 ℃ for 2 h to dissolve silicates. After dilution to 15 mL with deionised water, digests were directly analysed using an ICP-MS instrumentation equipped with an HF-inert sample introduction system. Relative measurement errors varied, depending on both the reference material matrix (NIST SRM 1573a (tomato leaves), SRM 1575 (pine needles), CRM 1547 (peach leaves) and SRM 1572 (citrus leaves)) and the ICP-MS measurement mode (standard or kinetic energy discrimination). The authors aim to improve Si stabilization prior to acid evaporation to reduce loss of the analyte in future work.

### 4.3.2 Analyte separation and preconcentration

*Separation and preconcentration methods with solid sorbents* included a DGT method by Han *et al.*[172] for determination of labile $As^{III}$ and $As^{V}$ in soil using a $Fe_2O_3.xH_2O$ binding gel. Uptake of As species, elution conditions, and applicability to natural soils were tested and optimised. In solution, accumulation of As species (approx. 490 ng) on the binding gel was achieved in 90 min. In soils, samplers were directly inserted into soil paste (100 g) at 25 °C, with an accumulation time of 48 h. Optimum elution of the binding gel was achieved by heating with 0.8 % $H_3PO_4$ in a water bath at 90 °C for 80 min. Concentrations were measured with HPLC-ICP-MS. The LODs were 0.01 and 0.005 μg $L^{-1}$ for $As^{III}$ and $As^{V}$, respectively. Moens *et al.*[173] developed a hydrogel-free DGT binding layer for the mapping of labile P in soils. Unlike conventional hydrogel-based binding layers, the polyimide-based layer contained a finely powdered titanium dioxide P binding agent for superficial binding of P, enabling its detection by synchrotron-based XFM. The novel method was applied to study the diffusion of P from three different fertilizers in soil-fertilizer incubation experiments. Results of selected XFM analyses were confirmed by LA-ICP-MS. Data harvested regarding fertiliser P diffusion radii and concentrations can potentially be used to improve fertilizer efficiency. Determination of Be in plants by ICP-MS is challenging since, in addition to the complex organic matrices, concentrations are lower relative to other essential plant nutrients. To remove matrix effects and achieve preconcentration, a single step separation-purification method was developed[174] based on cation-exchange with a AG R  50W-X12 resin (BioRadTM, USA). Between 100 and 500 mg of plant sample were digested using a multi-step digestion procedure with $HNO_3$, $H_2O_2$, HF.  The digests were then loaded onto cartridges made from Pasteur pipettes, equipped with frits, which were packed with the resin. Elution of Be was achieved with 5.5 mL of 0.3 M HF, the first 1.5 mL of which were added incrementally in 0.5 mL aliquots. The eluate was evaporated to dryness and re-dissolved in 0.3 M $HNO_3$ (4 mL) for ICP-MS analysis with Li (5 ng/g) as an IS. Seven RMs were analysed with, and without, the purification process: WEPAL IPE 100 (grass), WEPAL IPE 151 (grass), WEPAL IPE 176 (reed), and WEPAL IPE 220 (willow wood), NIST SRM 1515 (apple leaves) (not certified for Be) and SRM 1573a (tomato leaves), and ERM-CD 281 (rye grass) (not certified for Be). Concentrations of Be determined following purification were consistently significantly lower than certified values indicating further research is necessary.

In the *determination of radionuclides*, a novel method was developed[175] for the simultaneous determination of Pu and Np in soil samples using a TK200 resin. Optimised loading was obtained with 6-12 M $HNO_3$ with addition of 0.01-0.12 M $NaNO_2$ for valence adjustment. Elution was achieved with a solution of 0.1 M HCl, 0.05 M HF, and 0.01 M $NH_2OH.HCl$ (40 mL). The method was validated by analysing environmental soil samples (5 g) spiked with 0.2 g of IAEA-384 (Fangataufa Lagoon sediment) or 1 g of IAEA-385 (Irish Sea sediment). Measured values of $^{237}$Np, $^{239}$Pu, and $^{240}$Pu, obtained by ICP-MS/MS, were consistent with their certified values within a 95% CI, and method precision was <6%. Results were superior to those obtained with TEVA and AGMP-1M resins. Method LODs (10 g samples) were 0.13 fg $g^{-1}$ for $^{239}$Pu, 0.07 fg $g^{-1}$ for $^{240}$ Pu, and 0.27 fg $g^{-1}$ for $^{237}$Np, adequate for monitoring of the radionuclides in soil and sediment samples.

Other separation and preconcentration methods for the analysis of soils, plants or related materials, or those developed for other sample matrices that used soil or plant CRMs for validation, are summarised in Tables 5 (LPE methods) and 6 (SPE methods).

**Table 5:** Preconcentration methods involving liquid-phase (micro)extraction used in the analysis of soils, plants and related materials

| Analyte(s) | Matrix | Technique | Extraction mode/ reagent(s) | Comments/ findings | LOD | Validation | Reference |
|---|---|---|---|---|---|---|---|
| Cd, Pb | Sediment, soils (agricultural, tea–planted, basalt, forestry), livestock feed, sea salt | LLE FAAS | sodium diethyldithiocarbamate and ammonium pyrrolidine dithiocarbamate chelating solution, 8-hydroxyquinoline masking agent to chloroform (5 mL) | 0.5-3 g sample for sediment, soil and livestock feed, 35-40 g sample for sea salt, re-extraction in $HNO_3$ (5-10 mL, 2 M) | Soil 6.9 (Cd), 72 (Pb) µg kg$^{-1}$, live feed 8.5 (Cd), 82 (Pb) µg kg$^{-1}$, sea salt 7.5 (Cd), 76 (Pb) µg kg$^{-1}$ | Spike recovery (0.15 µg g$^{-1}$ Cd, 5 µg g$^{-1}$ Pb in soil, and 0.1 µg g$^{-1}$ Cd, 1 µg g$^{-1}$ Pb in salt) | 176 |
| $Cr^{VI}$ | Spinach | LLME FAAS | DES DL-menthol and formic acid | 0.25 g sample, 80 µL DES | 0.63 µg L$^{-1}$ | Spike recovery (25, 50 and 100 µg kg$^{-1}$) | 177 |
| Cu | Rose bud samples | Emulsification LLME FAAS | DES choline chloride + phenol (1 + 2), THF emulsification agent | 2.2 g sample, 0.4 mL DES | 2.5 µg kg$^{-1}$ | Spike recovery (50, 76, 99 and 172 µg kg$^{-1}$ in rose tea brand 1, and 27, 50, 101 and 118 µg kg$^{-1}$ in rose tea brand 2) | 178 |
| Cu, Pb, Sn | Corn, soil | CPE ICP-AES | 2-(4-sulphonylamidebenzo)hydrazide-1-dithiocarbamate ligand, polyethylene glycol tert-octylphenyl ether (Triton X-114) surfactant | 1 g for corn, 0.25 g for soil, 0.01 M dithiocarbamate (1 mL) and 5% (v/v) Triton X-114 (0.1 mL) for CPE | 0.00021 (Cu), 0.0024 (Pb), 0.0004 (Sn) µg L$^{-1}$ | Chinese CRM GBW10011 (wheat flour) and GBW10012 (corn flour), spike recovery (0.5 mg kg$^{-1}$ of Cu, Pb and Sn in 3 corn and 3 soil samples) | 179 |
| Pb | Canned vegetables | electromembrane assisted | 1-octanol on supported liquid membrane hollow | 0.5 g sample, hollow fibre and electric system applied in 30 mL | 0.011 µg L$^{-1}$ | NRCC CRM SLRS-6 (river water) and | 180 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | (corn, cucumber, green lettuce, mustard), chili pepper, garlic, onion, tomato paste, water (drinking, tap) | hollow-fibre LPME ETAAS | fibre with DES choline chloride + phenol (1 + 2) | sample volume, 30 V applied for 25 min throughout extraction | | NIST SRM 1515 (apple leaves), spike recovery (0.3 and 0.5 µg $L^{-1}$ in all sample matrices) | |
| Se | Black tea leaves | Air-assisted CPE HG AAS | 1-(2-hydroxy-5-ptolylazo-phenyl)-ethan-one ligand, Triton X-100 surfactant | Air agitation performed at room temperature, 0.2 g sample, 1 mL ligand, 0.5 mL surfactant. Cloud point layer dissolved in 1 mL ethanol prior to analysis | 0.02 µg $L^{-1}$ | Chinese CRM GBW08513 (tea leaves), spike recovery | [181] |

**Table 6:** Preconcentration methods involving solid-phase (micro)extraction used in the analysis of soils, plants and related materials

| Analyte(s) | Matrix | Technique | Extraction mode/ reagent(s) | Comments/ findings | LOD | Validation | Reference |
|---|---|---|---|---|---|---|---|
| As | Rice | Magnetic SPE ICP-AES | $Fe_3O_4$@DTPMP | 0.5 g sample in 50 mL, 20 mg sorbent, 10 % $HNO_3$ for elution (2 mL) | 1.08 µg $kg^{-1}$ | NIST SRM 1568b (rice flour) | 182 |
| Cd | Chocolate, spice, tea, tobacco, wastewater, water (dam, river, sea, spring, tap) | Magnetic dispersive µSPE HR-CS-FAAS | $Fe_3O_4$-$SiO_2$-MIL-53 magnetic MOF nanomaterial | 0.25 g sample in 20 mL, 20 mg sorbent, 1.0 M $HNO_3$ for elution (4 mL) | 1.3 µg $L^{-1}$ | NIST SRM 1573a (tomato leaves), NIST SRM 1570a (spinach leaves), ECCC RM TMDA - 64.3 (fortified water) | 183 |
| Cd, Cu | Cocoa powder, juice (apple, cherry), plants (carrot, garlic, leek, lettuce, parsley, radish, rice, scallion, spinach, potato, pepper, tomato, walnut), water (drinking, mineral, tap) | Vortex-assisted dispersive SPME FAAS | Magnetic polystyrene-b-poly dimethyl siloxane block copolymer sorbent | 1-2 g sample in 50 mL, 250 mg sorbent, 0.5 M HCl for elution (1 mL) | 1.7 (Cd), 0.8 (Cu) µg $L^{-1}$ | NIST SRM 1570a (spinach leaves) and IRMM CRM BCR M032 (phosphate rock), spike recovery (20 and 40 µg $L^{-1}$) | 83 |
| Cu | Plants (lettuce, mint, rice), soil, water (bottled mineral and tap) | dispersive magnetic SPME FAAS | $Fe_3O_4$ MNPs modified with an $SiO_2$ shell and creatine to obtain inorganic-organic nanosorbent ($Fe_3O_4$@$SiO_2$-CRT) | 1 g for lettuce, mint and rice in 10 mL, 0.2 g for soil in 100 mL, 20 mg sorbent, 0.5 M | 1.5 µg $L^{-1}$ | Spike recovery (5, 20 and 100 µg $L^{-1}$ for aqueous samples; 5, 20 and 100 µg $kg^{-1}$ for solid samples) | 90 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | $HNO_3$ for elution (0.5 mL) | | | |
| Cu, Ni | Soil, water (natural) | µSPE FAAS | ZnMnAl layer double hydroxide NP sorbent | 1 g soil in 30 mL, 5 mg sorbent, 0.1 M $HNO_3$ for elution (2 mL) | 0.75 (Cu), 0.57 (Ni) µg kg$^{-1}$ | IRMM CRM BCR 505 (estuarine water) and Chinese CRM GBW GSS-15 07429 (soil) | 184 |
| Cu, Pb | Plants (celery, lettuce radish, spinach), wastewater, water (lake, sea) | magnetic dispersive SPME FAAS | Magnetic mesoporous carbon ($Fe_3O_4$@C) sorbent | 0.5 g for solid samples in 20 mL, 100 mg sorbent, 2 M HCl for elution (3 mL) | 0.87 (Cu), 2.8 (Pb) µg L$^{-1}$ | ECCC RM TMDA-53.3 (fortified lake water) and NIST SRM 1573a (tomato leaves), spike recovery (100 and 200 µg L$^{-1}$ for lake water and wastewater, 75 and 150 µg L$^{-1}$ for sea water and waste water, 3 and 6 µg g-1 for celery, radish and spinach, 6 and 12 µg g$^{-1}$ for lettuce) | 185 |
| Hg | Soil | Mini lithium-battery-powered Headspace SPME, miniature point discharge AES | gold-coated tungsten (Au@W) SPME fiber | 0.5 g in 50 mL, 20 s desorption time, 2.5 W power consumption | 0.008 mg kg$^{1}$ | Chinese CRM GBW07980 | 186 |
| Mn, Pb | Plants (cinnamon, tea), wastewater, water (dam, sea) | dispersive SPME FAAS | $NiCo_2O_4$@$ZnCo_2O_4$ ternary nanocomposite sorbent | 0.5 g in 50 mL for Mn, 0.5 g in 100 mL for Pb, 50 mg sorbent, 2 M HCl for elution (3 mL) | 1.7 (Mn), 4.0 (Pb) µg L$^{-1}$ | IRMM CRM BCR 482 (lichen), ECCC RM TMDA-70.2 (lake water), and NIST SRM 8704 (Buffalo River sediment), spike recovery (75 and 150 µg L$^{-1}$ for waters, 120 and 240 µg g$^{-1}$ for tea, | 187 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | | | 300 and 600 μg g$^{-1}$ for cinnamon) | |
| Ni | Sediments, water | SPE FAAS | mini-column of bamboo fibres modified with 2-(5-Bromo-2-pyridylazo)-5-(diethylamino) phenol sorbent | 1 g sediment, sample vol. 100 mL, 0.4 g sorbent, 1 M HCl for elution (2 mL) | 0.75 μg L$^{-1}$ | NIST SRM 1944 (New York/New Jersey Waterway Sediment), spike recovery (20 and 50 μg L$^{-1}$) | [188] |
| Pb | Baby food, cocoa powder, plants (coriander, carrot, dill, starch, tea, tobacco), water, wastewater | Magnetic SPE FAAS | magnetic *Luffa*@$TiO_2$ sorbent | 0.25 and 1 g for solid samples in 50 mL dep on matrix, 5 mg sorbent, sample volume, 3 M $HNO_3$ for elution (1 mL) | 0.04 μg L$^{-1}$ for liquid samples, 0.159 μg kg$^{-1}$ for solid samples | NIST SRM 1577b (bovine liver), ECCC RM TMDA-53.3 and TMDA-64.3 (fortified water), spike recovery (0.1 and 0.2 mg L$^{-1}$ for water and 0.1 and 0.2 μg kg$^{-1}$ for starch and tea) | [189] |
| Pb | Automobile battery water, water (river, sea), cigarettes and soil | Vortex-assisted SPE HR-CS-FAAS | Magnetic adsorbent with poly(N-isopropylacrylamide) | 15 mg sorbent, 20 mL samples, mass of solid samples not reported, 3.0 M $HNO_3$ for elution (1.0 mL) | 0.05 μg L$^{-1}$ | ECCC RM TMDA 64.3 (fortified water) and Polish certified RM e INCT-OBTL-5 (oriental basma tobacco leaves), spike recovery (between 2 and 9 μg g$^{-1}$ depending in matrix) | [190] |
| Pb | Chicken, plants (rice, tea powder tomato) | CPE, μSPE ET-AAS | Montmorillonite sorbent, 4-(2-pyridylazo) resorcinol monosodium salt (PAR) as chelating agent and triton X-114 surfactant | 0.2 g in 50 mL, 2 mg sorbent, 0.5 M $HNO_3$ for elution (1 mL) | 0.006 μg L$^{-1}$ | NIST SRM 1643 f (trace element in water) and SRM 3255 (green tea extract), spike recovery (0.2 and 0.3 μg g$^{-1}$for chicken, rice and tomato, 3 and 6 μg g$^{-1}$ for tea) | [191] |

## 4.4 Instrumental analysis

### 4.4.1 Atomic absorption spectrometry

There has been considerable interest in the development of *new analytical methods based on HR-CS-AAS.* A procedure for the determination[192] of Tl in plant leaves involved MAD in $HNO_3$, CPE, and the use of 100 µg Zr + 10 µg Ir as permanent chemical modifier. The LOD was 0.05 ng $mL^{-1}$ and the LOQ 0.17 ng $mL^{-1}$. Accurate results were obtained for BCR CRM 060 (aquatic plant) and NIST SRM 1572 (citrus leaves) according to a Student’s t-test at 95% CI. A cold vapour HR-CS-QT-AAS method[193] for Hg proved applicable to a wide range of sample types – not only soil, sediment and mushrooms but also fish and (bio)polymers – with an LOD of 0.014 ± 0.001 mg $kg^{-1}$ for environmental samples. The same group of researchers also developed[194] a HG-HR-CS-QT-AAS method for total and inorganic As, a key advantage of which was avoidance of an LLE step in the sample treatment protocol for measurement of the inorganic As fraction. The LOD was 0.006 mg $kg^{-1}$ for both species; the results obtained for total As in soil and sediment CRMs were accurate; and spike recovery for inorganic As was 95 ± 10%.

Aramendia *et al.*[195] optimised *a new HR-CS method for the direct determination of B in solid samples* based on molecular, as opposed to atomic absorption. The analyte was quantified by detection of the BF molecule created by a gas-phase reaction with methyl fluoride. Both a W permanent modifier (250 µL, 1000 mg $L^{-1}$) and a mixed liquid modifier (10 µL of a 15 g $L^{-1}$ citric acid solution + 10 µL of a 1000 mg $L^{-1}$ Ca solution) were required, giving a LOD of 0.6 mg $kg^{-1}$. The result obtained for NIST SRM 1570a (spinach leaves) was 35.6 ± 9.4 mg $kg^{-1}$ *cf.* certified value 37.6 ± 1.0 mg $kg^{-1}$ and for SRM 1573a (tomato leaves) 28.5 ± 6.8 mg $kg^{-1}$ *cf.* 33.3 ± 0.7 mg $kg^{-1}$. The interesting possibility of measuring B isotope ratios based on wavelength shifts in the $^{11}BF$ and $^{10}BF$ molecular signals was also explored.

### 4.4.2 Atomic emission spectrometry

A key requirement for the successful development of portable AES instrumentation is low power consumption. Two approaches with potential for use in *the field determination of Hg in soil* were described. The first method used[186] a gold-coated tungsten fibre for SPME of $Hg^0$ – produced by $NaBH_4$ reduction of $Hg^{2+}$ in aqua regia digests of soil samples – as a Au/Hg amalgam. The fibre was then heated using a 3.7 V lithium battery to desorb the analyte vapour into a point discharge microplasma. Overall power consumption was reduced from 60 W to 2.5 W compared to conventional external heating desorption devices and the instrument was more compact. The second method incorporated[196] a novel piezoelectric transformer driven microplasma, thereby eliminating the need for a high voltage power supply, and HG for analyte separation and interference elimination. A LOD of 2.8 µg $L^{-1}$ was obtained and the result for NRCC CRM GBW07405 (soil) was identical to the certified value. Although the spectroscopic aspects of these works show great promise, the need to acid digest the samples prior to analysis remains a challenge for actual field deployment.

*A rapid HPLC-ICP-AES method for Fe speciation* analysis in soil, sediment and archaeological pottery[197] featured a short (50 mm) cation-exchange column (Dionex IonPac CG5A) in place of the standard (250 mm) length column (Dionex IonPac CS5A). Adequate separate of $Fe^{II}$ and $Fe^{III}$ was achieved in 240 s (as opposed to 480 s) and both mobile phase consumption and power use were significantly lowered,

A *method for the determination of total and labile Cd, Cu, Pb and Zn in soil based on a miniature ETV-µCCP-AES system* in accordance with the principles of green analytical chemistry was developed[198]. The accumulation of analytes by DGT eliminated previously challenging non-spectral interferences, and improved LODs by at least one order of magnitude. Relative measurement errors for the analysis of four soil CRMs ranged from -15 to + 23% and the LODs ranged from 0.03 (Zn) to 0.4 (Pb) mg $kg^{-1}$.

