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Atomic spectrometry updates: Review of advances in atomic spectrometry and related techniques

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This review covers developments in 'Atomic Spectrometry'. 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 other related reviews in the series.[1–6] A critical approach to the selection of material has been adopted, with only novel developments in instrumentation, techniques and methodology being included. A number of themes have emerged from this year's review. Novel developments in sample preparation include the use of magnetic nanoparticles for solid phase extraction and an increase in the number of viable methods for use in quantitation of peptides, proteins and DNA by elemental tagging, particularly the development of multiplexed techniques. There were also some advances in electrochemical vapour generation, such as the use of reducing reagents immobilized on electrodes and development of electrolytic membrane diffusion cells. New instrumentation has been to the fore, with research into some novel and interesting miniaturized plasma sources being of particular interest, plus the development of a new distance of flight (DOF) mass spectrometer. There have been some insightful fundamental studies of particle atomization and ionization in ICP-MS, and subsequent space-charge effects after ion sampling, which should enable practical steps to solving some of these problems. One of the main drivers of research in isotope ratio analysis has been to increase detection power to enable smaller and smaller quantities of analyte to be

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measured, which yields advantages in geochronology and nuclear forensics. Laser ablation has played a large part in many types of analysis where high resolution is required, including analysis of single particles, small inclusions or elemental mapping of tissues, so the development of LA methods with extremely small spot sizes and efficient sample transport to the source has been key. In addition, several novel methods have been developed, such as laser ablation molecular isotopic spectrometry (LAMIS) for isotope ratio analysis, and stand-off LIBS techniques such as 'underwater LIBS'. In contrast, very little research into the use of chemometrics has been reported, and fundamental studies are generally confined to characterization of new plasma sources.

1 Sample introduction

1.1 Liquids

Liquid sample introduction relates to methods wherein the sample is introduced into the instrument in the form of a liquid, such as through nebulization or into a thermal vapourizer; whereas in vapour generation the sample is initially in the form of a liquid but is converted to a vapour prior to introduction into the instrument.

1.1.1 Sample pre-treatment

1.1.1.1 Solid phase extraction. A predominant theme in this review has been the use of magnetic nano-particles for solid phase extraction (SPE). The use of MNPs is advantageous because they can be easily separated from the sample after preconcentration by immobilisation in a magnetic field, then the analyte is eluted into a much smaller volume. This property of immobilisation also makes them ideal for preconcentration from a flowing stream. The field has been reviewed (74 references) by Giakisikli and Anthemidis[7] in which they gave a clear overview of the literature, separating applications into those utilising 'inorganic' and 'organic' coated NPs used for metal pre-concentration, with comprehensive application tables arranged by analyte. They focused on the benefits of MNP-SPE for automated methods, particularly the convenience of incorporating them into flowing systems. The same authors[8] reported the use of octadecylsilane functionalised maghemite MNPs as a SPE medium. They used two NdFeB magnets to immobilise the MNPs in a FI system, thereby avoiding the use of frits, and used this for online formation and preconcentration of a DDTC–Cd complex from waters. Analysis by ETAAS yielded an LOD of 3 ng L^{-1} and RSD of 3.9% at the 50 ng L^{-1} level, with stable column operation for 600 cycles. In a similar approach, Chen *et al.*[9] utilised 'on-chip' SPE for speciation of Se yeast cells. For this, they prepared a column on a microfluidic chip packed with sulfonated, polystyrene-coated MNPs (Fe_3O_4@PSS). The chip had seven separate inlets to allow introduction of sample solutions, reagents and standards at flow rates of approximately 1 μL min^{-1}, thereby allowing on line enzyme digestion of selenium-enriched yeast cells followed by SPE, subsequent elution with 0.5 mol L^{-1} Na_2CO_3 and analysis using HPLC-ICP-MS. Close reading of the paper seems to suggest that the principal advantage of using MNPs in this application was the ease with which the microfluidic column could be packed in the presence of a magnetic field, rather than to hold the MNPs in place. The authors compared the performance of on-line and off-line MSPE for speciation of $SeCys_2$, MeSeCys, SeMet, GluMeSeCys, and SeEt, and achieved LODs in the range from 0.022 to 0.149 μg L^{-1}, with the latter method yielding LODs at the lower end of the range. They validated the method by analysis of selenium-enriched yeast cells (*S. cerevisiae* BY4742), obtaining recoveries of between 85.3 and 106% for a 50 μg g^{-1} spike.

Cui *et al.*[10] have coated Fe_3O_4@Si–OH MNPs with the ionic liquid methyltrioctylammonium chloride ($MTOA^+$ Cl^-) for use in extracting Cd, Cu and Zn from biological samples. The target analytes were determined in the final eluate solution of 0.8 mL of 1.0 mol L^{-1} HNO_3, with LODs of 0.33, 0.54 and 0.56 μg L^{-1}, respectively. The method was found to be tolerant of concentrations of other transition and heavy elements such as Co, Cr, Fe, Mn, Ni and Pb up to between 1 and 4 mg L^{-1}, but also much higher concentrations (*ca.* 1000×) of polyanions, alkaline and alkaline earth elements. The method was validated by analysis of the CRMs GBW09103 human urine and GBW07601 human hair, and spiked samples, with recoveries between 89 and 120%.

Selectivity in SPE has long been a goal of the analyst, and ion-imprinted polymers (IIPs) are a class of adsorbent that holds some promise. Ebrahimzadeh *et al.*[11] have developed a novel IIP for Au preconcentration, by incorporating a dipyridyl ligand in ethylene glycol dimethacrylate, then coating it onto porous silica particles. They achieved an LOD of <0.2 ng mL^{-1} using FAAS and selectivity of preconcentration in the presence of palladium and platinum. Another novel IIP has been reported by de Lima *et al.*[12] who formed the polymer by reduction of Se^{IV} to Se^0 prior to reaction with 4-vinylpyridine and vinylimidazole, hence they designated the product as an atom imprinted polymer (AIP). Preconcentration of Se was achieved in FI mode by first reducing the analyte to Se^0, using 0.5% (w/v) citric acid, then preconcentration on the AIP which was immobilised in a mini-column. The Se^0 was then eluted by oxidation to Se^{IV} using hypochlorite, subsequently reduced to SeH_2 using $NaBH_4$ and analysed by HG-FAAS. The method was optimized using a Doehlert design to give an LOD of 53 ng L^{-1} and preconcentration factor of 232. Validation was by the determination of Se in DORM-2 dogfish muscle, with 98% recovery. Selenium was also successfully determined in Brazil nuts, apricot, white beans, rice flour and milk powder with recoveries in the range 100 to 109%. It is worth noting that significant matrix interferences (>10%) were observed in the presence of less than 10-fold excess of Cr^{3+} and Cu^{2+}, so the authors recommended that the method of standard additions be used.

Bauer *et al.*[13] reported a novel SPE method whereby trace metals were preconcentrated from environmental waters using silica NPs. The NPs were functionalised with strong cation exchange ligands based on 3-mercaptopropyltriethoxysilane modified with acetonitrile, trifluoroacetic anhydride and urea hydrogen peroxide. These particles had diameters in the range from 300 to 700 nm so could be suspended as a slurry and nebulized directly into ICP-OES without the need for elution of the analytes. The authors found that the analytical signal initially decreased by 10% 2.5 min after initial ultrasonic suspension of the slurry, but stayed constant thereafter up to 12.5 min. They attributed the initial decrease to settling out of larger particles. An average preconcentration factor of 10.4 was achieved, yielding LODs between 0.03 μg L^{-1} for Be to 0.48 μg L^{-1} for Fe, and the method was validated by the determination of Al, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb in NIST1643e fresh water.

Ozdemir *et al.*[14] have reviewed (160 references) the use of microbacteria as SPE media, with particular attention paid to preconcentration of metals using bacteria immobilised on resins.

1.1.1.2 *Liquid phase extraction.* The method of dispersive liquid–liquid microextraction (DLLME) has been reviewed (126 references) by Andruch *et al.*,[15] who outlined the basic principles and produced application tables ordered by analyte for quick reference. Another review (99 references) by Miro and Hansen[16] covered liquid phase microextraction (LPME) and solid phase microextraction (SPME), taking a selective approach to illustrate key developments in on-line methods and covering the various manifestations of these techniques. The attraction of LPME methods is that they minimise the amount of organic solvent used for the extraction step by using small amounts of highly dispersed droplets of the extraction solvent (usually an organic solvent), in either batch or sequential injection mode. An alternative approach was adopted by Boucherit *et al.*[17] whereby they directly nebulized an aqueous sample into an organic extracting solvent. In this way the principle of fine dispersion was retained but the advantage of reducing the amount of organic solvent was lost. Nevertheless, they found an improvement in the speed of extraction (compared with traditional solvent extraction) of Mo from aqueous HCl (into tributyl phosphate in *n*-hexane) and H_3PO_4 (into bis(2-ethylhexyl) phosphoric acid in *n*-hexane) solutions. Equilibration was achieved almost instantaneously between the aerosol and the extractant, but took up to 180 s and 900 s for the respective traditional extraction methods. The analysis was performed using ICP-OES with an LOD of 2 μg L^{-1} and a 10-fold enrichment.

Two of the key requirements for DLLME are the initial dispersion of the extracting solvent and subsequent centrifugation of the mixed phases in order to separate the highly dispersed organic droplets from the aqueous phase. This can also be achieved using an ionic liquid (IL) in place of an organic solvent. The role of ILs in extraction methods has been reviewed (113 references) by Han *et al.*,[18] covering liquid and solid phase extraction utilising hollow fibres, single drop and dispersive methods for both organic and inorganic analytes.

There have been some novel variations on the standard procedure. Naeemullah *et al.*[19] extracted a vanadium-8-HQ complex (0.1–1.0 mL of a 0.1% w/v solution of 8-HQ) from waters using 1-butyl-3-methylimidazolium hexafluorophosphate (20–70 mL of a 1 : 1 mixture of the IL and chloroform). In this case dispersion of the IL was aided by using chloroform in the mixture and high pressure argon (15 kPa for 5 min). The sample was centrifuged for 10 min at 3000 rpm and dissolved in 200 mL of 0.1 mol L^{-1} HNO_3 in ethanol–water (1 : 1 v/v) before analysis using ETAAS, to yield an LOD and enrichment factor of 20 ng L^{-1} and 100, respectively. The use of a hollow fibre, in conjunction with room temperature ILs, has been reported by Zeng and Tang.[20] They used butyl- octyl- or hexyl- 3-methylimidazoliumhexafluorophosphate (or tetraborate) ILs to aid complexation of Au with dithizone, with subsequent extraction into 9 μL of 1-octanol trapped inside a hollow fibre. This solution was then flushed out with a microsyringe, mixed with 65 μL of 95% (v/v) alcoholic solution with 1% (v/v) HNO_3 and siphoned into a FAA spectrometer for analysis. They found that the use of the ILs improved extraction efficiency by five-fold to give an enrichment factor of 130 and LOD of 0.9 ng mL^{-1} for Au. Shah *et al.*[21] performed a microextraction of Pb using an IL inside a 10 mL syringe. The pH buffered sample was placed in the syringe with 0.01% (w/v) dithizone, then 500 μL of 0.075% (v/v) Triton X-114 and 100 μL of 1-Butyl-3-methyl-imidazolium hexafluorophosphate added to extract a Pb–dithizone complex. Separation of the IL phase was effected by decanting from the syringe and diluting in 0.5 mL of methanol, before injecting 100 μL aliquots into the sample uptake tube of FAAS. The method yielded an enrichment factor of 82.6 and LOD of 0.281 μg L^{-1}.

