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Atomic Spectrometry Update: Review of Advances in Atomic Spectrometry and related techniques

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SUMMARY OF CONTENTS

This review of 177 references covers developments in 'Atomic Spectrometry' published in the twelve months from November 2019 to November 2020 inclusive. It covers atomic emission, absorption, fluorescence and mass spectrometry, but excludes material on speciation and coupled techniques which is included in a separate review. It should be read in conjunction with the previous review¹ and the other related reviews in the series.²⁻⁶ A critical approach to the selection of material has been adopted, with only novel developments in instrumentation, techniques and methodology being included. The analysis of nanoparticles is of current interest, with several novel developments in single particle ICP-MS methods of analysis. Nanoparticles have also been used extensively for elemental tagging to determine proteins and biomarkers, which is now becoming a routine method. Matrix effects in ICP-MS have come under scrutiny, with several studies pointing to a re-evaluation of space charge effects in instruments with newer designs of ion lenses. The DBD, and similar miniature plasma sources, are becoming increasingly popular in compact portable instruments, and for vapour generation and trapping. Developments in laser-based spectroscopy have slowed somewhat, but there were some novel developments in double-pulse and microwave assisted LIBS. Data treatment is one area which looks to be attracting some attention, particularly ways to reduce the huge LIBS dataset to a manageable size for processing. Methods of analysing isotopes continued to be refined using high-impedance resistors, but also with the development of ATONA-based Faraday collectors (ato- to nano- Amp detection) in certain instruments. There were also a number of studies utilising chemical reaction cells to remove isobaric interferences and reduce scatter: a development that will continue to smooth a path towards

high precision isotope ratios from vanishingly small amounts of analyte. Double spiking continued to be the mass fractionation correction method of choice in a variety of stable isotope, radiogenic isotope and nuclear environmental applications.

1. Sample Introduction

1.1 Liquids

1.1.1 Sample pre-treatment.

1.1.1.1 Extraction methods. Extraction methods using gas, liquid or solid phases (or a combination), with physical adsorption, ion-exchange, chelation, electrochemical or magnetic means, have long been used to remove interferences and/or preconcentrate the analyte. Hence, few novel developments now present themselves, and research in recent years has gravitated to making these processes on-line or miniaturised. However, there has been some activity in the development of new phases or techniques. For example, *3D printing has opened the possibility of in-house manufacture* of solid phase supports, columns and manifolds. This approach was adopted by Su and Lin⁷ who 3D-printed 6 cm rectangular outer columns from acrylonitrile butadiene styrene (ABS) filled with the microporous composite filaments Lay-Fomm 40, Lay-Fomm 60, Gel-Lay, and Lay-Felt. This was achieved using a dual head printer so that the microporous filaments were laid down at the same time as the ABS outer shell, stacked as interlacing cuboids arranged layer by layer with a 45° twisting angle for each layer. The columns were incorporated into an FI-ICP-MS system and operated at an optimised flow-rate of between 1 and 2 mL min⁻¹ at pH 8. Metals were eluted using 0.5% HNO₃ with >99% extraction of Cd, Co, Cu, Mn, Ni, Pb, and Zn ions from natural water samples (using the Lay-Fomm 40 column) for samples containing a matrices of up to 4.5% NaCl. The LODs were between 0.3 and 6.7 ng L⁻¹.

Li *et al.*⁸ developed a *novel demineralisation device*, that made use of ion imprinted materials (IMMs), for the analysis of high salinity waters by ICP-MS. The silicon-based IMMs were synthesised using a one-step method and imprinted with Ca²⁺, Mg²⁺ and Na⁺ ions. The material (10 g) was ground and packed into a helical tube using a syringe. Sample solutions were pumped through this tube, where Ca²⁺, Mg²⁺ and Na⁺ target ions were absorbed preferentially. The maximum adsorption capacity of the target ions was in the range from ~ 94 mg g⁻¹ to 105 mg g⁻¹, whereas adsorption of competing ions was less than 5 mg g⁻¹. After

passing through the demineraliser tube the sample continued into a standard pneumatic nebuliser and spray chamber set-up, used with ICP-MS. Using this device, the LODs for As, Cd, Cu, Mn, Ni, Pb, Sb, and Tl were improved 10-fold to within the range from 0.002 (Tl) to 0.024 (Cu) $\mu\text{g L}^{-1}$. Recoveries of these elements were between 80% and 120% for the analysis of samples containing 120 mg L^{-1} of Ca^{2+} , Mg^{2+} , and Na^{+} , for over 10 h of continuous operation. The method was also evaluated in batch mode by the analysis of CASS-5 seawater, with deviation from the certified values of less than $\pm 5\%$.

1.1.1.2 Elemental tagging. For several years, elemental methods have been developed for the indirect quantitation of proteins, peptides and nucleic acids. This can be performed in a number of ways: by quantitation *via* an intrinsic hetero-atom in a protein, such as sulfur or selenium; chelation or covalent bonding of a metal tag to the target molecule and subsequent quantitation by direct calibration or ID-MS; labelling using an antigen-antibody immunoassay approach; or hybridisation of target strands of DNA or RNA with complementary labelled probes. There are also variations which combine all of the foregoing. After peaking several years ago, the number of publications in the research literature has declined. This may reflect either that workers are now tackling the problems of routine implementation, or that the routine nature of many applications no longer warrants publication. Xu *et al.*⁹ published *a short overview (57 references) of recent progress in metalloproteomic approaches* for the identification of protein targets of anticancer and antibacterial metallodrugs. They focussed on two coupled techniques: gel electrophoresis (GE) coupled with ICP-MS for on-line separation and identification of *e.g.* Ag anti-bacterial drugs; and LA-ICP-MS for *in situ* analysis of *e.g.* Pt anti-cancer drugs. They concluded that metallomics and metalloproteomics are 'emerging fields' with 'increasing applications' for therapeutics and diagnostics, so perhaps these techniques have yet to enter the mainstream of routine analysis. However, some of the recent research published suggests that this is now more than a near possibility.

One major advantage of these techniques is the *ability to amplify the signal*. This can be achieved in several ways, but the method which is perhaps closest to routine application is the use of metal NPs for tagging. Lores-Padin *et al.*¹⁰ reviewed this area (158 references). The review includes: an overview of the most common NP-labelled reaction probes; their synthesis and bioconjugation; and applications involving SPE with magnetic NPs, SP-ICP-MS and LA-ICP-MS. They included some useful tables of applications, one detailing the most common approach of using AuNPs for labelling via specific recognition reactions, and

another which compiled a list of applications in which other metals were used. They concluded that NPs offer better amplification than other approaches, but blanks can be high if common metals are used - that is unless SP-ICP-MS is used for detection. Another issue was high background in LA-ICP-MS caused by non-specific absorption of NPs in biological tissues due to unreacted sites on the NPs. Lastly, they observed that the advent of ICP-TOFMS should make detection of multiplexed analytes easier, particularly for SP sample introduction. The same research group¹¹ investigated the use of Pt nanoclusters (NCs) as bimodal labels in a competitive immunoassay for immunoglobulin E (IgE), which nicely illustrated the amplification advantage. Each nanocluster was calculated to contain an average of 116 Pt atoms, and each antibody was labelled with an average of 11.13 PtNCs, corresponding to ~1300 Pt atoms per antibody, thereby imparting a high degree of amplification. The synthesis of the NCs was optimised to achieve a narrow size distribution (1.49 ± 0.025 nm for $n = 1800$, 99% CI) and strong fluorescence for excitation/emission wavelengths of 455/620 nm. A comparison between fluorimetry and ICP-MS detection yielded LODs for IgE of 0.6 ng mL^{-1} and 0.08 ng mL^{-1} respectively.

Chang *et al.*¹² used *AuNPs and a magnetic immunoassay* to detect circulating cancer cells. In order to avoid the problem of non-specific binding of background cells, $\text{Fe}_3\text{O}_4@\text{Au}$ NPs were coated with leukocyte membranes and then conjugated with antibodies (Ab) of the epithelial cell adhesion molecule to form an $\text{Fe}_3\text{O}_4@\text{Au-Ab}$ complex. Lysed human blood samples were spiked with cancer tumour cells which were incubated with and captured by $\text{Fe}_3\text{O}_4@\text{Au-Ab}$. Magnetic separation allowed quantitation using ICP-MS to detect the Au content. A ~2/3 capture ratio was observed with an LOD (3σ) of 83 cells. The authors noted that concentrations of cancer tumour cells in clinical samples were much lower than the LOD, but that the LOD of this method was lower than others such as some cytosensors and electrochemical detection. A similar study was presented by Cao *et al.*¹³ who used a combination of AuNPs, AgNPs and ZnSe QDs with SP-ICP-MS to achieve multiplexed detection of cancer biomarkers in human lung serum. Simultaneous capture of cytokeratin fragment antigen 21–1 (CYFRA21-1), carcinoembryonic antigen (CEA) and carbohydrate antigen (CA15–3) was initially achieved using biotinylated, antibody-coated magnetic beads. Then, second antibody complexes of the AuNPs, AgNPs and ZnSe QDs were added to form sandwich complexes. Unbound biotinylated magnetic beads were removed and the complexes magnetically separated before analysis using SP-ICP-MS. The LODs were 0.02 ng mL^{-1} , 0.006 ng mL^{-1} and 0.25 mU mL^{-1} for CYFRA21-1, CEA and CA15–3, respectively.

The multiplexing advantage has previously been demonstrated by using lanthanides (Ln) elements as multiple tags. This approach was used by Shuck *et al.*¹⁴ who performed metal-assisted protein quantitation (MAPq) with lanthanide-conjugated antibodies to simultaneously quantify up to 35 proteins. The initial conjugation to form unique Ln³⁺-antibody combinations was achieved using a commercial kit containing a maleimide-functionalised linker. An LOD of 0.5 pg mL⁻¹ and LOQ of 5 pg mL⁻¹ were achieved with ICP-MS detection, which was a 10-fold improvement compared to Western Blotting. This demonstrated that the approach could be simplified and perform well as a high-throughput method. Improved performance when using Ln elements as tags was promised by Clases *et al.*¹⁵, this time for immuno-mass spectrometry imaging using LA-ICP-MS. They optimised the ion lenses and quadrupole to maximise ion transmission by reducing the mass resolution for Ln elements. Part of the rationale was that there were unlikely to be many interferences in this mass range when using a dry plasma, providing that well separated isotopes were chosen. This approach increased ion transmission and improved SNRs 6-fold for ¹⁷²Yb-labelled antibodies in the imaging of brain tissue.

An alternative to Ln, Au or Ag tags was reported by Corte-Rodriguez *et al.*,¹⁶ who investigated the use of ¹⁴³Nd-tagged antibodies to target the transferrin receptor 1 (TfR1) in tumour cells. The TfR1 receptor is used as a biomarker in breast cancer tissues and two cell models of breast cancer with different malignancy (MCF7 and MDA-MB 231) were investigated. The monoclonal antibody anti-TfR1 was first labelled with a polymeric chelator using a commercial kit, then ¹⁴³Nd was incorporated resulting in a stoichiometry of 21 Nd atoms per antibody molecule. Single cell ICP-MS was used to detect individual event signals for ¹⁴²Nd⁺, with ³¹P¹⁶O⁺ at m/z 47 monitored as an internal control. Thus, quantitative analysis of TfR1 at the single-cell level was possible.

1.1.2 Nebulisation. *The fundamental parameters and analytical performance of four commercial nebulisers*; Concentric, Mira Mist, OneNeb series 1, and OneNeb series 2, were evaluated for MIP-OES.¹⁷ Estimated fundamental plasma parameters indicated that the Mira Mist nebuliser provided a plasma with the highest T_{exc} and n_e , but the lowest solvent transport efficiency. OneNeb series 2 showed the lowest T_{exc} and n_e with the highest solvent transport efficiency. The OneNeb series 2 presented the lowest RSD and LOD values in all matrices studied, while the concentric nebuliser presented the highest RSD. The accuracy was evaluated using several CRMs and addition and recovery experiments performed using

sugarcane spirit as the sample. Taking into account the sensitivity improvement, solvent transport efficiency and analytical precision, the OneNeb series 2 was concluded to provide the best analytical performance. A *multinebuliser combined with on-line standard dilution analysis* (SDA) was developed for the determination of wear metals in used lubricating oils using ICP-OES.¹⁸ Analytes Cd, Cr, Cu, Fe, Mn, Ni and Pb were determined in oils with LODs of 20, 10, 6, 20, 4, 30 and 200 ng g⁻¹, respectively. The analysis of spiked commercial lubricating oil samples resulted in recovery values ranging from 91 to 108%. The results were compared with values obtained with conventional standard addition calibration and both LODs and recovery values were of the same order of magnitude. The method avoided the use of organic calibration standards and was suggested as a simple, fast, relatively economic, environmentally friendly, direct and reliable method of wear metal monitoring in used lubricating oils by ICP-OES. A *multiple channel-type concentric grid nebuliser* (m-CGrid) was developed for online standard addition in ICP-OES without premixing of liquids before nebulisation.¹⁹ The system could nebulise two separate liquids without premixing due to the two independent liquid-flow capillaries situated inside a single nozzle and a grid screen placed on the hole of the nozzle. The grid acted as both a flow damper and sieve; the two liquids were mixed with a gas flow in a small space just before the grid screen, so the mixture broke up into small droplets by passing through the grid. The spray performance of the m-CGrid nebuliser produced finer primary aerosols with a diameter below which 50% of aerosol by volume is contained (D_{50}) of 2.9 and 3.1 μm for two channels. This compared well with that of a conventional Meinhard nebuliser type C ($D_{50} = 19.5 \mu\text{m}$). The signal intensities obtained with two liquid channels were found to be 2- to 3-fold higher than those obtained with the Meinhard nebuliser for 23 elements. Two CRMs (NIST SRM1577b bovine liver and NIES No. 3 Chlorella) were analysed using the m-CGrid with online standard addition and the results obtained were found to be in good agreement with their certified values.

When coupled online with ICP-MS, water-in-oil droplet-based microfluidics for *single cell analysis* encounters problems, particularly in sample introduction. Zhou *et al.*²⁰ considered cells as "droplets" with a hydrophilic surface and an elastic hydrophobic membrane. Hence they developed an oil-free passive microfluidic system (OFPMS) consisting of alternating straight-curved-straight microchannels and a direct infusion (dI) micronebuliser for ICP-MS. The OFPMS permitted single cell isolation using a thermo-decomposable NH_4HCO_3 buffer, eliminating the use of any oil or polymer carriers.

Quantitative single-cell transportation and detection efficiency greater than 70% was obtained using the system. Using this approach, cell-to-cell heterogeneity could be detected through the determination of metals in individual cells.