*Microwave induced plasmas* continued to be of interest. Stoitsov *et al.*[199] modified the sample introduction system (specifically, widened the inlet to the GLS) to improve sample mass transfer in their PVG-MP-AES method for the determination of Hg. Following optimisation, the LOD was 0.25 ppb and there was no significant difference between measured and certified values for two soil CRMs (at 95% confidence). Serrano *et al.*[200] demonstrated the capability of MICAP-AES for the analysis of complex samples by measuring 12 elements in a range of CRMs, including biological materials, polyethylene, and BCR 483 (sewage sludge amended soil). A detailed evaluation of spectral and non-spectral interferences was also performed.

**4.4.3 Inductively coupled plasma mass spectrometry** Several *review articles* have focussed specifically on ICP-MS. Naozuka *et al.*[201] (101 references) summarised the contribution of the technique to improved understanding of the behaviour and impact of NPs in edible plants; Ermolin and Fedotov[26] (69 references) discussed methods for the study of NPs in soil and dust, with particular emphasis on sp-ICP-MS; and Nguyen *et al.*[202] (136 references) proposed that ICP-MS with data analysis by PCA could be a standard approach for authentication of the geographical origin of plant-based foods. Kierulf and Beauchemin[203] (46 references) wrote a useful tutorial review on the ability of continuous on-line leaching coupled with ICP-MS to improve PTE bioaccessibility testing in food safety assessment. As well as being faster than batch extraction methods, the dynamic nature of the information obtained provides clues to the origins of any contaminants present. For example, two peaks observed in a leaching profile of a corn bran RM were found to have different Pb isotope ratios, indicating the presence of Pb from two distinct sources.

A high-efficiency miniaturised USN[204] offered *improved sample introduction efficiency in ICP-MS* by decreasing the mean aerosol particle size. The LODs for REE ranged from 0.03 (Tm and Lu) to 1.07 (Sc) ng $L^{-1}$ (similar to those for pneumatic nebulisation but with a ten-fold reduction in sample consumption), and results for soil and sediment CRMs were predominantly within 5% of certified or indicative values. A novel slurry sampling apparatus[205] reduced the problem of sample deposition during transport to the plasma in ETV-ICP-MS. It incorporated a “gas turbulator line” – a second stream of Ar gas introduced at right angles to the carrier gas via an annular aperture to create turbulence – and a signal delay device that meant an increased number of points could be recorded over the course of the transient signal. Precision for the direct determination of As, Cd, Pb and Se in plant-based foods was improved from 15-16% to 1-9%, with LODs in the range 0.3 to 0.6 ng $g^{-1}$ for 10 µL slurry samples.

The ability of transition metals to *improve sensitivity in PVG-ICP-MS* has been exploited for the determination of As in sediment[137]. Optimal generation efficiency was obtained with a 100 s UV irradiation in the presence of 10 % (*v*/v) acetic acid + 5.0 mg $L^{-1}$ $Sb^{III}$ + 20 mg $L^{-1}$ $Cd^{II}$. This gave a 50-fold increase in sensitivity relative to that of conventional pneumatic nebulisation and a LOD of 2.1 ng $L^{-1}$. Similarly, a method[206] for simultaneous determination of Se and Te involved a 30 s irradiation with 15% (*v*/v) formic acid + 15 % (*v*/v) acetic acid + 50 mg $L^{-1}$ $Co^{II}$ sensitizer. The LODs were 0.5 ng $L^{-1}$ for Se and 0.6 ng $L^{-1}$ for Te. Results for analysis of 11 geological CRMs, including two soils, were consistent with certified and literature values.

*New analytical methods coupling chromatographic separation with ICP-MS* continued to be developed. Examples included a fast HPLC-ICP-MS procedure[207] for the quantification of inorganic As in seaweed that used $HNO_3$ sample extraction to remove potential interference from arsenosugars, and an IC-ICP-MS method[208] that was used to study the distribution of $Ge^{IV}$, monomethylGe and dimethylGe in soil from the vicinity of an e-waste processing plant. An important contribution to analytical capabilities for study of trace element speciation in soil solution was an HPLC-ICP-MS method[209] that could separate metal-organic species in DOM. A key feature was the use of a second HPLC pump to deliver a post-column compensation gradient that inversely mirrored the separation gradient, meaning the mobile phase was of constant composition on entering the ICP. Application to samples from saturated and unsaturated soil horizons revealed differences in Cu, Fe and Ni speciation in different redox environments.

A multi-facetted ICP-MS approach[210] for *Se speciation analysis in soil* involved simultaneous extraction of Se NPs, inorganic $Se^{IV}$, $Se^{VI}$, and organic selenides by use of 5 mM $Na_4P_2O_7$ + 1.2 µM $KH_2PO_4$ followed by filtration through a 0.45 µm pore size nylon membrane filter. The NPs were retained on the filter then digested in $HNO_3$ for determination of their Se content, whilst species in the filtrate were separated and quantified by HPLC-ICP-MS. Total Se was determined following MAD and the concentration of non-extractable metal selenides calculated by difference.

*In vitro* fossilisation[211] was *a novel means to improve the analysis of plant tissues by LA-ICP-TOF-MS*. Replacing water with a silicate matrix by treating samples with sodium metasilicate at pH 13-14 for 24 hours not only preserved the complex 3D-structure of the biological material but also meant that the laser ablation craters had clean-cut edges (in contrast, ablation of dried leaves caused uneven removal of material outside the crater) and that Si could be used as an IS, allowing quantitative element imagining to be carried out at high spatial resolution. Mapping was performed on leaves of plants grown in unamended and Cd-spiked soil for Cd and Cu (soybean) and Cd and Zn (sunflower).

Several articles addressed *the preparation of improved matrix-matched calibration standards for LA-ICP-MS analysis of plants or fungi*. Standards based on a (8 + 2) mixture of gelatin and hydroxypropyl methyl cellulose[212] were stable, homogenous, and proved suitable for use in the quantitative mapping of Cu, Mn, Sr and Zn in leaves of *Trigonotis peduncularis*. The incorporation[213] of 5 mmol $L^{-1}$ L-cysteine improved the stability and element distribution in gelatin-based droplet standards, allowing the distribution of Hg and Se to be studied in the fruit bodies of porcini mushrooms. Incorporation of chitosan was also investigated but, despite being a better match to the composition of mushroom tissue, it gave poorer precision. Finally, a method[214] for wood analysis used standards prepared from finely ground *Pinus taeda*. Both conventional and one-point calibrations were used to quantify Ba, Cd and Pb in samples of *Tipuana tipu*.

Understanding *the uptake and distribution of NPs in plants* is important to assess their environmental fate and impact. A high throughput LA-ICP-MS method[215] developed using animal (woodlice) tissue was shown to be applicable for the mapping of Ag to a wide range of aquatic and terrestrial biota, including wheat, following exposure to $Ag_2S$ NPs or $AgNO_3$ spiked soil. By doping[216] polystyrene NPs with Eu it was possible to follow their uptake in cucumber root, stem and leaf by LA-ICP-MS. A cryogenic chamber suppressed the evaporation of water and maintained the structure of the fresh sample.

Optimisation of the reaction cell gas mixture is key to *the successful determination of analytes by ICP-MS/MS*. A detailed assessment[138] of the reactivity of NO with 50 elements revealed $MO^+$ as the dominant product, with a few elements also forming a small amount (<4%) of $MN^+$. In the first application of this gas in actinide analysis, a NO flow rate of 0.37 ml $min^{-1}$ was found to be optimal for the determination of Pu in mass-shift mode as $PuO^+$. Impressive results within 6% of target values were found when digests of NIST SRMs 4250b (river sediment), 4354 (lake sediment) and 2711a (Montana soil) were spiked with 0.05 pg/g $^{239}Pu$, even when 1 µg/g $^{238}U$ was also added, with no need for a complex matrix separation procedure prior to analysis. A method[217] for the determination of $^{237}Np$, $^{239}Pu$ and $^{240}Pu$ involved optimisation of an analyte separation based on TK200 resin and use of He (7.5 mL $min^{-1}$) + $CO_2$ (1.1. mL $min^{-1}$) to eliminate interference from $UH^+$ and peak tailing from $U^+$. The LODs were 0.14, 0.51, and 0.08 fg $mL^{-1}$ for $^{237}Np$, $^{239}Pu$, and $^{240}Pu$, respectively. A new ICP-MS/MS method was also reported[218] for the determination of Se in soil and maize.

*New sp-ICP-MS methods for the study of NPs in soils* continue to be developed and applied. Systematic investigation[219] and optimisation of MAE-based procedures for recovery of Ag-, Au-, Se- and Pt NPs from spiked soils with a range of physicochemical properties, showed that Au NPs and Pt NPs could be recovered intact with 66-95% efficiency in 6 min using 0.1 M NaOH and 800 W (except for clay-rich soil where the recovery was <10%). Although 75% of added Ag NPs were also successfully retrieved, they had decreased in size, indicating partial dissolution, whilst the Se NPs degraded almost entirely (recovery < 2%). The authors highlighted that there is a trade-off to consider between extraction efficiency and NP preservation. Other workers studied[220] naturally occurring Si NPs in soil. First, sp-SF-ICP-MS was used to optimise a NP extraction procedure (the double-focussing magnetic sector analyser was used to overcome polyatomic ion interference from isotopes of C, N and O). A solution of 40 mM $Na_4P_2O_7$ gave highest extraction efficiency, with less particle agglomeration than $Ca(NO_3)_2$, $Mg(NO_3)_2$ or $BaCl_2$. Then sp-TOF-ICP-MS was used to study the composition of the NPs. Over 46% were found to contained both Al and Si, and were therefore classified as aluminosilicates. Only Si was detected in almost 35% of cases, but this was considered an upper limit for $SiO_2$ NPs since secondary elements may have been present at concentrations too low to be detected.

In *applications of sp-ICP-MS in plant analysis*, a review[221] (83 references) on the use of the technique for the determination of inorganic NPs in food and food additives included studies on leafy vegetables, radish and edible seaweed. A 48 h multi-enzyme extraction procedure[222] was recommended to study concentrations and distribution of ZnO NPs – commonly applied to crops as a foliar spray – in the roots, leaves, stems and grains of rice. Recoveries were over 85%, and the size distribution of ZnO NPs was unaffected by the digestion procedure. The sp-ICP-MS variant single cell ICP-MS was used[223] to analyse individual pollen grains of *Arabidopsis thaliana*. The effects of soil amendment with iron and manganese were investigated.

### 4.4.4 Laser-induced breakdown spectroscopy

In *sample preparation procedures for the determination of trace elements in soil*, a ‘solid-phase conversion’ method[224] gave more stable signals and repeatable results than either direct analysis or analysis of tabletted samples by reducing the influence of particle size. The procedure involved spiking a soil sample with up to 500 mg kg$^{-1}$ of either $CrCl_3$ or $PbCl_3$ (a somewhat unexpected oxidation state for Pb). Samples then underwent a “soil-liquid-solid” conversion by shaking in distilled water (2 g in 20 mL), followed by filtration through a nitrocellulose membrane and heating of the filter paper to 50 °C to create the LIBS target. The authors claimed that improvements were due to the sample “being dissolved in water and then adsorbed onto the surface of nitrocellulose filter membrane absorbent paper”. However, since soil dissolution requires much more vigorous treatment e.g. exposure to hot mineral acid, a perhaps more likely explanation is that the Cr or Pb spike dissolved and then was re-sorbed onto particles comminuted by the shaking procedure, followed by deposition of the resulting fine soil slurry onto the filter.

Efforts have continued to *enhance LIBS signal intensity and thereby improve sensitivity and LODs*. One approach[225] recommended (in Chinese with English abstract) for the determination of Cd in soil was addition of NaCl to improve coupling between the laser and the sample and thereby increase ablation yields. With 90% NaCl doping, LODs were improved from around 30 mg kg$^{-1}$ to < 2.5 mg kg$^{-1}$. Magnetic field plasma confinement[226] (optimal field strength 0.98 T) gave signal enhancement factors ranging from 2.4-fold for Ba to 2.8-fold for Cr. When combined with a grid search and cross validation quadratic optimisation network chemometric approach, the method was able successfully to classify soils from different mining areas in China. A dual-enhancement LIBS system[227] that used both cylindrical cavity confinement and a $N_2$ atmosphere increased signal intensity more than 3-fold for the determination of Sr. The S/N increased to >700 and the LOD decreased to 34.6 mg $kg^{-1}$ *cf.* <350 and 58.1 mg $kg^{-1}$ in air without confinement. Finally, a LIBS-LIF procedure [228] for estimation of readily-soluble P increased signal intensity for the P I line at 213.6 nm up to 40-fold, relative to conventional LIBS, and improved selectivity by decreasing spectral overlap with the Fe I line at 213.85 nm. Different soil types required different calibration graphs. The LODs were 0.12 mg $kg^{-1}$ for clay soil and 0.27 mg $kg^{–1}$ for silt loam/loam.

A novel means to *reduce the influence of variations in laser energy on spectral line intensity* involved[229] addition of a second optical path to the spectrometer for collection of polarised light from the plasma. Although the signals obtained with this "micro-linear spectrum model" were less intense than those of conventional LIBS, the correlations between found and target concentrations for a series of Cr-spiked soils were improved.

Noteworthy amongst other *improvements in LIBS methods* was a study[230] that compared two laser wavelengths for the determination of C in air dried soil samples without pelletisation. Better performance (prediction error 2.7% and LOD 0.34-0.5 *w/w* %) was obtained at 532 nm than at 1064 nm. Also in the area of soil C measurement was a detailed evaluation[231] of the advantages and limitations of 13 univariate and 22 multivariate calibration strategies that provided useful guidelines for method selection. The critical influence of soil pellet compactness on the laser ablation process was demonstrated[232] for Cd and Pb using a portable LIBS instrument and a suite of 60 Chinese CRMs. More compact targets produced less (or no) dust and smaller ablation craters than less compact targets. To account for this, samples were divided into six compactness categories, a separate calibration curve was constructed for each, and then then method was applied to >300 soil samples. Whilst many of the soils had Cd concentrations below the LIBS LOD of 3 mg $kg^{-1}$, comparisons between the values that could be obtained and results from ICP-MS were promising ($r^2$ values > 0.95).

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Further examples of *LIBS methods for the analysis of soils, plants and related materials* that involved comparison with results of other analytical methods, or their use in construction of LIBS calibration models, are provided in Table 7 (soils and sediments) and 8 (plants).

**Table 7**: Methods for the LIBS analysis of soils and sediments

| Analyte(s) | Matrix | Sample preparation | Comparison or validation | Ref |
|---|---|---|---|---|
| Al, Ba, C, Ca, Co, Cr, Cu, Fe, Mg, Mn, Na, Sr, Si, Ti | Nile river sediments | Dried, ground and pressed into pellets; no binder | Qualitative analysis only | [233] |
| C | Agricultural soils | Dried, ground and pressed into pellets; no binder | Results compared with those obtained by dry combustion | [234] |
| C | Tropical and subtropical soils | Sieved (< 2 mm) and pressed into pellets; no binder | Results compared with those obtained by dry combustion | [235] |
| Ca, Cu, Fe, K, Mg, Mn, N, P, Zn | Agricultural soils | Dried, ground and pressed into pellets; no binder | Results compared with those obtained by WD-XRF | [236] |
| Cr | Yellow brown soil and lateritic red soil | Dried, ground and pressed into pellets; no binder | Results compared with those obtained by ICP-MS | [237] |
| Pb, Zn | Soils from contaminated areas | Fixed to adhesive tape | Results compared with those obtained by ICP-AES | [238] |

**Table 8:** Methods for the LIBS analysis of plants

| Analyte(s) | Matrix | Sample preparation | Comparison or validation | Ref |
|---|---|---|---|---|
| Al, Ba, C, Ca, Fe, H, K, Li, Mg, Na, Si, Sr, and Ti | *Saussurea simpsoniana* | Dried, ground and pressed into pellets; no binder | CF-LIBS results compared to those obtained by EDX | 239 |
| Al, Cu, Mg, Pb, Zn | Lily bulbs | Dried, crushed, sieved and pressed into pellets; no binder | Samples analysed by ICP-MS | 240 |
| C, Ca, Cu, Fe, K, Li, Mg, Na, Pb, Si, Sr | *Peganum harmala seeds* | Dried, ground and pressed into pellets; no binder | CF-LIBS results compared to those obtained by EDX and XRFS. techniques | 241 |
| Ca, Cu, Fe, K Mg, Mn and Na | Rice leaves | Dried, ground and pressed into pellets; no binder | Samples analysed by ICP-AES or ICP-MS | 242 |
| Ca, K, Mg | Soy leaf | Dried, ground and pressed into pellets; no binder | Samples analysed by ICP-AES | 243 |
| Extractable Ca, K, Mg, Na | *Yerba mate* | Dried, ground, sieved and pressed into pellets; polv(vinyl alcohol) binder | Samples analysed by LIBS before and after extraction with ultrapure water at 80 °C for 30 min. Results obtained by difference and compared with analysis of extracts by AAS | 244 |

**4.4.5 X-ray fluorescence spectrometry** In a *review of advances in synchrotron-based applications*, methods for the *ex situ* and *in situ* study of the biogeochemical movement of elements, were outlined by Smieska *et al.*[245] (122 references). The need for a micro-focusing synchrotron beam-line covering 2D and 3D μXRF, as well as time- and spatially resolved μXAS and μXRD, was emphasized, as were the benefits of facilities with additional imaging techniques such as IR and Raman spectrometries, and MS. Methods for the characterization of soils, minerals and organic material with XRF, XPS, XAS and XRD, and the benefits of mega-science facilities, were reviewed by Kirichkov *et al.*[246] (116 references).

*Advances in XRF instrumentation* included a prototype spectrometer for underwater Hg determinations[247]. The waterproof PVC casing housed a CdTe detector and $^{57}$Co excitation source at $90^0$, since this arrangement was found to lower background noise compared to other geometries. Copper pieces inside the casing enabled submersion and lowering of the prototype to the ocean floor. Despite the relatively high LOD of 2,880 ppm and the relatively short half-life for the $^{57}$Co K shell excitation source of 272 days, the spectrometer has potential as an *in situ* screening tool for Hg in contaminated sites.

A novel XRF setup was designed[248] *to overcome the limitations of small analysis chambers and plant sizes* associated with *in vivo* plant analysis. The in-house ‘spectrometer for *in vivo* plant analysis’, or SIPA, consisted of a 4 W Ag X-ray tube and a silicon drift detector, mounted at 45° and 135°, respectively, from the sample surface. The confocal point was determined by a two-laser convergence system. The SIPA experimental chamber was appropriate for tomato and coffee plants with heights of about 15 and 30 cm, and could be operated remotely with its door open, allowing parts of the plant not being analysed to remain outside the equipment. Using tomato plants as a model species and Rb and Sr as physiological tracers for potassium and calcium respectively, transport of the foliar-applied minerals throughout the plant tissues was successfully monitored, making the SIPA a useful tool for the long-term *in vivo* study of mineral absorption and transport.

## 5 Analysis of geological materials

### 5.1 Reference materials and data quality

The ongoing development of *new RMs for accurate microanalysis and dating, as well as further characterization of existing materials*, in terms of their trace element and isotopic composition, was reviewed[249] (22 references). The trends recognized were: obtaining more information on existing RMs, and the development of new materials for isotopic measurements and for *in-situ* and microanalysis applications using techniques such as SIMS or LA-ICP-MS. Within the field of U-Pb dating, to make full use of the spatial capabilities of LA-ICP-MS, homogeneous RMs are required for external calibration so 10 columbite-tantalite minerals were evaluated[250] as potential RMs but only four of them were determined to be suitable.