1.1.1.3 *Elemental tagging.* Quantitation of proteins by elemental tagging and ICP-MS detection is a method which has threatened to become mainstream for a number of years, but has yet to be adopted on a routine basis. Several reviews have been published over the past year which highlighted the current status and possible future applications. Yan *et al.*[22] emphasised protein-labelling and element-tagging strategies based on bio-specific interactions, ranging from protein to whole cell quantification. Sanz-Medel *et al.*[23] reviewed (83 references) the last five years of research in this area and identified application niches for elemental tagging such as quantification of metalloproteins in biological systems, improved sensitivity, imaging of biological tissues and certification of peptides. Kretschy *et al.*[24] made a similar overview (140 references) with particular emphasis on the use of HPLC coupled with ICP-MS, including an application table of frequently used metal chelating molecules and conjugation reagents that have been used for elemental tagging. Giesen *et al.*[25] reviewed (125 references) the use and potential of ICP-MS as a detector for immunoassays. They pointed out that future developments, which capitalise on the high sensitivity and multiplexing advantage, rely on the development of high-throughput methods, and predicted that signal amplification and spatial analysis using LA-ICP-MS offers some potential for single cell analysis.

Normally, absolute quantitation of peptides and proteins by IDA requires the use of an isotopically enriched isotopomer of the target peptide, which will likely have to be synthesised for the purpose. This goes some way to explaining why the technique has not been widely adopted. Esteban-Fernandez *et al.*[26] have used the metal coded affinity tag (MeCAT) approach for absolute quantitation of proteins using ID-ICP-MS. The MeCAt reagent was loaded with (separately) natural and isotopically enriched Yb then tagged to various proteins *via* an iodoacetamide (IA) cysteine-reactive group on the reagent to form a MeCAT(Yb)-IA-Protein complex. Proteins were separated by gel electrophoresis (GE) and analysed either directly by LA-ICP-MS or after excision and digestion of the gel spots. Absolute quantitation was performed by IDA after spiking with standard proteins labelled with enriched Yb. Crucially, both natural and enriched MeCAT(Yb)-IA-Protein complexes migrated equally during the GE separation, and a stable ^{172}Yb:^{171}Yb ratio was observed along the spot when using LA-ICP-MS. The same group[27] used the same labelling strategy and compared this method with LC-ESI-MS, LC-ESI-MS-MS and HPLC-ICP-MS for the relative quantitation of alpha-lactalbumin, using Eu, Ho, Lu, Tb and Tm in a tetraplex labelling approach, and SDS-PAGE separation prior to analysis. They found that all three methods yielded quantitative results.

Liu *et al.*[28] reported a non-species-specific IDA method, using LC-ICP-MS, for absolute quantitation of bradykinin. They used commercially available 2′,2′′-(10-(2-((2,5-dioxopyrrolidin-1-yl) oxy)-2-oxoethyl)-1,4,7,10-tetraazacyclododecane-1,4,7-triyl) triacetic acid (DOTA–NHS–ester) to react with bradykinin, then labelled the resultant conjugate by forming a bradykinin-DOTA-Eu chelate at pH6, by using a two-fold molar excess of Eu to DOTA. Non-species-specific IDA was achieved by post-column perfusion of a ^{151}Eu spike solution (4.27 ng g^{-1}) *via* a three-way connector. The method was validated by comparison with a species-specific GC-MS method, in which the bradykinin sample was spiked with ^{13}C-labelled phenylalanine, then hydrolysed to yield free phenylalanine before derivatization with methyl chloroformate. The two methods agreed to within 4%, with 5% RSD at concentrations in the range from 20 to 500 pmol. An LOD of 7.3 fmol was estimated for the species-non-specific LC-ICP-MS method. Wang *et al.*[29] developed a different approach based on labelling standard peptides with Tb to act as an internal standard. They also used a DOTA–NHS–ester to form peptide -DOTA conjugates with synthesised standard peptides and the equivalent endogenous target peptide, which were then chelated with either Tb or Tm, respectively. Analysis was performed by LC-MRM-MS using external calibration, but also by using the Tb-DOTA-peptide:Tm-DOTA-peptide ratios ascertained from the widely separated mass fragments in co-eluting peaks as an internal standardisation method. They achieved an LOD of 0.8 fmol μL^{-1}, so the technique might well benefit from using ICP-MS as the detection method.

Yet another solution to this problem has been reported by Konz *et al.*[30] who utilised the intrinsic ability of the hormone hepcidin-25 to complex with Cu^{II} ions. They used two approaches, both involving IDA and LC-ICP-MS: post-column addition of a non-species-specific ^{65}Cu spike; and synthesis of a labelled ^{65}Cu-hepcidin-25 complex to use as a species-specific spike. The stability of the Cu-hepcidin-25 complex was checked using ESI-MS, and found to be stable under physiological conditions and to exist as an equimolar complex, however, they did note that spiking with the ^{65}Cu-hepcidin-25 complex should occur directly prior to species specific IDA because Cu-exchange reactions were possible; a problem that did not occur with post-column addition. They used both methods to determine hepcidin-25 in human serum samples and found an average concentration of 21.6 ng mL^{-1}, which agreed well with those reported in the literature of 19.2 ng mL^{-1}. In an unrelated but relevant paper Arnquist and Holcombe[31] studied metal-protein binding equilibria between Cu^{II} ions and bovine serum albumin (BSA) using preparative ultracentrifugation to separate bound and unbound Cu, with ICP-MS detection. In this way they determined the apparent (K_{app}) and intrinsic (K_{int}) binding affinities under different conditions of pH; information which could be used to predict the type of exchange reactions reported by Konz *et al.*[30]

Absolute DNA quantitation by elemental tagging poses a similar challenge to protein quantitation. Han *et al.*[32] have described a novel and elegant multiplexing approach to this problem. They utilised 15 DNA hybridisation probes for separate DNA targets, of 25–30 bases length, related to clinical diseases. The probes were 3′ end-functionalized with thiol, derivatized with maleimide-DOTA (MMA-DOTA), then individually labelled by complexation with a specific REE. A mixture of these DNA-MMA-DOTA-REE complexes was then added to the target DNA sequences to allow hybridisation to occur, and these were then captured by further hybridisation with capture probes which had been immobilised on MNPs. The MNPs with the attached probe-target-capture sequences were separated from the mixture containing the excess REE labelled probes. Finally, the REE labelled probes were released from the target sequences by raising the temperature to 95 °C and analysed by ICP-MS using external calibration with standard REE labelled probes. They further developed the method to allow an IDA approach to absolute quantification by using a spike-DNA-MMA-DOTA-REE probe complexed with an enriched isotope; in this case separate ^{161}Dy-enriched and ^{168}Er-enriched probes were tested. The method was as before, except that the MNP-immobilised capture probes contained an extra sequence which was complementary to the spike-DNA-MMA-DOTA-REE probe, and the quantitation step was performed by ID-ICP-MS. The method was applied to the analysis of *B. anthracis* and severe acute respiratory syndrome (SARS) targets and good agreement with a UV-vis method was obtained.

An alternative approach to DNA quantitation was reported by Leclerc *et al.*[33] who used ICP-MS (MC and Q) to quantify the total amount of DNA extracted from cells of *Legionella pneumophila* by determining the mass fraction of intrinsic P. They compared the results of the ICP-MS analysis with UV-vis and quantitative polymerase chain reaction (qPCR) methods, and found good agreement between the three. The ICP-MS method could be used with about 2 mL of DNA solution at about 30 ng g^{-1} P per measurement and had 11× lower uncertainty compared with qPCR because of the uncertainty in the qPCR standards. Swart[34] has addressed the important metrological difficulties of protein quantitation. The main problem seems to be that there are few SI-traceable reference materials for metallo-proteins, which is a serious lack when comparable results for samples of human origin are required. The author discussed the problems inherent in quantitative analysis and the production of traceable standards for this class of compounds using the examples of hemoglobin, transferrin, superoxide dismutase, ceruloplasmin, and C-reactive protein.

1.1.2 Nebulization. Miniaturization and automation in analytical sciences have evolved tremendously over the past decade, particularly within the framework of "green" analytical chemistry. Miro and Hansen described the merits of advanced flow methodology using mesofluidic platforms to simplify and speed up the overall analytical process.[35] Introduced in 2000, lab-on-a-valve (LOV), coupled with sequential injection analysis, has been developed as a downscaled analytical tool for pressure-driven sampling at the low μL level. Uses of this technique include on-chip sample processing involving renewable micro-solid phase extraction, non-chromatographic speciation and chemical vapour generation using programmable flow. These can be coupled with on-chip optical and electrochemical detection, or used as a front end to modern detection equipment or column separation systems. The authors provided a critical view of the future of LOV through a survey of currently used mesofluidic systems and identified what they consider to be the major challenges involved in the development of LOV for applications that are unsuitable for lab-on-a-chip microfluidic approaches.

Determination of metals in volume limited biological samples is critical to metallomics research and microfluidic chips provide an excellent platform for the miniaturization of extraction. In this context, Wang *et al.*[36] designed and fabricated a chip-based LPME device to combine with ETV-ICP-MS for the determination of trace Bi, Cd, Cu, Hg, Pb and Zn in cell and human serum samples. Using sodium DDTC as the chemical modifier for low-temperature ETV-ICP-MS and the extracting reagent for the chip-based LPME, the chip parameters influencing the extraction efficiency were optimized by orthogonal design experiments. Under optimized conditions, LODs were in the range from 6.6 to 89.3 pg mL^{-1} with the RSDs ranging from 4.23 to 8.15% ($n = 7$, $c = 1$ ng mL^{-1}) for the target metal ions. The linear range covered three orders of magnitude with correlation coefficients higher than 0.99. The method was validated by analysis of CRMs GBW07605 human hair and GBW09152 human serum. Metal determination in HepG2 cells, Jurkat T cells and a human serum sample was achieved with the recoveries between 86.6 and 119%. This rapid and sensitive method has low sample and reagent consumption and offers potential for the analysis of quantity-limited biological samples such as cells.

The analysis of engineered nanoparticles continues to be a subject of some interest, requiring the development of new methods for characterisation of size, mass, elemental composition, and number concentration. Elzey *et al.*[37] developed a sample introduction system to allow the separation and analysis of gold nanoparticles. An ES-differential mobility analyser (ES-DMA) was used to achieve real-time upstream size discrimination. A condensation particle counter and ICP-MS were employed as downstream detectors, providing information on number density and elemental composition, respectively, of aerosolized nanoparticles *versus* the upstream size selected by ES-DMA. A gas-exchange device was designed and optimized to improve the conversion of air flow (from the electrospray) to argon flow required to sustain the ICP-MS plasma, the key compatibility issue for instrumental hyphenation. This initial work demonstrates successful measurement of the key analytical factors for nanoparticle characterisation.