Al Hejami *et al.*²¹ described an *infra-red heated modified cyclonic spray chamber* (MCSC) system for ICP-OES that operated with a total sample consumption up to 75 $\mu\text{L min}^{-1}$. The analytical performance of the MCSC was compared with the Apex E desolvation system and the IsoMist programmable temperature spray chamber. A baffled cyclonic spray chamber (BC) at room temperature was used as a reference sample introduction system. Sample uptake rates of 25, 50 and 75 $\mu\text{L min}^{-1}$ were tested. At a sample uptake rate of 50 $\mu\text{L min}^{-1}$, the improvement in the sensitivity and detection limit of the MC and Apex were comparable and significantly higher than for IsoMist. At a sample uptake rate of 75 $\mu\text{L min}^{-1}$, however, the order of the improvement in the sensitivity and LOD was Apex > MC > IsoMist. In general, at sample uptake rates of 50 and 75 $\mu\text{L min}^{-1}$ and in contrast to IsoMist, the sensitivity and LOD for the MC and Apex were similar to those obtained with the BC at a regular sample uptake rate of 1 mL min^{-1} . The MC system provided the highest plasma robustness. At a given sample uptake rate, the MC also provided a shorter washout time than the Apex and IsoMist. Accurate ICP-OES analysis of two CRMs of drinking and waste waters was obtained with the MC, using external calibration without internal standardisation, giving similar results to those obtained using the BC, IsoMist and Apex. The results of the study demonstrated the suitability of the MC as a sample introduction system for ICP-OES. The same authors posed the question: ‘How much aqueous sample can an ICP withstand?’²². To provide an answer, the IR-heated sample introduction system was used. This consisted of a modified cyclonic spray chamber with a ceramic rod heater within a baffle at its centre and a ceramic rope heater wrapped around the base of the torch. It was operated at 200 °C or 280 °C, and sample uptake rates of 100, 150, 200, 250 and 300 $\mu\text{L min}^{-1}$ in combination with ICP-OES. The plasma was not extinguished although it flickered at 200 and 250 $\mu\text{L min}^{-1}$. At 280 °C no liquid was evident from the drain up to 250 $\mu\text{L min}^{-1}$, indicating total consumption. This volume represents more than double the highest sample uptake rate previously used for total sample introduction. Sensitivity was similar or improved compared to that obtained with a BC at room temperature operating at 1 mL min^{-1} . Plasma robustness, assessed using the Mg II 280.270:Mg I 285.213 nm signal ratio, of at least 8 was achieved at 100 and 150 $\mu\text{L min}^{-1}$ at 200 °C, and at 100 $\mu\text{L min}^{-1}$ at 280 °C, but degraded to 7 and 3 at 250 $\mu\text{L min}^{-1}$ at 200 °C and 280 °C, respectively. The LOD for all sample uptake rates at 280 °C was better than that obtained at 200 °C and also better than that obtained with a BC at room

temperature. Although the precision at 280 °C was better than that obtained at 200 °C, the LOD was generally degraded because a single set of ICP operating conditions, established with the reference system, was used in all cases. Hence, re-optimisation of ICP operating conditions might enable total sample consumption at up to 250 $\mu\text{L min}^{-1}$ with improved sensitivity as well as similar or improved LODs, precision and plasma robustness.

1.1.3 Single particle analysis. *SP-ICP-MS has become an important tool for the characterisation of NPs.* The method allows determination of size, size distribution, and particle number concentrations of NPs in suspensions, in several minutes of measurement time. A review²³ modelled on the concept of ‘an ideal method for atomic spectroscopy’, introduced by Gary M. Hieftje in his publication dedicated to Howard Malmstadt, discussed the instrumental developments in SP-ICP-MS in recent years. The authors identified necessary improvements and suggested directions for further developments which have the potential to bring the method closer to the concept of an ideal method. The review also discussed the literature on coupling SP-ICP-MS to separation and fractionation techniques including CE, FFF, and DMA. The second part of the review covered applications of SP-ICP-MS. Key steps in sample preparation and selected instrumental conditions that were used in the published literature are summarised in tables. It was observed that the most frequent use of SP-ICP-MS is for Ag, Au, and TiO₂ nanomaterial analysis. Data acquisition was typically performed with millisecond dwell times in the earlier reports while a time resolution of hundreds of microseconds has been used more often in the last five years. The tables provide a useful guide to choose an experimental procedure depending on the matrix that is present in the sample under investigation.

SP-ICP-MS offers unique features for the detection of particles, as well as for their quantification and size characterisation. The detection capabilities of SP-ICP-MS are therefore not limited to the concentration domains (of particles and dissolved related species), but also to the mass of element per particle and particle size domains. Discrimination and detection of particle events, based on the use of robust LODs (also known as critical values), and the estimation of the LODs in the different domains, require standardised methods that have not yet been clearly established. Laborda *et al.*²⁴ summarised and reviewed the different approaches applied to date in relation to detectability in SP-ICP-MS. A holistic approach with criteria and expressions for the estimation of the different critical values and LODs, in terms of the different instrumental and experimental parameters

involved, was proposed. It included a calculation tool for estimating and predicting critical values and LODs under different experimental conditions. Although SP-ICP-MS has been identified as one of the best techniques for detecting NPs, it is limited by relatively high size detection limits for several NPs, including many of the oxides. The use of a high sensitivity ICP-SF-MS, microsecond dwell times, and *dry aerosol sample introduction systems* were examined with the goal of lowering the size detection limits of the technique.²⁵ For samples injected as a wet aerosol, size LODs as low as 4.9 nm for Ag NPs and 19.2 nm for TiO₂ NPs were determined. By using a dry aerosol, a significant gain in ion extraction from the plasma was obtained, which resulted in a noticeable decrease of the size detection limits to 3.5 nm for Ag NPs and 12.1 nm for TiO₂ NPs. The improved conditions were applied to the detection of TiO₂ NPs in sunscreen lotions, rainwaters, and swimming pool waters.

SP-ICP-MS can be used for the determination of the size and concentration of NPs suspended in solution. Using a dilute suspension to introduce a single NP into the plasma allows for quantification of the mass of the NP (and thus its size, if its density and shape are known) based on signal intensity. Conventional sample introduction using continuous nebulisation is typically used. However, heating of the sample introduction system can improve the transport efficiency by enhancing the formation of small droplets after nebulisation, which enables more sample to reach the plasma. A new method, involving *IR heating the sample introduction system for SP-ICP-MS* was investigated by Williams *et al.*²⁶ The number of detected NPs per minute increased from 540 at room temperature to 600 at 60 °C and 840 at 80 °C. As the IR heating was applied outside the torch box, condensation could occur inside the torch box. As a result, no significant change in size detection limit was obtained at 60 °C and degradation occurred at 80 °C. Sample introduction efficiency can be improved using mono-segmented flow analysis (MSFA), where FI is carried out within an air bubble. MSFA was tested with the SP-ICP-MS system. Transport efficiency for Au NPs was improved to 840 NPs min⁻¹ without heating and to 900 NPs min⁻¹ with IR heating at 60 °C. Both approaches improved the precision of NP size measurements. *A dual inlet system consisting of a pneumatic nebuliser and a microdroplet generator for sample introduction in SP-ICP-MS* was described by Rosenkranz *et al.*²⁷ The system enabled sequential introduction of ionic metal calibrant solutions and NP suspensions via various combinations of two inlets, allowing three independent modes of analysis. A new interface, assembled using standard analytical components (a demountable quartz ICP-MS torch, flexible non-conducting silicon tubing and various connectors), was used to interface the dual inlet system to an ICP-MS. This setup provided three ways to independently determine the metal mass fraction and NP number concentration. All three analyses were carried out within a single analytical run lasting

approximately 20 min. Commercial Au, Ag and CeO₂ NPs were analysed and the determined average diameters for Au (56.7 +/- 1.5 nm), Ag (72.8 +/- 3.4 nm) and CeO₂ (69.0 +/- 6.4 nm) NPs were found to be in good agreement for all three modes of analysis, and with the values provided by suppliers for Au and Ag NPs (56.0 +/- 0.5 for Au, 74.6 +/- 3.8 nm for Ag). However, the average value for CeO₂ was much higher than the expected 28.4 +/- 10.4 nm. It was proposed that this was due to NP agglomeration and poor detection of NPs in the lower size range. The determined NP number concentrations, using two of the analysis modes, gave recoveries between 91 and 100% for the Au and Ag NP number concentrations. The third analysis mode gave recoveries of between 70 and 88% for the same materials.

SP-ICP-MS can be used to quantify NPs with element mass down to single-digit attogram levels. *Monodisperse microdroplets* composed of elemental solutions are vehicles for the transport of discrete amounts of elemental species into the ICP, and signals produced from microdroplets closely match those produced by NPs. Temporal durations and element sensitivities obtained from microdroplets and NPs are so similar that microdroplets can be used as NP proxies. Unlike NPs, microdroplets offer a flexible platform for SP-ICP-MS measurements because the absolute mass of elements injected into the plasma in each droplet can be accurately controlled. Gundlach-Graham and Mehrabi²⁸ have used the measurement of microdroplet-based element signals with ICP-TOFMS to expand the versatility and the general understanding of SP-ICP-TOFMS measurements. The authors described the use of microdroplets for online calibration of analyte NP element mass and particle-number concentration. The measurement of microdroplets with tailored analyte masses was also used to refine, test and validate SP-ICP-TOF-MS data analysis strategies. The results of these experiments were used to describe how monodisperse microdroplets can be used to design better SP-ICP-MS experiments.

A range of techniques were compared for the characterisation of Ni NPs.²⁹ Synthetic ferromagnetic NPs prepared with and without polyvinylpyrrolidone stabiliser were characterised using TEM, SEM, XRD, SP-ICP-MS and FI coupled SP-ICP-MS. Single NPs analysed using XRD yielded nominal diameters of 13.7 and 16.6 nm with and without the stabiliser respectively. However, a diameter of 100-130 nm was obtained by TEM and SEM with or without stabiliser, indicating that extensive agglomeration occurred during preparation for microscopy. In contrast, without stabiliser, mean and mode sizes of respectively 35 +/- 18 and 21 nm by SP-ICP-MS and 33 +/- 15 and 20 nm by FI-SP-ICP-MS were obtained for suspensions of Ni NPs using external calibration with Ni standard solutions. With stabiliser present, the mean and mode sizes respectively decreased to 27 +/- 12 and 18 nm by SP-ICP-MS and 25 +/- 10 and 16 nm by FI-SP-ICP-MS. No degradation in performance was reported using FI-SP-ICP-MS instead of SP-ICP-MS, despite

measurement of NPs mass using the former FI-SP-ICP-MS being carried out without knowledge of the transport efficiency and the sample uptake rate.

Addition of N₂ to the plasma (outer) flow increases the power density of the plasma in an ICP. This reduces matrix effects and may improve the atomisation and ionisation of NPs. Kofsky and Beauchemin³⁰ compared the use of Ar and mixed gas plasmas (Ar-N₂ and Ar-N₂-H₂) for the determination of 37 elements as NPs only (*i.e.* in the absence of dissolved analyte) using SP-ICP-MS. For each plasma, the selected operating conditions provided a compromise in sensitivity for multielemental analysis. An Ar plasma was found to provide significantly lower LOD (size) than the mixed-gas plasmas, except for ³³S, ³¹P, and ⁴⁴Ca, where oxygen scavenging by N₂ within the Ar-N₂ plasma significantly improved the measured LOD (size). With the Ar-N₂-H₂ plasma, an accompanying loss of sensitivity largely negated the LOD (size) improvement from oxygen scavenging. Further improvements in the LOD (size) for S, P, and Ca could be obtained by optimising the Ar-N₂ mixed-gas plasma for the individual determination of each element.

1.2. Vapour generation

Chemical vapour generation (CVG) has been applied for a long time, but the *mechanisms* are still not fully understood. Pagliano *et al.*³¹ investigated the mechanism of reduction of dimethylarsinic acid (DMA) with aqueous NaBH₄ under non-analytical conditions, *i.e.* 1000 µg mL⁻¹ As. Two different CVG systems were tested and coupled with direct analysis in real time (DART)-HRMS, which revealed a large number of ions, any of which might have originated from gas-phase reactions in the ion source, so extensive interpretation was necessary. However, the species Me₂As-AsMe-AsMe₂ and the arsonium species [Me₃As-AsMe₂]⁺ and [Me₂As-AsMe₂-AsMe₂]⁺ were identified. This information, in conjunction with earlier GC-MS studies, was used to further develop a number of hypotheses previously published by the same group regarding reaction mechanisms of DMA with NaBH₄. One of their main conclusions was that the formation of some arsonium species, not containing oxygen, could be confirmed with certainty and that ≥ 98% of total arsenic remained in solution. This observed reactivity was at odds with previous studies of organic-phase reactions of methylated arsanes and polyarsanes, where the lability of As-As and As-H bonds, and a non-ionic redistribution mechanism were considered to control the reactivity. Interested researchers are advised to read the paper in order to gain a fuller understanding. While the practical (if not theoretical) aspects of CVG are well established, there are still gains to be made in optimising the instrumental configuration. This was illustrated by

Stadlerova *et al.*³² who assembled a highly sensitive, non-dispersive system for the determination of Bi. The instrument was based around a shielded flame atom cell which was basically a miniature diffusion flame shielded with Ar. An EDL was used as the excitation source in conjunction with an interference filter and PMT. The LOD was 0.9 ng L⁻¹ using a 307.1 nm interference filter, but interferences from Sb and Hg were identified using 202 nm and 223 nm filters.

Vapour generation using a plasma or discharge has come to the fore in the last few years. It is normally used as way of promoting and adding to reaction pathways normally achieved using CVG and PVG, because a large number of reactive species, such as free radicals, ions, and molecules, are generated at the plasma-liquid interface. Liu *et al.*³³ reviewed research in this area (113 references), focussing on developments and applications of liquid electrode GD and DBD plasmas used for plasma-induced CVG. It also includes a section on possible mechanisms and comparison with PVG. The authors summarised the advantages as: simpler reagents; high efficiency; simple instrumentation; insensitivity to elemental speciation; fast reaction speed; and small sample size. However, they also concluded that there was scope to develop the method so it has wider applicability to a greater number of elements without changing operating conditions, a role in which catalysts may offer potential advantages. He *et al.*³⁴ used a nebulised film DBD to generate volatile species of 16 REEs. In this approach, an aqueous sample solution of REEs was nebulised onto the outside surface of a quartz tube to form a liquid thin film. This tube itself was enclosed inside a DBD discharge tube such that the volatile species formed at the interface between the liquid film and the plasma, and were then swept into an ICP-MS for detection. The authors reported improvements of between 4- and 10-fold in LODs for Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu compared with conventional nebulisation. There were no obvious interferences from up to 10 mg L⁻¹ of Ba²⁺, Zn²⁺, Cu²⁺, Fe³⁺, Co²⁺, Ni²⁺ and 1000 mg L⁻¹ of Na⁺ and Mg²⁺.