Instrumental advances can influence the suitability of a selected RM for an application. An in-house non-matrix-matched primary standard, Rutile TB-1, was initially proposed[251] as a non-matrix-matched standard for *in situ U-Pb dating* of ilmenite by LA-ICP-SF-MS but was found to be unsuitable as a primary standard, so use of RM Zircon 91500, which possesses a similar U-Pb fractionation and average normalized Pb-U ratio to ilmenite BC269, improved the accuracy of the determinations. There are currently a limited number of matrix-matched secondary RMs for U-Pb dating of geological samples and advances in the development of such materials are summarised in Table 9.

Whilst the advent of new analytical instrument variants has facilitated *the isotopic analysis of sulfur*, there is a requirement for new RMs and a natural stibnite, BJ-Snt, was proposed[252] as a potential candidate. Homogeneity of the material was verified by BSE mapping, and determination of the mineral phases and elemental compositions undertaken. Further verifications were conducted by comparing isotope values obtained by LA-MC-ICP-MS with those obtained using IRMS, as well as undertaking an intercomparison with two external laboratories.

A novel synthetic laser ruby crystal RM (HD-LR1) was proposed for the matrix-matched SIMS analysis[253] of *oxygen isotopes* in corundum. Homogeneity testing of the material at the mg scale was undertaken using laser fluorination isotope ratio mass spectrometry (LF-IRMS) whereas homogeneous O-isotopic values at the ng-scale were determined using SIMS. The authors reported that the topography of the sample surface had to be considered to avoid $\delta^{18}$O bias at grain boundary edges. The proposed material was a chemically pure crystal with trace Cr concentrations at 276 µg $g^{-1}$ with Be concentrations <0.002 µg $g^{-1}$ so for this reason it use as a blank material for SIMS or LA-ICP-MS analysis of corundum was also proposed .

Suitable *sample preparatory steps* in the development of matrix matched RMs need to be considered. A sintering process used[254] in the production of dolomite RMs for C and Mg isotopic microanalysis by LA-MC-ICP-MS demonstrated negligible isotope fractionation with respect to natural dolomites. Development[255] of a matrix-matched RM with S isotope ratios similar to those of natural barites was possible using a fast hot-pressing sintering method. The resultant $\delta^{34}$S data for the material obtained by IRMS, solution nebulization MC-ICP-MS and LA-ICP-MS assays performed in six independent laboratories were comparable. A new method for preparing[256] a magnetite RM based on sintering at 500 ºC at 1.2 GPa yielded a material with an Fe content and isotopic distribution that were homogeneous

A *process for certifying geological RMs* was clearly established in the ISO Guide 35:2017 that recognizes a role here for proficiency testing. Within the GeoPT scheme, use of this certification protocol was successfully applied[257] to the certification of nine major elements and 39 trace elements in a new candidate CRM IAG GMN-1 (Meissen Granite). Procedures based those described within ISO Guide 35:2006 and JJF 1343-2012 were used in the development and preparation[258] of new synthetic phosphate RMs for LA-ICP-MS. The candidate materials were prepared by co-precipitation of a series of analytes within a hydroxyapatite matrix for use in the multielemental analysis of apatite, monazite or other phosphates.

*Additional certification of existing RMs* is reported in Table 10. Ebihara *et al.*[259] determined the mass fraction of Br, Cl and I in 17 USGS geochemical RMs by radiochemical NAA, three RMs were also analysed by INAA and the results were within

4% of each other. Whilst the new data for Br and Cl concentrations did not differ from the those previously published values by the same authors, new data for I were 1/4 to 1/8 lower and so the authors concluded that their former determinations were biased.

Sometimes, *newly reported values for RMs disagree with previously established ones*. One example was the heterogeneity encountered in microscale $\delta^{56}$Fe analyses of aliquots of Balmat pyrite RM, a material previously thought to be homogeneous. Pasquier et al.[260] combined $\delta^{56}$Fe data obtained by solution-based MC-ICP-MS and *in situ* SIMS assays of Balmat-UNIL and Balmat-Original and found that these two populations had different $\delta^{56}$Fe values of -0.39 ± 0.18‰ and -1.46 ± 0.25‰ despite having similar petrological and chemical characteristics.

*Gallium* is a moderately volatile element, used in tracing geochemical evaporation-condensation processes but reported $\delta^{71}$Ga values in geological RMs can vary, highlighting the importance of appropriate sample preparation protocols for volatile species. A reported purification method based on the use of an anion AG1-X8 and a cation AG50W-X8 column avoided[261] isotope fractionation and enabled $\delta^{71}$Ga values for three USGS RMs to be obtained.

In an instructive guide for geologists, recommendations[262] for the standardised *reporting of ID-TIMS U-Pb geochronological data and associated metadata* were presented so as to maximize the long-term utility and comparability of published results. The inclusion of all contextual information was recommended so as to allow the correct reproduction of experiments and data manipulations to be performed by others. Additional suggestions were rigorous separation of the radioisotopic results from age interpretation (and the inclusion of clear explanations of the inherent hypothesis) and the provision of information for preferred interpretations *e.g.*, age. Measurement precision is continuously improving, so the publication of data in a standardised format was advocated to more readily identify potential biases and the adoption of AI techniques for data-mining recommended.

**Table 9**: New geological reference materials for isotope measurements

| Determinands | Matrix | Technique | RM Name | Comments | Reference |
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| Major (Al, Ca, K, Na, and Si), trace elements, (Ba, Ce, Cr, Eu, Fe, Ga, La, Mg, Mn, Nd, Ni, P, Pr, Rb, Sr, Ti, and Zn) and Sr isotopes | Plagioclase | LA-ICP-MS | MGP-1 | Natural plagioclase sample from Madagascar. MGP-1 homogeneous at the µm–mm scale for major (Al, Ca, K, Na, Si and RSD < 4%), most trace (Ba, Ce, Cr, Eu, Fe, Ga, La, Mg, Mn, Nd, Ni, P, Pr, Rb, Sr, Ti, Zn, and RSD < 15%) elements and $^{87}Sr/^{86}Sr$ ratio (2SD = 0.00013); verified by PMA, LA-ICP-MS and LA-MC-ICP-MS. Major and trace elements also analyzed through XRF and solution ICP-MS with good agreement (10%) with the in-situ performed measurements. $^{87}Sr/^{86}Sr$ mean ratio (TIMS): 0.703459 ± 0.000028 (2SD) | 263 |
| Al, Na, Si isotopes | Albite | LA-ICP-MS | Piz Beverin Albite (PB Ab) | The homogeneity of three natural K-feldspar samples was verified by EPMA (nine independent laboratories), variation in Al and Si content in the order of ± 0.5% (within the EPMA error). Absolute Al, Na and Si contents verified by XRF and agreed with those for LA-ICP-MS. Three additional K-feldspar samples (yellow sanidine crystals from | 264 |

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| | | | | Itrongay, Madagascar) confirmed homogeneity at the cm and µm scale (EPMA) | |
| B, Sr isotopes | Tourmaline megacrysts<br>(borosilicate) | LA-MC-ICP-MS | GIGT, XJ-1 and XJ-3 | RMs homogeneity in B isotopic compositions at the tens of µm scale (demonstrated with LA-MC-ICP-MS). Average $\delta^{11}$B: −12.63 ± 0.51‰ (2SD, n = 74) for GIGT, −11.90 ± 0.64‰ (2SD, n = 78) for XJ-1 and −11.91 ± 0.64‰ (2SD, n = 73) for XJ-3. Tourmaline IAEA RM B4 (Tourmaline) taken as external standard. Uncertainty 0.38‰. The values agreed with the results found in solution MC-ICP-MS. $^{87}$Sr/$^{86}$Sr (for XJ-1) = 0.70827 ± 0.00021 (2SD, n = 176) | [265] |
| C isotopes | Graphite | LA-MS-ICP-MS | LSTM, CSY | Two in-house graphite RMs from the Lutang deposit in Hunan Province and the Changshouyuan deposit in Jiangxi Province, China. Carbon isotope composition relatively homogeneous (RSD uncorrected $^{13}$C/$^{12}$C ratios: ~0.030 %). A slight matrix effect was observed between graphite and dolomite and a strong matrix effect existed between graphite and calcite. Agreement in $\delta^{13}$C values from the mutual calibration of the two graphite samples in previous and current studies using IRMS | [266] |

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| C and Mg isotopes | Dolomites | LA-MC-ICP-MS | GBW07217, DOL-8 | $\delta^{26}$Mg and $\delta^{25}$Mg: 0.11‰ and 0.09‰, respectively. The materials were homogeneous; $\delta^{13}$C, $\delta^{25}$Mg and $\delta^{25}$Mg = 0.37‰, 0.11‰ and 0.06‰ (2SD, n =15), respectively | 254 |
| Nine isotopes<br>(Co, Cr, FeO, Mg, Nb Sc, $TiO_2$, V,) | Ilmenite | LA-ICP-MS | LY | The ilmenite sample was homogeneous with respect to Cr, FeO, Mg, Sc, $TiO_2$, V, whilst Co and Nb were unevenly distributed | 267 |
| Cu, Fe, and S, isotopes | Chalcopyrite, pyrrhotite, sphalerite | IRMS (S)<br>Solution analysis MC-ICP-MS (Fe) | Ll-Cpy, Ll-Po, Ll-Sp | Bulk S isotopic compositions determined by 7 independent laboratories (IRMS).<br>Preferred $\delta^{34}S_{V\text{-}CDT}$ for Ll-Cpy, Ll-Po, Ll-Sp: 6.13 ± 0.37‰ (2SD), 6.42 ± 0.37‰ (2SD) and 6.28 ± 0.38‰ (2SD), respectively. Recommended $\delta^{56}Fe_{IRMM\text{-}014}$ for Ll-Cpy and Ll-Po (MC-ICP-MS): 0.57 ± 0.07‰ (2SD) and -0.62 ± 0.07‰ (2SD), respectively. Determined $\delta^{65}Cu_{NIST\ SRM\ 976}$ for Ll-Cpy (MC-ICP-MS): 0.57 ± 0.06‰ (2SD). Data in agreement with LA-MC-ICP-MS and homogeneity of materials was verified at the 30-40 mm scale by LA-MC-ICP-MS | 268 |

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| Fe isotopes | Olivine, Garnet, Amphibole, Biotite | SIMS | YY11-12, YS-42, YS-37, YS-20 | Proposed as matrix-matched in-house standards for SIMS Fe isotopic analysis. Homogeneous for Fe isotopic compositions. External reproducibility for YY11-12 olivine, YS-42 garnet, YS-37 amphibole and YS-20 biotite: 0.23 ‰, 0.28 ‰, 0.23 ‰ and 0.25 ‰ for $\delta^{56}$Fe values (2SD), respectively | [269] |
| Fe and S isotopes | Pyrite | fs-LA-MC-ICP-MS | IGGPy-1 | Pyrite grains were homogeneous in terms of major elements as confirmed by EPMA. fs-LA-MC-ICP-MS: variances in $\delta^{56}$Fe and $\delta^{34}$S of 0.07 ‰ (2SD, n = 105) and 0.13 ‰ (2SD, n = 105), respectively. $\delta^{34}S_{VCDT}$ (EA-IRMS): 17.09 ± 0.30‰ (2SD, n = 6); $\delta^{56}Fe_{IRMM-014}$ and $\delta^{57}Fe_{IRMM-014}$ (solution-nebulization MC-ICP-MS): −1.31 ± 0.06 ‰ (2SD, n = 21) and −1.94 ± 0.12 ‰ (2SD, n = 21). Fe, S and Co contents (wt%): 46.25 ± 0.13 (1SD), 52.03 ± 0.26 (1SD) and 1.47 ± 0.1 (1SD), respectively | [270] |
| $^{4}$He dating | Detrital Pt-Alloy Grains | Magnetic sector mass spectrometry | RS-Pt | Native platinum grains from placer deposits in the Santiago River, Ecuador, analysed by two independent centres, yielded constant $^{4}$He contents (n =17). $^{4}$He concentration: $215 \pm 4 \times 10^{11}$ at $g^{-1}$ (2SD); mean $^{190}$Pt-$^{4}$He age: 39.6 ± 0.7 Ma (2SD) | [271] |
| Hf/W dating | Zircon | NanoSIMS | Std-A Std-B | The RMs were applicable to the analysis of Mesosiderite (a meteorite). Hafnium oxide, tungsten | [272] |

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| | | | | oxide and high-purity zircon powder were subjected to high temperature (1000ºC) and pressure (6 GPa). Hf/W ratios homogeneity was tested by SEM-EDS, EPMA and LA-ICP-MS. Hf/W ratios measured by NanoSIMS. Relative sensitivity factor (RSF) of Hf and W: 0.585 ± 0.180. Absolute zircon Hf-W age: $4536.5^{+4.6}_{-7.2}$ Ma | |
| Nd-Sm isotopes | Vesuvianite | LA-MC-ICP-MS | M6635,<br>M784,<br>M1377,<br>M1450, M659 | In-house vesuvianite standards; external correction for Nd and Sr isotopes *in situ* determinations. Eleven samples were analysed from different locations. Sr and Sm-Nd isotopic compositions were consistent with those obtained by solution nebulization MC-ICP-MS. M659 recommended for *in-situ* Sm-Nd isotope analysis (low Sr content, ~20 µg $g^{-1}$; $^{147}Sm/^{144}Nd$ low variations, RSD ~ 9.5%; and $^{143}Nd/^{144}Nd$, 2SD:~0.00005). M6635, M784, M1377, and M1450 recommended for *in situ* Sr isotope analysis, with high Sr (>1000 µg $g^{-1}$) and low Rb (<0.5 µg $g^{-1}$) contents and relatively homogeneous $^{87}Sr/^{86}Sr$ ratios (2SD < 0.0001) | [273] |
| O isotopes | Corundum | SIMS | HD-LR1 | Synthetic laser ruby crystal as a new matrix-matched RM for SIMS. LF-IRMS averaging $\delta^{18}O_{V\text{-}SMOW}$ = +18.40 ± 0.14 ‰ (95% confidence interval, n = 23). Material was homogeneous at the mg scale, as | [253] |

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| | | | | verified by LF-IRMS, and O-isotopic values at the ng scale. EPMA revealed that only Cr impurities were found and HD-LR1 could be used for Cr determination | |
| O isotopes | Chromitites, Harzburgite | SIMS | | SIMS $\delta^{18}$O measurements confirmed the homogeneity of eight chromite samples with a range of Al, Cr, Mg and Fe contents. Magnetite and spinel affected the SHRIMP instrumental mass fractionation, IMF. The most important variable being the proportion of magnetite in the chromite sample (IMF > 4 %) | [274] |
| O isotopes | Barite | SIMS | NJU-Ba-1 FJ barite | Recommended $\delta^{18}O_{VSMOW}$ of NJU-Ba-1 and FJ determined by GS-IRMS: 7.94 ± 0.30‰ (2SD, n = 11) and 7.52 ± 0.34‰ (2SD, n = 8), respectively. SIMS analyses proved homogeneity of both NJU-Ba-1 and FJ barite at the ~20 µm level, (2SD): 0.36‰ (n = 383) and 0.58‰ (n = 325), respectively | [275] |
| O isotopes | Cassiterite | SIMS | Piaotang-Cst | SIMS measurements confirmed the homogeneity of this RM at the micrometer scale. Average 2SD: 0.49 ‰ (n = 626). $\delta^{18}O_{VSMOW}$: 5.33 ± 0.07‰ (2SD, n = 5), determined by IRMS with no matrix effects | [276] |

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| | | | | for cassiterite samples having variable concentrations of trace elements | |
| O and S isotopes | Barite<br>Anhidrite<br>Gypsum | SIMS | Barite: ROM-13898 ROM-48628 ROM-48628<br>Anhydrite: ROM-13491 ROM-40347<br>Gypsum: ROM-16655 ROM-37603 | Three barite, two anhydrite, and two gypsum samples were selected from the Royal Ontario Museum. SIMS repeatabilities better than ± 0.39‰ and ± 0.37‰ (1SD) for oxygen and sulphur isotope ratios, respectively. GS-IRMS analyses in independent laboratories gave narrow variation in $\delta^{18}O_{SMOW}$, although higher in $\delta^{34}S_{VCDT}$. GS-IRMS analysis provided good reproducibility within laboratories: $10^3\delta^{18}O$ values between ± 0.24‰ and ± 0.44‰ (1SD) and $10^3\delta^{34}S$ values ranging from ± 0.07‰ to ± 0.99‰ (1SD) | 277 |
| Os-Re dating | Molybdenite | LA-ICP-MS/MS | MDQ0252 and MDQ0221 | Two RMs from the Merlin deposit in Queensland and Q-MolyHill from the Preissac pluton in Quebec. Spectral interference of $^{187}$Re on $^{187}$Os resolved by using $CH_4$ as reaction gas. Homogenous Re-Os isotope ratios. $^{187}$Os/$^{187}$Re ratio (ID-TIMS): 0.025649 ± 0.000105. Re mass fraction 65 – 5100 µg g$^{-1}$ (MDC0252) and 60 – 1300 µg g$^{-1}$ (MDC0221). Ages verified by ID-TIMS Re-Os measurements: 1520 ± 4 Ma for MDQ0252. LA- | 278 |

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| | | | | ICP-MS/MS ages: 1518 ± 4 Ma for MDQ0252 and 1516 ± 6 Ma for MDQ0221 | |
| REEs | Scheelite | LA-ICP-MS | CaW-0, CaW-1, CaW-3 | $CaWO_4$ homogeneous crystals were dopped with REEs at 50, 250 and 5000 µg g$^{-1}$. REEs within and between unit major elements variation ($s_r$) for LA-ICP-MS: 0.53 and 5.56 %, respectively. Preliminary mass fractions determined by ICP-MS: from 15.5 ± 0.8 (Lu) to 36.2 ± 1.7 (Gd) µg g$^{-1}$ in CaW-0; from 49 ± 10 (Lu) to 209 ± 20 (Eu) µg g$^{-1}$ in CaW-1; and from 906 ± 29 (Lu) to 2851 ± 136 (Gd) µg g$^{-1}$ in CaW-3. Errors taken as 1SD | 279 |
| S isotopes | Chalcopyrite | SIMS | IGSD | Large grains of natural chalcopyrite were taken, and the homogeneity of major elements was tested by EPMA and four laboratories with SIMS. An LA-MC-ICP-MS confirmed homogeneity for S isotopes. Recommended $\delta^{34}$S based on IRMS: 4.21±0.23‰ (2SD, n = 30) | 280 |
| S isotopes | Stibnite | LA-MC-ICP-MS | Bj-Snt | Recommended $\delta^{34}$S (determined by IRMS) was -0.71 ± 0.32 ‰ (2SD, n = 15). The material contained Sb and S as major elements, and hundreds to thousands of mg kg$^{-1}$ of trace elements such as As, Cu, Pb and Si | 252 |

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| S isotopes | Barite | LA-MC-ICP-MS | NWU-Brt | Barite crystals from the Xiefang fluorite ore, Ruijin, Jiangxi province, China. The material was sufficiently texturally and chemically homogeneous; analytical uncertainty of 0.40‰ for $\delta^{34}$S (2SD). Recommended mean $\delta^{34}$S value obtained by bulk isotope analyses by GS-IRMS and MC-ICP-MS: 14.21 ± 0.33‰ (2SD) | 255 |
| Sb isotopes | Stibnite | fs-LA-MC-ICP-MS | DC, BJS | There were no matrix effects between the two samples. Homogeneity of RMs tested through MC-ICP-MS and backscattered electron maps (BSE). Sn was used as an internal standard to correct for isotopic fractionation. The $\delta^{123}$Sb precision was 0.02‰ and 0.04‰ (2SD) within 1 and 3 h, respectively. fs-LA-MC-ICP-MS $^{123}$Sb/$^{121}$Sb ratios: DC; 0.04±0.07‰ (2SD, n = 62) and BJS; 0.39±0.06‰ (2SD, n = 62), consistent with solution nebulization MC-ICP-MS results | 281 |
| Sr isotopes | Calcite | LA-MC-ICP-MS | TLM LSJ07 | m-XRF images indicate they are roughly homogeneous with respect to Ca, Mg, and Sr, (except for Sr in LSJ07). Rb/Sr ratios < 0.0002 and low Sr contents (< 200 mg g$^{-1}$). For independent grains, $^{87}$Sr/$^{86}$Sr: 0.70969 ± 0.00023 (2SD, n = 219) and 0.71006 ± 0.00015 (2SD, n = 219) for TLM and | 282 |