A similar approach, to determine the size and mass of metallic engineered nanoparticles, was reported by Gschind *et al.*[38] using a monodisperse microdroplet generator (MDG) for sample introduction into ICP-MS. Vertical and horizontal sample introduction configurations were evaluated. The horizontal introduction system resulted in shorter measurement time by reducing temporal jitter. Quantitation of Ag, Au and CeO_2 nanoparticles of different sizes and polydispersities was achieved. Results were compared to those obtained using TEM and asymmetric flow FFF, and the advantages and limitations of the proposed technique were discussed.

Finally, Pereira *et al.*[39] have developed a multiple nebulizer based on flow blurring hydrodynamics and used it to reduce matrix effects on As and Se determination by ICP-OES. This so-called flow blurring multiple nebulizer (FBMN) is essentially an array of three pneumatic nebulizers arranged in close proximity to each other which produces droplets <53 μm diameter (Sauter mean diameter = 16.3 μm) when operated at gas and liquid flow rates of 0.6 L min^{-1} and 0.3 mL, respectively. They studied matrix effects caused by Ca, K, Mg and Na when using the FBMN (with and without internal standardisation using In, Ge or Y) and compared the results with a standard pneumatic nebulizer. It is not clear what advantage the FBMN nebulizer affords, given that internal standardisation is an established approach to matrix correction and the propensity for the authors to present key comparative findings in the electronic supplementary information rather than the main body of the paper.

1.1.3 Thermal vapourization. Badliei *et al.* described electrothermal, near-torch vapourization (NTV) sample introduction system for micro- or nano-volume samples.[40] Samples were pipetted onto coiled-filament assemblies that were purposely developed to be removable and interchangeable. These were inserted into a small-volume vapourization chamber, that could be clipped onto any ICP torch with a ball joint, dried and then vapourized *in situ*. Interchangeable assemblies of various volume capacities were constructed to be small and lightweight so that they could be portable. This horizontally-operated, NTV sample introduction system was interfaced to an axially-viewed ICP-OES and optimized for 8 elements (Ba, Be, Ca, Cd, Mg, Pb, V and Zn). Precision and LODs obtained were comparable with existing ETV systems. Analytical capability and utility was demonstrated using the determination of Pb at pg mL^{-1} levels in a diluted natural water CRM, and the determination of Zn in 80 nL volumes of the liquid extracted from an individual vesicle. In a further paper, this system was applied to Cr speciation in seawater.[41] Samples were electrodeposited in the field on portable coiled-filament assemblies made from Re. Assemblies with dried residues of Cr^{III} and $Cr^{III} + Cr^{VI}$ were transported to the lab for determination by NTV-ICP-OES. Electrodeposition allowed selective species deposition, preconcentration and matrix clean up from seawater samples. Free Cr^{VI} was electrodeposited at −0.3 V and $Cr^{III} + Cr^{VI}$ at −1.6 V (both *vs.* Ag/AgCl). Interestingly, at 0 V and in the absence of an electrodeposition potential only Cr^{VI} was spontaneously and selectively adsorbed onto the coil. Due to preconcentration afforded by electrodeposition, the detection limits obtained after 60 s at the voltages stated, using buffered (pH = 4.7) artificial seawater spiked with either Cr^{III} or Cr^{VI}, were 20 and 10 pg mL^{-1}, respectively. In comparison, the LOD for Cr obtained by pipetting 5 μL of diluted standard solution directly onto the coil was 500 pg mL^{-1}, demonstrating that electrodeposition offered between 40 and 60 fold improvement. The method was validated in the lab using buffered artificial seawater and it was used in the field for the first time by sampling seawater, buffering it and immediately electrodepositing Cr species on portable assemblies on-site. Electrodeposition in the field helped avoid species transformation during sample pre-treatment, such as acidification during transport and storage. An additional benefit was the ability to ship the portable assemblies with Cr species on them rather than shipping large volumes of sample to the lab.

1.2 Vapour generation

1.2.1 Chemical vapour generation. Gao *et al.*[42] have reviewed (101 references) the application of VG in ICP-MS, covering most of the common methods developed in the last twelve years, with particular reference to CVG-ID-ICP-MS. The review contains a number of tables arranged alphabetically by analyte for ease of reference.

Yilmaz *et al.*[43] have investigated the efficacy of using $K_3[Mn(CN)_6]$ as an additive for HG of Pb reduced to plumbane using $NaBH_4$. The point being that this reagent should enhance the reaction in the same way that $K_3[Fe(CN)_6]$ has been shown to do by other workers. They did indeed find that a 1% v/v solution improved sensitivity, when coupled with ICP-MS, by as much as 48-fold. The method did suffer from severe signal suppression in the presence of Cu at a concentration of 0.1 μg mL^{-1}. This was eliminated by increasing the $K_3[Mn(CN)_6]$ concentration to 1%, but does not bode well for the analysis of real samples. Kratzer *et al.*[44] used radioactive ^{212}Pb to investigate the HG and trapping efficiency of plumbane using a similar method which also utilised $NaBH_4/K_3[Fe(CN)_6]$ as an enhancing reagent. They prepared the ^{212}Pb tracer by precipitation of PbS from $Th(NO_3)_4$ with subsequent purification by ion exchange separation to yield $^{212}PbCl_2$. The efficiency of plumbane generation, trapping and subsequent volatilization was determined by measuring the activity of gamma radiation from the ^{212}Pb tracer with a scintillation detector. The HG apparatus was made in-house from a reagent mixing manifold and gas–liquid separator, which was interfaced with an electrically heated quartz trap or charcoal column depending which part of the process was to be investigated. Results showed that the efficiency of HG was *ca.* 96%; trapping efficiency was 88% at 300 °C; and volatilization efficiency was 85% at 800 °C. They also found that the presence of Bi at a concentration of 400 ng mL^{-1} reduced the volatilization efficiency to 13%.

A novel method of CVG has been developed by Zhu *et al.*,[45] who used a cylindrical dielectric barrier discharge (DBD) plasma reactor made from two concentric glass tubes with a copper wire in the centre, and the outer tube wrapped with copper foil to act as the other electrode. The sample solution was run down the outside surface of the inner tube to form a thin film, from which hydrides of Cd were generated by reaction with hydrogen, produced after instigation of an 18 W DBD between the electrodes. Detection was performed using FI-QF-AFS to yield LODs of 0.03 ng mL^{-1} and 0.008 ng mL^{-1}, using DBDs generated with argon and helium, respectively. No interference from first row TMs at concentrations of 1 mg L^{-1} was observed, but signal suppression down to as low as 40% (for Ni) occurred at 10 mg L^{-1}.

Ai *et al.*[46] used Fe_3O_4 MNPs for the oxidation of Hg species prior to CVG. The system involved mixing an HPLC eluent with H_2O_2 prior to a column containing the MNPs, in which organo-Hg species were oxidised by $OH^{\bullet}$ free radicals formed as a result of the catalytic breakdown of H_2O_2. Subsequent CVG using KBH_4 and AFS detection yielded LODs of 0.7, 1.1, 0.8 and 0.9 mg L^{-1} (as Hg) for Hg^{2+}, MeHg, EtHg and PhHg, respectively. The method was validated by determination of MeHg in CRM DORM-2 dogfish muscle, with 95% recovery.

1.2.2 Electrochemical vapour generation. Zhang *et al.*[47] have developed a novel method for speciation of Hg^{2+} and $MeHg^+$ using an L-cysteine modified graphite electrode. The cleaned electrode surface was conditioned by applying a +1.8 V, 6 min potential step in 0.1 mol L^{-1} H_2SO_4 to create carboxylic acid surface groups. The electrode was then immersed in 15 g L^{-1} of L-cysteine for 8 h at room temperature to ensure peptide bond formation. They found that only Hg^{2+} was reduced at a low current of 0.2 A, whereas both Hg^{2+} and $MeHg^+$ were reduced at 2.2 A, thereby allowing electrochemical speciation to be performed. The LODs were 0.098 and 0.073 μg L^{-1}, respectively, using AFS detection. The system was relatively free from interference due to Ni, Fe and Co up to 100 mg L^{-1}, but Cu and Pb caused signal suppression at a concentration above 0.5 mg L^{-1}. Validation was performed by analysis of the CRM DORM-2 dogfish muscle, with excellent recovery, however, the authors also reported that the electrode required renewal after *ca.* 20 cycles.

Hranicek *et al.*[48] constructed and evaluated fifteen different electrolytic cells of varying types (non-membrane, thin-layer and tubular) for electrochemical vapour generation (EVG) of H_2Se and detection by QF-AAS. In all of the cells lead and platinum were used as cathode and anode, respectively, and a Nafion membrane was used to separate the chambers. After optimization, the EVG efficiency, and spatial distribution of the analyte, for the five best-performing cells was evaluated using ^{75}Se as a radioactive tracer. In this way it was possible to use autoradiography to determine the distribution of ^{75}Se-containing compounds in the various parts of the cells by means of an activity budget. The LODs were sub-ng mL^{-1} for all five cells, approaching the performance of CHG (using $NaBH_4$) which was used as a benchmark. The tubular cell, with an LOD of 0.4 ng L^{-1}, was deemed the best-performing cell for FI because it had the highest efficiency (78%), lowest cathode volume (43 mm^3) and fastest response time. The thin layer electrolytic cell was performed similarly, with cathode volume, LOD and efficiency of 225 mm^3, 0.31 ng mL^{-1} and 75%, respectively, but did not have such a rapid response.

An EVG cell comprising a Ti anode, separated by a cation exchange membrane between two Pb cathodes, was designed and tested by Shen-Tu *et al.*[49] Using an electrolysis current of 3.5 A, and with anolyte (0.4 mol L^{-1} H_2SO_4) and catholyte (0.3 mol L^{-1} HCl) flows of 4.0 and 1.5 mL min^{-1}, respectively, they were able to generate and determine AsH_3 and SbH_3 with LODs of 0.65 and 0.9 μg L^{-1}, respectively, using AFS. Various types of cation exchange membrane were tested, including polyethylene and Nafion 324. The authors found that longevity was greatly increased to several months continuous use by including porous epoxy resin spacers either side of the membrane. The method was validated by analysis of the CRMs GBW07405 and GBW07406 soil, with recoveries of between 96 and 107%.

1.2.3 Photochemical vapour generation. Suzuki *et al.*[50] utilized a tandem UV photochemical vapour generation (PVG) system for the quantitation of Se species using QF-AAS. The dual lamp system consisted of a 40 W lamp for oxidation followed by an 8 W, 254 nm germicidal UV-lamp. The 8 W lamp was arranged in parallel with 3 mm i.d. × 4 mm o.d. quartz tubing, coated inside with TiO_2 to act as a catalytic reactor. Selenite, selenomethionine, L-selenocystine, γ-glutamyl-Se-methylselenocysteine and selenocystamine were directly photolysed to volatile Se species (presumed to be SeCO and SeH_2) using only TiO_2 catlaysed photolysis with the 8 W lamp (*i.e.*, without the 40 W lamp), with efficiencies of between 73 and 100%, in the presence of 5% acetic acid. However, selenobetaine and selenate required pre-oxidation with the 40 W lamp to obtain Se^{VI} first. The system was optimized for post-HPLC detection of Se species.

Sturgeon and Luong[51] developed two PVG reactors constructed from arrays of UV LEDs with either 0.3 mW and 245–260 nm output, or 0.3 mW and 360 nm output. They compared the results of PVG of inorganic and methylmercury using formic acid as the reducing medium, with those obtained using a thermal reactor at 85 °C. No reduction of the species was observed using the 360 nm LEDS but the 245–260 LEDS were effective. An LOD of 0.68 ng was obtained using the 245–260 nm LEDs using a 9 min irradiation time. Analysis of PACS-2 marine sediment and DOLT-4 fish liver tissue using the method of standard additions resulted in recoveries of almost 100%.