Li *et al.*³⁵ developed a novel variation on plasma induced CVG by using a He-H₂ DBD directly on the surface of a solid sample to generate volatile Se species for introduction to AFS. Three solid samples, mixed with solid boric acid at 0.05% w/w, containing different valence states of Se were investigated; namely Na₂SeO₄, Na₂SeO₃, and elemental Se. Enhanced fluorescence was only observed when H₂ was included in the DBD gas. The authors proposed a mechanism which included collisions between H₂ and He* to form H₂⁺, then electron collision to form H species, and another electron collision to form H⁻. Hence, they proposed that the H radicals (E_{red} = 2.3 V) were thermodynamically capable of reducing

Se^{VI}, Se^{IV} (and even Se^{II}) to Se⁰. The LOD was 19.7 pg using AFS detection. The presence of Fe, Cu, Ag, Au, Sb and Te did cause signal enhancement, but the method was applied for the determination of selenomethionine, selenocystine and methyl selenocysteine in water CRMs with apparently acceptable results.

The DBD can also be used as a preconcentration trap after CVG, as reported by Liu *et al.*³⁶. They preconcentrated Pb, from PbH₄ generated using CVG, on the quartz surface of a DBD discharge tube in the presence of O₂. This was then regenerated as a volatile species and released in a H₂-containing atmosphere. The LOD for Pb was 4.1 pg (1.2 mL sample) using AFS detection, and the LDR was from 0.05 to 100 µg L⁻¹. These workers used a similar system for the VG and preconcentration of As generated from blood samples.³⁷ However, this time, the volatile As species were generated and trapped *in situ* (*i.e.* in the DBD itself rather than externally by CVG) using 11 kV DBD at 110 mL min⁻¹ air, and released with 13 kV at 180 mL min⁻¹ H₂. The LOD was 7 pg using AFS detection.

Photochemical vapour generation (PVG) shares some similarities with plasma-induced vapour generation in so far as free radicals are involved. Another aspect of PVG is the use of organic solvents and catalysts, to increase reaction efficiency for compounds which do not easily form volatile species using traditional CVG methods. Vyhnanovsky *et al.*³⁸ used a flow-through photoreactor with a 19 W low pressure mercury discharge lamp (≈720 µL internal volume) for the PVG of volatile W species - probably W(CO)₆ - using formic acid (40% v/v) as the reaction medium. It is notable that the addition of 500 mg L⁻¹ of Cd acetate to the samples, as a sensitiser, enhanced the PVG reaction by 30,000-fold. The LOD for W was 0.9 ng L⁻¹ (0.4 pg) using FI-ICP-MS detection. However, this was blank limited by contamination from the Cd acetate addition and an instrumental LOD of 0.06 ngL⁻¹ was estimated in the absence of this. The method did suffer from variable suppression interference caused by HNO₃ (70% signal suppression from 30 mM), HCl (23% at 30 mM) and H₂SO₄ (14% at 100 mM). This was attributed to the presence of the anions in solution rather than a pH effect. An attempt was made to investigate the reaction mechanism but no firm conclusions were drawn. Interested researchers should refer to several previous publications from this group in order to gain a fuller insight into VG of non-traditional elements in general. Similarly, Yu *et al.*³⁹ used the same make of photoreactor and Co²⁺ as an enhancer for the PVG of Bi with ICP-MS detection. In this case the reaction medium was 10% v/v formic acid, 30% v/v acetic acid and 80 mg L⁻¹ Co²⁺. They observed that the presence of 50 mg L⁻¹ of Cl⁻, NO₃⁻, SO₄²⁻ and PO₄³⁻ did not cause any obvious interferences, however, these

concentrations were more than 10x lower than in the previous study. Likewise, Fe^{3+} at 100 mg L^{-1} did not cause an interference. The reaction mechanism was investigated using GC-MS, leading to the tentative identification of the volatile species $\text{Bi}(\text{CH}_3)_3$ and $\text{Co}(\text{CO})_4\text{H}_2$. Novakova *et al.*⁴⁰ investigated the PVG of Cd using a 6 W low-pressure Hg lamp and AFS detection. They used quite a low concentration of formic acid (1.5 % v/v/), in comparison to other studies. The addition of 100 mg mL^{-1} of Fe^{II} enhanced the PVG by 2.6-fold. Adjustment of the pH to 2.7 and addition of Triton X-100 further enhanced the signal. The LOD was 1.8 ng mL^{-1} but practical application was limited by the interferences caused by HNO_3 .

The problem of *nitrate interference on the PVG* of Se was addressed by Mollo and Knochen⁴¹ by the simple expedient of removing it at the Se^{VI} to Se^{IV} reduction stage by boiling with HCl. This was effective for up to 7% w/w NO_3^- and 40% w/w H_2CO was used for concentrations up to 21%. The LOD and LOQ (10s) were 0.98 and 3.3 $\mu\text{g L}^{-1}$ respectively for the determination of Se in water and spiked rice flour digest CRMs using QT-AAS detection.

A simple *electrochemical vapour generation (EVG)* system was reported by Liu *et al.*⁴² for the determination of Cd by AFS. The system comprised two serially-connected graphite tubes as two electrolysis cells with 18 V DC power supplied from a wall-plug adapter. The signal was stable even when the HCl electrolyte varied between 8 and 20% v/v. Analyte signal suppression in the presence of 10 $\mu\text{g mL}^{-1}$ of Cu^{2+} , Fe^{3+} , Zn^{2+} and Ni^{2+} was observed to be 30, 21, 36 and 42%, respectively; but this was eliminated when 10 $\mu\text{g mL}^{-1}$ thiourea was added. The LOD was 0.05 ng mL^{-1} and the EVG efficiency was calculated to be 38.4%.

1.3 Solids

In recent decades, direct solid sample analysis has been reported in the literature as an alternative to traditional methods of sample preparation, becoming well established in the atomic spectrometry field. Recent advances in the most commonly used techniques for solid sample analysis (such as, FAAS, GFAAS, HR-CS-GFAAS, ETV, LA, LIBS, XRF, GD-OES, GD-MS and arc/spark OES) have been reviewed by Machado *et al.*⁴³ Advantages and limitations of the approach were outlined. The possibilities for non-metal detection through molecular emission or absorption signals, speciation analysis, portable instrumentation for *in situ* analysis, and surface elemental mapping for obtaining chemical imaging were discussed. The potential ability to overcome spectral interference and matrix effects through the development of calibration strategies was highlighted.

1.3.1 Direct methods. *HR-CS-ETAAS for the direct analysis of solid samples* of various compositions was reviewed by Filatova *et al.*⁴⁴ The review covered determinations using aqueous reference solutions, analysis of suspensions and adsorbates after adsorption separation, use of various modifiers, and optimisation of the programme for heating the graphite furnace. The authors also discussed the potential of HR-CS-ETAAS for: the simultaneous and consecutive monitoring of atomic lines; the possibility of molecular absorption spectrometry for the determination of analytes whose atomic absorption lines are outside the continuous spectrum range of 190-900 nm; and a promising approach to the determination of S, P, halogens, and Al by absorption lines of diatomic molecules. *Spectral interferences affecting the determination of P* due to the molecular absorption of PO at 213.647 nm using HR-CS-GF molecular absorption spectroscopy was studied by Pomarolli *et al.*⁴⁵ Interestingly, the study revealed how observation of the background signal, which typically goes unnoticed, can provide valuable information for method development. In this case, the background signal suggested the formation of a concomitant polyatomic molecule in solid samples that was more volatile than PO and that can cause disturbances in the absorption of the target molecule. This information was used to optimise the conditions for analysis. The most effective modifier to achieve quantitative PO molecule formation and better thermal stability was found to be a mixture of Au and Ca and the pyrolysis and vapourisation temperatures were set to 1500 and 2200 °C, respectively. Using these conditions, CRMs (NIST 1547, NIST 1570a, and NIST 1573a) were analysed using external calibration with P aqueous solutions. The LOD was 0.078 µg (n= 5), or 78 µg g⁻¹ when using one mg of the sample.

1.3.2 Indirect methods.

1.3.2.1 Laser ablation. A review of recent developments in LA-spark induced breakdown spectroscopy (SIBS) for material analysis, undertaken by Zhou *et al.*,⁴⁶ included a summary of the fundamentals of the technique and an overview of the instrumentation. The method can be used in compact instrumentation as an alternative to LIBS methods for the analysis of rocks and soils for planetary missions.⁴⁷ LODs were enhanced up to 4-fold compared with those obtained using LIBS. The signal intensity for SIBS is three orders of magnitude higher than for LIBS, due to the higher energy of plasma generated.

A review by Martinez and Baudelet⁴⁸ described *the calibration strategies used for the analysis of biological samples by LA-ICP-MS and LIBS*. The review focused on the calibration materials used to quantify trace elements in samples such as soft tissues (brain, liver, hair) and hard tissues (bones

and teeth). The promise of matrix-matched, biological reference materials appears to be imminent and should lead to improved quantitation using LIBS and LA-ICP-MS. A simple and general *dried droplet calibration approach* was developed for the quantitative analysis of elements in inorganic non-metallic materials using LA-ICP-MS.⁴⁹ For quantitative analysis, the elemental distribution in dried droplets was improved by optimising both the concentration of surfactant (Pluronic F-127) added to the calibration solutions and the drying temperature. Under optimal conditions, at 2.0% w/w Pluronic F-127 in the calibration solutions and a drying temperature of 85 °C, the RSD of the signal intensity obtained from multi-line ablation mode was less than 20% for dried droplets. The experimental results demonstrated that dried droplets had no effect on the ablation of the sample and could be totally ablated in a single ablation raster. The method was applied to the analysis of inorganic non-metallic materials such as yttrium aluminium garnet (YAG) ceramics, BaF₂ crystals, and NIST SRM 612 glass. The linear correlation coefficients of the calibration curves ranged from 0.9936 to 0.9999 without internal standard correction and the results obtained agreed well with those obtained using ICP-OES, ICP-MS and with certified values.

LA-ICP-MS imaging has been used extensively to determine the distributions of metals in biological tissues for a wide variety of applications. To be useful for identifying metal biodistributions, the acquired raw data needs to be reconstructed into a two-dimensional image. Several approaches have been developed for LA-ICP-MS image reconstruction, but less focus has been placed on software for more in-depth statistical processing of the imaging data. Software written in Python that automatically reconstructs, analyses and segments images from LA-ICP-MS imaging data has been used by Castellanos-Garcia *et al.*⁵⁰ The value of the described algorithms has been demonstrated for LA-ICP-MS images of nanomaterial biodistributions. The image reconstruction and processing approach revealed that nanomaterials distribute in different sub-organ regions based on their chemical and physical properties. This work opens new possibilities for understanding the impact of nanomaterials *in vivo*.

Single particle analysis of solid biomatrices, involving sizing and counting, using LA-SP-ICP-MS, is prone to produce erratic results when non-optimal operational conditions are used. Results from a study by Materapi and van Elterne⁵¹ produced insights into the analysis of NPs by LA-SP-ICP-MS based on modelling the chain of events from NP release to LA cell washout to ICP-MS detection, as a function of the biomatrix characteristics, instrumental specifications and variable operational settings. By processing the computational data via an ‘outlier’ filter to differentiate between metal NPs and dissolved metal, guidelines were established for instrumental setup and

operation. An online app (<http://193.2.14.6:9988/webapps/home/>) was developed, based on the model, to predict the SP analysis capabilities of LA-ICP-MS setups using a custom detectability criterion.

The application of LA-ICP-MS for *in situ microanalysis in solid samples* has traditionally been hampered by a lack of matrix-matched and homogeneous reference materials. Ke *et al.*⁵² described a method for preparing these reference materials using a multiple REE doped CaWO₄ single crystal prepared by the Czochralski technique. The matrix composition and crystal structure were confirmed by XRD and EMPA, which indicated that these crystals had a matrix composition of CaWO₄ and were matrix-matched with natural scheelite. The homogeneity of REE distribution was studied and the results demonstrated that REEs were distributed homogeneously in the CaWO₄ crystal with slight fluctuation (RSD ~ 4%). The synthesised CaWO₄ crystal was then used to quantitatively calibrate REE concentrations in natural scheelite. An approach for the quantitative and SI-traceable analysis of solid materials with LA-ICP-MS was described by Michaliszyn *et al.*,⁵³ using an LA and nebuliser system connected to the torch using a Y-piece. Several standard solutions, having well-known element contents, were introduced one after the other into the plasma simultaneously with the ablated material. The solid sample itself served as the reference and the content of an analyte element was calculated based on the known content of the matrix element (such as Si in a glass sample). Equations to describe the method were derived based on the standard addition method. Pb and Rb were determined in two CRMs (NIST SRM 610 and 612 glass samples). The solid samples were analysed together with solutions of different mass fractions of Si as the reference element. The mass fractions of Pb and Rb measured in the CRMs were equal to the certified values within the limits of given uncertainties. Compared to other quantification methods, this method allowed SI-traceability for the measurement results without the need for matrix-matched solid reference materials. This represents a benefit for the use of LA when matrix-matched CRMs are sometimes unavailable. The method is best-suited to determine impurities in very pure samples with a mass fraction of the matrix element close to 1 g g⁻¹.

Microwave plasma torch (MPT)-OES is a technique that conventionally requires digestion and desolvation steps when analysing solid samples. *A new Z-shaped LA chamber used with MPT-OES* was developed for direct solid analysis by Wang *et al.*⁵⁴ The ablation chamber was sealed with a flat surface of the solid sample (> 3 mm x 2 mm). The chamber internal volume was 0.04 cm³, washout time 0.5 s, and the RSD of the signal when analysing pure Cu samples was found to be 1.2% (n=11). Under the optimal experimental conditions, 12 elements (Si, Mg, Fe, Al, Mn, Ca, Ba, Sr, Na, Li, K, Rb) were determined in a rock-polyethylene tablet, and the LODs ranged from 0.00002

to $362 \mu\text{g g}^{-1}$, with RSDs between 3.7% and 9.1% ($n = 11$). The LA-MPT-OES system described offers sensitivities comparable to LA-ICP-OES at lower cost. The performance characteristics of a guard electrode (GE) in LA-ICP-SFMS for multiple element quantification were studied by Wu *et al.*⁵⁵ The GE shaped and increased the ion density of the plasma prior to injection into the sample cone, shifting the ionisation zone back to the sample cone and requiring a larger carrier gas flow rate for compensation. The signal intensity of 55 elements were found to be enhanced by a factor of 3-20 with the use of GE compared to that without. However, this enhancement was accompanied by higher oxide and doubly charged ion yields. Elements with low m/z showed a larger sensitivity improvement than those with higher m/z . The ion transmission efficiency improved by between 3x and 20x using the GE but LODs were not improved due to enhanced background intensity. The linear relationship between m/z and transmission efficiency obtained without the GE changed to a quadratic relationship when the GE was used. Mass discrimination appears to be limited to lower m/z species. The ion profile in the ICP demonstrated that use of the GE increased the ion density of the plasma, which was attributed to the reduced ion kinetic energy distribution. Analysis of several glass reference materials demonstrated improvements in precision by factors of between 2 and 4, and comparable accuracy between GE and non-GE modes.