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| | | | | LSJ07, respectively. In agreement with data for TIMS and MC-ICP-MS | |
| Sr isotopes | Plagioclases | LA-MC-ICP-MS | AMNH-107160,<br>G29958,<br>Hrappsey 14-2 | Most accurate and precise $^{87}$Sr/$^{86}$Sr were obtained by a combination of $^{84}$Kr-baseline subtraction, Rb-peak-stripping using βRb derived from a bracketing glass RM, CaCa or CaAr correction for plagioclase and $^{84}$(CaCa or CaAr) + REE$^{2+}$ correction for rock glasses. $^{87}$Sr/$^{86}$Sr uncertainties better than 100 ppm (2SD) with a 100 µm laser spot size and materials with Sr mass fractions from 500 to 1000 µg g$^{-1}$. $^{87}$Sr/$^{86}$Sr ± 2SD (solution MC-ICP-MS): 0.704371 ± 24 (n = 9) AMNH-107160; 0.707551 ± 22 (n = 7) G29958; 0.703168 ± 18 (n = 8) Hrappsey 14-2. $^{87}$Sr/$^{86}$Sr ± 2SD (TIMS): 0.704365 ± 15 (n = 2) AMNH-107160; 0.707547 ± 15 (n = 1) G29958 | 283 |
| Ti isotopes | Ilmenite, titanite, perovskites | LA-ICP-MS | Ilmenites SIN1, CZE2, PAK122 and RUS10<br>Titanites PAK8, AUS10, NAM12 and MAD8 | Twelve Ti-rich minerals from Singapore, the Czech Republic, Pakistan, Russia, Australia, Namibia, USA and Italy. Isotopic composition was determined through SSB and fs-LA-MC-ICP-MS with identical $\delta^{49}Ti_{OL-Ti}$ values for each mineral. The natural samples were mostly homogeneous in terms of Ti isotopic composition. Intermediate precision: ± 0.13‰ to ± 0.17‰ (2SD) on $\delta^{49}Ti_{OL-Ti}$ | 284 |

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| | | | Perovskites ITA4, RUS5, RUS1 and RUS2 | | |
| Sr isotopic composition and trace elements (Mn, Sr, REE, and Y) | Calcite | LA-MC-ICP-MS | BZS, WS-1 | Homogeneity of Sr isotopes and trace elements (Mn, Sr, Y, RSD <10%, and REEs for BZS, RSD<20%) verified through LA-MC-ICP-MS. Recommended $^{87}$Sr/$^{86}$86 values: 0.71181 ± 0.00013 (2SD, n = 183) and 0.70872 ± 0.00009 (2SD, n = 184), for BZS and WS-1, obtained by solution MC-ICP-MS | [285] |
| U-Pb dating and trace elements | Apatite | SIMS | BR2, BR5, BR96, AFG2, AFB1, MADAP, SLAP, GR40, OL2, OL3, OL4, NUAN | Twelve apatite samples examined as secondary RMs. Homogeneity of SLAP, NUAN, GR40 demonstrated with LA-ICP-MS in terms of trace elements. Homogeneous SIMS U-Pb data. ID-TIMS ages: 2053.83 ± 0.21 Ma, 2040.34 ± 0.09 Ma, 868.87 ± 0.25 Ma, 478.71 ± 0.22 Ma and 473.25 ± 0.09 Ma, respectively. Eight of the RMs had homogeneous S isotopic composition (2SD for $10^3\delta^{34}$S and $10^3\delta^{33}$S < 0.55‰). BR96 and SLAP useful as RMs for sulphur isotope microanalysis of apatite. AFG2 and BR5: best suited for U-Pb isotope measurement by SIMS. ABF1: High Th content, useful as RM for SIMS Th-Pb apatite dating. ID-TIMS $^{87}$Sr/$^{86}$Sr between 0.704214 ± 0.000030 and | [286] |

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| | | | | 0.723134 ± 0.000035. MADAP and OL3: Best approaches for Sr isotope analysis | |
| U-Pb dating | Andracite-rich garnet | LA-ICP-MS | IUC-1 | Four different laboratories for LA-ICP-MS analysis, one for ID-TIMS and EPMA measurements, demonstrated homogeneity of the material IUC-1 from the Miocene trachyte dome near Ankara city (Turkey). This RM contained relatively high U levels (57 mg kg$^{-1}$). ID-TIMS $^{207}$Pb/$^{235}$U and $^{206}$Pb/$^{238}$U ages: 20.9 ± 0.4 and 20.6 ± 0.8 Ma, respectively, consistent with U-Pb LA-ICP-MS analyses | 287 |
| U-Pb dating | Apatite | LA-ICP-MS | MAP-2 | Young apatite RM collected from Myanmar (22 Ma). Chemically and isotopically homogeneous material, free from inclusions. U concentrations: 161 – 231 mg g$^{-1}$. ID-TIMS isotopic ratios: $^{206}$Pb/$^{238}$U = 0.00345 ± 0.00003, $^{207}$Pb/$^{235}$U = 0.0243 ± 0.0039, $^{207}$Pb/$^{206}$Pb = 0.0512 ± 0.0082. ID-TIMS $^{206}$Pb/$^{238}$U weighed ages: 22.18 ± 0.22 Ma (2SD, MSWD = 0.01, n = 6). Results obtained with LA-ICP-MS were consistent with those measured by ID-TIMS | 288 |
| U-Pb dating | Rutile | LA-HR-ICP-MS<br>ID-TIMS SIMS | RKV01 | RKV01 grains from Kaap Valley pluton, South Africa. Major and trace elemental concentration was obtained by means of EPMA and LA-HR-ICP-MS, | 289 |

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| | | | | respectively. The material contained high U (~83 µg g$^{-1}$), extremely low Th (~0.003 µg g$^{-1}$) mass fractions and U-Pb homogeneous isotopic composition with no compositional zoning. Recommended ID-TIMS mean $^{207}$Pb/$^{206}$Pb age: 3225.61 ± 0.64 Ma ($2s_r$, MSWD = 0.83), consistent with LA-ICP-MS and SIMS determined ages | |
| U-Pb dating | Calcite | LA-ICP-MS | TARIM | Natural low Mg megacryst calcite RM. Homogeneity for trace elements and U was tested through EPMA and LA-ICP-MS. ID-TIMS U-Pb analysis provided an intercept age of 208.5 ± 0.6 Ma (2SD, MSWD = 1.04). LA-ICPMS U-Pb showed ages of 208.0 ± 0.4/3.2 Ma (2SD, MSWD = 3.0), 515 isotope analyses | [290] |
| U-Pb dating and Lu-Hf isotopes | Zircon megacrystals | LA-ICP-MS | OZ | Zircons from the Kawisigamuwa carbonatite in Sri Lanka with moderate lo low radiation damage. ID-TIMS weighted mean $^{206}$Pb/ $^{238}$U age: 532.39 ± 0.66 Ma (2SD). Hf content ranged from 6630 to 9960 mg g$^{-1,}$ while the *in situ* mean $^{176}$Hf/ $^{177}$Hf ratios of ten crystals agreed within the error bands. Recommended $^{176}$Hf/$^{177}$Hf ratio: 0.282003 ± 0.000020 (2SD). Homogeneity of the material, verified by LA-ICP-MS. Two oscillatory zoned | [291] |

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| | | | | megacrysts yielded $\delta^{18}O_{VSMOW}$ of 12.1 ± 0.4‰ and 12.2 ± 0.4‰ (2SD) | |
| U-Th and U-Pb double dating | Zircon | ID-TIMS | SA01 | (U–Th)/He ages for three different fragments: 350.4 ± 18.8 Ma (n = 5, MSWD = 0.66), 369.6 ± 11.4 Ma (n = 12, MSWD = 0.60), and 368.6 ± 14.4 Ma (n = 7, MSWD = 0.59). Ages were consistent with traditional single-crystal laser fusion He determination and U–Th isotope dilution. No evidence of fragment zoning was reported, and the material proved to be homogeneous at the 100–500 µm scale as revealed by cathodoluminescence, Raman spectroscopy, LA-ICP-MS and conventional chemical methods. Raman spectrometry analysis suggested that the material experienced a low degree of radiation damage | 292 |
| U isotopes | Glass | LA-ICP-MS | CAS glasses<br>SAC glasses | Six different RMs for spatially resolved nuclear fallout analyses prepared by melting and quenching of $SiO_2$, $Al_2O_3$ and $CaCO_3$ powders. Materials with three different $^{235}U$ isotope enrichment (natural or 0.72%, 53% and 94%) and three U mass fractions: 5 µg $g^{-1}$, 50 µg $g^{-1}$ and 500 µg $g^{-1}$. Heterogeneous bulk elemental data was detected with a 10% RSD | 293 |

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| U-Th-Pb dating | Xenotime | LA-ICP-MS | XN01 | Material with similar $^{206}Pb/^{238}U$ and $^{208}Pb/^{232}Th$ ratios and calibration factors to bastnaesite (K-9) proposed as primary standard for bastnaesite dating. Ages for both materials: 118 ± 1 Ma with <2% offsets. Single spot LA-ICP-MS analysis data reduction was performed through calculation of the ratio-of-the-mean intensity. XN01 was more homogeneous than K-9 and useful as primary RM for in-situ LA-ICP-MS U-Th and Th-Pb bastnaesite dating | [294] |

**Table 10.** New data for existing geological reference materials

| Determinand | Matrix | Technique | Comments | Reference |
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| Ag isotopes | Basalt, granite, andesite, rhyolite, and ferromanganese crusts | MC-ICP-MS | Seven USGS RMs: BCR-2 and BIR-1 (basalt) GSP-2 and G-2 (granite), AGV-2 (andesite), RGM-1 (rhyolite) and NOD-P-1 (ferromanganese crusts), were analysed. Ag consumption lowered down to 5 ng. Instrumental mass bias corrected using the Pd-doping and SSB. Samples analysed with a precision better than 0.05‰. $\delta^{109}Ag_{SRM978a}$ for silicate rocks: from −0.24 ± 0.05‰ to 0.20 ± 0.05‰, and uncertainty for granite G-2: (2SD, 0.08‰) | 295 |
| B isotopes | Basalt | MC-ICP-MS | New data for Mid Ocean Ridge Basalt (MORB) glass were obtained: $\delta^{11}B_{SRM\ 951}$ (-5.6 ± 0.3‰ to -8.8 ± 0.5‰, 2SD), implying some upper mantle $\delta^{11}B_{SRM\ 951}$ heterogeneity. The results were fully in agreement with SIMS assays, although for low mass fractions MC-ICP-MS provided better precisions | 296 |
| Ce isotopes | Manganese nodules, diabase, granite | MC-ICP-MS | Analysis according to a sample–standard combined with a Sm-doping method done by | 297 |

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| | gneiss, stream sediment | | two different laboratories. $\delta^{142}$Ce, USGS RM NOD-P-1 (manganese nodule): 0.177 ± 0.035‰ (2SD, n = 7) and 0.172 ± 0.034‰ (2SD, n = 8) for the two laboratories; USGS RM NOD-A-1 (manganese nodule): 0.116 ± 0.028‰ (2SD, n = 8) and 0.104 ± 0.028‰ (2SD, n = 9), respectively. The $\delta^{142}$Ce of two USGS RMs W-2a (diabase) was - 0.036 ± 0.046‰ (2SD, n = 3), USGS RMs BHVO-2 (basalt) was - 0.019 ± 0.036‰ (2SD, n = 4). Ce isotopic compositions of three Chinese RMs GBW07121 (granite gneiss), GBW07123, and stream sediment GBW07301a were: 0.039 ± 0.033‰ (2SD, n = 5), 0.068 ± 0.027‰ (2SD, n = 5) and 0.046 ± 0.015‰ (2SD, n = 3), respectively | |
| Hf and Lu isotopes | Mafic and ultra mafic rocks | ID-MC-ICP-MS | Hf and Lu mass fractions and $^{176}$Hf/$^{177}$Hf isotopic ratios were measured in ten mafic-ultramafic rock RMs, including IAG RM OKUM (komatiite), CCRMP RM WPR-1 (serpentinised peridotite), MINTEK RM NIM-N (norite), MINTEK RM NIM-P (pyroxenite), ANRT RM UB-N (serpentinised peridotite), GSJ RM JP-1 (peridotite), MINTEK RM | 298 |

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| | | | NIM-D (dunite), IAG RM MUH-1 (serpentinised harzburgite), IAG RM HARZ01 (harzburgite), USGS RM DTS-2b (dunite), with low contents of Lu and Hf (Lu, 2-150 ng g-1; Hf, 5-500 ng $g^{-1}$). Variability in Hf mass fraction and isotopic composition were observed for: NIM-N, NIM-P and MUH-1 at test portion masses of 0.1 to 0.3 g. For the remaining materials, precision was lower than 60 ppm (2SD) for test portions of 0.06 to 0.3 g | |
| Mg-isotopes | Basalt, granodiroite , andesite, carbonate, sediments, soil, rhyolite, amphibolite, limestone, clay, sandstone, shale, syenite, gabbro | MC-ICP-MS | The RMs studied were: six USGS RMs: (BHVO-2 and BCR-2, basalts), RGM-2 (rhyolite), AGV-2 (andesite), GSP-2 (granodiorite), COQ-1 (carbonate), two rhyolite Geological Survey of Japan RMs (JR-1 and JR-3), sixteen RMs from CRSRI (GSS-2, soil, GRS-11, rhyolite, GSR-15, amphibolite). For these RMs, $\delta\ ^{26}$Mg values (2SD, n = 3) agreed with previously published ones. $\delta\ ^{26}$Mg values for GSR-6, limestone, GSD-1, GSD-3A, GSD-4, GSD-5, sediments, GSS-1, soil, GSS9, sediment, GSS-15, clay, GSS-16, clay, GSR-4, sandstone, GSR-5, shale, GSR-7, syenite, and GSR-10, gabbro, | [299] |

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| | | | were reported to be (2SD, n = 3): -1.42 ± 0.02‰; -1.11 ± 0.12‰; -0.08 ± 0.06‰; -0.12 ± 0.04‰; -0.24 ± 0.06‰; -0.71 ± 0.12‰; -0.54 ± 0.07‰; -0.40 ± 0.11‰; -0.06 ± 0.01‰; -0.07 ± 0.09‰; 0.21 ± 0.08‰; -0.50 ± 0.03‰; -0.33 ± 0.08‰, respectively | |
| Nd, Rb, Sm, and Sr elemental concentrations and Sr and Nd isotopic ratios | Silicates | TIMS, MC-ICP-MS | 13 Chinese silicate rock certified RMs were analysed. Test portions were spiked with tracers enriched in $^{87}$Rb–$^{84}$Sr and $^{149}$Sm–$^{145,146,150}$Nd and digested with HF, $HNO_3$, and $HClO_4$. For GBW07111, GBW07112, GBW07121, GBW07122, GBW07123, GBW07124 and GBW07125, the Nd and Sr isotopic compositions were reported for the first time | 300 |
| Nd, Sm, Sr isotope ratios | Basalt | ID-TIMS | Instrumental bias and fractionation corrections were performed based on repeated measurements of the certified RMs JNdi-1 (Neodymium oxide) and NIST SRM 987 (Strontium carbonate). RM Basalt Ribeirao Preto BRP-1: $^{143}$Nd/$^{144}$Nd = 0.512408 ± 0.000010 (2SD); $^{87}$Sr/$^{86}$Sr = 0.706011 ± 0.000017 (2SD). Respective Sm and Nd mass fractions: 11.0 ± 0.2 and 51.9 ± 0.6 μg $g^{-1}$. | 301 |

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| | | | Accuracy of the methods tested with the following USGS RMs: AGV-1, BCR-1, BHVO-1, G-2 and GSP-1 | |
| Rb-Sr dating | Mica | LA-ICP-MS/MS | ZBH-25 biotite, a Chinese national primary RM (GBW04439) for K-Ar dating, was characterized for aging according to the Rb-Sr dating method. A younger age was determined with respect to the K-Ar age when using synthetic glass RM (NIST SRM 610) as the RM for external calibration (*i.e.*, there was a significant matrix effect). $^{87}Sr/^{86}Sr$ ratios were 0.7100 ± 0.0020 (2SD, n = 15), in agreement with the recommended value | [302] |
| U isotopes | Coal | MC-ICP-MS | Samples were dry ashed and high pressure digested; instrument isotopic fractionation was calibrated through $^{233}U$-$^{236}U$ double-spike. $\delta^{238}U_{CRM-145}$ of seven USGS coal RMs (SARM18, SARM1, SARM20, GBW11156, GBW11157, GBW11159, GBW11160) and a NIST SRM 1633c (fly ash) values ranged from -0.69 ± 0.04‰ (2SD) to - 0.29 ± 0.03‰ (2SD) | [303] |
| U isotopes | 28 Igneous, metamorphic and | MC-ICP-MS | The $^{233}U$-$^{236}U$ double spike technique was used. U mass fractions ranged from 0.11 to 18.7 µg g$^{-}$ | [304] |

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| | sedimentary rocks and sediments RMs | | $^{1}$. $\delta^{234}/^{238}$U values were provided for all RMs for the first time | |
| U-Pb dating | Ilmenite | LA-SF-ICP-MS | Zircon 91500 and garnet PL-57 had similar U–Pb fractionation and average normalized Pb/U ratio with ilmenite BC269. Ilmenite samples HG79 ($^{206}$Pb/$^{238}$U age of 259.3 ± 1.3 Ma), LX32333 ($^{206}$Pb/$^{238}$U age ~196.0 ± 2.7 Ma), and BC269 (2055.0 ± 3.9 Ma) contained appropriate U and Pb contents and were useful as potential RMs for *in situ* U–Pb dating of ilmenite | [251] |
| U-Pb dating | Apatite | Fission-track dating | McClure Mountain Syenite (MMS) Apatite recommended as a RM for LA-ICP-MS fission track and U-Pb double dating. Overall central age: 254.1 ± 5.1 Ma (n = 238) in analyses over two years.<br>The MMS apatite is widely used as a secondary RM for U-Pb dating. It was also proposed as a secondary material for trace element as well as fission track assays. | [305] |
| U – Pb isotopes and trace elements | Three titanite geochronology RMs | LA-ICP-MS | EPMA results revealed intragrain heterogeneity of titanite materials; RSD for trace elements | [306] |

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| | (Ecstall, McClure and FCT) | | from 5 to 40%. For U, RSD = 70% (n = 26), 265% (n = 22) and 202% (n = 26) for Ecstall McClure and FTC, respectively meaning these RMs were not suitable for trace element analysis | |
| U, Th and Pb dating | Titanite and apatite | LA-ICP-MS ID-MC-ICP-MS | Ten titanite (MKED-1, BLR-1, OLT-1, YQ82, Khan titanite, Mud Tank titanite; in-house: ONT-A, ONT-B, ONT-C and EPMA titanite RM Renfrew) and five apatite (MAD-UCSB, MRC-1, BRZ-1, Tory Hill apatite; in house: ONTAPA) RMs were analysed. A good concordance with the results from EPMA in the MKED-1 titanite RM $^{238}$U/$^{206}$Pb, $^{235}$U/$^{207}$Pb and $^{232}$Th/$^{208}$Pb ages was found. Spectral overlapping made it necessary to perform a careful selection of EPMA primary RMs to minimize inaccuracies | 307 |
| Zn isotopes | Dolerite, gabbro, microgabbro, andesite, diorite, syenite, granite, rhyolite, shale, | MC-ICP-MS | The RMs analysed in this study included the following USGS RMs: GSP-2 (granodiorite), AGV-2 (andesite), W-2 (diabase), BCR-2 (basalt), BHVO-2 (basalt), BIR-1 (basalt), DNC-1 (dolerite) and NOD-P-1 (manganese nodule); Geological society of Japan, GSJ RM JB-1b (basalt); CRPG RMs: PM-S | 308 |

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| | limestone, and hornblendite | | (microgabbro) and DR-N (diorite); CNRCG RMs: GBW07103 (GSR-1, granite), GBW07104 (GSR-2, andesite), GBW07105 (GSR-3, basalt), GBW07107 (GSR-5, shale), GBW07108 (GSR-6, limestone), GBW07109 (GSR-7, syenite), GBW07111 (GSR-9, diorite), GBW07112 (GSR-10, gabbro), GBW07113 (GSR-11, rhyolite), GBW07122 (GSR-15, hornblendite). Long-term reproducibility better than 0.03‰ (2SD). New $\delta^{66}$Zn values for eleven CRMs were provided whereas, for four RMs (basalt JB-1b and GSR-3, diabase W-2 and dolerite DNC-1) an improved characterisation of $\delta^{66}$Zn was performed | |
| Zn isotopes | Ultramafic, felsic igneous rocks, carbonatites, sediments soils | MC-ICP-MS | CRMs from USGS, the Geological Survey of Japan, and the Institute of Geophysical and Geochemical Exploration, People's Republic of China (peridotite, JP-1, basalt, BCR-2, BHVO-2 and BIR-1a, andesite, AGV-2, rhyolite, GSR-11, granite, GSR-1, JG-1, granodiorite, GSP-2, carbonatite, COQ-1, soil, GSS-11, GSS-13, and sediment, GSS-33). | [158] |

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| | | | Long-term external reproducibility for $\delta^{66}Zn$ values: ±0.04‰ (2SD) | |

## 5.2 Sample preparation, dissolution and chemical separation

Developments in *digestion and fusion* procedures were reported. A rapid (30 min) standardised sample digestion[309] performed at high temperature (250 ºC) and pressure (80 bar) using a SCR microwave system enabled the complete dissolution of the geological RMs (ANRT CRM GP-13, spinel lherzolite, ANRT CRM UB-N, serpentinite, and USGS SRM BHVO-2, basalt) to be performed. The subsequent digests were purified by means of an ion-exchange column and the results of determinations carried out by ID-HR-ICP-MS agreed with those previously reported. In an improved alkaline fusion procedure, undertaken in silver crucibles at 710 ºC, use[310] of hydrated $Na_2O_2$ as a fusion reagent resulted in the complete dissolution of eight international silicate standards and where the uncertainty associated with blank subtraction was reduced by the lower reagent consumption required for dissolution of the fusion cake. An in-house built[311] induction furnace enabled rapid lithium metaborate fusions in graphite crucibles to be performed (5-10 min) on five powdered USGS silicate rock RMs.