Matusiewicz and Slachinski[52] combined an ultrasonic nebulizer and UV photolysis spray chamber by inserting an 8 W, UV pen lamp directly into a cyclonic spray chamber. This enhanced the production of As, Bi, Sb, Se and Sn hydrides, Hg vapour and volatile Cd species by PVG to yield LODs of 11, 22, 16, 19, 20, 15 and 11 μg L^{-1}, respectively. Acetic acid (40% v/v) was used as the generation medium and detection was performed by MIP-AES. The main advantages were the ability to use a very small (<30 μL) sample size by ultrasonic nebulization and the relative lack of reducing agents.

1.3 Solids

Methods of solids analysis are either direct, where vapourization, atomization and excitation of the sample occurs together, such as arc/spark ablation, glow discharge analysis and secondary ion mass spectrometry; or indirect, where vapourization is separate to atomization and/or excitation, such as laser ablation or thermal vapourization coupled with a separate atomization/excitation source.

1.3.1 Direct methods. The processes occurring during slurry sampling of Al_2O_3 for ICP-OES were investigated by Wang *et al.*[53] The conditions for sampling were optimized with relation to aerosol mass transport, with a cut-off point for aerosol particle size being set at between 7 and 10 μm for the sample introduction system. By using a customized computer model and experimental results, the maximum particle size for complete vapourization was found to be approximately 7 μm. For a gas flow of 0.8 L min^{-1}, particles with a diameter of up to 8 μm could be evaporated with an efficiency of 68% and particles as large as 5 μm could be evaporated completely within the nebulization gas flow region. In order to produce slurries for analysis an Al_2O_3 sintering block was ground using a mortar combined with a mixer mill device for particle reduction. The sample slurry was prepared by directly dispersing powdered Al_2O_3 in an aqueous solution with an addition of 0.5 wt% poly(acrylate amine) as the dispersant. The accuracy of the results was compared with the data obtained through high-pressure digestion with acid. The NIST SRM 699 alumina was analysed and good agreement was found with the certified values.

1.3.1.1 Glow discharge. In a review by Ganeev *et al.*,[54] various types of GDMS systems and their applications were considered. Special attention was paid to RF and pulsed GD combined with TOF-MS. Applications of GDMS were reviewed, with focus on analysis of semiconductors, polymers, and dielectrics, as well as isotope analysis and depth profiling. Methods of standard-free MS analysis of solids were considered and some interesting prospects for combining GDMS with preliminary chromatographic separation were also discussed.

Depth profiling with pulsed GD is a promising technique that has been the subject of investigation for a number of years. The use of a pulsed voltage for sputtering reduces the sputtering rate and thermal stress, and thereby improves the analysis of thin layered and thermally fragile samples. Pulsed glow discharge has not been widely studied, however, and this has limited its practical use. Efimova *et al.*[55] investigated the factors that must be optimized when pulsed mode is used, *i.e.*, duty cycle, frequency and pulse length, in order to obtain the best sputtering and crater shape. Pulse length was found to be a crucial parameter for the crater shape and thermal effects. They compared pulsed DC and RF modes and found that they produced similar sputtering effects.

Combinatorial and high-throughput techniques have become well-established in materials science to aid in the accelerated discovery of novel functional materials. Thin film composition spreads are frequently used for this purpose by performing localized measurements and exploring different properties throughout the phase diagram. The thin film composition map has to be determined in order to understand the behaviour of the compound or alloy of interest. There are several established techniques that can give elemental composition maps of large areas but the total mapping time can range from several hours to tens of hours or more. Thus, faster elemental mapping techniques are needed. In a study by Gamez *et al.*,[56] the applicability of GD-AES elemental mapping for combinatorial and high-throughput screening samples was explored by characterizing a CuNi thin film composition spread. Qualitative analysis images showed that Cu and Ni composition gradients can be obtained in a very short time period. In addition, the use of reference materials allowed quantitative elemental analysis maps to be extracted from the emission intensity images. The images of emission intensities and curve fitting parameters are discussed. Finally, the GD-AES results are compared to profiles obtained by EDXRF. The GD-AES figures-of-merit relevant to elemental mapping were compared with selected alternative techniques from the literature to put their potential impact into perspective.

An approach to the analysis of non-conducting materials using GD-MS was suggested by Qian *et al.*[57] A thin coating of molten indium was placed on the sample surface allowing the sample to be sputtered and ionized. After optimization of the plasma conditions, the prepared samples were analyzed directly by DC-GD-MS with satisfactory detection limits, stability and reproducibility. Two NIST SRMs were used to validate the precision, accuracy and reproducibility of this method. The results showed that this method could avoid grinding, sustain the relatively stable discharge and enhance the stability of signals compared to the method of using a cathode made from an In pin rolled in the sample powder.

1.3.2 Indirect methods

1.3.2.1 Laser ablation. LA for direct solid analysis has advanced over the past 50 years and has applications in many disciplines. The choice of laser is normally dependent on the application requirements, however, there are fundamental effects attributed to the laser pulse duration that drive the ablation sampling process. A comparison of nanosecond and femtosecond LA by Russo *et al.*32 (ref. 58) provides a useful discussion with respect to analysis based on the optically induced plasma at the sample surface (such as LIBS or LA molecular isotopic spectrometry), and transport of the ablated mass aerosol to ICP-MS. The same authors provided a useful review of LA[59] covering fundamental research, applications based on detecting photons at the ablation site (LIBS and LAMIS), collection of particles for excitation in a secondary source (ICP), and future directions for the technology.

A method has been developed for the determination of Ba, Cu, Ni, Pb, Sr and Zn in solid geological and environmental samples by LA-ICP-MS using a spinning sample platform.[60] The platform, containing a sample and a standard, is spun during the ablation, allowing the quasi-simultaneous ablation of both materials. The aerosols resulting from the ablation of sample and standard were mixed in the ablation cell allowing quantitation of the analytes by standard additions. The proportion of standard *versus* sample could be increased by performing the ablation further from the axis of rotation. The ablated masses were determined using a strategy based on IDA. This spinning LA method has been applied to the Allende meteorite and four powdered CRMs fused in lithium borate glasses. SRM 612 trace elements in glass was also analyzed. Deviations from the certified values were found to be less than 15% for most of the elements and samples studied, with an average precision of 10%. The results demonstrated the validity of the method for the direct analysis of solid samples using a single standard.

The advantages and possibilities of using LA-ICP-MS for IR measurements were discussed by Urgast *et al.*[61] A comparison of quadrupole, sector-field and multi-collector systems revealed the limitations of the respective set-ups. The report focused on the possibility of using LA-ICP-MS to image isotope ratios for biological tracer studies. The authors concluded that this application has significant potential in this important field.

Isotope ratio measurements using LA-ICP-MS in air under atmospheric pressure has been performed.[62] Samples of brass and two minerals (galena and zircon) were ablated in air and the laser-generated aerosol aspirated into a gas exchange device, where the air was replaced with argon and transported into an MC-ICP-MS instrument. Results were compared to those obtained using conventional LA-MC-ICP-MS in helium in a sealed cell. Comparable in-run (0.03 to 1.61%) and external (0.002 to 0.254%) precision was obtained, and the accuracy of both methods was comparable. However, the atmospheric sampling method gave up to 5-fold lower intensities and visualization of the aerosol extraction indicated that some material was lost prior to gas exchange. Nevertheless, this method is suitable for isotopic determination of bulk materials for samples which are too large to fit into an ablation cell or too valuable to be cut into smaller pieces.

The quantitation capabilities of LA-ICP-MS are known to be restricted by elemental fractionation as a result of ablation, transport, and atomization/ionization effects, which may result in inaccuracies whenever non-matrix matched standard materials are used for calibration. Flamigni *et al.*[63] studied the vapourization processes of laser-produced aerosols and subsequent diffusion losses occurring inside the ICP. Both ICP-OES and ICP-MS detection was used. Na- and Ca-specific AES of aerosols produced by LA of silicate glasses or metals revealed variations in the onset and maximum position of atomic emission in the axial channel, which were in the range of a few mm. These shifts were found to arise from composition-dependent particle/aerosol penetration depths which determined the starting point of axial vapourization in the ICP. This was also found to influence ion extraction efficiency through the ICP-MS sampling orifice, with differences observed for oxide *vs.* metallic aerosols caused by differences in the rate of diffusion-driven expansion from the central channel. Analysis of individual particles by ICP-MS resulted in $1/e$ half-value signal durations of approximately 100 μs, which agree with modelled values if AES maxima are assumed to coincide with positions of instantaneous vapourization and starting points for atomic diffusion. Results suggested that differences of up to 15% in the relative ion extraction efficiency could be explained depending on whether analytes were metals or oxides. Implications of these findings on the accuracy achievable by state-of-the-art LA-ICP-MS systems were discussed.

1.3.2.2 Thermal vapourization. Two different approaches to the direct determination of Cl using ETV have been investigated. Antes *et al.*[64] developed a system for the analysis of coke by ICP-MS. The ETV system consisted of a high power lamp enclosed in a glass chamber equipped with solenoid valves. The system was controlled by a printed circuit board and software developed in LabVIEW. Temperature and heating time were optimized and samples of up to 5 mg of petroleum coke were analysed. Calibration was performed by standard additions using the CRM SARM 19 coal. The RSD was $< 9\%$ ($n = 4$) and the

LOQ (10σ) of Cl was 3.5 μg g^{-1}. Results obtained for the determination of Cl in petroleum coke were in agreement with those obtained using other validated methods. The benefits of the proposed method were the reductions in: analysis time (approximately 2 min per sample); risk of contamination; analyte losses; and waste generation in comparison with techniques that require sample digestion. Hashimoto *et al.*[65] determined Cl in ceramics using a tungsten boat vapourizer with ICP-OES. The powdered sample was vapourized in the tungsten boat and subsequently introduced into the plasma. Calibration was by standard additions with an LOD and RSD of 0.71 ng (59 ng g^{-1}) and 3.2%, respectively, for Cl in solid ceramic materials. A number of ceramic materials were analysed and accurate determination of Cl was achieved.

2 Instrumentation, Fundamentals and chemometrics

2.1 Instrumentation

This section covers the development of novel atom cells, excitation sources, monochromators, mass spectrometers and detectors.

Plasma sources for MS and OES continue to be the focus of much development. Jankowski and Reszke[66] have published a tutorial review (133 references) of microwave plasma sources for OES and MS. They cover the generation and classification of the different types of microwave plasmas, recent advances in construction and their applications in selected fields, particularly as OES detectors for GC. They also focus on the development of mini-discharges for miniaturized spectroscopic systems and developments in elemental and molecular ionization. The review is not comprehensive and tends to concentrate on recent developments in selected laboratories.