1.3.2.2 Thermal vapourisation. ETV-ICP-OES with a mixed Ar-H₂-CF₄ carrier gas was used to directly determine minor and trace elements in Ni foam samples.⁵⁶ The carrier gas was supplemented with 20 mL min^{-1} H₂ and 9 mL min^{-1} CF₄ to increase analyte volatility. Also, 45 mL min^{-1} N₂ was introduced into the central channel of the plasma via a sheathing device to improve plasma robustness, sensitivity and LODs. The Ar 415.859 nm emission line was used for internal standardisation to compensate for sample loading effects on the plasma, before computing the peak area of the transient signal observed for each analyte during the vaporisation and final cooling steps. External calibration was carried out using NIST 2710 (Montana soil) CRM. The measured concentrations of Cd, Cr, Mn, Mo, Pb, V, and Zn agree with those obtained by PN-ICP-OES after digestion with HNO₃. The method allowed accurate determination of minor and trace elements in Ni foam without sample preparation.

2. Instrumentation, Fundamentals and Chemometrics

2.1 Instrumentation

Advances in electronics have meant that much of the hardware necessary for power supply, control and data-processing has shrunk in size. Spectrometers are now available which fit on a chip, diode lasers can be used as sources, and even mass spectrometers have become much smaller and compact. However, the greatest challenge has proven to be developing an atom cell or source which can accept a liquid, gas or solid sample, and convert it to atoms or ions with minimal interferences without the requirement for expensive gases or high power. It is perhaps for this reason that advances in miniaturisation have focussed on particular niche areas, such as the *in situ* analysis of a particular solid, or on-line analysis of samples with an unvarying matrix.

Recent developments in microplasmas have pointed the way towards the promise of a wider application for miniaturised instruments. Yamamoto⁵⁷ reported (in Japanese) on the development of an ultra-compact elemental analyser based on a LEP. The plasma was generated in liquid electrolyte contained in a narrow channel on a quartz or PDMS chip, by application of a DC voltage (between 500 and 1500 V). The chip, a micro-spectrometer and syringe pump were all contained in a relatively small desktop instrument. LODs ranged from $\sim 10 \mu\text{g L}^{-1}$ up to 10 mg L^{-1} for a variety of transition and metalloid elements. In comparison, another chip-based device, this time based on an atmospheric GD with a liquid drop anode, was developed by Swiderski *et al.*⁵⁸ The GD was sustained between a tungsten micronozzle (cathode) and a liquid sample drop (anode). The sample was introduced into the hollow of a ceramic microchip, He gas was passed through the nozzle at a rate of 300 mL min^{-1} and a DC discharge potential of up to 1.5 kV was applied. The LOD for Hg was 47 g L^{-1} for a $15 \mu\text{L}$ sample and the calibration was linear up to 30 mg L^{-1} . Recoveries for spiked tap-water samples were within the range 96% to 122%. It is instructive to compare this with the previous paper: in this case, while the source was reduced to the size of a chip, other parts of the instrument were not miniaturised so it was still a lab-based instrument. Another type of microplasma, a DBD, was used as both as a hydride preconcentration trap and excitation source for OES.⁵⁹ This in itself is not novel, but the authors claimed that this was the first report of its use for multielement analysis, using a fibre-optic spectrometer. They reported LODs for As and Sb as $0.5 \mu\text{g L}^{-1}$ and $0.2 \mu\text{g L}^{-1}$ respectively so the multielement claim was technically correct. The instrument also required an Ar/H₂ gas supply, thereby limiting its portability.

One way of introducing the sample into miniaturised plasmas is the use of ETV, which has the advantage that solids can be directly analysed. Commonly, this was achieved using a resistive heating device, such as a graphite furnace or metal coil, however, Liu *et al.*⁶⁰

have developed a compact and portable instrument built around a DBD microplasma with an *electromagnetically heated tungsten boat* for sample introduction. A copper coil (1 mm i.d. and 2 mm o.d.) was wound around the W boat and inductively heated by a 45 V a.c. current (of unknown frequency) supplied from a battery. This was enclosed in a quartz chamber and connected to the DBD by a quartz tube. The device was only 40.5 x 30 x 15 cm in size, 7 kg in weight with an average power consumption of 118 W. The LODs for Hg, Cd and Pb in soils were 8.0, 17.8 and 3500 $\mu\text{g kg}^{-1}$ respectively.

Muller *et al.*⁶¹ reviewed (112 references) N₂-MIP-OES as a competitive technique to ICP-OES. They described the performance of MIPs generated using Okamoto and Hammer cavities, and the microwave inductively coupled atmospheric plasma (MICAP) method. An extensive applications table was also included. They concluded that N₂-MIP-OES is more sensitive than FAAS for many elements but LODs are higher than ICP-OES; however the use of a dry sample introduction system should result in lower LODs. The most recent of these developments, *the MICAP, was more fully evaluated, in comparison with ICP-OES*, by Wiltche and Wolfgang.⁶² They determined LODs and LOQs for 30 elements based on 72 emission lines and found that LODs for the MICAP were ~10x higher than those obtained by ICP-OES when using the same spectrometer, detector and data processing software. In comparison, the LODs were similar to a commercial MIP-OES instrument with a Hammer cavity. It is worth noting that the most sensitive ICP-OES emission lines did not always result in the lowest LODs for the MICAP, probably due to a combination of the lower excitation energy of N compared with Ar, different excitation mechanisms and the highly structured background in the N₂ plasma. On the plus side, N₂ is significantly cheaper than Ar.

Polyatomic species are often considered to be problematic in atomic spectrometry, but they can also be put to good use, as described by Resano *et al.*⁶³ in a review (195 references) of atomic spectrometric methods used for molecular analysis. The review covers how LIBS, high-resolution CS-AAS and ICP-MS (*via* a collision/reaction cell) have been used for monitoring molecules or polyatomic ions containing the target analyte. From the point of view of optical spectroscopy, the technique of LAMIS is covered in some detail, and the advantage of the large molecular isotopic shift to obtain isotopic information from high resolution spectra. Also, the use of collision and reaction cells in tandem ICP-MS-MS has meant that polyatomic ions which were once purely regarded as interferences can now be taken advantage of to avoid interferences and access difficult to determine analytes.

Methods for the analysis of nanoparticles have been much studied over recent years, primarily by using SP-ICP-MS, however, Cheng *et al.*⁶⁴ developed a near field desorption ionisation mass spectrometry (NDI-MS) instrument for imaging single cells. The instrument comprised a TOFMS with a shear-force scan probe microscope (SPM) placed in the ion source region. The 355 nm desorption laser ionisation source was tightly focused onto the sample using a customised optical fibre. A high precision nano-positioner enabled pixel-by-pixel scanning of the sample, acquiring MS signals at a sampling rate of 2.5 G s^{-1} for 100 ms, leading to a m/z range from 0 to 1200. One advantage of this technique was that the feedback control maintained a constant tip-to-surface distance regardless of the surface roughness. The instrument was used to image the occurrence of Au and Ag NPs in single, cultured mouse macrophage cells on 1 cm^2 glass slides, and the results compared with confocal laser scanning microscopy (CLSM) of the same samples. A mean crater diameter of 310 nm and single cell imaging with 250 nm pixel size was obtained, enabling the imaging of NPs as well as ligands at the organelle scale. Correlated imaging with CLSM verified that the AuNPs were located in endosomes/lysosomes after the entering cells.

Another new technique for the analysis of individual particles by MIP-OES was developed by Borowska *et al.*⁶⁵ The sample introduction tube, which was the key part of the device, consisted of a vertical glass tube, flared to include a conical dilution chamber. A few mg of sample NPs were placed on a frit at the bottom of the tube, the whole thing mechanically agitated, then particles transported up the tube to the dilution chamber using He carrier gas, so NPs were directly introduced into a MIP-OES instrument one particle at a time. The data acquisition system allowed NP signals to be measured with a time resolution of between 4 and 20 ms. The instrument provides a potentially lower cost approach for the analysis of NPs compared with ICP-MS.

Finch *et al.*⁶⁶ developed a transmission-type triple grating spectrograph (TGS), with high numerical aperture (0.25)/contrast ($\leq 10^{-6}$ at $532 \pm 0.5 \text{ nm}$)/stray light rejection ($\sim 1.8 \times 10^{-8}$ at $532 \pm 22\text{--}32 \text{ nm}$) for Thompson scattering experiments on low density plasmas such as the ICP, MIP and GD. The TGS performance was evaluated by probing an RF GD *via* Thomson scattering at closer distances from the cathode surface compared with previous studies with a double monochromator instrument. Successful measurement of absolute value of T_e and n_e yielded LODs of $\sim 1 \text{ eV}$ and $\sim 10^9 \text{ cm}^{-3}$ respectively. The instrument has a large spectral window of $\sim 64 \text{ nm}$ which allows analysis of plasmas with relatively high n_e and T_e , such as

LIPs, and the authors noted that the Abel transform should be easy to implement if radial resolution of non-homogenous plasmas is required.

2.2 Fundamentals

2.2.1 Fundamental constants. Dojic *et al.*⁶⁷⁻⁶⁹ used a reduced pressure (<300 mbar) LIP in He to *investigate the Stark broadening* of a number of atom and ion lines. In the first of these papers⁶⁷ five Al II and eight Al III lines were investigated. The n_e was determined to be between 0.98 and $4.86 \times 10^{23} \text{ m}^{-3}$ using the H_β line broadening method, and T_e in the range between 20,000 and 28,000 K using Boltzmann and Saha-Boltzmann methods. Stark broadening parameters for Al II and Al III spectral lines were compared with available experimental and theoretical results. The authors compared their results with Stark widths published in the last few decades, with reasonably good agreement for similar n_e environments. They also reported Stark widths and shifts for the He 388.86 nm spectral line for $n_e > 1 \times 10^{23} \text{ m}^{-3}$. The two other papers by the same authors dealt separately with Stark broadening of 18 Mo I and 18 Mo II lines⁶⁸ and 43 Mo II lines⁶⁹ under similar conditions of $n_e \approx 1.5 \times 10^{23} \text{ m}^{-3}$ and $T_e \approx 13000 \text{ K}$. It should be noted the three studies also included an Abel inversion to account for radial inhomogeneity. In contrast, Kumar *et al.*⁷⁰ determined Stark widths of Al I lines in a LIBS plasma using a different method of calculation to estimate self-absorption. They utilised experimental values of the line width and peak intensity, obtained from time resolved LIBS measurements, which were fitted with calculated values for the optically thin case. The authors noted that the advantage of this was that derivation of the instrument factor and absorption path length no longer posed a challenge. Yet another approach was adopted by Poggialini *et al.*,⁷¹ who used a time-independent, extended C-sigma approach for the determination of the Stark broadening of four Ta I and nineteen Ta II lines in a LIBS spectrum with reasonable precision (RSD ~ 30%). This was proposed as another way of accounting for self-absorption in an optically thick plasma.

The hyperfine, structure and isotopic shifts of U transitions in a LIP were studied by Harilal *et al.*⁷² They observed that the hyperfine structure of ^{235}U overlapped with the isotopic shifts between ^{238}U and ^{235}U when a natural U target was analysed. Furthermore, LIF measurements were affected by the high absorbance of ^{238}U , resulting in a nonlinear dependence of LIF signal on atomic number density. The authors recommended that lower concentrations (at least in terms of ^{238}U) would yield better results.

Several groups contributed to the body of work on fundamental constants; namely oscillator strengths of transitions from the $6d7p\ ^3F_2^o$ to the $7s6d\ ^3D_1$, $7s6d\ ^3D_2$, and $7s6d\ ^1D_2$ states in $^{226}\text{Ra}^{73}$; transition probabilities and line strengths for transitions between different types of $5s^25p^5$, $5s^25p^46s$, $5s^25p^46p$ and $5s^25p^45d$ states of atomic I⁷⁴; and transition probabilities of Ag I lines at 827.35 and 768.77 nm.⁷⁵

2.2.2 Diagnostics

2.2.2.1 Plasmas. Plasma modelling studies are useful because they provide valuable insights into atomisation and excitation mechanisms and the role of interferences. Bogaerts⁷⁶ presented an overview of plasma modelling work undertaken by the group over the last 25 years. Plasmas such as GDs and ICPs, and LA for sample introduction were covered. In particular, plasma-liquid interactions such as those that arise in DBDs and atmospheric pressure GDs were addressed. The important point was made that models developed in other fields often provide important insights for analytical chemistry. One example of such a model was reported by Oks⁷⁷ who produced a general analytical result for the shape of hydrogenic spectral lines under a multi-mode non-monochromatic linearly-polarised electric field $E(t)$, whose power spectrum had a Gaussian (as opposed to Lorentzian) form. They posited that this kind of electric field is caused by the Langmuir turbulence in plasmas, hence could be used to investigate this property and its power spectrum in dense plasmas. While the method was developed using the Ly-beta line of hydrogenic atoms and ions, the authors proposed that it should work using other intense hydrogenic spectral lines that do not have the central Stark components, *e.g.* Ly-delta, Balmer-beta, and Balmer-delta. Ortiz-Mora *et al.*⁷⁸ presented a method to reduce computation time for the determination of H I line profiles by expanding the experimental profile as a sum of Voigt profiles, computed in terms of Faddeeva functions. The calculated profiles fitted well with experiment profiles for n_e between 1×10^{14} and $1 \times 10^{16}\text{ cm}^{-3}$.