Implementation of *suitable sample surface treatments* was critical for U-Pb dating purposes. Annealing at 1400ºC was proposed[312] to minimise morphological damage caused by alpha particles with resultant homogeneity in U-Pb dating confirmed by LA-ICP-MS and SIMS assays. An alternative chemical abrasion surface treatment method combined[313] annealing at a lower temperature alongside partial dissolution using HF performed over 4-12 h at 180 to 210 ºC. In a companion paper by the same authors[314], data obtained using microscale X-ray computed tomography, SEM, and Raman spectroscopy, revealed a mechanism for dissolution of zircons. It was found that HF permeated into the crystal core either through fractures caused by radiation damage, via inclusions within soluble high U-zones or via acid percolation through faults. This study demonstrated that the duration of chemical abrasion treatment processes and the temperature at which such processes are performed, can affect resultant U-Pb ratio determinations because elements like lead can be lost. Continuing this theme of elemental losses, it was highlighted[315] that the perturbed U–Pb isotopic ratio distribution obtained was the superposition of two signals, namely a Gaussian distribution, reflecting the MU of the true isotopic ratio and a skewed distribution that characterised Pb loss. A correction was successfully applied to model the distribution of apparent Pb loss in 10 different igneous samples previously analysed by LA-ICP-MS or SIMS. It was demonstrated[316] that a chemical abrasion treatment nevertheless can be successfully applied because no systematic bias in the U-Pb dates were observed when 13 zircon RMs were analysed by LA-ICP-MS.

Following sample dissolution, *analyte purification through coprecipitation to minimise matrix effects* with iron(III) hydroxide ensured[317] more accurate determinations by HG-MC-ICP-MS of $^{82}$Se/$^{78}$Se isotopes in geological samples. Use of coprecipitation with $Fe(OH)_3$ followed by purification with a AG1-X8 resin was also proposed[318] for U-Th dating of gypsum so as to concentrate analytes and to remove the calcium matrix.

The use of *resins for sample purification* is well established and several reported studies are summarised in Table 11. Of note were the purification[319] of digested samples for subsequent Mo and Zn isotopic assays using a double-stack column which shortened the separation time by a factor of two but maintained recoveries of 92% for Mo and 96% for Zn. Caution nevertheless should be exercised so as to avoid isotopic fractionation. In the isotopic analysis of Ce[297] and Nd[320] in rocks samples, it was noted that use of a TODGA type resin led to the preferential retention of lighter isotopes. In the determination[321] of the S mass fraction in carbonate-associated sulfate minerals, samples was mixed with an aqueous suspension a of weakly acidic cation-exchanger whose exchange group (*i.e.* -COOH) facilitated the decomposition of the carbonate minerals thus releasing soluble sulfates. This approach was successfully applied to the analyses of NMIJ CRMs JDo-1 (dolostone), JLs-1 (limestone) and ML-2 (limestone) with resultant S recoveries in the 74 to 94% range.

*Boron determinations* in NIST SRM 8301f (marine carbonate) were carried out[322] following matrix removal by mixing the dissolved sample with Amberlite™ resin (IRA-743) and analysing the supernatant by MC-ICP-MS following centrifugation. The advantages of this approach over column clean-up methods included: no column blocking; lower procedural blanks of 10 ± 16 pg; and higher sample throughput, with the ability to process 24 samples within *ca.* 5 h. Excellent reproducibilities with results of 14.58 ± 0.11‰ (2SD) that agreed with the certified value achieved when 15 sample aliquots (10 ng sample masses) were processed .

In *Pb isotope ratio determinations* on small sample sizes (*ca.* 3 mg) by MC-ICP-MS, use of matrix removal steps were deliberately skipped[323], which improved the sample throughput four-fold. However to overcome the resultant potential interferences, an IS procedure or an optimised regression method (ORM) was successfully applied as verified when accurate lead isotopic data when USGS CRM G-2 (granite) was analysed.

*Photochemical vapour generation* enabled[206] volatile species $Se^{IV}$ and $Te^{IV}$ to be liberated from digested samples within 30 s following UV irradiation in the presence of formic and acetic acids with cobalt(II) as a catalyst. The approach was confirmed by the successful analysis of several CRMs including soils, sediments and rocks.

The leaching and assaying of ore samples for *total U determinations* using an on-line ICP-MS approach[324] required samples to be ground and sieved to a particle diameter of < 74 µm. The extractant was a mixture of $HNO_3$, HF and $H_2O_2$, only a mg of sample was consumed, and measurements were performed within 15 min resulting in recoveries > 95%.

A commercially available *high-temperature pyrolyser* (Rock-Eval® 7S) coupled[325] to a MC-ICP-MS instrument enabled pyrolysable organic and pyritic sulfur fractions to be thermally differentiated. To minimise matrix interference effects, the samples were initially acidified to remove carbonates as $CO_2$ thus enabling $\delta^{34}S$ values ($\delta^{34}S_{organic}$ and $\delta^{34}S_{pyrite}$) to be sequentially determined on 5 to 90 mg of now decarbonated samples. Assays were performed within 30 min with an average measurement precision of 0.5‰ for those samples that contained > 5 nanomole of S.

A triple silicon *isotope ratio* ($^{29}Si/^{28}Si$, $^{30}Si/^{28}Si$, expressed as $\delta^{29}Si$ and $\delta^{30}Si$) measurement protocol involved heating silica-containing samples using an infrared laser in an atmosphere of $BrF_5$ gas; the resultant $SiF_4$ gas was analysed[326] by gas source-MS, allowing changes in triple silicon isotope ratios at the ppm level to be determined. Gas source-MS was also used[327] in the high-precision triple ($\Delta_{47}$, $\Delta_{48}$, $\Delta_{49}$) clumped isotopic analysis of $CO_2$ liberated from carbonates following acidification with phosphoric acid. Here a fully automated gas extraction system, connected to the dual inlet system of the gas source-MS instrument, enabled excellent (external) repeatabilities to be obtained *i.e.*, close to those predicted by the shot noise limit. A newly described[328] analytical method to liberate oxygen from geological samples combined high-temperature conversion

(HTC), in which oxygen-containing organics, phosphates, sulphates, nitrates, carbonates, and silicates were converted to CO within a glassy carbon reactor at temperatures >1400 ºC, with a subsequent methanation-fluorination (HTC-M-F) process step wherein the newly generated CO was reacted with hydrogen at 560 ºC over an iron catalyst to facilitate the transfer of oxygen from CO to oxygen in $H_2O$ (methanation reaction), which ultimately yielded $O_2$ when this $H_2O$ was subsequently fluorinated using $CoF_3$. The oxygen yield was essentially quantitative and in the determination of $\delta^{17}O$ and $\delta^{18}O$ by MS that followed, excellent reproducibilities in $\Delta^{17}O$ of <10 ppm (1SD) were achieved.

## 5.3 Instrumental analysis

**5.3.1 Laser-induced breakdown spectroscopy** In a recent[329] *review* (167 references) on LIBS, applications within the field of geosciences were summarised. The review described calibration-free methods that, together with their applications, are increasingly more widely used. Also discussed were use of ANN, SVM, and other chemometrics together with applications within the field of geotechnical engineering. Another review (140 references) discussed[330] new strategies and applications of calibration-free LIBS. under non – local (and partially local) thermodynamic equilibrium conditions. The application of ANN and columnar density calibration-free LIBS approaches were included. The paper concluded that some of the challenges with using LIBS that are reported *e.g.*, self-absorption, could be addressed by calibration-free LIBS.

A recurring problem in the quantitative analysis of geological samples using LIBS is the *mismatch in analytical performance between raw samples and RMs* especially when the latter are used as pressed pellets. A learning transfer component analysis was applied[331] to overcome this problem. By using machine vision technology to automatically detect raw rock samples and a machine learning optimum algorithm (XGBoost), the contribution of the sample irregularities to inaccuracy was eliminated. Multivariate regressions based on machine learning were efficient in minimising matrix effects in the determination[332] of Cl in a simulated Mars environment. The impact of confounding variables *e.g.*, strong signals caused by cations associated to Cl, was mitigated and a sample weighting procedure implemented that decorrelated the features in the model training phase. Two sets of samples (training and matrix matched) were prepared to test the trained models: and good LODs (0.16% w/w) and rmse of prediction of 0.57% *w/w* and 0.59%, *w/w* were obtained for both sets of samples. The quantitative analysis capabilities of LIBS were further extended[333] by improving the models that account for matrix effects. The determination of EC and fixed C in coals was improved once it was verified that fixed C was less impacted by matrix effects in different coal samples than EC. Correct determination of EC content was of great importance when estimating $CO_2$ emissions from burning of coal. A method based on a dual-cycle variable selection mechanism with competitive adaptive reweighted sampling to optimise PLS regression improved the accuracy of such determinations. In fact, the $CO_2$ emissions estimated in this way were within 1.7% of the predicted values.

In support of *future analysis of Martian rocks and soils*, sufficient LIBS data were required[334] to build a component inversion model for predicting the collected spectra, which could then be transferred to other instruments. A domain-adaptive fully connected neural network that can realise knowledge transfer between different LIBS spectrometers was discussed.

Improvement of *the analytical figures of merit of LIBS* by means of LIBS-LIF was possible as exemplified in the determination[335] of Pt in ore samples where excitation at 235.71 nm with secondary fluorescence emission measured at 269.84 nm resulted in the S/N being boosted and interferences reduced. Synthetic calibrants were used, and following 200 laser shots, the LOD improved from 21 mg kg$^{-1}$ using BS to 0.15 mg kg$^{-1}$ using LIBS-LIF.

Detailed *multielemental compositional maps* of geological samples in the order of $10^7$ pixels were achieved[336] by employing a hf (kHz) µ-LIBS analyser that could survey areas of tens of cm$^2$ at high lateral resolutions < 20 µm. The quantity of data generated however required automated fast data treatment methods. This approach enabled small discrete mineral phases to be identified in samples that would otherwise go undetected in conventional LIBS assays.

LIBS measurements supported EPMA measurements in determining[337] *U oxidation states* in siliceous materials From the LIBS spectra of oxygen and hydrogen it was proposed that U existed as $Ca[(UO_2)_2(SiO_3OH)_2]\ 5H_2O)$ because the U oxidation state was inferred from the intensity of the O signal and the hydroxyl environment inferred from the intensity of the H signal. From the superimposition of images obtained using LIBS and EPMA, detection of primary and secondary U mineralisations were possible.

**5.3.2 Dating techniques** *Applications of ID-TIMS to U-Pb radioisotopic dating* were reviewed[338] (173 references) wherein the utility of measuring zircons was initially discussed. The paper then proceeded to cover various sample preparation procedures e.g. abrasion, dissolution, and purification steps and the use of ID protocols and isotopic tracers in TIMS assays. Finally, data treatment methods, age interpretation and the advantages and disadvantages of this technique were discussed.

The application of laser ablation coupled to ICP-MS for dating of geological materials, relies on the *appropriate selection of suitable standards*. It was reported[339] that poor accuracies were obtained when using the MicaMG pressed nano-powder pellet as a RM because of the different ablation yield for this material compared to real mica samples. Other RMs *e.g.*, natural biotite, muscovite, and phlogopite also yielded different fractionation trends compared to this standard. So to alleviate such issues, the authors proposed use of the NIST SRM 610 (trace elements in glass) both as a primary RM for normalisation and for drift correction together with a natural mineral such as phlogopite with similar fractionation behaviour to account for ablation yields. Use of this protocol resulted in accurate Rb-Sr age determinations for minerals such as biotites and K-feldespars. In another study[340], NIST SRM 610 was also used, with a subsequent correction for the Rb/Sr offset based on the age of isochronous calibration micas. This approach afforded a <3% deviation in age determination with respect to that obtained using a solution-based method. A similar two-step methodology was reported[302] using NIST SRM 610 for instrumental calibration and Chinese CRM GBW04439 (ZBH-25 biotite), originally developed for K-Ar dating, but used here as a second standard to correct matrix effects in Rb-Sr dating. The difficulty in finding a mica mineral with homogeneous $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios was overcome[341] by using LA-ICP-MS/MS for *in situ* Rb-Sr dating. Under optimized measurement conditions, it was found that there was now no need for a matrix matched RM. For micas with an age > 15 Ma, this methodology was accurate and precise but for younger micas < 5 Ma, dating was less accurate because of the shorter radiogenic accumulation time. The U-Pb dating[342] of sulfates in a variety of carbonate-based matrices was improved by matrix matching using carbonate RMs, so ensuring comparable ablation yields.

Using *LA-ICP-MS in fission-track analysis* was advantageous over the use the conventional external detector method (EDM), because of a higher achievable sample throughput and for safety considerations. Both methodologies provided[343] similar results for samples with a wide range of fission track ages (from < 1 to 2 Ga) when a common calibration approach was used, but measuring more isotopes was possible with LA-ICP-MS.

The *in situ mapping by LA* of geological samples for dating purposes using $^{87}$Rb/$^{86}$Sr and $^{87}$Sr/$^{86}$Sr measurements was improved[344] using a high repetition rate (> 100 Hz) inline scan mode. Use of a 3-4 µm laser spot size enabled 2D Rb-Sr maps to be generated with good lateral resolution and minimised the ablated sample mass thirty-fold compared to a static spot ablation mode. Performance of this approach was verified by analysis of muscovite and biotite with matrix matched crystalline mica used for interference correction. Reverse depth profiling with LA was proposed[345] as an alternative approach to U-Pb dating and multielemental analysis of zircons with complex structures. In this method, samples were embedded in resin as usual but then over-polished so revealing the internal zircon structures, when visualised by cathodoluminescence imaging, they were then ablated from the core to rim wherein the identified zircon age rim was determined to be as narrow as 0.6 µm. Geochronological information gleaned from analysis of leucogranites and granitic gneiss samples was consistent with that obtained using conventional LA-ICP-MS dating.

The *age of young uranium ore concentrates* was determined[346] by LA-MC-ICP-MS using the $^{230}$Th–$^{234}$U chronometer with reported ages that ranged between 3.5 to 4435 y. To overcome problems associated with sample impurities that can compromise the accuracy of results for ages > 100 y, multiple measurements of $^{230}$Th/$^{232}$Th and $^{232}$Th/$^{234}$U ratios were taken at an interval of about 2 to 5 y. Interestingly, significant variations in the former ratio were detected as a function of age.

The timing of the *magmatic crystallization of mafic rocks* using the Lu-Hf dating system was[347] determined using LA-ICP-MS/MS where addition of $NH_3$ to the reaction cell enabled $^{176}$Hf and $^{178}$Hf to be measured in mass shift mode at *m/z* 258 and 260, thus resolving the isobaric interferences on Lu. The $^{177}$Hf values were calculated from the $^{178}$Hf signal using their natural abundance ratios. Measurement of $^{175}$Lu enabled $^{176}$Lu isotope abundance to be calculated using the $^{176}$Lu/$^{175}$Lu natural ratio.  NIST SRM 610 RM (trace elements in glass) was used as the primary standard, RM OD306 (apatite) was used to correct for LA matrix-induced fractionation effects, and in-house prepared apatite RMs Bamble (Lu–Hf age: 1097 ± 5 Ma) and Harts Range (Lu–Hf age: 343 ± 2 Ma) were analysed to assess accuracy.

The *in situ double-dating by laser-ablation – ICP-MS* through the measurement of (U-Th-Sm)/He and U/Pb couplets used[348] two different ablation assays: the first determined the radiogenic He content; the second the U-Th-Sm-Pb isotopic ratios and mass fractions. The age error associated with *in situ* double ablation, with concentric and successive ablations, was evaluated for 249 zircons from the Fish Canyon Tuff locality. The application of this procedure to minerals with U-Th-Sm zoning generated a significant (U-Th-Sm)/He age error. Nevertheless, the method allowed a comparison of the intra- and inter-sample maximum age and a deconvolution of a multimodal age spectrum. One of the main problems of this methodology was that U, Th, and He measurements must be expressed in units of molar concentration, rather than molar abundance. This means matrix-matched U-Th concentration standards were required together with accurate He ablation pit measurements. To overcome[349] this challenge, proton-induced $^{3}$He measurements substituted for ablation pit volume, and use of standards of known U-Th-He age were proposed. The use of relative rather than absolute concentration measurements yielded more accurate results. Double dating U-Pb and U-Th methods were recommended[350] in the application of LA-ICP-MS for dating of samples with low Pb contents. It was verified that the Toya tephra's weighted mean U-Pb age determination of 0.103 ± 0.029 Ma (2SD) was accurate, but, due to the low $^{206}$Pb intensity, the age determination for SS14-28 zircon of (0.25 ± 0.10 Ma) was inaccurate. In contrast, both materials yielded accurate ages when U-Th dating approaches was applied.