Miniaturized plasma sources have attracted much research interest because of the desire to place as much analytical capability as possible onto a ‘chip’. Luo and Duan[67] have reviewed this area (70 references), focusing on the microfabrication of various types of microplasma discharges used for atomic and molecular analysis by OES and MS. Most of the applications are for gaseous analysis but they also cover solids and liquids to a lesser extent, with the attendant problems of sample introduction to the fore. Frentiu *et al.*[68] have developed a miniaturized system comprised of a Hg CVG device with a gold filament preconcentrator, and a CCP microtorch (20 W power and 200 mL min^{-1} argon gas flow rate), interfaced with a microspectrometer. The preconcentrator was made from an 80 μm i.d. gold filament wound into a 43-turn spiral placed inside a quartz capillary, such that preconcentrated Hg could be rapidly desorbed to achieve maximum signal after 3 s. The system was used to determine Hg in waters and polymer leachates in the concentration range 0.06 to 57.4 ng L^{-1}, with an LOD of 0.02 ng L^{-1} (0.5 pg absolute). Liu *et al.*[69] constructed a low power (2 W) microplasma made from two platinum electrodes inside an alumina chamber of 150 nL volume, for determination of P and S in gas by AES. The argon plasma was operated at atmospheric pressure, 280 V (DC) and 8 mA, and excited emission at 253.6 and 469.4 nm to yield LODs of 68 ppb and 1.0 ppm for P and S, respectively, when using a palm-sized spectrometer for detection. A liquid electrode plasma (LEP) has been characterised for use in AES by Kohara *et al.*[70] The plasma was generated directly in solution between two platinum electrodes, by applying a pulsed (3 ms) voltage of up to 2500 V in a narrow channel (100 μm) etched in fused silica. They observed the plasma and Pb emission at 405.78 nm using an array of detection equipment, including a high speed camera, CCD interface with a microscope, and a CCD spectrometer with a fibre optic interface. They estimated $T_e \sim 10\,000$ K (using Wien's displacement), $T_{exc} =$ 8150 K (using a Boltzmann plot of Cu emission lines) and $n_e =$ 1.4×10^{15} cm^{-3} (using Stark broadening of the H_β line). Time resolved monitoring of the emission revealed a double peak over a period of several ms. Spatial imaging showed that maximum emission occurred at the centre of the expanding plasma bubble in the confines of the 100 μm channel, but also at the anode side bubble–liquid interface where the background was much lower. An LOD of 4.0 μg L^{-1} was obtained for Pb. The same group[71] then went on to integrate the LEP onto a PDMS chip and obtained an LOD of 0.27 ppm for Pb. The PDMS chip could be used for ‘tens’ of measurements before degradation reduced performance.

New sources for MS and OES are constantly under development. Pfeifer *et al.*[72] developed a low consumption argon ICP-MS. The design included an air-cooled, bulb-shaped quartz torch which fitted inside a standard rf coil, and up against a modified sampling cone with an extended tip. This arrangement allowed the torch to be operated at an argon flow of 1.5 L min^{-1} and ions to be sampled from inside the torch, but prevented entrainment of the cooling air. The modular design allowed a variety of sample introduction systems to be interfaced, including solution nebulization, HPLC and GC, with LODs between 0.002 and 0.046 μg L^{-1} for Al, As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, V and Zn for solution nebulization, compared to LODs which were between 2 and 10 times lower in conventional ICP-MS mode.

A dielectric barrier discharge (DBD) was investigated by Muller *et al.*[73] as a possible soft ionization source. The DBD was generated in a 30 mm long glass capillary at a helium gas flow of 600 mL min^{-1}, and from 3.5 to 6.5 kV at 21.5 kHz. The discharge was examined spectroscopically in various discharge modes to determine the populations of N_2^+ and N_2 as indicators of the suitability of the plasma for soft ionization. They concluded that soft ionization should be favoured by operation in homogeneous mode (below 4 kV) which had the highest production of N_2 metastable atoms. Another type of DBD, developed by Liu *et al.*,[74] was used as a desorption/atomization source for AFS. The argon plasma (10 kHz, 2.5 kV, 100 mL min^{-1}) was generated between two copper rings in a quartz capillary, and used to desorb and atomize Hg species from a TLC plate. The analytes were subsequently determined by QF-AFS with LODs of 0.51, 0.29 and 0.34 pg for Hg^{2+}, MeHg and PhHg, respectively.

The solution-cathode GD (SC-GD) source is attractive because it can be used for the direct analysis of a liquid. Progress in this area has been reviewed (55 references) by Jamroz *et al.*,[75] with emphasis on the design and analytical figures of merit of different types of system over the last 20 years. The review contains a table of LODs arranged alphabetically by analyte for those wishing for a quick lookup guide. The mechanism of solution-to-plasma transport and excitation in this type of source was investigated by Schwartz *et al.*[76] by high speed imaging and laser scattering. They found that the surface of the solution deformed on plasma ignition and a number of high powered plasma nodes formed across it at timescales of 100 ns to 100 μs, which were the source of most of the analyte emission. They also concluded that these nodes only occurred at low pH which also corresponded with an increase in sample transport into the plasma. Zhu *et al.*[77] have used a SC-GD in a novel way, as a method of generating OsO_4 vapour for introduction into an ICP-OES instrument. An LOD of 0.51 ng mL^{-1} was obtained without the need for oxidising reagents, though there was the requirement to prepare the samples in approx 0.1 M acid solution (*i.e.*, pH = 1). Xiao *et al.*[78] improved the performance of an a.c. SC-GD by adding organic compounds to the electrolyte. They found that adding 3% (v/v) formic acid enhanced emission by 13-, 17- and 78-fold for Ag, Cd and Pb, respectively, to yield LODs of 1, 17 and 45 μg L^{-1}.

There have also been new developments in spectrometers. Gundlach-Graham *et al.*[79] coupled an ICP with a distance of flight (DOF) MS. As the name suggests, this is similar to TOF-MS in that ions must be pulsed into the spectrometer however, m/z separation was effected by using a spatially selective, commercially available microchannel plate (MCP)/phosphor detector. The MCP detector elements were stacked in a chevron arrangement and ions were selectively deflected into the plane of the detector. The instrumental setup allowed for a high-to-low mass range of 1.11 : 1 with $m/\Delta m$ resolution (FWHM) of between 440 and 670 with an ICP source. LODs of between 2 and 30 ng L^{-1}, LDRs of 10^5 and IR precision of 0.1% RSD were obtained. One of the main advantages of DOF-MS is that low-cost, commercial detectors are available which are sufficiently large (100 mm) to allow a high-to-low mass range of 1.45 : 1, sufficient for simultaneous detection of the lanthanide elements.

Bhatia *et al.*[80] have developed novel zoom optics which allowed Faraday detectors with wide apertures to be fixed in place and dispersion varied using a DC quadrupole and deflection optics. This arrangement resulted in flat-topped peaks for ^{87}Sr:^{86}Sr IR measurement with precision of 8 ppm. A new type of ion funnel has been designed by Egorova *et al.*[81] to replace the conventional second stage, ion optics in an ICP-MS instrument. The funnel was made from 54 ring electrodes each of 0.5 mm thickness with 0.5 mm spacing between. The electrode apertures were circular with continually decreasing inner diameters, so that the stacked arrangement formed a funnel with a 35 mm i.d. at the entrance and 2 mm i.d. at the exit. Radiofrequency and DC potentials could be applied to the electrodes and adjusted to optimize the transmission of ions of different m/z. Ion transmission was found to be lower by one order of magnitude compared with conventional ion optics, but it was possible to introduce gases such as N_2 and H_2 to reduce the abundance of Ar-based polyatomic ions by one and three orders of magnitude, respectively.

2.2 Fundamentals

Coverage is confined to a consideration of fundamental studies related to instrumental methods used primarily for analytical atomic spectrometry, and excludes studies related to *e.g.* astronomy and sputtering sources, except where particularly relevant.

2.2.1 Fundamental constants. New measurements of fundamental constants often crop up, generally in the context of physics or astronomy, but some have direct relevance to atomic spectrometry. Ruffoni[82] developed software which can be used to simplify atomic emission spectra obtained from FT spectrometers. This so-called F(TS) atomic spectrum tool (FAST) is intended for calculating atomic branching functions, transition probabilities and oscillator strengths (and uncertainties) for use in astrophysics, but there are obvious uses in analytical atomic spectrometry. The programme is written in C++, runs on Linux/Unix/Windows and has a graphical user interface. Doidge[83] has observed forbidden transitions in the ICP-OES spectra of singly ionized Ba, Ca and Sr, with $n = 6, 4$, or 5, respectively, of the type $ns^2S_{1/2}$-nd $^2D_{3/2}$ and $ns^2S_{1/2}$-nd $^2D_{5/2}$. Transitions had the following wavelengths: 216.5943 and 217.5622 nm for Ba; 175.8755 and 175.9348 nm for Ca; and 187.3609 and 187.6660 nm for Sr. Manrique *et al.*[84] have identified transition probabilities for 48 lines of the transition array $3d^84s$–$3d^84p$ of Ni(II) using LIBS. They found good agreement between their measurements and other workers, including the NIST Atomic Spectra Database, and also reported 17 new measurements.

2.2.2 Diagnostics. Konjevic *et al.*[85] reported a procedure for measurement of low n_e densities using the Stark broadening of hydrogen Balmer lines. In particular, they address the problem of analysing the line profile to determine half-width and presented several formulae to correct for inaccuracies in the Voigt function, and to correct for van der Waals broadening which is significant at low n_e density close to the fine structure limit (FSL). They recommended that careful measurements of atomic hydrogen temperature and determination of the reduced mass emitter–perturber parameter (μ) was necessary, and that data tables for Stark broadening should only be used for n_e above the FSL (6×10^{20} m^{-3} for H_α, 4×10^{19} m^{-3} for H_β and 10^{19} m^{-3} for H_γ). Rincon *et al.*[86] characterised an atmospheric argon MIP known as the "Torche à Injection Axiale sur Guide d'Ondes" (TIAGO), which is the latest iteration of an axial MIP in which the torch is a nozzle forming part of the waveguide. The T_{rot} was measured using a Boltzmann plot of the P branch of N_2 ($B^2\Sigma_u{}^+ \rightarrow X^2\Sigma_g{}^+$) to yield temperatures in the range 6000 to 2000 K, which decreased markedly with gas flow rate (0.5 to 5.0 L min^{-1}). The effect of power (250, 450 and 650 W) depended on gas flow rate, with temperature increasing with power when a gas flow of 1.5 L min^{-1} was used, but the trend reversing when the gas flow was increased above this. They also measured n_e using Stark broadening of H_α by using Levenberg–Marquardt nonlinear fitting algorithm to divide the Voigt width into its Gaussian and Lorentzian contributions, and taking into account both Doppler and van der Waals broadening. They assumed a T_e of 15000 ± 5000 K in order to calculate n_e, which showed an increase from *ca.* 0.5×10^{15} cm^{-3} to 3.0×10^{15} cm^{-3}

as gas flow rate was increased from 0.5 to 1.5 L min^{-1}, but remained relatively constant with power. Orejas *et al.*[87] have taken 2D images of an atmospheric pressure, helium GD source using zoom lenses coupled to an intensified CCD detector. Wavelength regions were isolated using bandpass filters to isolate emission produced by He*, N_2^+ and O* revealing that He*, N_2^+ were concentrated in regions close to the electrodes whereas O* emission appeared in most of the plasma volume. They also observed that higher helium flow rate and greater interelectrode distances lead to higher emission signals for all species.