Tsivilskiy *et al.*⁷⁹ developed a *3D, non-stationary numerical model* of an ICP by considering the gas, as a temperature-dependent conductor, interacting with the inductive field. Thus, they were able to simultaneously solve Maxwell's equations in conjunction with gas-flow and energy equations to take into account the effect of Joule heating and the Lorentz force on gas flow. The model also predicted the temporal evolution of the 3D magnetic field, pressure, gas velocity and temperature, both in the plasma torch and a chamber used for powder sample introduction. The authors noted that the model was suited to simulate typical

spectrochemical and technological plasma torches, but also acknowledged the limitation that it was only currently applicable to unloaded plasmas, potentially with dry injection of powder particles. Apaydin and Celik⁸⁰ developed a *collisional radiative model* of a low pressure Ar plasma by making use of collisional and radiative rate coefficients, from Los Alamos National Laboratory and NIST, for 101 atomic and 222 ionic energy levels. The model simulated the spectrum for 146 Ar I lines between 86.68 and 2397.3 nm and 303 Ar II lines between 71.8 and 6985.3 nm. The simulated spectrum was compared with the experimental spectrum of a helicon plasma (RF power = 1000 W; magnetic field intensity = 1800 Gauss; Ar flow rate of 20 cm³ min⁻¹) and thus enabled the prediction of the plasma parameters $T_e = 1.31$ eV, $n_e = 3.73 \times 10^{14}$ cm⁻³, $n_{Ar} = 2.57 \times 10^{14}$ cm⁻³, $n_{Ar+} = 3.73 \times 10^{14}$ cm⁻³.

van der Mullen *et al.*⁸¹ investigated a long-standing discrepancy between the results of the 'global plasma model' and Thompson scattering (TS) diagnostics of an MIP (NB: no discrepancy was found for the ICP). The differences were ascribed largely to a much higher value of T_e determined by TS experiments. The authors concluded that the discrepancy resulted from poor Gaussian fitting of the TS spectrum, which was very sensitive to the method employed, leading to a low value for n_e . A number of causes for this were identified, in particular the transient nature of the plasma affecting the reliability of TS measurements. The authors concluded that, in this case, '... it is not the experiment that validates the model but, conversely, that the model points to shortcomings in the experiments'.

One of the problems with diagnostic models of inhomogeneous plasma sources is that emission intensity measurements are integrated along the line-of-sight, so radial information is lost. Commonly, an *Abel inversion* is used to extract this information, but this can lead to accumulation of errors towards the axial region, which is the area of most interest. These shortcomings were addressed by Shi *et al.*,⁸² who developed a Fourier Transform Abel inversion method designed to spread the error evenly across the radial profile. The method used OES images collected with a pushbroom hyperspectral imaging system using a sub-pixel shifting (SPS) sampling protocol in the direction of the radial reconstruction. This was done to improve the fidelity by increasing the number of data points. The software utilised a 350 x 246 x 40 3D hyperspectral model datacube. A 3D median noise filter with 3-pixel radius, a minimum of 50 points and 8 cosine expansions was found to be optimum to keep the RMSE < 8%. A micro-capillary DBD was imaged to construct radial profiles of He, N₂ and N₂⁺ emission, revealing a hollow-cone shape, with axial profile peak intensities at different positions compared to the line-of-sight images.

It is not always necessary to develop complex mathematical models to gain insight into atomisation and ionisation mechanisms in the ICP. This approach was exemplified by Ebert *et al.*,⁸³ in the latest addition to a series of papers from Houk and co-workers. They used a *high-speed camera with short exposure time* (10 μs) and fast framing rate (5000 frames s^{-1}) to film particles resulting from a nebulised solution of high Y concentration. The movies clearly showed the dried particles moving along the axial channel of the ICP and the associated red (probably YO), pale red (probably Y atom) and blue (probably Y^+) emission surrounding them. The nature of the emission cloud was observed to change from red to a faint white streak (attributed to a solid residue) with a surrounding cloud of blue Y^+ emission. The velocity of the droplet and subsequent particle was measured to be 28 m s^{-1} . These observations confirmed results of other studies of droplets and particles in the ICP central channel.

Modelling studies of plasmas used for MS often follow a different approach than those for OES, largely because some type of interface is required between the plasma and much lower pressure in the MS, and this affects ion energies and formation of polyatomic ions. This point was well made in the paper by Thompson *et al.*⁸⁴ who studied the effect of H_2O , He, N_2 and H_2 on *ion kinetic energy (KE)* in wet and dry Ar ICP used in ICP-MS. They found that there was a minor, but consistent, difference in the relationship between analyte ion mass and ion KE in dry plasma compared to wet plasma, at least for ions with $m/z > 23$ using the instruments under study. Calculated values for T_{gas} obtained using two different instruments were: shielded wet plasma between ~ 3055 and 3905 K ; unshielded dry plasma between ~ 2441 and 3164 K . These were significantly lower than T_{gas} previously determined using ion KE measurements and much lower than typical T_{gas} temperature found in ICPs used for OES (between 5000 and 7400 K), possibly due to the presence of ion optics, gas collisions in the interface, and/or use of the quadrupole as the ion stop. The presence of H_2O resulted in higher plasma potentials and addition of small amounts of H_2 to a dry plasma made it behave more like wet plasma, *i.e.* ion KEs increased. Shielding a wet plasma lowered ion KEs and decreased their spread, but shielding a dry plasma had little effect. Differences in ion KEs for polyatomic species suggested different mechanisms or locations of formation between wet and dry plasma.

Galbacs *et al.*⁸⁵ used classical thermodynamics to predict the *equilibrium concentration of polyatomic species* formed from Ar, H, D and O in the ICP, with a view to

the analytical determination of D by monitoring a polyatomic ion. They predicted that the species ArD^+ , OD^+ , HD^+ , and D_2^+ (at m/z 42, 18, 3, and 4 respectively) were sufficiently present at $T = 5000$ K to make them useful for determination of D. After optimisation of the operating conditions, calibration curves were constructed for ions at m/z 4 and 42 using mixtures of D-depleted (with 1 ppm D) and D-enriched (99.96 atom % D) waters. The LODs were 78 ppm at $m/z = 4$, and 3 ppm at $m/z = 42$. The paper also included a useful appendix which detailed the methodology used to calculate the partition functions and the sources of fundamental data.

Bufkova *et al.*⁸⁶ investigated the spatial atomisation of TeH_2 in a DBD using LIF. The DBD was operated with an Ar carrier gas flow rate of 75 mL min^{-1} and peak-to-peak high voltage of 18 kV. Hydride generation was employed to deliver TeH_2 gas to the DBD. Free Te atoms were identified throughout the length of the quartz discharge tube covered by the electrodes. An atomisation efficiency of up to 100% was estimated. Addition of O_2 enabled *in situ* collection, with a trapping efficiency of $\sim 50\%$. It should be noted that experiments were performed on the wet gaseous hydride because the gas-liquid separation tended to remove the TeH_2 .

2.2.2.2 Graphite furnaces. Kulik *et al.*⁸⁷ studied the degradation of longitudinally heated furnaces for ETAAS in the presence of W, Zr and Pd compounds used as modifiers. Visual changes in the furnaces and the loss of carbon material over time were reported. The absorption profiles obtained during the atomisation of Ag and Cu at different stages of degradation of modified and unmodified furnaces were discussed. Furnaces used with modifiers were observed to experience accelerated damage to the pyrographite coating and subsequent destruction of the polycrystalline graphite base compared with furnaces used without modification. Possible explanations for these observations were provided.

2.2.2.3 Flames. Diagnostic studies of flames have somewhat fallen out of fashion. However, Obrusnik *et al.*⁸⁸ developed a computational model of gas flow and hydrogen combustion in a diffusion flame using an open-source computational framework and selected species from the GRI-MECH 3.0 reaction mechanism. The species (namely Ar, H_2 , H, OH, HO_2 , H_2O , H_2O_2 , O, O_2 and N_2) were chosen to simulate an Ar-diluted H_2 flame in air. The distribution of H radicals were both simulated using the model and experimentally determined by LIF with

reasonably good agreement; the main difference being that the experimental H density profiles were more diffuse.

2.2.3 Interferences. *Space charge effects* are generally thought to be a major cause of *non-spectroscopic matrix effects* in the ion beam of ICP-MS, however, a study by Jiao and Olesik⁸⁹ has questioned this. They investigated matrix effects in ICP-SFMS, caused by high concentrations of concomitant elements as a function of analyte mass, matrix mass, matrix element concentration, lens voltage, and nebuliser gas flow rate. Their premise was that, given the high accelerating voltage (-2 kV), space charge effects should be less evident because of the resultant relatively smaller spread in ion KE between low and high mass ions. The effects of matrix elements Na, Cu, Y, In, Cs, Tb, Lu, and Tl on signals for analyte elements ${}^7\text{Li}^+$, ${}^{11}\text{B}^+$, ${}^{24}\text{Mg}^+$, ${}^{45}\text{Sc}^+$, ${}^{71}\text{Ga}^+$, ${}^{75}\text{As}^+$, ${}^{88}\text{Sr}^+$, ${}^{111}\text{Cd}^+$, ${}^{138}\text{Ba}^+$, ${}^{153}\text{Eu}^+$, ${}^{172}\text{Yb}^+$, and ${}^{238}\text{U}^+$ were characterised. When the guard electrode was grounded (shielded torch), the effect of the matrix on analyte ion sensitivities increased with increasing matrix mass and concentration, consistent with space charge effects. However, the effect was similar for all analyte ions irrespective of m/z , contrary to the expected space charge effect. Furthermore, matrix effects on analyte signals were similar to those observed using a ICP-QMS with a small +ve accelerating voltage; despite the fact that the much high beam current in ICP-SFMS would be expected to increase the severity of the space charge effect. Lens voltages and operating conditions had a large effect on the severity of the matrix effects. When the guard electrode was ungrounded (unshielded torch), there was no correlation between matrix-induced analyte ion signal suppression and the mass of the matrix or analyte. Clearly, the causes of matrix effects in ICP-MS cannot be reduced to a simple explanation solely due to space charge effects in the ion beam, and other factors are likely to be at play. Barros *et al.*⁹⁰ also studied the effect of matrix elements Na, Cu, Y, In, Tb, Lu and Tl on analyte signals for ${}^{11}\text{B}^+$, ${}^{24}\text{Mg}^+$, ${}^{45}\text{Sc}^+$, ${}^{60}\text{Ni}^+$, ${}^{71}\text{Ga}^+$, ${}^{75}\text{As}^+$, ${}^{111}\text{Cd}^+$, ${}^{138}\text{Ba}^+$ and ${}^{172}\text{Yb}^+$ using ICP-QMS. They observed that matrix effects were more severe when high mass matrix elements were present but were not correlated with analyte m/z , such that a single internal standard IS could be used to correct for matrix effects for most analytes with $m/z > 50$. They drew the not unreasonable conclusion that changes in the design of ions lenses used in the newest generation of ICP-MS instruments mean that a re-evaluation of the causes of matrix effects is necessary.

Grotti and Todoli⁹¹ investigated the matrix effect caused by HNO_3 in ICP-MS. They observed an increase in ion signal for elements with an IP < 7.5 eV and a decrease for less easily ionised elements. Spatially resolved measurements suggested that the increase for

elements with low IPs was caused by a delay in ionisation and consequent reduction in the ion lateral diffusion. They ascribed the decrease for elements with high IPs to the cooling effect caused by the thermal dissociation of HNO_3 in the plasma, and subsequent dissociation of N–O ($E_{\text{diss}} \sim 7 \text{ eV}$) and N–N ($E_{\text{diss}} = 9.8 \text{ eV}$). Hence, the distinction between elements with IPs $> 7.5 \text{ eV}$ which were not suppressed and those with IPs $> 9 \text{ eV}$ which were suppressed. It is noteworthy that they did not observe different effects for analytes with different m/z , giving further support to the conclusions of the previous two papers.

Spectroscopic interferences in ICP-MS can often be addressed using a collision/reaction cell, of which there are various designs extant. Narukawa *et al.*⁹² compared Ne and He used as collision gases. They computed a 'cell gas index' to indicate the relative tendency of reaction between an analyte and collision/reaction gas. The index was calculated from two factors, the energy factor (α) and probability factor (β). The former was the energy gap in IP or E_{diss} between analyte and a cell gas; and the latter was calculated from the mass ratio (β_1) of the analyte and the cell gas, the relative mean free path of the cell gas (β_2) and the atomic diameter of the analyte (β_3). For example Ne, with an index value 6x greater than He, attenuated analyte sensitivity by 5x more in practice. In contrast, the cell gases H_2 , O_2 , and N_2 could have both positive or negative values. A negative value meant that a gas did not work as a reaction cell gas at all, whereas a positive value meant that it reacted with analyte ions to produce addition products. Its utility is somewhat tempered by the fact that the cells gases are in such excess that reactions are driven to completion, hence little can be inferred from the absolute positive or negative values of the index.

Carter *et al.*⁹³ evaluated eight different supervised learning models to predict the *severity of matrix effects caused by Ca and Na in ICP-OES*. The models were trained on nine species of Ar, H and O and used to predict analyte recoveries for Cd, Co, Cr and Pb. These predictions were then used to help choose the best approach to use, *i.e.* simple external calibration, internal standardisation using a non-analyte signal, or matrix matching. The Ar atomic line at 737.212 nm and Y were both used to successfully correct for matrix effects when the optimised models (GLM, regularised GLM and PLS regression) predicted absolute errors of $< 30\%$. The main advantage of the technique was that it could be used in real time by simply monitoring non-analyte elements. For predictions of matrix effects $> 30\%$ the authors conceded that any correction strategy was likely to fail, but the value of the predictive model in this context is that the analyst would be alerted to the fact.

Two related papers from the same group addressed the problem of *matrix effects in a high power nitrogen MIP-OES instrument*. In the first,⁹⁴ the effect of matrix elements (Na, In, Bi, Zn, Cu), HNO₃ and HCl on the analytical signals of elements present as impurities in the nitrogen MIP (1 kW), were investigated. No change was observed in analytical signals for acid concentrations up to 0.5 M (0.9 M in the case of REEs). Significant changes in analytical signals were observed when concentrations of matrix elements were >1%, but whether these effects were caused by matrix effects in the plasma or sample introduction system was not addressed. In the second paper,⁹⁵ matrix effects in an MIP sustained using a H₀₁₁ cylindrical microwave resonator (up to 1.65 kW) were investigated. Emission signals for atomic lines with $E_{exc} < 5$ eV were enhanced in the presence of Na, Cu, Pb but suppressed atomic and ionic lines with E_{exc} or $E_{sum} (E_{exc} + E_{ion}) > 5$ eV. Matrix elements with lower ionisation potentials were observed to have a greater matrix effect on signals for both atomic and ionic emission lines. A plasma temperature of 5,200 K was determined using the Boltzman plot method for Fe lines, and $n_e = 1.9 \times 10^{13} \text{ cm}^{-3}$ was determined using the Saha equation. The plasma temperature was unaffected by up to 1% Cu, Cd, Pb and Zn, whereas the n_e increased in the presence of Na, Pb and Cu.