The potential of γ-rays to extract geochronological information, introduced in the 1970s, was re-investigated[351] by means of the production of $^{38}Ar_K$ from $^{39}K$. The established $^{40}Ar/^{39}Ar$ dating procedure is based on irradiation with fast neutrons. In this study, various age RMs commonly used for the established $^{40}Ar/^{39}Ar$-method were co-irradiated for 60 h at 17.6 MeV maximum energy. The γ-ray bremsstrahlung was low and, hence, the total production of $^{38}Ar_K$ was depressed. Ages of young RMs could be reproduced within error, whereas older age RMs showed discrepancies due to the low production rate. The advantages of this methodology over the irradiation with neutrons is a reduction in radioactivity produced during the irradiation process, instrumental availability and the possible absence of recoil effects of produced $^{39}Ar$.

**5.3.3 Inductively coupled plasma mass spectrometry** A wide ranging review[352] (119 references) of *advances in LA-ICP–MS/MS* covered the determination of halogens, noble metals and REEs, as well as *in situ* dating of U-Pb minerals. The review paid particular attention to analysis methods and the reduction of polyatomic interferences. A companion section provided a valuable overview of different applications of LA-ICP-MS/MS for $^{176}Lu$-$^{176}Hf$, $^{87}Rb$-$^{87}Sr$, $^{187}Re$-$^{187}Os$ and U-Pb radiometric dating.

Several *reviews on specific elemental determinations in geological materials by ICP-MS* were published. The difficulties[353] (81 references) associated with Sn determinations by LA-ICP-MS included: memory effects and their impact on the transient signal shape; isobaric interferences due to doubly charged uranium ions; and other challenges arising from elemental fractionation and matrix effects. The authors also discussed homogeneity issues when interrogating standards at the µm scale. A review[354] (121 references) of V isotopic analysis by MC-ICP-MS, paid particular attention to the use of different sample pretreatment approaches dependant on the nature of the mineral encountered *e.g.*, silicates, metal oxides, carbonates. The potential challenges for *in-situ* V isotopic analysis using fs LA were also addressed. Applications of ICP-MS and X-ray related techniques *i.e.*, XRF, XRD, XPS, XAS, XANES, μ-XAS for Tl determinations were reviewed[355](332 references) and suitable RMs for determining the Tl isotopic ratio and mass fractions tabulated.

In ICP-MS isotope ratio determinations, *liquid sample introduction systems* are still recognized as critical components. Rodríguez-Díaz et al.[356] evaluated, for the first time, the performance of sample introduction systems in the isotopic analysis of B by MC-ICP-MS in marine biogenic carbonates *e.g.* clams and corals. A Scott type PFA spray chamber with a PFA MicroFlow nebulizer operating at 30 μL min$^{-1}$ provided the best results in terms of sensitivity *i.e.*, signal per mass of B aspirated by the nebulizer. The detector configuration was also varied, and it was found that by combining an ion counter for detecting $^{10}$B with a FC fitted to a 1012 rd amplifier for $^{11}$B afforded more accurate results for total B signals with an intensity < 0.35 V compared to the use of two FCs.

Advances in MC-ICP-MS have led to the use of *iron isotopes as markers of geochemical history* in a wide range of environments. King-Doonan et al.[357] developed a new mathematical correction procedure for those situations in which the Fe concentration in the samples and isotope standards were mismatched by > 10%, producing the so-called self-induced matrix effect that can induce mass bias.

The *application of ICP-MS/MS for overcoming spectroscopic interferences* in geochemical analysis is still expanding. Using $N_2O$ as a reaction gas, it was possible[358] to overcome the $BaO^+$ interference on $Eu^+$ even at Ba/Eu ratios as high as 125,000. Another study proposed[359] $NH_3$ as a reaction gas to yield $Ag(NH_3)_2^+$, for Ag determination. The isobaric interferences caused by $ZrO^+$ and $NbO^+$ were also removed by the generation of $ZrO(NH_3)_4^+$, $ZrO(NH_3)_5^+$, and $NbO(NH(NH_3)_3)^+$, species thus improving the LOD to < 0.53 ng g$^{-1}$. For *in situ* Rb-Sr geochronological applications, undertaking[360] simultaneous $^{87}$Sr/$^{86}$Sr and $^{87}$Rb/$^{86}$Rb isotope ratio determinations was possible using $SF_6$ as a reaction gas, because Sr was now measured as $SrF^+$. The now simultaneous measurement of Rb and Sr isotopes with improved precision by LA-MC-ICP-MS/MS, enabled integrations of signals from individual laser shots. Time-resolved signals demonstrated that individual laser spots contained multiple isochronous subpopulations.

*Matrix effects, elemental fractionation or representative sub-sampling* remain as issues in LA studies. For instance, when andradite-grossular garnets were ablated[361] using a 193 nm excimer laser, there was evidence of melting and sample evaporation. In the case of rutile, examination of the craters revealed non-uniform ablation with melting, splashing and thermal stress cracking effects. One possible solution[362] was to use a -30 ºC cryogenic ablation cell. Here sulfide minerals such as pyrite, chalcopyrite, and galena were ablated and examination of the resulting crater verified that cooling the sample led to a reduction in melting and vapor redeposition at the area affected by heat. The LA-ICP-MS signal precision (RSD) improved from 28-39% to 11-24% when samples were chilled. The application of fs-LA-MC-ICP-MS also minimized[363] analyte fractionation effects encountered in the determination of the $^{34}S/^{32}S$ isotope ratios in apatite samples in so far that results obtained now were in good agreement with those obtained using SIMS.

In the determination[364] of Li isotopes in 11 spodumene samples by fs-LA, the impact of *plasma operating conditions and data reduction protocols* on measurement accuracy were investigated. Adding small amounts of water to the carrier gas before the ablation cell improved stability of the baseline signal and the reproducibility of the isotope ratios determined. The Li ratios obtained using NIST SRM 610 (trace elements in glass) as a calibrant agreed with those measured by solution MC-ICP-MS because matrix-matched calibrants were now not required. The use of a wet plasma also minimized[269] matrix effects when determining Fe isotopes in silicate minerals such as olivine, garnet, amphibole and biotite by LA-MS-ICP-MS. With the aid of a ns ArF 193 nm excimer laser, scheelite samples were also successfully analyzed[365] with NIST SRM 610 (trace elements in glass) as calibrant coupled with He as a carrier gas and tungsten as an IS. Measured CaO concentrations agreed with those results obtained by EPMA and data obtained for both major (Ca, W) and trace elements (Fe, Mo, REEs, Si and Y) were in agreement with those obtained by ICP-MS following dissolution.

*Additional sources of measurement inaccuracy* can be attributed to the MS hardware itself, as demonstrated[366] when B isotopic compositions were measured by LA-MC-ICP-MS. Here it was demonstrated that scattering of both Ca and Ar ions within the spectrometer flight tube degraded the accuracy of B isotope determinations, but this issue was eliminated when deflectors to focus and guide B ions were used. Furthermore, mass fractionation effects were influenced by the plasma operating conditions employed, hence use of hot plasma conditions was preferred but at the expense of accuracy when low boron concentrations were measured because of the inherent reduction in instrumental sensitivity when using such plasma conditions.

There is an increasing interest in performing *spatially-resolved trace element mapping* studies. The coupling[367] of LA with ICP-ToF-MS enabled 2D ultra-fast mapping of solid materials at a scan rate of between 0.3 and 30 $mm^2 h^{-1}$ to be performed, thus enabling several elements in geological RMs and in melted and partially melted micrometeorites to be quantified. Fast data acquisition across the full periodic table within several tens of microseconds was now possible and the use of a low dispersion LA chamber enhanced the spatial resolution. Quantification was achieved using glass bead calibrants prepared by fusion of matrix-matched geological RMs and normalising data by summing element oxide content to 100%. Unfortunately, for those analytes that provided a low analytical signal or for those elements, such as As, Cd, Ge, In and Sn, for which suitable RMs were lacking, generation of indicative data were only possible. Analytical issues arising by an irregular distribution of the IS, added to correct for ablation rate differences, within- and between- samples and standards were addressed[368] by use of an optical profilometer to measure the ablation volume per pixel so enabling elemental mapping data to be normalised with respect to volume.

Undertaking *quantitative imaging* by ID-ICP-MS was possible by combining[369] the sample aerosol from the ablation chamber with that generated from standards using a conventional nebuliser – cyclonic spray chamber system. Use of isotopically spiked solutions enabled transport effects to be accounted for thus enabling the quantitative imaging of Fe and Sr in NIST SRM glasses 610, 612 and 614 to be performed without recourse to matrix-matched solid calibrants.

Accurate *in situ multielemental analysis of single fluid inclusions* by LA-ICP-MS in complex geofluids *e.g.*, multi-solute basinal brines, magmatic-hydrothermal fluids or pegmatitic fluids, was possible[370] by combining microthermometric and LA-ICP-MS data in conjunction with thermodynamic modelling. This approach was applied to quantifying elements in chloride-dominated fluid inclusions where element to sodium ratios were calculated from the LA-ICP-MS data. The unknown Na concentration was calculated from modelling the chemical equilibrium between the aqueous phase and the last melting solid phase within the fluid inclusion. This was accomplished by applying the Pitzer ion-interaction model for aqueous electrolytes.

**5.3.4 Secondary ion mass spectrometry** SIMS is often the technique of choice in analysis of special samples, such as lunar samples or meteorites, because of its inherent advantages such as low sample consumption, high spatial resolution, and high sample throughput. However because of the severe matrix effects, measuring complex samples required *calibrations generated by assaying several RM*s, which was accommodated here by modifying[371] split mounts that could deploy several RMs within instrumental sample holders. Such mounts were independently prepared and could be reused many times thus reducing RM consumption. Their applicability was demonstrated in the successful determination of O and U-Pb isotopes in various CRMs (91500 zircon, Plešovice zircon, Qinghu zircon, ZN3 zircon, and NIST SRM 610 glass).

There have been issues with *data reduction protocols and error propagation algorithms* used in U-Pb geochronological studies involving SIMS that can degrade the precision and accuracy of the determinations namely: different results were obtained dependent upon how data were treated e.g. use of $^{206}$Pb/$^{238}$U or $^{238}$U/$^{206}$Pb; use of symmetrical confidence intervals could be unrealistic and that random and systematic uncertainties propagate separately, but a new algorithm written[372] in R addressed such concerns.

The *trace $H_2O$ content in quartz glasses* was determined [373] by LG-SIMS The problems associated with such measurements, *i.e.*, low vacuum caused by the large volume including the transfer and coupling column, were alleviated and the vacuum within the analytical chamber could be increased. This could create other issues such as desorption of water molecules from instrumental surfaces and challenges in maintaining the required vacuum because of the large internal volumes of such instruments. However, installing a Peltier-cooling trap step instead of a liquid nitrogen tank trap, enabled stable trap operation at -80 ºC and a vacuum pressure of 1.7 x $10^{-9}$ mbar to be maintained. To prepare test samples, small pieces of about 200 mm were selected, placed on a double adhesive tape and cast within a melted Sn-Bi alloy at 90ºC. These modifications improved the LOD from 50 mg $kg^{-1}$ to 0.15 mg $kg^{-1}$.

Data obtained by *nanoSIMS* can be strongly affected by matrix effects requiring empirically derived correction factors to be used. For example, when Li isotope ratios were determined[374] in silicate glasses, during the simultaneous measurement of $^{6}$Li, $^{7}$Li and $^{30}$Si ions, a matrix effect on $\delta^{7}$Li was clearly observed with a 19‰ maximum instrumental mass fractionation . The extent of this mass fractionation correlated with the silica content in samples, so an offline correction method was developed whereby preliminary Si concentrations were determined to subsequently derive the required correction factors. When compared within an online method where the corresponding factors were calculated using measured $^{30}$Si signals, similar performance was noted but the online method was faster and more accurate. To estimate accuracy, the absolute difference between the instrumental mass fractionation factors from the analytical data and those corrected using the calibration equation was calculated. It was observed that $\delta^7$Li was within 3‰ of the reference values for five glass standards.

**5.3.5 X-ray fluorescence spectrometry and related techniques** In *a review*[375] (90 references), the instrumental attributes (energy, energy range, resolution and sensitivity) of various commercially available WDXRF were tabulated as were a number of geological applications. Advice was provided on the selection of the most suitable instrument for a particular given application.

In the quantification[376] of *light elements,* such as C, H, O and N, in coals by means of WDXRF, coherent and incoherent spectral scattering was used in conjunction with PLS regression techniques to generate required calibrations so enabling low-Z elements to be quantified without recourse to use of instruments equipped with specialised optics. Results agreed with those obtained using an alternative elemental combustion-based analyser approach.

An instrument that incorporated both pXRF and pXRD capabilities, enabled[377] *field-based, in-situ elemental mapping* to be performed on a harzburgite material over a circular area with a 10 cm perimeter. Fast (< 30 min) analysis with a LOD of *ca*. 1% (*m/m*) was possible and data obtained for Al, Ca, Cr, Fe, Mg, Mn, Ni and Si agreed with data obtained using laboratory-based EPMA, SEM-EDS, XRD and XRD assays.

The *thickness of geological layers* was analysed by XRF [378] by interrogation of multi-element count data obtained from each layer. The shape of their resultant data frequency distributions and how well such distributions correlated were criteria for determining whether there was a degree of similarity between layers. Along similar lines, use[379] of XRF-derived data in conjunction with PCA aided the identification and estimation of the thickness of layers in deposits arising from tsunami events.

*Spectral interferences* can be problematical in the analysis of geological samples using ED TXRF as exemplified [380] in the determination of U and Th in ashes and ores where it was identified that the Th Lα signal overlapped those from Fe Kα and Rb Kα, and where the U Lα signal overlapped those from Rb Kα and Sr Kα. Use of PLSR improved the determination of Th and U in rubidium-rich samples *i.e.*, under conditions of strong line overlapping. However, in rubidium-depleted samples, spectral deconvolution was the suggested solution for U determinations. Another study addressed[381] the influences on the analyte X-ray emission signals arising from nearby atoms. Here $CaF_2$, $Na_3AlF_6$, NaF and $MgF_2$ calibrants prepared as pressed pellets, together with fused bead samples of granite (CG-1a), basalt (SMB) and limestone (KN) were analysed to obtain three sets of F calibration lines. It was noted that the $CaF_2$ calibrants were best for the analysis of fluorites, apatites or sphenes; whereas $MgF_2$ calibrants were best suited in the analysis of micas and NaF calibrants were best suited in the analysis of villiomite or cryolite materials.

The potential of synchrotron X-ray fluorescence microscopy (XFM) and X-ray backscatter diffraction mapping (XBDM) as a combinational tool for the *rapid acquisition of structural and elemental information* in geological materials, enabled[382] data to be obtained at µg $kg^{-1}$ concentrations and at scales that spanned from that of the crystal lattice ($10^{-10}$ m) to that of the specimen ($10^{-2}$ m) within a single measurement. The XFM/XBDM combination shortened assay times by two orders of magnitude compared to the time taken using the independent techniques of SEM and electron backscatter diffraction. Furthermore, complex sample preparation techniques were now not required, and it was possible also to examine features at grain and sub-grain boundaries as well as interrogate fractures.

In an attempt to obtain *speciation information*, WDXRF was used to determine $Fe^{II}/Fe^{total}$ ratios in geological samples of complex mineralogy by recording [383] the fluorescence emission from the Fe $L\alpha_{1,2}$ line which was inversely correlated with these ratios. To separate Fe $L\alpha_{1,2}$ emission peaks efficiently from the close Fe $L\beta_{1,2}$ peaks, spectral deconvolution was undertaken using the commercially available OriginPro 2022b software. Matrix effects were overcome through the calculation of a chemical index factor that enabled the accurate determination of $Fe^{II}/Fe^{total}$ ratios in different matrices. In another reported study, it was highlighted[384] that the chemical nature of the sample did not have any impact on the ratios of the close Fe $K\beta_5$/ Fe $K\beta_{1,3}$ lines that correlated linearly with the $FeO/Fe_2O_{3total}$ (*w/w*) ratios, so allowing Fe speciation to be elucidated. Although, a high-resolution WDXRF setup was required for such speciation measurements *i.e.*, use of a LiF analyzer crystal with a 0.13º collimator, this approach offered important advantages such as high sample throughput, and minimum sample preparation without recourse to using radioactive sources.

A transition-edge sensor (TES) was applied for the first time as a *new detector* for analysis[385] by µ-XANES in the hard X-ray region. This TES included a thermometer with the ability to measure temperature changes after X-ray absorption and determination of both U distribution at the micro-scale in biotite, together with information on the U chemical species was now possible. Unlike when utilising a conventional SDD, effective separation of the fluorescent emissions of U Lα1 and Rb Kα lines was now possible when using the TES, which enabled the accurate mapping of trace U in the presence of high amounts of Rb. Furthermore, the S/B was close to 46 times higher than that achieved using a conventional SDD.

**5.3.6 Other techniques** The quantification[386] of *bromine in glasses and minerals* was undertaken by EPMA by measuring the Br $K_\alpha$ X-ray emission (11.909 keV) in combination with use of a LiF diffracting crystal because, unlike at the Br $L_\beta$ line, aluminium emissions did not interfere. Results obtained for scapolite-group minerals by EPMA compared favourably with those results obtained using alternatives techniques such as INAA, LA-ICP-MS, noble gas method or SIMS. No matrix-matched calibrants were required and other advantages of EPMA were exploited namely: its high spatial resolution (≤10 µm) capability; its ability to perform non-destructive assays and the fact that the EPMA instrument is typically less expensive than some of the alternatives.

Use of MC SHRIMP was reported[387] for determining *isotope ratios* in Fe-Mg containing oxidic and salicaceous materials. The Earth's magnetic field caused isotope-dependent trajectory deviations for $^{24}Mg^+$, $^{25}Mg^+$ and $^{26}Mg^+$ within the instrument's sample chamber that significantly affected the isotope ratios determined, but such deviations were corrected by applying a current to two Helmholtz coils so aligning the three Mg ion beams. Under these circumstances, instrumental mass fractionation was dependent on the mineral structure, whereas it was negligibly affected by the chemical composition. As such differences were constant however for a given mineral *i.e.*, structure, it was possible to calculate fractionation correction factors for any given mineral thus permitting the analysis of different specimens with a good accuracy ($\delta^{26}$Mg = 0.3 ‰) using a single stated mineral as RM.

*Multimodal assays* offer new possibilities, such as the synergistic combination of LIBS with hyperspectral imaging (NIR-SWIR)[388], for mineral identification. Two distinct approaches were explored: a traditional sensor fusion, that allows increasing the information supplied by the two techniques; and, a knowledge distillation approach, in which knowledge is condensed and transferred from a complex to a simpler model, where LIBS was used as an autonomous supervisor for hyperspectral imaging. In this second approach, a teacher – student scheme was adopted and in assessing accuracy and robustness of a measurement mode, the teacher, was used to generate labels for a training dataset, subsequently giving support to the supervised training procedure using the dataset of the second spectral imaging modality, the student. This novel approach was used to train a model taking only NIR-SWIR data as input using the LIBS as a supervisor during training.

Planetary mineralogical samples typically contain *osmium* at low concentrations, an impediment for undertaking highly precise $^{184}$Os/$^{188}$Os, $^{186}$Os/$^{188}$Os, and $^{187}$Os/$^{188}$Os isotopic ratio measurements. However such measurements were possible by operating[389] a NTIMS instrument in a mode that allowed the three ratios to be simultaneously measured. The mode required the system to be equipped with 9 FCs with $10^{12}$ Ω and $10^{13}$ Ω amplifiers together with two compact discrete dynodes (CDDs). The precisions reported for a 12 ng Os sample were 2, 0.061, and 0.050‰ (2 RSD), for the $^{184}$Os/$^{188}$Os, $^{186}$Os/$^{188}$Os, and $^{187}$Os/$^{188}$Os ratios, respectively. The method avoided non-linear signal change in the instrument during the analysis and removed oxygen isobaric interferences caused by $PtO_2$ and $PtO_3$.