The use of mixed gas plasmas, or gases other than argon, in ICP-OES has been around since the first reports of the technique in the 1960s, whether for economic reasons or to modify the temperature of the plasma in some way. Scheffler and Pozebon[88] found that addition of nitrogen (20 mL min^{-1}) to the nebulizer gas flow of an axially viewed argon ICP improved its robustness by a factor of two, as evaluated by the Mg(II) 280.270 nm : Mg(I) 285.213 nm ratio. They studied matrix effects, caused by 5 g L^{-1} of Na or K, on ten spectral lines with excitation energies between 11.5 and 15.5 eV and found that they were generally reduced by the addition of nitrogen without degrading the LOD or linear range. In some cases (for high excitation energy) an enhancement was observed, and the matrix effect of Ca was more variable. Any number of theories can be proposed for these observations but it is generally the case that changes to the size and shape of the central channel must be considered in addition to atomization and excitation mechanisms. This influence of plasma shape was well illustrated by Miyahara *et al.*[89] who studied the effect of nitrous oxide addition to an air ICP. Addition of 40% nitrous oxide increased the plasma volume by two-fold, but atom and ion line intensities increased, and they observed a decrease in T_{rot} from 3200 to 2700 K when nitrous oxide was increased from 0 to 100%.

Similar in some ways to the use of mixed gases, Grindlay *et al.*[90] reported on the effect of carbon (in the form of glycerol, citric acid, potassium citrate and ammonium carbonate) on the signal for hard-to-ionize elements: As, Au, B, Be, Cd, Hg, I, Ir, Os, P, Pd, Pt, S, Sb, Se, Te and Zn in ICP-MS. They found that some elements showed an enhancement while others were unaffected, and put this down to a combination of changes in the ion distribution in the plasma and charge transfer reactions between some of the enhanced elements and carbon-containing species in the plasma.

Single particle analysis has attracted much interest in recent years. Chan *et al.*[91] have studied the effect of single aerosol droplets on plasma impedance by using two methods: an RF-probe coil placed inside the torch; and by tapping the phase-detector signal of the impedance matching network. They found that there was a direct correlation between temporal spikes in the impedance and H_α atomic emission, which was linearly proportional to the volume of the introduced droplet. The measurements were made over short (*ca.* 10 ms per pulse) timescales and the method was proposed as a trigger for single droplet introduction into the ICP with appropriate tuning of the threshold value. In addition, the authors estimated that the energy change coupled to the plasma caused by a 50 μm droplet was between 8 and 11 W (0.03 to 0.04 J).

Niemax[92] published an overview of the single droplet approach to diagnostic studies in ICP-MS, with recommendations on how to improve detection efficiency. He emphasised the spatial nature of analyte atomization, ionization and diffusion processes in the plasma, and how this interacts with the position and size of the sampling orifice. He recommended the use of a narrow injector and high gas flow rate to shift the point of atomization downstream so as to optimize the position where temperature is high and analyte ions have not had much time to diffuse away from the particle origin. However, he pointed out that optimization is a complex business that also depends on analyte mass (heavier elements diffuse more slowly) and other operating conditions. In a related report, Flamigni *et al.*[63] studied aerosols and single particles produced by LA in the context of atomization, ionization and diffusion effects on ion sampling in ICP-MS. They used LA to generate aerosols containing Na_2O and CaO from NIST610 silicate glass, and elemental Na and Ca from their metals, and observed that maximum emission for the oxides occurred further along the central channel than the elemental forms, *ca.* +3 mm for Ca and +1.5 mm for Na. This spatial shift in vapourization resulted in a discrepancy between the relative extraction efficiencies of metallic *vs.* oxide aerosols of 25% for Ca/CaO to 97% in case of Na/Na_2O. Modelling of penetration depth revealed that this was more pronounced for particles larger than 1 μm. The main conclusion of this interesting study was that the inherent difficulty of calibrating LA-ICP-MS without matrix matched standards will require an approach which addresses this spatial difference in vapourization of particles. Some insight into these effects might be gained by studies such as that of Aghaei *et al.*,[93] who developed a computational fluid dynamics model to investigate the effect of varying the pressure behind the sampler, gas flow rates and applied power in an ICP-MS instrument. This allowed them to model gas pathways through the sampler cone, concluding that it is possible to control whether only the injector gas flow passes through the orifice, or if it is accompanied by some auxiliary gas flow. In a further paper[94] they used this to predict the effect of sampling cone position and orifice diameter on plasma temperature, electron number density, gas density and gas flow velocity; and the implications for extraction of ions formed from vapourizing particles travelling through the plasma. They conclude that a large sampler orifice favours extraction of both injector and auxiliary gas, and consequently large ion clouds, while a smaller orifice favours extraction of small ion clouds.

As if spatial heterogeneity in the ICP itself was not enough to contend with, there is also the time-worn problem of space charge effects in the post-sampler ion beam. Bergeson *et al.*[95] used LIF to study space charge effects on Ca, caused by the matrix species Cs, Mg, and Pb, in the second vacuum stage of a commercially available ICP-MS instrument with right-angle ion-reflecting geometry. They used a CW-Ti:Sapphire laser, frequency doubled to 393.4 nm, to excite the Ca(II) $4s^2S_{1/2} \rightarrow 4p^2P_{3/2}$ transition, and monitored the subsequent fluorescence at 854.2 nm from the ion beam at the entrance aperture to the third vacuum stage using a CCD detector. Interestingly, they found that the Pb matrix (1.5 mM) caused an off-centre deflection in the Ca ion beam rather than the more commonly assumed defocusing effect. They concluded that this could be corrected for by on-the-fly adjustment of the ion optics, with the caveat that this effect may well be specific to the type of ion optics studied.

Houk's group[96] have continued their studies of metal argide (MAr^+) polyatomic ions of Co, Cr, Cu, Fe, Mn, Ni, Ti, V and Zn in the ion extraction interface of an ICP-MS instrument. They compared experimental measurements of MAr^+/M^+ ratios with theoretical ratios calculated from the expected thermodynamic equilibrium at $T_{gas} = 6000$ K, and found that the experimental ratios were far lower than the calculated ratios, with the weakest bound species exhibiting the largest discrepancy. Increasing the ion kinetic energies by increasing the plasma potential, *via* a homemade guard electrode between the RF coil and torch, was observed to further reduce the experimental ratios, and adjusting the skimmer cone geometry also had an effect. Taking this evidence in total they postulated that the low experimental ratios were caused by collision induced dissociation (CID) due to a shock wave at the tip of, or in the throat of, the skimmer cone, thereby yielding far fewer MAr^+ ions than expected. Bouchoux *et al.*[97] published a theoretical investigation into interferences on Se in ICP-Ms. They estimated heat of formation, ionization energy (IE), and proton affinity (PA) for Se, SeH, SeH_2, ArH, ArH_2, Ar_2, Ar_2H, Ar_2H_2, ArCl and ArHCl using quantum mechanical methods. Three composite methods (G3, G4, and W1) were used with accuracy better than 5 kJ mol^{-1} for ΔH_f°, PA, and IE. They also used CCSD(T) calculations using the aug-cc-pVTZ basis set for the neutral non-covalent complexes which were thought to mainly involve dispersive forces. Hence, they were able to make predictions about the thermochemical reactions between the ions $Se^{\bullet+}$, SeH^+, $SeH_2^{\bullet+}$, SeH_3^+, $Ar_2^{\bullet+}$, Ar_2H^+, $Ar_2H_2^{\bullet+}$, $Ar_2H_3^+$, $ArCl^+$, $ArClH^{\bullet+}$, and $ArClH_2^+$ with neutral gases H_2, CH_4, NH_3, O_2, CO, CO_2, NO, and N_2O used in DRC-ICP-MS. Results were presented in tables of data and as thermochemical ladders, including previously unreported values for Ar and Ar_2 hydrides and ArCl-containing neutral and ionized species. A full discussion of these results is beyond the scope of this review so readers interested in optimizing the performance of DRC-ICP-MS for Se determinations are advised to refer to the full paper.

2.2.3 Interferences. Dettman and Olesik[98] have used a pLTE model applied to ICP-OES to correct line-dependent changes in analyte sensitivity caused by matrix-induced changes in plasma temperature. Coupled with an Mn internal standard to correct for sample transport efficiency, they reduced matrix effects caused by 1.0 mol L^{-1} Ba and Na and 1.5 mol L^{-1} Li and Ca to less than 20% for a range of analytes. Errors caused by 1.5 mol L^{-1} La were likewise reduced to less than 40%. In a two part study, Chan and Hieftje[99,100] used spatial measurements of analyte emission across an axially-viewed ICP to indicate the presence of spectroscopic interferences, or those related to either the plasma or sample introduction system. They measured the relative analyte intensity (defined as the signal from the analyte in the presence of the matrix divided by the signal without the matrix present) over the cross-section of the axially viewed ICP to give a spatial pattern equivalent to the analyte concentration in the presence of the interferent. This was done using Ba to induce plasma-related matrix interferences, mineral acids to cause sample introduction effects, and two spectrally interfering line pairs (As and Cd at 228.81 nm, and Er and Co at 239.73 nm). In an elegantly simple approach, they interpreted a flat profile to mean absence of interference and a curved profile to mean that an interference was present. In the second study, they developed a statistical protocol to decide whether the profile was flat or curved and hence flag the presence of an interference.

2.3 Chemometrics

For the purposes of this review, chemometrics relates to a range of mathematical techniques and algorithms used for optimization, interpretation of analytical data, correction of interferences, and instrument calibration. Very little novel work has been published during the review period, except in the area of metrology wherein Mermet and co-workers have published two related papers[101,102] on accuracy and precision. In the first paper they computed an accuracy profile, based on the ISO 5725-1, 5725-4 and 21748 standards which are normally used to estimate the standard deviation of interlaboratory experiments. They used these methods to determine tolerance intervals as a function of concentration by computing the intermediate precisions for a range of analytes, in simple solutions, measured by ICP-OES and ICP-MS. This is rather time consuming so they conceded that it is best suited to method validation when a range of possible sample concentrations is likely. In the second paper[102] they applied the method to determine the LOQs for Pd (ICP-MS), U and B (ICP-OES). They concluded that the LOQ determined by the accuracy profile method was the most pessimistic (and hence most realistic), and that the weighting of the calibration regression was important, with a 1/*y* weighted regression being a good compromise.

3 Laser-based atomic spectrometry

This section highlights the most recent developments in laser-based atomic spectrometry. In particular, it relates to the main atomic spectrometry techniques where the laser is used as either an intense energy source or a source of precise wavelength, including laser induced breakdown spectroscopy (LIBS), laser atomic absorption spectroscopy (LAAS), cavity ringdown spectroscopy (CRS), laser induced fluorescence (LIF), and other tandem techniques. The use of lasers for fundamental studies of the properties of atoms and for thin film deposition will not be covered here. Studies related to laser ablation (LA) as a method of sample introduction are covered in Section 1.3.2.1.

3.1 Laser induced breakdown spectroscopy (LIBS)

Laser induced breakdown spectroscopy is one of the most important techniques where the laser is used as an energy source to induce an optical plasma. This section describes the latest instrumental developments and fundamental studies related to LIBS, but not applications.