Greda *et al.*⁹⁶ investigated matrix effects caused by Na, K, Mg, Ca, Al, Cu, Fe, Mn, Ni, and Zn, in flowing liquid anode GD-OES. They observed suppression in analyte signals of ~10% for Hg and Tl, ~20% for Cd and Ag, and up to ~80% for Zn and Pb in the presence of 0.24 mmol L⁻¹ of individual matrix elements. Values of $T_{rot}(\text{OH})$ and the $H_\beta:H_\alpha$ line intensity ratio remained unchanged in the presence of the matrix, suggesting that the atomisation/excitation conditions were unaffected. Hence, the reason for the decrease in analytical response was ascribed to a reduction in analyte transport from the liquid to plasma phase. The use of masking agents to reduce the effect of the matrix elements was partially successful providing that a stable complex could be formed, hence transition metals were easier to mask than alkali and alkaline earth metals.

2.3 Chemometrics

Large spectroscopic datasets are often difficult to handle because of the computational requirements. In order to address this Vr  bel *et al.*⁹⁷ developed a restricted Boltzmann machine method for dimensional reduction of large spectroscopic datasets obtained using LIBS. Initial studies compared its performance to PCA, with variable results. The PCA

performed better in some respects but worse with regard training time and applicability to very large datasets.

3 Laser-based atomic spectrometry.

Key fundamental studies and instrumental developments in laser-based atomic spectrometry are highlighted in this section. Progress in this area during the previous years can be followed here.¹ Atomic spectrometry techniques where the laser is used as either an intense energy source or a source of precise wavelength (e.g. LIBS or LIF) are considered. Studies related to LA used for sample introduction are reviewed in a section 1.3.2.1. The use of lasers for fundamental studies of the properties of atoms or for thin film deposition are not reviewed.

3.1 Laser induced breakdown spectroscopy (LIBS).

This section describes the latest instrumental developments and fundamental studies related to LIBS, but it does not cover detailed applications. Ji *et al.*⁹⁸ reviewed recent developments in the use of LIBS for aerosol analysis in atmospheric monitoring and/or industrial processes. The review included information about new instrumentation, analytical methods, plasma-particle interactions and applications. New developments and applications of remote LIBS were reviewed by Li *et al.*,⁹⁹ including a discussion on existing problems related to inferior efficiency and lower collected signal from a remote distance.

Current trends in LIBS were comprehensively reviewed by Fernandes Andrade *et al.*,¹⁰⁰ including information about key analytical variables for proper sample treatment, signal enhancement, data processing and qualitative & quantitative approaches. Guezenoc *et al.*¹⁰¹ reviewed the different spectral-based normalisation methods used for LIBS quantitative analysis. They encouraged users to compare the different normalisation methods to choose the most appropriate one according to the analytical context. Methods to improve the detection sensitivity of LIBS were reviewed by Fu *et al.*,¹⁰² including a discussion about the pros and cons of the different physical, chemical, and mathematical approaches.

3.1.1 Fundamental studies. The direct determination of halogen elements by LIBS is difficult due to their low excitation efficiency in the plasma. Hence, molecular emission, from halogen containing compounds formed in the plasma is employed as an indirect calibration method. For example, a method based on the detection of emission signal from SrF was recently used by Tang *et al.*¹⁰³ to determine the concentration of F in copper ore.

The *spatio-temporal distribution* of atomic and molecular LIBS emission signals plays an important role in optimisation of detection of the molecular emission from the halogen compounds. Fernandez-Menendez *et al.*¹⁰⁴ investigated the spatio-temporal distributions of atomic and molecular LIBS emission signals from samples containing different amounts of Ca and F. Results confirmed that excited CaF molecular species were mainly formed by recombination processes. At short delay times, it was observed that molecular emission was predominant closer to the sample surface (between 0 and 480 μm). This spatio-temporal splitting of atomic and molecular signals was used to maximise the CaF molecular emission while keeping the atomic emission at low levels. Using this method, it was possible to improve the sensitivity for F detection by more than 4-fold, in comparison to that obtained using typical molecular acquisition conditions. In the case of Ca-free samples, the simultaneous nebulisation of a Ca-containing solution during LIBS analysis can be used to achieve a CaF molecular emission that is proportional to the amount of F in the sample. Mendez-Lopez *et al.*¹⁰⁵ investigated these interactions between the nebulised solution and the plasma for different nebulisation conditions, using Cu as a model substrate sample. When a solution of Ca was nebulised the decay intensity of the Cu lines changed, with lower average Cu T_{exc} and increased ablation rates. Also, asymmetry of the excited species in the plasma plume and partial detachment of the plume was observed. Spatio-temporal studies of CaOH molecular emission in underwater LIBS were performed by Tian *et al.*¹⁰⁶ The longer persistence of CaOH molecular emission was employed as an alternative method to the detection of Ca I and Ca II emission lines, resulting in higher stability, less self-absorption, similar LODs and reduced matrix effects. This method provided an improvement in the analytical performance of underwater LIBS.

Measurement of the effect of *self-absorption on the measured line* intensities and line broadening in LIBS spectra can be used to determine fundamental parameters, such as transition probabilities, oscillator strengths and Stark broadening coefficients. In a recent review, Aberkane *et al.*¹⁰⁷ critically discussed the application of LIBS for the determination of these fundamental parameters, which are of paramount importance for plasma diagnostics or for quantitative analysis using a calibration-free LIBS methods. The mechanism of the multi-elemental self-absorption effect in LIBS was also studied in detail by Cai *et al.*¹⁰⁸, who combined different models to create a self-absorption effect value model. Numerical simulations were then applied to determine plasma spatial distribution characteristics. The experimental results were in good agreement with those of the theoretical simulation. They

also studied emission of Na, K and Al atom lines using LIBS with and without microwave assistance. Results showed that microwave assistance could enhance emission intensity and inhibit or reduce self-absorption. Rezaei *et al.*¹⁰⁹ reviewed current strategies used for the estimation, compensation and exploitation of self-absorption effects in order to improve the analytical potential of LIBS.

Nanoparticle enhanced (NE) LIBS was investigated by De Giacomo *et al.*¹¹⁰. They studied the plasmonic nature of the signal enhancement during NE-LIBS of noble metal NPs deposited on metal samples. Shielding of the NPs due to the plasmonic effect was thoroughly studied using laws of conservation of energy and the spectral features of the atomic emission during plasma evolution. Negligible differences in the ablated mass (as measured with profilometry) were measured with and without plasmon enhanced ablation. However, NE-LIBS signal enhancement was observed which correlated with electromagnetic field enhancement. Liu *et al.*¹¹¹ evaluated the merits and demerits of NE-LIBS, paying a special attention to the effect of pre-ablation and signal repeatability.

The excitation of ablated target atoms by Penning-like energy transfer processes, through collision between the ablated atoms in their ground state with metastable excited He atoms, was studied by M. Pardede *et al.*¹¹² They found that suppression of the self-absorption effect in LIBS was demonstrated as a consequence of this excitation mechanism. Hedwig *et al.*¹¹³ employed a double-pulse technique in which the first laser was used to create a strong He plasma (a He flow of 5 l/min was kept parallel to the sample surface), and the second laser (after a short optimised delay) was used to ablate the target. The method provided linear-calibration curves even for high concentrations of alkali elements or for highly concentrated Al samples.

3.1.2 Instrumentation. A new approach to further improve the sensitivity of orthogonal double pulse (DP-) LIBS was developed by Bai *et al.*¹¹⁴ The method was based on the use of a concentric multipass cell to form a repeatedly reheating plasma. This enhanced the emission intensity of spectral lines and lowered the LOD of doublet lines of Mn I at 403.08 nm and 403.31 nm by 2.3-fold, compared to orthogonal reheating DP-LIBS. The effect of reflection times in the cell was evaluated, confirming the contribution of the reflected laser pulses. A new collinear long-short DP-LIBS was developed by Cui *et al.*¹¹⁵ and used to generate Fraunhofer-type signals from an underwater copper sample. A compact laser head that

consisted of two independent channels (with and without Q-switch units) was constructed to reduce the external path of the laser beam for collinear long and short pulse duration double pulses. The early structure of underwater plasma generated by collinear long-short DP-LIBS is similar to a solar structure, *i.e.* hot core and cold shell. During the early stage of plasma evolution the hot core emits broadband continuum radiation, which is selectively absorbed by the outer cold shell (like Fraunhofer lines). The authors found that, under conditions of underwater and collinear long-short DP-LIBS excitation, the cold shell had sufficient thickness and number density to generate a strong and stable Fraunhofer-type signal, from the ablation of a Cu sample placed at 100 mm below a deionised water surface, at very short delay times (~ 10 ns). They maintained that further analysis of a Fraunhofer-type signal may contribute to more precise under-water quantitative LIBS measurements. The addition of a pre-ablation laser pulse and a reheating laser pulse to LIBS were investigated by Prochazka *et al.*¹¹⁶ The energies of the pre-ablation and reheating laser pulses were kept constant and the energy of the ablation pulse was set to the minimum value to detect analyte signals above the LOD. Once the delay times of the three laser pulses were optimised, an enhancement of signal:background ratios was observed in comparison to DP- and SP-LIBS. They demonstrated that pre-ablation caused a higher ablation rate per pulse and that re-heating increased the plasma temperature.

Laser ablation at high repetition rate, sequentially coupled to LIBS for analysis of non-matrix matched standards, was described by Diaz *et al.*¹¹⁷ The approach was used to overcome matrix effects during the analysis of non-matrix matched standards. The performance of kHz-LA-LIBS was evaluated for the analysis of relatively homogenous metal alloys, achieving a significant reduction in analysis time and improved SNR and LOD, which was related to the larger amount of ablated mass. The authors claimed that the reduction of matrix effects, together with the larger sampling volume achieved with kHz-LA-LIBS, could provide a robust analytical tool for geological applications where analytes may be discrete and non-homogenously distributed.

A novel method for elemental analysis of airborne particles was developed by Heikkilä *et al.*,¹¹⁸ based on the use of *electrodynamic balance trapping* followed by LIBS. A novel corona-based aerosol charger was used together with a double-ring electrodynamic balance trap. The experimental set-up allowed the elemental composition analysis of single particles (with diameters as low as 1 μm), from ambient air at low concentrations ($\sim 1 \text{ cm}^{-3}$). The authors claimed that this technique had great potential for any application that might

require real-time single particle elemental characterisation, especially for low ambient concentrations.

A new prototype of a *microwave-enhanced fibre-coupled LIBS* instrument was developed by Ikeda *et al.*,¹¹⁹ who used a 2.45 GHz semiconductor microwave oscillator to enhance the LIP. This enhanced line intensities by >1000-fold in the analysis of Al₂O₃ test samples. Pulsed microwave oscillations were also used to sustain a non-thermal plasma that avoided the sputtering of the microwave antenna, eliminating any potential source of sample contamination. The authors highlighted the great capability of the technique for applications in screening nuclear fuel debris; *e.g.* decommissioning the post-accident Fukushima Daiichi nuclear power station set to begin in 2021.

LIBS combined with resonance Raman scattering was developed by Zhang *et al.*¹²⁰ for the determination of the sulfur content in alumina. It is known that standard LIBS configurations show low efficiency for the detection of S. In this work, disulfide radicals, which are formed in the LIP after the ablation of a S-containing sample, were excited by resonance Raman scattering using a 306.4nm wavelength laser, while their Raman shift was observed at 710 and 1420 cm⁻¹. Calibration curves from alumina samples with different amounts of S showed improved linearity and LODs.

3.1.3 Novel LIBS approaches. Automated or semi-automated preprocessing of LIBS data, from samples of similar composition, was developed by Ewusi-Annan *et al.*,¹²¹ using machine learning tools. For this purpose, PLS regression and artificial neural networks were applied on two LIBS datasets, obtaining relatively high accuracy on the prediction of preprocessed spectra of geological samples analysed by a laboratory model of ChemCam and by ChemCam as it interrogates Martian targets, respectively.

An extensive dataset of LIBS spectra was provided by Kepes *et al.*¹²² for pre-training and evaluation of classification models. The dataset consisted of LIBS spectra from 138 soil samples belonging to 12 distinct classes, and included the composition of each sample as well as estimated uncertainties. A classification contest was organised for the EMSLIBS 2019 conference using this dataset. The five best classification approaches were selected, and their algorithms discussed in detail by Vrabel *et al.*¹²³ Chen *et al.*¹²⁴ investigated a convolutional neural network (CNN) with 2D input for the identification of rock samples (*e.g.* dolomites, granites, limestones, mudstones and shales). The performance of the method was compared with other identification methods, concluding that a CNN has great potential for lithological identification and could be a feasible and useful tool for LIBS spectral data processing.

Often, when using LIBS, calibration is performed by plotting the elemental concentration as a function of the emission signal (inverse model) rather than the normally accepted way (direct model). Duponchel *et al.*¹²⁵ demonstrated statistical differences in the predictive ability of the direct and inverse model. The authors recommended the use of the inverse model as it is potentially more efficient, in particular at small SNR, or when the number of calibration samples is low. However, Poggialini *et al.*¹²⁶ argued that some peculiar characteristics of the LIBS signal, including the non-homoscedasticity of the data employed in the calibration plot, make the application of inverse models less convenient in most cases. For instance, the authors demonstrated, using spectral signals acquired on brass samples, that inverse calibration led to less precise analytical results. The authors highlighted that these two calibration methods sparked multiple discussions and included a reference to a previous publication (Meija *et al.*, *Anal. Chem.* 86 (2014) 8563–8567) that described coordinate swapping properties.

Other calibration methods based on CNNs have been investigated for use as classifying and quantifying approaches that can improve the prediction accuracy of LIBS regression models. Cao *et al.*¹²⁷ used a CNN model for the quantitative analysis of ChemCam spectral data, produced using LIBS under the Mars-like atmospheric conditions. The model resulted in superior performance for the quantification of oxides compared to models based on support vector (SV) and PLS regression. A deep CNN model was developed by Li *et al.*¹²⁸ for multi-component quantitative analysis of 23 China national standard reference materials. The method was implemented for the LIBS system in MarSCoDe, the Mars Surface Composition Detector on the rover of China's first Mars exploration mission.

Imaging using LIBS results in several million spectra from a single sample in a few hours. Nardecchia *et al.*¹²⁹ developed a spectral analysis strategy which enabled simultaneous detection of major and minor compounds and the generation of associated localisation maps. This novel approach was employed for the analysis of a complex rock sections with different phases and traces. An image features assisted line selection method was developed by Yan *et al.*¹³⁰ as an automatic line selection tool. The method improved the classification performance of LIBS, which was investigated using 24 metamorphic rock samples and conducted with a linear discriminant analysis algorithm. Classification accuracy was increased compared to manual line selection.