Four modifications were made[390] to an EA-IRMS instrument to *boost sensitivity in the determination of the N isotope ratio* ($\delta^{15}$N) in geological samples that contained only trace nitrogen concentrations. These included: reducing the diameter of the reaction tube and hence the dead volume; replacing magnesium perchlorate in the water trap with soda lime; using a needle valve to better control split flow rates and modifying GC operational parameters through selection of an appropriate GC column with optimal carrier gas flow rates and split flow ratios. Provided that a sample containing > 12 µg N could be analysed, a SD of <0.2 ‰ was achievable.

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

| Element | Matrix | Sample preparation | Technique | Comment | Reference |
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| Ag | Silicate rocks: basalt, andesite, granite, rhyolite and ferromanganese crusts | Four-step chromatographic procedure involving the use of an anion resin Bio-Rad AG® 1-X8, to separate first the major elements and, afterwards, Zn and Cd, and a cation AG® 50 W-X8 resin to further separate Ag from Nb and minor elements | MC-ICP-MS | Recoveries > 95%. $\delta^{109}Ag_{SRM978a}$ value of doped solutions: (0.00 ± 0.05‰; 2SD, n = 4) in agreement with the recommended values. External precision: 0.05‰ (2SD). Seven USGS RMs were analyzed: basalt (BCR-2 and BIR-1), andesite (AGV-2), granite (GSP-2 and G-2), rhyolite (RGM-2), and ferromanganese crusts (NOD-P-1). $\delta^{109}Ag_{SRM978a}$ varied from −0.24 ± 0.05‰ to 0.20 ± 0.05‰, *i.e.*, Ag isotopes fractionated in silicate rocks | 295 |
| B | Silicates | HF sample digestion with low temperature evaporation and sequential chemical purification with Dowex AG® 50W-X8 cation-exchange resin; and an amberlite anion exchange B-specific (IRA 743) resin | MC-ICP-MS | $\delta^{11}B_{SRM\ 951}$ carbonate values (NIST RM 8301, (Coral): 24.24 ± 0.11‰. Intermediate precision: <±0.2 and 0.6 ‰ for carbonate and silicate RMs, respectively. Good agreement between $\delta^{11}B$, for carbonate and silicate RMs, with the mentioned sample preparation method and a fusion and purification procedure | 296 |
| C and O isotopes | Silicate | Quartz (Polaris, $\delta^{18}O$ = 13.0‰) grinding with a layer of alcohol and three different carbonate sources (KH-2 | CF-IRMS | Results affected by instrumental non-linearity for small amounts of gas, the amount of $CO_2$ (blank effect) and the content of neutral silicate particles (matrix effect). The second factor precludes the determined carbonate | 391 |

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| | | limestone and Ko and MSA-8 calcites) in a polished agate mortar. Then drying at 105 ºC | | fraction by shifting the isotope ratios towards an underestimated content of heavy isotopes ($^{13}$C and $^{18}$O). Low carbonate fractions (1-2%) induce ppm deviations from the true $\delta^{13}$C and $\delta^{18}$O with an 20-40 % underestimation in carbonate content | |
| Ca | Basalt, andesite, ferromanganese nodules, granodiorite, carbonatite, dunnite | Digestion with HF and $HNO_3$ at 120ºC for 12 h, evaporation and acid dissolution cycles. Purification with N,N,N',N'-tetra-n-octyldiglycolamide (TODGA) chromatography resin | MC-ICP-MS | $^{44}$Ca/$^{40}$Ca ratios were determined in eight different geological RMs. To avoid isobaric interference caused by $^{40}$Ar, cold plasma conditions were selected. Matrix effects removed by keeping the concentration of interferents (*i.e.*, Al, Mg, K, Na, and Sr) below 1% that of Ca and below ‰ for Fe. Long term precision for $\delta^{44/40}$Ca and $\delta^{44/42}$Ca values < 0.10‰ | 392 |
| Cd isotopes | Soil, rock and manganese nodules | Digestion and Cd purification with an AG® MP-1M macroporous anion-exchange resin followed by a UTEVA resin | Double spike MC-ICP-MS | The combination separates Cd from Sn, Mo, organic matter and avoids the P-related anomalous shifts in the Cd isotope measurement. Recoveries > 99% and procedural blank < 20 pg. $\delta^{114/110}$Cd values of rock, soil and manganese nodule RMs determined with respect to NIST SRM 3108 (cadmium standard solution) agree within analytical uncertainty with previous studies. Long-term external precision of $\delta^{114/110}$Cd BCR-2: 0.04‰ (n = 10, 2SD). Minimum sample size: 10 ng | 393 |
| Cd isotopes | Mn nodule, igneous rock, shale, soil, | Digestion and single-step Cd purification with an AG® | Double spike MC-ICP-MS | >99% of Sn removed. $\delta^{114/110}$Cd with respect to NIST SRM 3108 (cadmium standard solution): USGS RM BHVO-2 (basalt) = 0.055 ± 0.026‰ (2SD, n = 2); | 394 |

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| | and sediment RMs | MP-1M macroporous anion-exchange resin | | USGS RM GSP-2 (granodiorite) = -0.191 ± 0.035‰ (2SD, n = 4); USGS RM COQ-1 (carbonatite) = 0.143 ± 0.053‰ (2SD, n = 6); CNRCG RM GSR-2 (dolomite) = 0.162 ± 0.044‰ (2SD, n = 9); USGS RMs NOD-P-1 and NOD-A-1 (manganese nodules) = 0.185 ± 0.048‰ (2SD, n = 9), 0.184 ± 0.057‰ (2SD, n = 11), respectively; USGS RM SGR-1b (shale) = 0.076 ± 0.046‰ (2SD, n = 6); Chinese IGGP RMs GSD-4a, GSD-5a, GSD-3a (stream sediments) = 0.004 ± 0.047‰ (2SD, n = 9), 0.062 ± 0.046‰ (2SD, n = 6), -0.095 ± 0.055‰ (2SD, n = 6), respectively; NIST RMs 2711a, GSS-1a (soils) = 0.568 ± 0.057‰ (2SD, n = 7), -0.078 ± 0.050‰ (2SD, n = 8), respectively | |
| Cr isotopes | Dunite, harzburgite, serpentinite, basalt, rhyolite, syenite, stream sediment, dolomite | Sample dissolution with HNO$_3$ and HF, evaporation, redissolution in appropriate reagents depending on the sample. Three-step ion exchange chromatography with an AG® 50W-X8 cation-exchange resin | TIMS | Using DS-TE-TIMS the method lowered sample consumption to ~20 ng per $^{53}$Cr/$^{52}$Cr measurement. Cr procedural blank <0.5 ng. Cr recovery: 93 ± 8% (2SD, n = 7). External precision: 0.01 – 0.07 ‰ (2SD) | [395] |
| Fe isotopes | Rich Cr oxide minerals | Fe$_2$O$_3$ and Fe$_3$O$_4$ NPs were combined with pure chromium solutions | fs LA-MC-ICP-MS | A fs laser and ICP-MS under wet conditions are used to overcome matrix effects. The Cr fractionation factor was obtained for isobaric interference correction (*i.e.*, $^{54}$Cr on $^{54}$Fe). Corrected δ$^{54}$Fe for hematite and magnetite | [396] |

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| | | | | samples with Cr/Fe ratio = 1.27 agreed with reference values. Long term reproducibility uncertainty = 0.1 ‰ | |
| I | Soil and sediments | Drying and sodium carbonate and zinc oxide semi-melting by heating at 750ºC in a muffle furnace. Then hot water washing, addition of anhydrous ethanol and boiling of the mixture, addition of Rh as internal standard, and addition of ascorbic acid to the supernatant. Addition of cation-exchange resin and liquid phase analysis | ICP-MS | The method avoided problems such as incomplete melting, strong memory effects, and poor stability during the analysis and testing process of iodine. Accurate results were obtained with an RSD (n = 12) of 1.83–2.80% and LOQ = 0.13 µg $g^{-1}$ | [397] |
| Li isotopes | Silicate glass | *In situ* analysis. Single 120 – 150 µm spot diameter and focusing the laser on the sample surface | ns-LA-ICP-MS | $^{6}$Li and $^{7}$Li observed signal spikes were removed according to a 2SD rejection criterion. Best results were achieved for samples with >40 ppm Li based on matrix-matched standard. An internal precision of 3‰ was achieved for these samples. $SiO_2$ contents deviating from the bracketing standard caused matrix effects, thus giving rise to $\delta^{7}$Li fractionation | [398] |
| Lu-Hf dating | Apatite | Dissolution of apatite in HCl, addition of $^{176}$Lu-$^{180}$Hf tracer. Use of two-stage | ICP-MS | DGA-normal chromatography column eliminated the interfering elements (Yb, Lu, and W), less than 1 pg of Lu in the analyzed apatite Hf solution. Hf recovery: | [399] |

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| | | chromatographic separation. Elution through an Eichrom Ln resin and further purification of the Hf fraction by means of a Eichrom DGA-normal resin, coated with chelate forming extractant and combining with trivalent metal ions after drying and re-dissolution | | 100%. Apatite Lu–Hf ages of Otter Lake, Bancroft, and Durango: 1047.6 ± 3.4 Ma, 1092 ± 17 Ma, and 31.1 ± 1.1 Ma, respectively. Apatite Lu–Hf isochrons independent of the initial isotopic composition. The Hf content in apatite was low and a big sample was required. Both points challenged the applicability of the method to rocks where apatite was a minor phase (*e.g.*, igneous and metamorphic) | |
| Nd | Basalts, granites, sediments and sedimentary rocks | Digestion with a $HNO_3$-HF mixture and dissolution with HCl. A single cation-exchange column (AG® 50W-X8 resin) was used to extract Nd. The eluate was dried and re-digested | TIMS | The method was rapid (2-3 h) The $^{145}$Nd/$^{146}$Nd ratio was used to correct for fractionation on $^{143}$Nd/$^{146}$Nd ratio. The isobaric $^{144}$Sm interference was eliminated | 400 |
| Nd | Carbonatite, dolerite, andesite, basalt, granite, rhyolite, granodiorite, manganese | Samples were digested for 5 days at 120ºC with HF and $HNO_3$, drying and re-dissolving several times. Purification with a Eichrom DGA resin (TODGA type). Double spike used to correct | DS-TIMS | Yields of the geological samples > 99%. $\delta^{146/148}$Nd for a total of twelve geological RMs (USGS RMs COQ-1 (carbonatite), DNC-1a (dolerite), AGV-1 (andesite), AGV-2 (andesite), BHVO-2 (basalt), BCR-2 (basalt), G-2 (granite), RGM-1 (rhyolite), GSP-2 (granodiorite), NOD-A-1 (manganese nodule), NOD-P-1 (manganese nodule), and SDC-1 (mica schist)were reported. Radiogenic $^{143}$Nd/$^{144}$Nd of RMs were calculated by a | 320 |

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| | nodule, mica schist | for mass-dependent fractionation | | double spike deconvolution with a precision of ≤ 5 ppm (2SE) that agreed with published values | |
| Nd, Sr and Pb | Andesite, basalts, granite, granodiorite, rhyolite, nepheline syenite, andesite | Decomposition and purification on two tandem chromatographic columns filled with (CMPO) dissolved in tributyl phosphate and Sr specific resins (based on the crown ether ditert-butylcyclohexano-18 crown-6 in 1-octanol). Sr and Pb fractions suitable for isotopic analyses were directly isolated from the Sr resin. An additional column of DGA resin (based on tetra(n-octyl)diglycolamide) was used, to obtain a Nd fraction isolated from the other LREEs | ICP-MS | Eleven geological RMs spanning a wide range of major element concentrations were analysed: USGS RMs AGV-2 (andesite), BCR-2, BHVO-2 and BIR-1a (basalts), G-2 (granite), GSP-2 (granodiorite), RGM-1 (rhyolite), and STM-1 (nepheline syenite), GJS RMs JA-1 (andesite) and JB-3 (basalt), and CRPG RM BE-N (basalt). Satisfactory recoveries and blanks were obtained for the three studied elements. Measured isotope ratios agreed well with published values. All the steps were completed in just one day | [401] |
| Ni | Mafic and ultramafic rocks, basalt, granodiorite, manganese | Samples acid digestion. Purification with three columns in series: Chelex-100, for the removal of K, Na, Ca, Mg, Al, Fe, Mn, Ba, | MC-ICP-MS | Ni recovery > 96%; procedural blank below 1.2 ng and an overall precision better than 0.09 ‰ (2SD). $^{61}$Ni–$^{62}$Ni double spike corrected for fractionation in the chemical procedure and instrumental discrimination bias. $\delta^{60}$Ni$_{SRM986}$ for RMs (BCR-2, GSR-3 (basalts), GSP-2 | [402] |

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| | nodule, cobalt rich-crust, shale and sediments RMs | Cr, and certain amounts of Zn and Ti, AGMP-1M, to eliminate Fe, Mn, Co, Cu, Zn, V, and Ti, and AGMP-50, to remove any remaining Ca, Mg, and Al | | (granite), NOD-A-1 (iron–manganese nodule), GSMC-1 (cobalt rich crust), SDO-1, SGR-1 (shales), and GSD-5a and GSD-23 (river sediments) were consistent with previously published work | |
| Np, Pu | Soils and Sediments | Ashing, spiking with $^{242}$Pu, leaching, co-precipitation and use of a single extraction with a chromatographic column (TK200), with ($NH_2OH{\cdot}HCl$)/HCl as the eluent | ICP-MS/MS | Oxygen was used as reaction gas to remove the $UH^+$ interference on Pu isotopes. Recoveries were higher than 70%. $^{237}$Np, $^{239}$Pu, and $^{240}$Pu were determined at femtogram levels, with $^{242}$Pu as a reliable tracer in samples with U/Np and U/Pu atom ratios of up to $10^{17}$ and $10^{12}$. Uranium interference was reduced by a factor of $3.2 \times 10^7$ | 217 |
| Pu | Soils, Sediments | Ashing, leaching, co-precipitation and use of two sequential chromatographic columns (TK200), with HCl and $NH_2OH{\cdot}HCl$ as eluting solutions | ICP-MS/MS | $^{238}$Pu, $^{239}$Pu, $^{240}$Pu, and $^{241}$Pu were simultaneously determined at femtogram levels. Uranium interference was reduced by a factor of $2.12 \times 10^9$. He and $NH_3$ were used as reaction gases to remove the $UH^+$ polyatomic | 403 |
| Pu | Soils | Ashing (550ºC), leaching with nitric acid, spiking with $^{242}$Pu and addition of $NaNO_2$ to maintain the analyte as $Pu^{IV}$. Plutonium was | ICP-MS/MS | The method removed the spectral interference of U on Pu and was validated by analysing the sediment IAEA CRM 384 (Fangataufa Sediment). Recoveries improved from 61 to 87% ICP-MS/MS blanks: 0.012 ± 0.008 µg $kg^{-1}$ ($^{238}$U) and 0.066 ± 0.121 pg $kg^{-1}$ ($^{239+240}$Pu). Respective LODs were: 0.012 µg $kg^{-1}$ and 0.18 pg $kg^{-1}$ | 404 |

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| | | separated with a TEVA column | | | |
| REEs | Sediments, soils and basalts | $HNO_3$ and HF digestion with a high-pressure bomb method | ICP-MS | Micro-USN sample introduction for a 10 fold increase in sensitivity. Low registered ICP-MS oxide ratios ($^{139}La^{16}O^+/^{139}La^+$ = 0.79%, $^{140}Ce^{16}O^+/^{140}Ce^+$ = 0.73%, $^{150}Sm^{16}O^+/^{150}Sm^+$ = 0.06%, $^{159}Tb^{16}O^+/^{159}Tb^+$ = 0.10%) LODs for 16 REEs from 0.03 (Tm and Lu) to 1.07 (Sc) ng $L^{-1.}$ Repeatability (RSD, n = 8) between 0.3% (Eu, 10 ng $mL^{-1}$) and 3.4% (Lu, 1 ng $mL^{-1}$) | 204 |
| REEs | USGS BCR-2 and BIR-1A RMs | BCR-2: Flux fusion, iron coprecipitation and bulk REE separation with a column. BIR-1A: HF and $HNO_3$ dissolution, iron coprecipitation and bulk REE separation with an ion-exchange column | MC-ICP-MS | A commercial desolvation system was used. Spike/sample isotope ratios were measured in unseparated REEs with oxide-minimizing tuning. BCR-2: Concentrations for Ce, Nd, Sm, Eu, Dy, Er, and Yb fell within 2% of accepted values. BIR-1-: REEs concentrations within 3% of consensus values with 0.3% RSD (n = 3) | 405 |
| Re, Os | Organic rich sedimentary and mafic rocks | $HNO_3$ digestion at 230 ºC for 24 h | TIMS | The method increased the accuracy of Re-Os isotope analysis, because of the low blank levels. Os isotopes in mafic rocks did not produce fractionation at temperatures above 200ºC | 406 |
| Rh | Geological RMs | Rh preconcentration by $Sb_2O_3$ fire assay and further microwave digestion of the | ICP-MS | Cold plasma conditions were selected. The cell in KED mode removed interferences of $^{206}Pb^{2+}$ and $^{40}Ar^{63}Cu^+$ on $^{103}Rh^+$. LOD: 0.012 ng $g^{-1}$ | 407 |

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| | | granules employing 40% (*v/v*) *aqua regia* | | | |
| S | Carbonates and archaean rocks | Sample purification with an anion-exchange resin (AG1X8) | MC-ICP-MS | $\delta^{34}$S intermediate precision for 30 nmol S: 0.15‰ (2SD) at 95% confidence. $\Delta^{33}$S, Intermediate precision: 0.05‰ (2SD) | 408 |
| Si | Silicon oxide, basalt and diatomite | Alkaline fusion, dissolution with ultrapure water, loading on an AG® 50W-X12 resin and subsequent silicon elution with water. pH adjustment with nitric acid | MC-ICP-MS | Under dry plasma conditions, no significant offset in $\delta^{30}$Si values outside the range of analytical precision (±0.09‰, 2SD) were caused by chloride, sulphate or dissolved organic carbon. It was recommended to remove organic matter by UV photolysis | 409 |
| Sm | Basalt, andesite, granodiorite, granite, nepheline, syenite, manganese nodule, and marine sediment | $HNO_3$ – HF dissolution on a hot plate under reflux for 7 days; followed by drying and redissolution with concentrated HCl. Chromatographic isolation with AG® 50W-X12 and TODGA columns | MC-ICP-MS | Sm purification (90.4±0.3% yield) in complex matrices containing Nd, Eu and Gd. Procedural blank: < 30 pg. $\delta^{152/149}$Sm long term intermediate precision 0.04‰, 2SD, based on standard-sample bracketing with NIST SRM 3147a (Samarium standard solution), and Eu internal normalisation to correct for instrumental mass bias (4-8 times better than for the existing methods). For 11 RMs, $\delta^{152/149}$Sm values from -0.07‰ (andesite) to 0.15‰ (marine sediment) | 410 |
| Sm, Nd | Rock (basalt, mafic, andesite and granodioritic) | Sample digestion with concentrated HF–$HNO_3$–$HClO_4$ followed by chemical | MC-ICP-MS | Recoveries were 100% and isobaric interferences were corrected for by applying a mathematical method. The $^{147}$Sm/$^{144}$Nd and $^{143}$Nd/$^{144}$Nd ratios were simultaneously determined through a single analytical session for five | 411 |