3.1.1 Fundamental studies. Determination of plasma temperature and electron density from Mg(II) emission spectral line broadening was investigated by Choi *et al.*[103] using double-pulse LIBS. This configuration was employed because it provided enough energy to sustain the plasma emission during the time period when the line width was at a minimum. Cvejić *et al.*[104] used single-pulse LIBS and high speed photography to calculate Stark broadening parameters for Mg(I) and Mg(II) lines. The high speed photography was used to determine the time of plasma decay which provided the highest plasma homogeneity. Aguilera *et al.*[105] reported the measurement of Stark widths of 53 Ni(II) lines in the LIBS spectrum using an experimental procedure based on accurate measurement of the electron density through the Stark broadening of the H_α line. In a similar way, the Stark broadening of two Ti(III) lines were measured by Chen *et al.*[106] during the early phase (*i.e.*, between 60 and 200 ns) of the ablation process. At this point, it should be noted that Parigger[107] reviewed the limitations on the use of hydrogen Balmer series for the calculation of Stark broadening, and thus for the determination of electron number density under certain conditions. An alternative method, based on matching synthetic spectra (iteratively calculated from an equilibrium model of plasma radiation) and experimental emissivity spectra (obtained by Abel inversion of intensity spectra) has been developed by Merk *et al.*[108] This was used to make spatially resolved measurements of plasma temperature and number densities of plasma species in an argon LIBS plasma at atmospheric pressure. They concluded that the spectral fit method provided more accurate plasma diagnostics than the Boltzmann plot and Stark broadening methods.

The structure of the LIBS plasma was studied by Bai *et al.*[109] using dual-wavelength differential spectroscopic imaging. This involved the use of two filters, alternatively placed in front of the CCD detector, to eliminate the background continuum signal from a specific emission line. A pure aluminum target in an argon atmosphere was used to observe the distribution of ambient gas and target evaporated species inside the ablation plume using different ablation regimes (*e.g.*, different laser fluences and pulse durations). This study demonstrated the key role that laser fluence has on the internal structure of the LIBS plasma. Similarly, Eschlböck-Fuchs *et al.*[110] investigated the expansion dynamics and the optical emission of LIBS as a function of the temperature of sample materials such as aluminum alloys, silicon wafers and metallurgical slag. They observed that higher temperatures lead to larger plume volumes and brighter broadband plasma emission in air, though other plasma parameters were found to be independent of temperature, at least for the slag samples.

Freeman *et al.*[111] studied ns and fs LIBS operated in vacuum and at atmospheric pressure conditions. They investigated the dynamics of plasma evolution and characteristics of the emission spectra and observed that the fs-LIBS plasma plume expanded in a narrower angular distribution, probably due to a strong, self-generated magnetic field created at the onset of plasma expansion. They also noticed that ns-LIBS spectra showed transition lines from lower-charged ions, while fs-LIBS spectra were mainly dominated by neutral species emission. The fs-LIBS technique was employed by Banerjee *et al.*[112] for the detection of submicron buried layers inside a semiconductor material (*e.g.*, Si) by making use of the precise hole drilling capabilities of fs-LA. A correlation between depth resolution and processing speed was observed when carrying out these analyses. Ahmido *et al.*[113] used fs-LIBS to detect visible to NIR signatures from molecular fragments of the nitro (NO_x) group after the ablation of potassium nitrate (KNO_3) and sodium nitrate ($NaNO_3$) coatings. A potential application of this method could be the detection of nitro-group energetic materials at standoff distances.

3.1.2 Identification of spectral lines. Barefield *et al.*[114] reported the identification and assignments of complex atomic emission spectra of mixed actinide oxides (*e.g.*, UO_2, PuO_2, AmO_2, and NpO_2 simulated fuel pellets) using LIBS. They concluded that a resolving power of approximately 20,000 was adequate for analyzing complex mixtures of actinide elements within the same sample. Gaft *et al.*[115] studied the Zr LIBS spectra in the UV region (190–240 nm) at the onset (150–200 ns) of plasma formation in air. This allowed the identification of emission and absorption lines from highly ionized Zr ions (*e.g.*, Zr(III) and Zr(IV)). New emission lines from Zr(I) and Zr(II) were observed in this spectral region.

Spectra in LIBS are sometimes complex and difficult to interpret, thus Labutin *et al.*[116] have developed an algorithm to automatically identify emission lines. This simulates the spectra corresponding to different temperatures and electron densities, then searches for the best correlated pair of experimental and model spectra constructed using information about atomic and ionic lines, broadening mechanisms and the parameters of the spectrograph. The model then attributes lines to the peaks. The algorithm was successfully applied to interrogate the spectral range from 393.34 to 413.04 nm, identifying 41 peaks.

3.1.3 Calibration methods. A novel, optimized calibration procedure has been developed by Frydenvang *et al.*[117] The method was based on a combination of empirical and theoretical methods to determine elemental ratios. It was demonstrated to have potential for fast, real-time, *in situ* analyses due to the fact that sample preparation is minimized and processing time is negligible. Self-absorption is an important parameter that might affect calibration. Usually, self-absorbed emission lines are disregarded or corrected because they would otherwise introduce non-linear effects into the calibration. However, Cristoforetti *et al.*[118] have demonstrated that self-absorption might also provide useful information when characterising the composition of laser-induced plasmas. The poor reproducibility of LIBS also affects the calibration, and efforts have been made to improve it, including experimental optimization, chemometric techniques or the use of internal standards. Criteria used for selection of the most appropriate internal standard have included using the most intense spectral line of a matrix element, the closest matrix line to the analytical one, or the use of a spectral line with a close upper energy level. Labutin *et al.*[119] have investigated an alternative criterion, based on using the best correlated pair of lines observed for variations in laser energy, and successfully used it for the analysis of high alloy steels and soils. The approach was shown to work even under non-LTE conditions.

3.1.4 Instrumentation. A historical review of the first five years of laser based micro-spectrochemical analysis was recently published by Baudelet *et al.*,[120] covering the first measurement systems after the invention of the laser in 1960 to its evolution to conventional LIBS. Nowadays, very compact (palm-top size) and powerful sub-nanosecond pulse width lasers are being investigated. For instance, Bhandari *et al.*[121] have developed a megawatt peak power, 266 nm UV microlaser based on a passively Q-switched Nd:YAG/Cr^{4+}:YAG microchip laser, which might be of great interest for the design of portable-LIBS systems. Scharun *et al.*[122] have designed a LIBS setup with a multi-kHz fibre laser which can be used for handheld quantitative analysis of metallic samples without mechanical sample preparation.

Time-resolved, thermodynamic characterization of small, high-jitter powerchip LIBS plasmas was performed by Merten *et al.*[123] under a variety of atmospheres (*e.g.*, air, Ar and He). This fast-evolving plasma was evaluated for LTE in terms of both the McWhirter and temporal criteria. The former considers the electron/heavy particle collision rate required to guarantee that the total effective population and depopulation rates are dominated by electron collisions, and the latter examines the evolution of temperature and electron number density and compares their rate of change to the rate at which electron collisions can thermalize the change. These considerations were used to conclude that LTE might be present at the early stage of the powerchip LIBS plasma generation, especially under an argon atmosphere, making possible calibration-free LIBS measurements.

3.1.5 New developments. Laser ablation molecular isotopic spectrometry (LAMIS) is an interesting approach for real-time isotopic analysis of samples. It is known that isotope shifts in atomic spectra are small (*e.g.*, a few pm) because the electronic transitions are slightly affected by differences in isotopic masses. Hence, isotopic measurements in LIBS atomic spectra would require high spectral resolution and/or the use of low pressure conditions. In comparison, optical isotope shifts in molecular spectra are much higher (*e.g.*, hundreds of pm) because the vibrational and rotational energy levels are more affected by the differences in isotopic masses. Excited molecular species are produced during LIBS plasma expansion through different chemical reactions, the precise nature of which is still relatively unknown. In LAMIS, emission spectra are collected at longer delay times after the laser–matter interaction to allow the formation of the excited molecules in the plasma. LAMIS is considered of great interest for the fundamental understanding of plasma properties and for different isotopic applications. For instance, Dong *et al.*[124] used LAMIS to study C_2 molecular formation, by observation of the Swan bands, in laser ablation of fabricated carbon isotopic samples containing different amounts of ^{13}C. This was performed in a neon atmosphere at 0.1 MPa. Measurement of the emission band demonstrated that C_2 was formed by a recombination process and that the $^{12}C/^{13}C$ ratio varied with time after the laser pulse and the distance above the sample surface.

Another variant of conventional LIBS, called nanoparticles enhanced LIBS (NELIBS), was investigated by Giacomo *et al.*[125] The method is based on the deposition of a drop of noble metal colloidal solution on the surface of a solid conducting target, in order to enhance the LIBS emission intensity. It was shown that the NELIBS enhancements were related to changes in the ablation process because a significant decrease in the ablation threshold was detected for all of the investigated metal samples. However, no significant differences were observed in the temperature and electron number density for NELIBS compared with LIBS.

LIBS is a powerful analytical technique for the analysis of samples placed in a gas environment (*e.g.*, air, Ar, He) or in vacuum, but also for the analysis of samples immersed in liquids. Lazic *et al.*[126,127] studied LIBS plasma and vapour bubble formation after ablation of Al targets underwater, using dual pulse excitation, by fast photography and time resolved spectroscopy. Position-selective emission spectroscopy of a LIBS plasma produced on an Al target in water was investigated by Matsumoto *et al.*[128] They observed that the density at the edge of the plasma produced by long-pulse irradiation (*ca.* 100 ns) was low enough to achieve well-resolved, narrow spectral lines, even without time-gated detection. These results might change the current concept of the instrumentation for underwater LIBS and open new possibilities for *in situ* chemical analysis of solid materials in water.

The combination of LIBS with diode-laser LAAS and LIF has been investigated by Khater[129] to improve the analytical capability and figures of merit of LIBS for trace analysis of light elements (*e.g.*, C, S, P and N) in steel samples.

3.2 Laser atomic absorption spectroscopy (LAAS)

A method for time-resolved, tunable diode LAAS (DLAAS) has been developed by Adamek *et al.*[130] An electronic module was designed to provide two signals that were used to trigger the fine tuning of the laser wavelength and to control time-defined signal sampling from the absorption. This method was successfully used to obtain time-resolved measurement of density and temperature of Ar* in a pulsed discharge. On-line and real-time quantitation of Xe in argon was performed by Jacquet *et al.*[131] using tunable DLAAS in a DC glow discharge. Xe is a fission product of U that must be monitored, for safety reasons, on-line in the cover gas of a sodium cooled fast neutron reactor. In this study, continuous wave laser absorption from the lower metastable state at 823 nm was used to measure the isotopic and hyperfine structure of Xe isotopes, and to individually quantify the odd isotopes.

3.3 Cavity ringdown spectroscopy (CRDS)

The background and principles of CRDS and various applications of this technology were recently reviewed by Zhang *et al.*[132] Significant developments of plasma sources, lasers, and cavity optics were reported, highlighting the great analytical potential of plasma-CRDS for elemental detection and isotopic measurements. Nevertheless, it was pointed out that further efforts are still needed in fields such as cavity design, plasma source design, instrumental improvement and integration, and measurements of radicals and molecules.

Biscan *et al.*[133] investigated the production of 2^3S_1 metastable helium in a laser-induced plasma at low pressure. The absorption CRDS technique was employed to measure the density time evolution of metastable helium and ablated atoms, produced during the ns laser ablation process of various materials (*e.g.*, graphite, aluminum and iron) in a low pressure (*e.g.*, 0.03–2 mbar), helium atmosphere. They concluded that the width of ablated atom lines was mainly related to directional movement of atoms and that the appearance of metastable He might be attributed to excitation in collisions with ejected electrons and heavy excited particles.