Ultra-sensitive detection of trace metal levels in liquid samples was achieved by Liu *et al.*¹³¹ using a novel strategy that utilised metal-chelate induced NP aggregation to enhance

the LIBS signal. The authors showed that direct mixing of Au NPs and metal chelates enhanced contact area and adhesion forces of the analytes, resulting in improved LODs and recoveries (between 88% and 110%) for the evaluated analytes. It was claimed that this methodology pushed the potential of LIBS for practical liquid sample analysis.

Attributing an absolute depth to the laser-induced crater produced after a few laser pulses is a key parameter to achieve proper qualitative and quantitative depth profile analysis of coated samples. Weimerskirch *et al.*¹³² developed a novel method based on non-scanning, single-spot, optical coherence tomography to determine absolute depth of laser-induced craters.

3.2 Other developments

A compact *cavity ringdown isotope ratio laser spectrometer* instrument was developed by Cui *et al.*,¹³³ for precise and accurate measurements of water IRs using direct absorption spectroscopy. A distributed feedback laser (at 2.7 μm with tuning range of 4 cm^{-1}) was directed both to a home-made Fabry-Perot etalon, for frequency metrology, and (mainly) to a multi-pass absorption cell for detection of the absorption signal. The authors simultaneously measured $^2\text{H}/^1\text{H}$, $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ isotope abundance ratios in glacier water, obtaining results that agreed with IR-MS measurements. They claimed that the instrument was suitable for real-time and *in situ* measurement of water IRs.

A method based on LIBS, with orthogonal post-excitation using a tunable optical parametric oscillator to achieve *molecular LIF*, was employed by Nagli *et al.*¹³⁴ to improve detection of Cl in concrete samples.

4 Isotope Analysis

4.1 Reviews

With the diversity of stable isotope systems now being used in the fields of chemistry, geology, environmental geoscience and biosciences, there is a call for some degree of unity in the notations used to represent isotopic deviations. Meisel¹³⁵, in an editorial for *Geostandards and Geoanalytical Research*, put forward that future papers should express the difference between sample ratio and standard reference ratio as δ . This would be applied to all isotope systems, regardless of the magnitude of the difference. Effectively this depreciated the use of ϵ and μ as notations that combine difference, and the units of the difference (10^4 and 10^6). It

was suggested that the δ notation is preceded by a factor expressing the scale of the difference, for example: $10^3\delta(^{18}\text{O})_{\text{std}} = -9.5$, or $10^6\delta^{184/184}\text{W}_{\text{sample/std}} = -330$.

Where applicable, the *double isotope spike technique* is the current method of choice for mass fractionation correction. A study by Liu *et al.*¹³⁶ provided a practical overview and outlook on the use of double spiking. This summarised the principles of the technique, including the role of different fractionation laws, the choice of spike pairs, and the optimisation of spike-sample mixtures. Specifically the study examined the double spike principles in relation to Ca isotopes. One interesting feature of double spiking highlighted by the study was the possibility of double spike compositions, presumably of the lighter element, changing with time during storage. This has previously been observed (Young *et al.*, Earth Planet Sci. Lett., 2009, **288**, 524-533) in the storage of a Mg double spike where solutions in non-PTFE bottles and at concentrations <40 ppm where Mg isotope compositions were observed to drift over periods of months.

A review of sample preparation methods for elemental and isotopic analysis of geological samples was conducted by Zhang and Hu.¹³⁷ They considered the key methods of sample digestion, namely open vessel acid, high-pressure acid, microwave, NH_4F or NH_4HF_2 , and alkali fusion. The key advantages and disadvantages were discussed, but there was particular focus on the ammonium fluoride digestion. These reagents are noted to have the advantages of: safety; efficient high-temperature digestion; lack of insoluble fluoride formation; and purification via sub-boiling distillation. These were summarised in a useful table of applications and references. Sample preparation for LA-ICP-MS was also covered, including pressed powder pellets and glass fusion beads. Zhang and Hu¹³⁸ conducted a valuable review of isotopic fractionation and interference correction for IR measurement by LA-ICP-MCMS. This covered methods of fractionation monitoring during ablation: internal correction, utilising doping elements and sample-standard bracketing. The section covering interference corrections contained a useful figure assessing the effects of oxides, hydrides, argides and doubly charged ions, relative to the atomic mass spectrum. Zhang *et al.*,¹³⁹ also presented new software to process isotope data from LA-ICP-MCMS systems.

4.2 Radiogenic isotope ratio analysis.

Chu *et al.*¹⁴⁰ evaluated measurement of Pb isotopes, with ~50 pg Pb, using multiple ion counting TIMS. The study utilised a dynamic measurement routine switching ^{203}Tl - ^{204}Pb - ^{205}Pb - ^{206}Pb - ^{207}Pb through four ion counting detectors. The ^{205}Pb spike technique

demonstrated that $^{207}\text{Pb}/^{206}\text{Pb}$ could be measured to 0.1% (2RSD) and consequently would be suitable for U-Pb dating of zircon with picogram quantities of Pb.

A study by d'Abzac *et al.*,¹⁴¹ compared 1030 nm and 257 nm wavelength femtosecond laser ablation with reference to zircon U-Pb dating. These wavelengths, termed near-infra-red (NIR) and near-ultra-violet (NUV) respectively, were used to determine ages of standard zircons. Comparisons indicated that NIR energy developed non-linear crater shapes and provided a much lower yield than the NUV system. This resulted in a greater fractionation between U and Pb during ablation, the results showing a high bias from the Concordia curve and relatively poor precision. NUV was found to produce the most robust data from its high yield and potential for high spatial resolution (<10 μm) spot size. Liu *et al.*¹⁴² used LA-ICP-MS to assess the optimum configuration of spot size and co-introduction of 2% water-ethanol vapours. Results indicated that the vapour introduction produced higher precision results, broadly in line with TIMS literature values, while dry plasma analyses differed from published data. Problems of common Pb correction during LA-ICP-MS analysis of high-U minerals such as zircon, apatite, monazite and titanite were highlighted in a study by Gilbert and Glorie,¹⁴³ who investigated the correction of ^{204}Pb for isobaric ^{204}Hg , and the potential to remove the interference in a reaction cell. Adding ammonia to a reaction cell prior to mass separation instigated the charge-transfer reaction $\text{Hg}^+ + \text{NH}_3 \rightarrow \text{Hg}^0 + (\text{NH}_3)^+$. This effectively removed the ^{204}Hg from the ion beam allowing an accurate estimate of common Pb in age determination using high U-Pb minerals.

Pb isotopes are now routinely determined to high precision using a double spike protocol. However it is difficult to integrate and compare these data with Pb isotopes measured using less robust fractionation correction routines such as constant-f and Tl-spiking (Taylor *et al.*, *J. Anal. At. Spectrom.*, 2015, 30, 198-213). A method to correct less robust data was presented by Taylor *et al.*¹⁴⁴ The technique can only be applied to data where one of the Pb isotope parameters (*e.g.* $^{207}\text{Pb}/^{206}\text{Pb}$) can be predicted or is a constant value. However, where such a prediction can be made, the correction was demonstrated to produce tight data clusters approaching those measured using a double spike. Pb isotope measurements in seawater presents challenges in chemical separation and low Pb levels. Griffiths *et al.*¹⁴⁵ outlined a method comparing Nobias Chelate resin with $\text{Mg}(\text{OH})_2$ co-precipitation. ICP-MCMS analysis employing a double spike and Tl-spike were then used to correct for mass fractionation. They concluded that Nobias separation provided the most matrix-free and precise determinations out of all the methods used.

High resolution Nd isotope analysis is generally limited by detector noise, counting statistics and the ability to accurately correct instrumental mass fractionation. Fukai and Yokohama¹⁴⁶ investigated the potential for secondary instrumental fractionation, derived from material deposited on ion beam focus plates. These authors found that, following a fractionation correction to a known Nd ratio, a bias was observed in the $^{142}\text{Nd}/^{146}\text{Nd}$ ratio. A re-correction to $^{150}\text{Nd}/^{144}\text{Nd}$ resulted in an improvement in reproducibility by a factor of 1.3. This may enable a more accurate determination of $^{142}\text{Nd}/^{144}\text{Nd}$ in studies of terrestrial rocks. Stable Nd isotopes were also the focus of a study by McCoy-West *et al.*¹⁴⁷ Their work demonstrated the possibility of measuring the radiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ ratio alongside the stable IR ($\delta^{146}\text{Nd}$) and the Sm/Nd concentration in the same measurement. This was achieved using a ^{145}Nd - ^{150}Nd double spike to correct instrumental and preparation mass fractionation, and a ^{149}Sm spike for Sm concentration determination. As the precision of the results was essentially indistinguishable from individual isotope measurement protocols, it proved that the methodology could be used in a geological context for age-correction of Nd isotope data or geochronology. The work also highlighted the potential for stable Nd isotopes to provide information on the evolution of magmatic systems, where there is a potential correlation between higher SiO_2 in magmas and heavier $\delta^{146}\text{Nd}$.

Reimink *et al.*¹⁴⁸ explored the potential for cavity ion source TIMS to generate high ionisation efficiency measurements of Nd isotopes. Their system used a tantalum rod with a 1.5 mm diameter hole drilled to depths of 10-40 mm, with $\sim 2 \mu\text{g}$ Nd added to the cavity with colloidal graphite and Re powder as activators. Results indicated that this system had the potential to generate large ion beams ($>50 \times 10^{11}$ A) for several hours. When these levels of efficiency were translated to precision, the predicted $^{142}\text{Nd}/^{144}\text{Nd}$ was estimated to be between 0.5 and 1.5 ppm, which was a significant improvement on the 2 to 3 ppm precision achieved by regular flat-filament techniques. This may provide a more effective utilisation of Nd isotope decay systems in understanding early Solar System events.

As well as geological systems, Sr isotopes can be used in archaeological and biological investigations. Murphy *et al.*¹⁴⁹ examined the potential for the ecological use of ICP-MS-MS in determining Sr isotopes in insects. This study used a Thermo iCap TQ instrument with a N_2O reaction gas, with the aim of maintaining $^{87}\text{Sr}^{16}\text{O}^+$ while minimising $^{87}\text{Rb}^{16}\text{O}^+$. NIST SRM 987 Sr doped with Rb demonstrated that there was no noticeable effect on the measured $^{87}\text{Sr}/^{86}\text{Sr}$. This opened the technique to the measurement of single insects containing between 2 and 4 ng Sr, albeit with a precision of better than 0.2%.

4.3 New developments.

Davis¹⁵⁰ devised a new method to *calibrate the efficiencies of Faraday and ion-counting detectors*. This involved a single change in the collector positions rather than multiple relocations of the collectors. The result was that efficiencies could be measured by a simple division of ratios following exponential fractionation correction. Data acquired using Pb isotope standard SRM NIST 982 demonstrated that ion counter gain and dead time could also be determined by a similar method. A new type of Faraday cup ion detection system was tested with respect to U-Pb isotopes and geochronology by Symanowski and Schoene¹⁵¹. They use the Isotopx Phoenix TIMS instrument fitted with the ATONA detection system (attoAmp to nanoAmp). These detectors have potential to measure a wide dynamic range of signal without recourse to amplifier switching, while having fast response time and producing less noise relative to traditional Faraday signal processing. Tests conducted on solution standards indicated that the ATONA-equipped Faraday system outperformed traditional Faraday-Daly detector combinations with signal intensities >1 mV and were comparable down to 500 μ V levels. Overall, this system demonstrated that zircon geochronology using samples with around 10 pg radiogenic Pb could be measured without degradation of precision.

Isolating isotopes of an element for use in spikes is usually the domain of Calutrons and other large-scale isotopic separation equipment. Dion *et al.*¹⁵² continued their development of isotopic isolation by ICP-MS. Replacement of the collector system with a rotating conductive substrate enabled isolated deposition of isotopes in discrete domains across this substrate. The aim was to collect 2 ng of each isotope following aspiration of a 1000 μ g g⁻¹ Nd solution. Spatial analysis of Nd isotopes across the deposition region confirmed the purity of the isolated masses.

Thompson *et al.*¹⁵³ provided an interesting comparison between ICP-QMS and ICP-TOFMS. Their study evaluated the two instruments as a potential U-Pb laser ablation geochronological tool using a split-sample pathway to supply both instruments. The results indicated the known lower sensitivity of TOFMS relative to QMS, but the TOFMS had significantly higher data collection rates and provided a wide range of elements with an effective long-dwell time. U-Pb dating was found to be equivalent between the instruments, but with non-linearity in TOFMS at high signal levels.

A new data reduction software ‘Iso-Compass’ was launched by Zhang *et al.*¹³⁹ aimed at processing LA-ICP-MCMS data. This freeware is available for Windows-based computers and was aimed at processing the transient-spatial analyses from raw data to IRs of time segments. The program can remove backgrounds, correct isobaric interferences and deploy internal and external mass bias corrections. Output data can be visualised as ratios and other parameter variation through the course of the analysis, prior to selecting the appropriate time-window to recover the highest precision section of the ablation.

4.4 Geological studies

Purification of B from geological samples by macro-sublimation was the subject of a study by Wang *et al.*¹⁵⁴ They were able to increase the sublimated sample volume by a factor of 10 using a two-bottle device. The indications were that the sublimation purification was 100% efficient and resulted in negligible $\delta^{11}\text{B}$ fractionation. This purification technique will be particularly useful for B isotope analysis in geoscience samples with low B concentrations, such as river and rainwater.

Zr isotopes are a relatively new stable isotope field with potential applications in geological environments. Tompkins *et al.*¹⁵⁵ used a ^{91}Zr – ^{96}Zr double spike with ICP-MCMS to determine Zr isotopes across a zircon crystal originating from a carbonatite rock. Findings indicated that the zircon was homogenous from core to rim ($\mu^{94/90}\text{Zr}$ 55 ± 28 ppm), which indicated that zirconium isotopes had not been fractionated during the crystallisation process in carbonatite magmas. This provided a contrast to silicate-based magmas which may show evidence of Zr isotope fractionation.