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| | and powder CRMs | purification with a TODGA chromatography resin | | rock powder CRMs. Accuracy and precision were similar as for ID | |
| Sr | Rhyolite, basalt, diabase, granodiorite, biotite, phlogopite and $SrCO_3$ | Sample digestion with HF, $HNO_3$ and $HClO_4$ at 120 ºC for 1 week; with several evaporation and HCl re-dissolution cycles. Purification on AG® 50 W-X12 cation resin, combined with Chelex-100 chelating and AG50-X8 resins | MC-ICP-MS | The method was validated by $^{87}Sr/^{86}Sr$ determination in ten RMs: GSJ JR-1, JR-2 (rhyolite) and JB-2 (basalt); USGS BCR-2, BHVO-2 (basalt), W-2 (diabase) and GSP-2 (granodiorite); CRPG Mica-Fe (biotite) and Mica-mg (phlogopite); NIST SRM 987 ($SrCO_3$). Sr was purified in geological samples with high Rb/Sr mass ratios without the need for elution or evaporation steps, saving analysis time and costs even though large volume of eluent was required | [412] |
| Sr, Sm, Nd | Five igneous rock materials (basalts, andesite and granodiorite) and a meteorite (jilin) | Multiple dissolution to dryness steps with concentrated $HNO_3$ and HF; then HCl; followed by $HNO_3$ and centrifugation. Purification with a single-column separation procedure using TODGA-normal resin (DN-B100-S) | TIMS | Close to 3 mg sample mass were analysed with a total chemical procedural blank for Sr, Nd, and Sm of < 80, 7, and 3 pg, respectively. Recoveries > 91%. Static measurement of Sr, Nd, and Sm isotopes were performed with TIMS equipped with Faraday cups and $10^{12}$ and $10^{13}$ $\Omega$ amplifiers. Three single calibration solutions were used NIST SRM 987f (Strontium Carbonate) Sr, La Jolla Nd, and Alfa Aesar Sm yielding $^{87}Sr/^{86}Sr$, $^{142}Nd/^{144}Nd$, $^{143}Nd/^{144}Nd$, $^{149}Sm/^{152}Sm$ and $^{150}Sm/^{152}Sm$ ratios of 0.710248 ± 11, 141 846 ± 25, 0.511852 ± 13, 0.516845 ± 17, and 0.275998 ± 9 (2SD), respectively. All results agreed with the published data with a precision of 11–25 ppm (2 RSD) | [413] |

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| Sr | Apatite | Dissolution and purification | LA-MC-ICP-MS | Apatite ablated volumes from 3000 to 75000 $\mu m^3$. Two data reduction methods tested: *(1)* measured intensities corrected for gas blank and instrumental mass bias; and *(2)* additional correction for isobaric interferences of $^{87}Rb^+$, $^{166,168,170}Er^{++}$, $^{170, 172, 174,176}Yb^{++}$, $^{40}Ca^{44}Ca^+$, $^{40}Ca^{46}Ca^+$, $^{44}Ca^{43}Ca^+$ and $^{40}Ca^{48}Ca^+$. $^{87}Sr/^{86}Sr$ 100 ppm (2SD) precision with a 50 µm laser ablation beam (Method *2*, more accurate only when $^{173}Yb^{++}$ is above the $LOD_{global}$, 3 $s_{all\ the\ blank\ measurements}$) and better than 3000 ppm at 10 µm with Method *1* | [414] |
| Thirty-one elements including U, Th, and Pb, and REEs, | Zirconolite present in Lunar basaltic and granitic rocks | Carbon coating at a 25 µm thickness | EMPA | Age of the zirconolites: 4332 ± 14 Ma (2SD, n = 20), consistent with the U–Pb age (4340.9 ± 7.5 Ma; 2SD) of zircon grains from the same clast measured by an ion microprobe | [415] |
| U | Uranyl nitrate | High temperature dissolution with $HNO_3$, HF and further addition of $HClO_4$. Finally, samples were purified with a UTEVA resin | ICP-MS/MS | An efficient desolvation system and the addition of oxygen to the collision/reaction cell allowed the precise determination of the $^{236}U/^{238}U$ isotopic ratio. The method was validated with an in-house AMS standard of uranyl nitrate | [416] |
| V | Igneous rock, manganese nodules, carbonaceous | Two-stage chromatography method using cation- and anion-exchange resins for V purification and separation | MC-ICP-MS | V recovery was 99%, the total procedural blank was < 2 ng. The V isotope compositions of 13 RMs were measured. Long-term reproducibility was better than ± 0.10 %0 (2SD) for $d^{51}V$. $d^{51}V$ values of two in-house | [161] |

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| | siliceous shale, sediment and soil. | from interfering matrix elements (Ti and Cr) | | standard solutions were 0.04 ± 0.08 ‰ (2SD, n = 121) and −1.23 ± 0.08 ‰ (2SD, n = 91) | |
| W | Basalt | Samples were digested with HF-$HNO_3$ at 150ºC for 48 h, followed by multi-step treatment with different acid mixes. The final liquid phase was purified by using a TEVA resin | MC-ICP-MS | W recoveries lay between 93.6 ± 4.7 (2SD, n = 3) and 98.5 ± 1.3 % (2SD, n = 3). Total procedure blank was 0.46 ± 0.06 ng. Bracketed mean $^{182}W/^{184}W$ ratio was used to calculate $\mu^{182}W_{N6/4}$. This parameter was determined in basalt USGS RMs: BHVO-2, BCR-2 and JB-3 and the values were consistent with previously published works with an intermediate measurement precision as low as 5 ppm (2SD) | 417 |
| Zr, Lu-Hf, U-Pb isotope ratios | Zircon | Dissolution in a $HNO_3$ – HF mixture followed by a four-step chromatographic purification to allow separation of: U and Pb from the matrix, then a late purified $^{91}Zr$-$^{96}Zr$ double spike was then added; before separation of Zr from Hf, Hf from Ti, and Zr from Mo | MC-ICP-MS | Zr isotope results for four zircon RMs (91500, Mud Tank, Plesovice and Penglai) agreed with published values. $\delta^{94}Zr_{IPGP\text{-}Zr}$: -0.041 ± 0.015‰ (2SD, n = 11), 0.018 ± 0.013‰ (2SD, n = 6), 0.089 ± 0.020‰ (n = 3) and -0.117 ± 0.021‰ (2SD, n = 3), respectively. $^{176}Hf/^{177}Hf$ ratios for RMs agreed with published ones. Thus, addition of a purified Zr double spike (with a Zr/Hf ratio of ~ 18,000) did not affect the $^{176}Hf/^{177}Hf$ results | 418 |

### 5.4. Software and databases

The increasing volume of analytical data now being generated by novel, faster, more accurate and precise instrumental techniques necessitates *new ways for extracting geochemical information*. A review [419](240 references) highlighted selected applications of machine learning tools to help identify rocks and sediments, for digital mapping purposes, to assist in soil physical and chemical properties prediction, *e.g.,* predicting the abundance of major elements in dust, rocks, and soils under Mars conditions, and deep space exploration *e.g.,* elemental distributions of lunar surface, lunar surface $TiO_2$ abundance maps, to elucidate the Martian surface mineral distribution and to determine its surface age. These tools help to interpret spectroscopy data, to develop numerical modelling and molecular ML. In contrast, applying ML techniques was problematic when minerals exist as a solid (*e.g.,* chlorite) rather than a single, stoichiometric ideal. In these cases, sampling of the mineral phases surrounding that of interest can be a significant source of error. A dataset of more than 3,000 major and minor multielemental analyses of chlorite by means of LA-ICPMS and EPMA was interrogated[420] when, interestingly, it was verified that 7.4% of these assays were from non-chlorite materials. Therefore, ML screening could be a useful tool for generating robust data obtained from *in situ* analyses.

*Machine learning* was also applied to U-Pb dating studies where obtaining good results in certain minerals is often hampered by their extremely low U concentrations. Therefore in order to ascertain[421] U content in garnets, predictive analysis was undertaken drawing upon data for other major and minor elements obtained by EPMA. A database was compiled, mostly from the publicly available GEOROC database, which contains elemental data for 4,366 garnet samples, that PCA was able to classify into two independent groups, namely uranium-rich or -poor minerals. Additionally, a supervised machine learning method (neural network) was developed to train a data analysis model with the ability to discriminate between U-rich and -poor ($<2$ mg kg$^{-1}$) samples with a predictive accuracy as high as 92%. The discrimination tool was especially useful in the assessment of garnets from kimberlites, high-grade metamorphic rocks and intermediate to felsic magmatic rocks.

A novel *software algorithm*, Isoclock, to correct RM data obtained by LA-ICP-MS for common Pb and to calculate isotopic fractionation and written in Python was released[422]. Two calculation modes were possible: firstly where the age of an RM is known or, secondly in which the measured U–Pb isotope ratio data of the RM could be inputted.

Undertaking quantitative 2D mapping exercises is a challenge when heterogenous mineral phases are interrogated using LA-ICP-MS and here use of *data reduction and processing tools* were invaluable. One such open-source tool was XMapTools[423] that enabled 2D density plots to be automatically constructed. The use of the open-source LinuxCNC software, originally designed to control CNC machinery but applied here to better control the movement of the laser ablation stage, facilitated better depth profiling exercises to be conducted in the analysis of olivine crystals.[424]. The subsequent elemental data obtained agreed with EPMA measurements and the Mg and Fe isotopic data information was precise with $\delta^{24}$Mg ≤ 0.12 ‰ and $\delta^{56}$Fe ≤ 0.15 ‰.

Use of a customised *Iolite software package* improved[283] Sr isotopic measurements using LA-ICP-MS by performing baseline corrections in the removal of krypton (an impurity in the argon gas) interferences by calculating βRb and Rb-Sr fractionation factors (from repeated analyses of BCR-2G glass); by peak-stripping of the $^{87}$Rb interferent (using the measured $^{85}$Rb and canonical $^{87}$Rb/$^{85}$Rb) and by correction for other isobaric interferences *e.g.*, $Er^{2+}$, $Lu^{2+}$ and $Yb^{2+}$.

In a *new fundamental parameter approach* for the quantification of environmental matrices by EDXRF[425], the measured fluorescent intensities of samples were used together with either reference data of experimental absorption at a single energy or the known concentration of an internal standard in the sample. The claimed advantages of this procedure were: it provided information on the residual matrix and the analytes; it was based only on simple absorption calculations supported by tabulated fundamental parameters and absorption data; the determined concentration was independent of the number of elements quantified; quantification was possible if samples contained a known concentration of internal standard, and no special sample preparation methods were required. Validation was performed by analysing NIST SRM 2711 (Montana soil) and SRM 2704 (Buffalo River sediment) with relative measurement errors of 2-8%.

## Glossary of abbreviations

| | |
|---|---|
| AA | atomic absorption |
| AAS | atomic absorption spectrometry |
| AEC | anion exclusion chromatography |
| AES | atomic emission spectrometry |
| $AF_4$ | asymmetric flow field-flow fractionation |
| AI | Artificial intelligence |
| AMS | accelerator mass spectrometry |
| ANN | Artificial neural networks |
| AOF | adsorbable organic fluorine |
| APM | atmospheric particulate matter |
| BAM | Federal Institute for Materials Research and Testing (Germany) |
| BCR | Community Bureau of Reference (of the Commission of the European Communities) |
| BEC | background equivalent concentration |
| BSE | Backscattered electron |
| CCP | capacitively coupled plasma |
| CENA-USP | Centro de Energia Nuclear e Agricultura-Universidade de São Paulo |
| CF | calibration free |
| CI | confidence interval |
| CIMS | chemical ionisation mass spectrometry |
| CMPO | octyl(phenyl)-N,Ndiisobutylcarbamoylmethylphosphine oxide |
| CNACIS | China National Analysis Centre for Iron and Steel |
| CNC | Computer numerical control |
| CPE | cloud point extraction |
| CRC | collision/reaction cell |
| CRCCRM | Chinese Research Centre for Certified Reference Materials |
| CRM | certified reference material |
| CRT | creatine |
| CS | continuum source |
| CV | cold vapour |
| CVG | chemical vapor generation |
| DBD | dielectric barrier detector |
| DES | Deep eutectic solvent |
| DLS | dynamic light scattering |
| DOC | dissolved organic matter |
| DOM | dissolved organic matter |
| DS-TE-TIMS | Double spike-total evaporation-thermal ionization mass spectrometry |
| EA | elemental analyser |
| EA-IRMS | Elemental analyzer-isotope ratio mass spectrometer |
| eBC | equivalent black carbon |

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| EC | Environment Canada |
| ECCC | Environment and climate change Canada |
| ED | energy dispersive |
| EDM | External detector method |
| EDS | energy dispersive x-ray spectroscopy |
| EDTA | Ethylenediaminetetraacetic acid |
| EDXRF | Energy dispersive X-ray fluorescence |
| EF | enrichment factor |
| EOF | extractable organic fluorine |
| EPMA | electron probe microanalysis |
| ERM | European Reference Material |
| ESI | electrospray ionisation |
| ETAAS | electrothermal atomic absorption spectrometry |
| ETV | electrothermal vapourisation |
| FAAS | flame atomic absorption spectrometry |
| FC | faraday cup |
| fs | femtosecond |
| GC | gas chromatography |
| GC-CV-AFS | gas chromatography-cold vapor generation-atomic fluorescence spectroscopy |
| GC-IRMS | gas chromatography isotope ratio mass spectrometry |
| GEM | gaseous elemental mercury |
| GeoPT | Proficiency Testing Scheme organised by the International Association of Geoanalysts |
| GFAAS | graphite furnace atomic absorption spectrometer |
| GLS | gas liquid separator |
| GO | graphene oxide |
| GOM | gaseous oxidised mercury |
| GSR | gunshot residues |
| Hgp | particulate phase mercury |
| HG | hydride generation |
| HPLC | high performance liquid chromatography |
| HR | high resolution |
| HR-CS-GFAAS | high resolution continuum source graphite furnace atomic absorption spectrometer |
| HTC | High-temperature conversion |
| IAEA | International Atomic Energy Agency |
| IC | ion chromatography |
| ICP | inductively coupled plasma |
| ICP-MS | inductively coupled plasma mass spectrometry |
| ICP-OES | inductively coupled plasma optical emission spectrometry |
| ICP-TOF-MS | time of flight inductively coupled plasma mass spectrometry |

| | |
|---|---|
| ID | isotope dilution |
| ID-TIMS | Isotopic dilution thermal ionization mass spectrometry |
| IGGE | Institute of Geophysical and Geochemical Exploration |
| IMF | Instrumental mass fractionation |
| INAA | Instrumental neutron activation analysis |
| IRMS | isotope ratio mass spectrometry |
| IS | internal standard |
| IUPAC | International Union of Pure and Applied Chemistry |
| JSAC | Japan Society for Analytical Chemistry |
| KED | kinetic energy discrimination |
| KRISS | Korean Research Institute of Standards and Science |
| LA | laser ablation |
| LA-ICP-MS | laser ablation-inductively coupled plasma mass spectrometry |
| LF-IRMS | Laser fluorination isotope ratio mass spectrometry |
| LG-SIMS | Large-geometry secondary ion mass spectrometry |
| LIBS | laser-induced breakdown spectroscopy |
| LIBS-LIF | LIBS assisted by laser florescence |
| LLE | liquid-liquid extraction |
| LLME | liquid-liquid microextraction |
| LOD | Limit of detection |
| LOQ | limit of quantification |
| M@GO-TS | magnetic particles and graphene oxide functionalized with methylthiosalicilate |
| MAD | microwave-assisted digestion |
| MAE | microwave assisted extraction |
| MC | multicollector |
| MC-ICP-MS | Multicollector inductively coupled plasma mass spectrometry |
| MDG | microdroplet generator |
| $Me_2Hg$ | dimethlymercury |
| MeCo | methylcobalamin |
| MeHg | methylmercury |
| MeOH | methanol |
| MICAP | microwave inductively coupled atmospheric-pressure plasma |
| MIL | magnetic ionic liquid |
| MIP | microwave induced plasma |
| ML | Machine learning |
| MNP | magnetic nanoparticles |
| MOF | metal–organic framework |
| MP | micro plastic |
| MS | mass spectrometry |
| MS/MS | tandem mass spectrometry |
| MSWD | mean squared weighted deviation |

| | |
|---|---|
| MU | measurement uncertainty |
| mu CT | microscale X-ray computed tomography |
| NDIR | non dispersive infra red |
| NIM | National Institute of Metrology of China |
| NIST | National Institute of Standards and Technology |
| NO | nitric oxide |
| NP | nanoparticle |
| NRCC | National Research Council of Canada |
| NTIMS | negative thermal ionization mass spectrometry |
| OES | optical emission spectroscopy |
| ORM | optimised regression method |
| PCA | Principal component analysis |
| PFA | perfluoroalkyl |
| PFAS | per- and polyfluoroalkyl substances |
| PLS | partial least squares |
| PLSR | Partial least squares regression |
| PM1.0 | particulate matter (with an aerodynamic diameter of up to 1.0 µm) |
| PM10 | particulate matter (with an aerodynamic diameter of up to 10 µm) |
| PM2.5 | particulate matter (with an aerodynamic diameter of up to 2.5 µm) |
| PM2.5-10 | particulate matter (with an aerodynamic diameter of between 2.5 – 10 µm) |
| PS | polystyrene |
| PS-MP | polystyrene microplastic |
| PTE | potentially toxic element |
| PTFE | polytetrafluoroethylene |
| PTR | proton transfer reaction |
| PVDF | polyvinylidene difluoride |
| PVG | photochemical vapour generation |
| pXRD | portable X-ray diffraction |
| pXRF | portable X-ray fluorescence |
| QT | quartz tube |
| REE | rare earth element |
| RH | relative humidity |
| RM | reference material |
| rmse | root mean square error |
| RNAA | Radiochemical neutron activation |
| RSD | relative standard deviation |
| S/B | signal-to-background ratio |
| SBET | simplified bioaccessibility extraction test |
| SCR | single chamber reactor |
| SDD | silicon drift detector |
| SEM | scanning electron microscopy |
| SES | spark emission spectroscopy |

| | |
|---|---|
| SF | sector field |
| SF-ICP-MS | Sector-field inductively coupled plasma mass spectrometry |
| SHRIMP | multi-collector Sensitive high-resolution ion microprobe |
| SIMS | secondary ion mass spectrometry |
| SIMS-SSAMS | secondary ion mass spectrometry-single stage accelerator mass spectrometry |
| sp | single particle |
| SPE | solid phase extraction |
| spICP-MS | single particle inductively coupled plasma mass spectrometry |
| spICP-TOF-MS | single particle time of flight inductively coupled plasma mass spectrometry |
| SPME | solid phase microextraction |
| SR | synchrotron radiation |
| SRM | standard reference material |
| SSB | sample standard bracketing |
| SVM | support vector machine |
| SWIR | Shortwave infrared |
| TBAOH | tetrabutylammonium hydroxide |
| TBP | tributyl phosphate |
| TBT | tributyltin |
| TCA | transfer component analysis |
| TD | thermal desorption |
| TDLAS | Tuneable diode laser absorption spectroscopy |
| TEL | triethyllead |
| TEM | transmission electron microscopy |
| TES | transition-edge sensor |
| TET | triethyltin |
| TIMS | Thermal ionisation mass spectrometry |
| TML | trimethyllead |
| TMT | trimethyltin |
| TOA | thermal optical analysis |
| TOC | total organic carbon |
| TODGA | N,N,N’,N’-tetra-n-octyldiglycolamide |
| TOF | time of flight |
| TPhT | triphenyltin |
| TXRF | total-reflection X-ray fluorescence |
| TXRF | total reflection X-ray fluorescence |
| UAE | ultrasound-assisted extraction |
| UFP | ultra fine particle |
| USGS | United States Geological Survey |
| USN | ultrasonic nebuliser |
| UTEVA | Diamyl, amylphosphonate |
| WDX | wavelength-dispersive X-ray fluorescence |

| | |
|---|---|
| WDXRF | Wavelength dispersive X-ray fluorescence |
| WEPAL | Wageningen Evaluating Programs for Analytical Laboratories |
| XAFS | X-ray absorption fine structure |
| XBDM | X-ray backscatter diffraction mapping |
| XFM | X-ray fluorescence microscopy |
| XRD | X-ray diffraction |
| XRF | X-ray fluorescence |
| XRFS | X-ray fluorescence spectroscopy |
| μ-XANES | micro-X-ray absorption near edge structure spectroscopy |

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