Smith *et al.*¹⁵⁶ completed an interesting study of the concentration and *isotopic composition of Pb* in honey samples from around Paris. This was to assess the use of honey as an environmental monitor in the wake of the Notre-Dame fire in 2019. The fire released a significant amount of Pb into the air, directed to the north-western sector of the city. Isotopically, the Pb in the honey was found to not be distinct from other sources of Pb around the city, but indicated the benefit of utilising Pb isotopes as a biomonitor. Homrighausen *et al.*¹⁵⁷ provided an interesting isotopic study of tracing the spatial heterogeneities of the deep mantle. They examined the tracks of seamounts and on-land volcanics stemming from the Shona and Tristan-Gough mantle hot-spots in the southern Atlantic Ocean. Ages of volcanics, with respect to distance from the active volcanic centres, indicated that two distinct isotopic signatures were imparted on the crust. These types are best discriminated based on their Pb

isotopes, which conform to a low $^{206}\text{Pb}/^{204}\text{Pb}$ signature from a south-central Atlantic domain, and a high $^{206}\text{Pb}/^{204}\text{Pb}$ from a belt extending across the south-eastern Atlantic. The implication from these volcanic systems is that the contrasting signatures stem from material stored discretely at depths of >2500 km in the Earth.

4.5 Stable isotope ratio studies

Stable Pt isotope measurement using low-background 10^{13} Ω amplifiers was completed by Creech *et al.*¹⁵⁸. The study aimed to reduce the amount of Pt required to determine the isotope composition while retaining a useful level of precision. It compared traditional 10^{11} Ω amplifiers with 10^{13} Ω using the same ICP-MCMS method. Findings indicated that a 0.5 ng ml^{-1} Pt solution gave $\delta^{198}\text{Pt}$ of $\pm 0.37\text{‰}$ and $\pm 0.25\text{‰}$ (2RSD) with the 10^{11} Ω and 10^{13} Ω equipped detectors, respectively. This represented a ~ 4 times degradation in precision relative to measurement with 50 ng ml^{-1} Pt solutions and 10^{11} Ω detectors. The $\delta^{198}\text{Pt}$ determination using 10^{13} Ω would potentially enable various new types of sample with sub-ng amounts of Pt to be available for isotopic analysis.

Gonzalez de Vega *et al.*¹⁵⁹ assessed the potential of LA-ICP-MCMS to measure *Fe isotopes* in cosmic spherules. These authors used a nanosecond laser with rock-glass standards to validate their signal integration and mass fractionation corrections. Results were found to be in broad agreement with $\delta^{56}\text{Fe}$ data obtained by solution ICP-MCMS. Analysis of glassy cosmic spherules suggested an enrichment in heavier Fe isotopes with $\delta^{56}\text{Fe}$ of 0.3‰ to 25‰ relative to the terrestrial glass standards. Zhu *et al.*¹⁶⁰ reported a novel method for the separation of Fe prior to ICP-MCMS isotope determination by double spike. Their system used a Bio-Rad® AGMP-50 cation exchange resin (200 to 400 mesh) combined with HCL-HF acid elution. The key advantage of this procedure was its effectiveness in samples with a high Cu content and was hence appropriate for many geological materials.

Stable Zr IR measurements were assessed by Feng *et al.*¹⁶¹. Their study used TIMS to measure chromatographically-separated Zr fractions pre-spiked with a ^{91}Zr - ^{96}Zr double spike. A key feature was removing the bulk of the interference from Mo by filament pre-heating prior to analysis. Any remaining isobaric overlap was quantified by monitoring ^{95}Mo in the collection array. Results indicated that reproducibility of $\delta^{94}\text{Zr}$ was better than $\pm 0.06\text{‰}$ (2RSD), which was comparable to results measured by ICP-MCMS. The TIMS method could be utilised with high Mo samples and a simple chemical preparation.

Lithium IR measurement can be affected by the amount of Li recovered during chromatographic separation. Gou *et al.*¹⁶² quantified this effect by modelling the Li elution

curve as a normal distribution. From this they estimated that where recovery is >99.8% of the added Li, there would be no observable isotopic fractionation during purification. An issue with TIMS IR determinations is that ionisation conditions may differ significantly from sample-to-sample. Pacek *et al.*¹⁶³ examined the possibility of analysing two samples by alternating measurements between separate side filaments which share a common central ionising filament. Cross-contamination between the samples was assessed and found to be negligible in the case of Li IR measurement. This was ascribed to the parallel orientation of each filament, potentially shielding the opposite samples.

Ni isotopes are known to be fractionated by processes such as rock weathering and plant uptake, so a comprehensive suite of characterised reference materials is valuable in ensuring accurate and comparable data between laboratories. Li *et al.*¹⁶⁴ measured Ni isotopes in 26 geological reference materials using ICP-MCMS equipped with a Faraday cup array connected to $10^{11} \Omega$ resistors. Recorded reproducibility of $\delta^{60/58}\text{Ni}$ was between 0.03‰ and 0.07‰ which is comparable to previous studies. The study characterised a diverse range of materials from plants, soils, sediments, volcanics and plutonic rocks and will provide a baseline for future comparison and an opportunity to utilise matrix-matched standards.

Measurement of *K isotopes* was optimised by Li *et al.*¹⁶⁵. Their study used a 200–400 mesh cation exchange resin to isolate K in a single step with a mixed acid (HCl–HF) elution. Analysis was performed using ICP-MCMS, in which the collector array was modified to include a dummy bucket. This blank collector was set to receive the high intensity $^{40}\text{Ar}^+$ and $^{40}\text{Ca}^+$ ion beams and was found to capture, and hence suppress, scattered ion signals and secondary electrons. Results indicated that the external precision was 0.06‰ (2RSD) for the method, which was used to determine $\delta^{41}\text{K}$ values in a suite of 23 geological and biological reference materials.

Si isotopes were analysed by ICP-HRMS by Otopkova *et al.*¹⁶⁶. They used silicon tetrafluoride and crystalline silica enriched in ^{28}Si to produce results sufficiently precise to use as a control in the production of single-crystalline ^{28}Si from SiF_4 .

It is difficult to determine Se isotope composition using ICP-MCMS, due to low ionisation efficiency and requirement for HG during sample introduction. Pons *et al.*¹⁶⁷ set out a revised analytical scheme for Se using a ^{76}Se – ^{78}Se double spike. This was chosen over the ^{82}Se – ^{78}Se and ^{74}Se – ^{77}Se spikes as it was predicted to generate lower analytical uncertainties over a much larger range of spike–sample mixing. However, a disadvantage of ^{76}Se – ^{78}Se is that both masses are isobaric with Ar dimers, *e.g.* $^{36}\text{Ar}^{40}\text{Ar}$ and $^{38}\text{Ar}^{38}\text{Ar}$ on mass 76; $^{38}\text{Ar}^{40}\text{Ar}$ on mass 78. This study provided a comprehensive scheme to correct for all interferences on

the four masses used for the Se double spike deconvolution, very well illustrated in the paper by a flowchart. Long term assessment of reproducibility using this method resulted in a mean value of $\delta^{82/78}\text{Se}$ $0.989 \pm 0.034\%$ (2s) for the Se Merck standard.

Wasserman and Johnson¹⁶⁸ also used a HG system in conjunction with an ICP-MCMS to assess Te isotopic variation. This study utilised a ^{120}Te – ^{124}Te double spike with <10 ng Te. Their new purification process resulted in a clear separation from matrix and isobaric interferences. Trials that analysed a series of geological reference materials resulted in the largest spread of $\delta^{130/126}\text{Te}$ compositions to date.

Separation and measurement of *Cd isotopes* was the subject of a study by Tan *et al.*,¹⁶⁹ such that as little as 20 ng Cd was sufficient to measure isotope compositions. An interesting aspect of the study was that three instruments, the Nu II, Nu III and Neptune Plus, were used to measure the Cd isotopes using a ^{111}Cd – ^{113}Cd double spike technique. This provided an opportunity to evaluate cross-platform performance while maintaining consistent chemical and sampling protocols.

Cr isotopes in samples with very small amounts (10 ng) were successfully measured by Wu *et al.*¹⁷⁰ using ICP-MCMS with a desolvating nebuliser. Signal stability and sensitivity of the system was found to be radically improved by passing the waste gas line from the nebuliser to a bottle held in an ice chamber: effectively a 5 °C cold trap. A ^{50}Cr – ^{54}Cr double spike was used for fractionation correction, which resulted in a reproducibility for $\delta^{53}\text{Cr}$ of better than $\pm 0.04\%$ through a 6 month period.

Xu *et al.*¹⁷¹ investigated stable *Sr isotope* variations using ICP-MCMS. Their study compared the correction techniques of sample–standard bracketing with a fractionation estimation based on the addition of a known Zr solution. Analyses of BCR-2 and BHVO-2 rock RMs yielded $\delta^{88/86}\text{Sr}$ uncertainties of ± 0.028 .

A method to calculate absolute IRs was devised by Shuai *et al.*¹⁷². Their method integrated the double spike concept with analysis of element pairs with isobaric isotopes. It was applied to Ca–Ti, V–Ti, Cr–Ti, Ni–Zn and InSn. Following correction for mass fractionation factors between the elements, the absolute IRs agreed well with literature data. Using this technique it was considered possible to measure Ca isotopes with reference to a Ti standard.

4.6 Nuclear forensics.

A problem encountered with LA-ICP-MCMS is the effect of highly *transient signals* on analytical precision. Craig *et al.*¹⁷³ investigated the bias and scatter generated by the

incomplete recording of signals using short integration times (<200 ms). The missing signal, termed ‘blind time’, was found to be responsible for degradation of $^{235}\text{U}/^{238}\text{U}$ precision when ablating sub-micron uranium particles with detection using ion counting. Longer integration times (0.5 s) provided a solution, but may not have captured highly transient ablated material.

Determination of ^{236}U is key in identifying potential sources of uranium contamination in the environment. Jaegler *et al.*¹⁷⁴ examined the use of collision gasses in measuring U isotopes by ICP-MS-MS. Their study trialled O_2 and N_2O as reactants in a collision/reaction cell with the aim of reducing hydride interferences. N_2O produced the greatest reduction, enabling the $^{236}\text{U}/^{238}\text{U}$ ratio to be accurately characterised down to 1×10^{-10} . This brings ICP-MS-MS closer to AMS detection limits, the former of which may be reduced further with ongoing developments in reaction cells.

Aside from battery technology, Li is a potentially useful metal in nuclear reactors, where molten LiF salts can be used as a coolant. This uses high-purity ^7Li (99.995%), requiring accurate determination of isotope abundance. Scott and Shafer¹⁷⁵ developed a method to measure Li isotopes in very non-natural abundance using a Faraday ion counter combination with particular attention to abundance sensitivity and background effects from ^6Li . Results indicated that $\delta^7\text{Li}$ values agreed to within 1.5‰ with Faraday-Faraday techniques.

Wenting Bu *et al.*¹⁷⁶ detailed the analysis of *Ce isotopes* by TIMS. Following an oxide-based separation procedure, their technique measured Ce as Ce^+ , rather than CeO^+ , with ionisation from Re filaments with Re–Pt and TaF as activators. The results indicated that reproducibility of $^{138}\text{Ce}/^{140}\text{Ce}$ was an impressive 10x better than earlier Ce^+ techniques. Analysis of Ce isotopes in uranium ores obtained from different mines indicated that this technique has the potential to discriminate between geological sources of U.

Cs isotopes are important in environmental monitoring of nuclear discharge from weapons tests, accidents, reprocessing plants and power reactors. Zhu *et al.*¹⁷⁷ outlined an analytical method for the separation and measurement of Cs from solid environmental samples. The isolation of Cs was completed using AMP-PAN resin (100–600 μm) and elution with NH_4Cl , followed by an HNO_3 elution from AG50W-X8 to purify the Cs relative to Ba, Rb and K. Analysis was performed using ICP-MS-MS and N_2O as a reaction gas to eliminate Ba and polyatomic ions. The study determined the $^{135}\text{Cs}/^{137}\text{Cs}$ of environmental samples, estimating a 50% contribution of Chernobyl-derived radio-Cs in soil from Denmark.

5. Glossary of Abbreviations

Whenever suitable, elements may be referred to by their chemical symbols and compounds by their formulae. The following abbreviations may be used without definition.

Abbreviations also cover the plural form.

2D	two dimensional
3D	three dimensional
AAS	atomic absorption spectrometry
AFS	atomic fluorescence spectrometry
AMS	accelerator mass spectrometry
CE	capillary electrophoresis
CRM	certified reference material
CS	continuum source
CVG	chemical vapour generation
DBD	dielectric barrier detector
DC	direct current
DMA	dimethylarsenic
DNA	deoxyribonucleic acid
EDL	electrodeless discharge lamp
EMPA	electron probe microanalysis
ETAAS	electrothermal atomic absorption spectrometry
ETV	electrothermal vaporisation
EVG	electrochemical vapour generation
FAAS	flame atomic absorption spectrometry
FFF	field flow fractionation
FI	flow injection
GC	gas chromatography
GD	glow discharge
GE	gel electrophoresis
GF	graphite furnace
GFAAS	graphite furnace atomic absorption spectroscopy
GLM	generalised linear model
HR	high resolution
HRMS	high resolution mass spectrometry
ICP	inductively coupled plasma
ID	isotope dilution
IP	ionisation potential
IR	isotope ratio
KE	kinetic energy
LA	laser ablation
LAMIS	laser ablation molecular isotopic spectrometry

LDR	linear dynamic range
LEP	liquid electrode plasma
LIBS	laser induced breakdown spectroscopy
LIF	laser induced fluorescence
LIPS	laser induced plasma spectroscopy
LOD	limit of detection
LOQ	limit of quantitation
MCMS	multicollector mass spectrometry
MIP	microwave induced plasma
MPT	microwave plasma torch
MS	mass spectrometry
n_e	electron number density
NIES	National Institute for Environmental Studies
NIST	National Institute of Standards and Technology
NP	nanoparticle
OES	optical emission spectroscopy
PCA	principal components analysis
PDMS	polydimethylsiloxane
PLS	partial least squares
PMT	photomultiplier tube
PN	pneumatic nebuliser
PVG	photochemical vapour generation
Q	quadrupole
QD	quantum dot
QMS	quadrupole mass spectrometry
QT	quartz tube
REE	rare earth element
RF	radiofrequency
RMSE	relative mean square error
RNA	ribonucleic acid
RSD	relative standard deviation
SEM	scanning electron microscopy
SFMS	sector-field mass spectrometry
SNR	signal-to-noise ratio
SP	single particle
SPE	solid phase extraction
SRM	standard reference material
T_e	electron temperature
T_{exc}	excitation temperature
T_{ion}	ionisation temperature
T_{rot}	rotational temperature
TEM	transmission electron microscopy
TIMS	thermal ionisation mass spectrometry

TOFMS	time-of-flight mass spectrometry
VG	vapour generation
XRD	X-ray diffraction
XRF	X-ray fluorescence

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