3.4 Laser-induced fluorescence (LIF)

Frankevich *et al.*[134] have coupled LIF with a differential mobility analyzer in order to obtain two-dimensional information on the electrical mobility and fluorescence spectroscopy of gas-phase ions. The authors claim that this unique instrument combination could be of great interest to investigate the physical and chemical properties of fluorescent proteins.

Many light atoms (*e.g.*, H, O, C) have LIF transitions in the VUV spectrum that are difficult to excite. Two-photon LIF has been developed to overcome this difficulty by exciting the LIF transition by absorption of two photons. One problem with this approach is that amplified spontaneous emission (ASE), which is created by the population inversion between the excited and the de-excited states, might affect the linear response of the LIF signal with respect to the number density of the target species and laser intensity. With this in mind, Li *et al.*[135] investigated, using a Monte Carlo model, the effects of line-narrowing of ASE, which is due to the fact that ASE photons near the central frequency are amplified more effectively. Consideration of these line-narrowing effects was necessary to avoid significant errors in the interpretation of the LIF and ASE signals.

4 Isotope ratio analysis (IRA)

Isotope ratio analysis is dominated by plasma source ionization, with sample introduction either by laser ablation or solution nebulization. Thermal ionization is still a valuable low-blank method which contributes to a number of applications. Precise measurements of isotopic abundance are used in a variety of disciplines including nuclear forensics, geochronology, stable isotope fractionation, isotope dilution analysis, isotope tracer studies and archaeological provenance. Instrumental developments continue to allow isotopic measurements to be made on smaller samples and more robust precision has been achieved by the application of poly-spiking techniques.

It is always appropriate to periodically re-assess the principles and knowledge-base. In this respect, a review by Baxter *et al.*[136] was a welcome assessment of some fundamental aspects of SF-MS. Factors which influence the IR measurement, at all stages of the process from the true ratio, through the measured ratio, to the final corrected ratio, were deliberated. The effects of Poisson counting statistics and flicker noise on ratio precision were treated mathematically, and accuracy offsets *via* abundance sensitivity tailing were discussed. Usefully, a thorough consideration of mass discrimination was contained in this tutorial, reviewing both the correction functions and the methodology of internal and external normalisation, as well as sample standard bracketing. Finally there was a comprehensive evaluation of dead time correction including a systematic review of the differing estimation methods which will be of great use to novice and experienced users.

4.1 Instrumental developments

A common thread of much IRA research is a drive to lower the amount of analyte required to generate a particular, or at least useful, level of precision. Such error-reduction has often been achieved by increasing the sensitivity of the MS technique, thereby requiring less sample to achieve signals significantly above noise level. Where the amount of analyte is small, the method of sample introduction to the mass spectrometer, particularly for plasma ionization instruments, is crucial to maximising sensitivity. In such cases, the sample dilution needs to be minimised to maintain suitable signal levels of the isotopes of interest. At the same time, the volume of sample consumed during the analysis also needs to be restrained to allow acquisition of a statistically viable population of isotope ratio data. Paredes *et al.*[137] have furthered their previous investigations[138] into low-flow nebulization, using continuous sample introduction rates of <10 μL min^{-1}. Validation of IR determinations was completed with Sr isotopes using an internal ^{88}Sr/^{86}Sr mass bias correction. Best results were obtained by heating the spay chamber walls to 65 °C and using a flow rate of 9 μL min^{-1}. Sensitivity of the MC-ICP-MS still ultimately determined the amount of element consumed in the analysis and, in the optimal case, a sample solution of ~250 ng mL^{-1} was used to maintain ^{86}Sr signal levels at >0.1 V. In a companion paper[137] a torch integrated sample introduction system (TISIS) was evaluated with respect to how mass discrimination effects on Sr isotopes can be controlled by sample flow rate and spray chamber temperature. Essentially, heavy-biased mass discrimination effects increased with higher flow-rates (15 μL min^{-1}) and higher spray chamber temperatures (100 °C). The authors hypothesised that this was related to a more effective solvent evaporation process in the TISIS at higher temperatures, and a reduction in water load at low sample flow rates. The other interesting finding was that low flow rates (5 μL min^{-1}) and high temperatures resulted in a degradation of the exponential law correction model for the mass discrimination process. It was suggested that this stems from irregularities in the aerosol formation processes which, in turn, could affect mass-dependent diffusion processes in the plasma.

There have also been developments in detection systems, such as a new generation of Faraday detectors equipped with low-resistivity (10^{12} Ω) resistors reported by Koornneef *et al.*[139] These detectors were designed to provide lower baseline noise compared to the conventional 10^{11} Ω amplifiers, and were used to measure ^{87}Sr/^{86}Sr and ^{143}Nd/^{144}Nd for 1 ng amounts of analyte. Comparison with previous studies indicated that reproducibility was improved by factors of 2 and 1.4, respectively. Combined with increases in instrument efficiency, this has the potential to benefit applications such as radiometric dating or characterising isotopic disequilibrium in geological samples.

Hu *et al.*[140] assessed the effect on sensitivity of fast interface pumping and the X-skimmer and Jet-sampling cones in a commercial MC-ICP-MS instrument. Combinations of new and old cones were trialled for Hf, Lu and Yb with a view to optimizing Hf IR measurements in zircons by LA. Results indicated that the X- and Jet-cone combination improved Hf sensitivity by a factor of ~5 compared to the standard cone combination. An interesting feature of the analysis was that the Jet-sampling cone resulted in a non-linear mass-dependent fractionation that could not be corrected by standard fractionation laws. However, it was found that this fractionation effect was inhibited by the addition of small quantities of nitrogen to the central argon-helium flow from the collision cell.

The effects of mass discrimination in the sampling and post-sampling regions of ICP-MS was examined by Kivel *et al.*[141] Using tantalum or graphite targets positioned close behind the skimmer cone orifice, elements ranging in mass between Li and U were admitted under wet plasma conditions to the interface. Material deposited on the target was then analysed both in bulk by solution nebulization, and as individual points along a radial transect from the central axis by laser ablation. The bulk measurements revealed a heavy-isotope bias, indicating that extraction of ions from the plasma contributed in the order of 50% of the measured discrimination. Radial measurement of Cd isotope ratios demonstrated a heavy-isotope bias at the axis which progressed to a relatively light-isotope bias outwards. As the ion beam was subject to "clipping" downstream from the target position, this was taken by Kivel *et al.* to indicate that further light-ion removal completed the remaining fraction of the instrumental mass discrimination.

Sometimes major improvements in analytical efficiency may be too good to be true. This may well be the case with intracavity optogalvanic spectroscopy (ICOGS) for measuring radiocarbon isotope systematics. Initial reports of this technique (Murnick, D. E.; Dogru, O.; Ilkmen, E. Anal. Chem. 2008, 80, 4820–4824) suggested that it could match the LOD achieved by AMS for $^{14}C/^{12}C$. At the time, this report generated significant interest because of the potential to simplify the analysis, reduce costs and increase the size of datasets. However, Persson *et al.*[142] have produced a frank assessment of the technique based on a comprehensive dataset and they have not been able to reproduce the reported optogalvanic signal dependence on ^{14}C concentration and wavelength. In addition, they have now estimated that the detection limit for ^{14}C is likely to be > 2 orders of magnitude higher than originally estimated.

4.2 Double-spike systematics

Conventionally, double spiking is used for in-run instrumental mass-bias corrections in ICP-MS and TIMS. De-convolution using a double spike to give bias-free isotope ratios requires an element with a minimum of four accurately measurable isotopes in the natural or the with-spike mixture. However, by using gravimetric mixing of the sample with different proportions of an isotopic spike, Chew and Walczyk[143] have developed a modification of the double spike technique capable of high-precision IR measurements using only three isotope signals. This gravimetric spiking IDA (GS-IDA) approach has the potential to increase the precision of Mg isotope ratios, benefiting studies of metabolism in humans and elemental diffusion in mineral species. Application of this technique could open other suitable isotope systems to a similar spike correction protocol.

Instigation of the double spike or GS-IDA techniques for determining isotopic composition requires calculation of the appropriate spike composition and an understanding of the optimum sample-spike mixing proportions. John[144] has developed models where the concentrations of the spike and sample are allowed to vary independently, rather than restricting spike-plus-sample to a fixed concentration mixture (within the bounds of the signal capacity of the detector). The result was a decrease of up to 30% in the theoretical error, or greater reductions where isobaric interferences were present.

Double spike systematics have also been applied to the analysis of Pt stable isotope ratios.[145] Using two separate Pt double spikes, the $^{198}Pt/^{194}Pt$ ratio could be reproduced to within 10^{-5} amu^{-1}. These findings indicated that, despite variable amounts of isobaric ^{192}Os, accuracy of the Pt isotope ratio was unaffected because ^{192}Pt was not used in the double-spike de-convolution. Application of this technique provided a redefined Pt atomic weight and indicated that Pt stable isotope fractionation is quantifiable above the reproducibility of the method.

Stable Zn isotopes have been the focus of a study by Makishima and Nakamura,[146] who have developed a low-blank method for Zn separation using TEVA resin, followed by a double spike determination of $\delta^{66}Zn$. Blank levels were reduced from greater than 1 ng reported in earlier studies to around 50 pg, enabling $\delta^{66}Zn$ to be reproduced to 0.004% RSD (2σ) for 100 ng of Zn. This method will prove valuable in high-resolution studies of Zn where material is limited and Zn concentrations are low.

Shalev *et al.*[147] compared MC-ICP-MS and TIMS for measuring the non-radiogenic $^{88}Sr/^{86}Sr$ ratio using a double spike. Results of the double spike bias corrections were found to be more reproducible than sample-standard bracketing for MC-ICP-MS. The two instruments produced the same $^{88}Sr/^{86}Sr$ values, with TIMS having smaller within-run errors but needing a longer integration time to achieve this.

4.3 Nuclear forensics

Kraiem *et al.*[148] have introduced a method for determining the mass of uranium in single micron particles. This is driven by the need to develop particle reference materials for nuclear safeguards, which would be used to evaluate mass and isotope abundances of uranium in such materials. Their method used ID-TIMS, where individual or multiple uranium oxide particles were mounted on a filament and spiked with ^{233}U in an acid medium. A separate measurement of a particle was made without the spike to determine the U isotope ratios. The estimated error for the calculated U mass was better than 10%, thought to be related to incomplete dissolution of the particle on the filament. The precision of the $^{235}U/^{238}U$ measurement was found to be better than 1% (2σ).

The need for rapid yet accurate analysis of isotopic materials has made LA a potential sampling tool for safeguards and nuclear forensic investigations. Kappel *et al.*[149] used a nanosecond laser coupled with MC-ICP-MS to directly analyse U isotope ratios in single U-doped glass particles. Uncertainties were better that 1.4% and 6% (2σ) for the $^{235}U/^{238}U$ and $^{236}U/^{238}U$ ratios, respectively. A similar study of direct measurement of uranium isotopes in enriched uranium pellets and rods was undertaken by Marin *et al.*,[150] using a 266 nm Nd:YAG LA–SF–ICP-MS. A combined precision and accuracy of <2% RSD (σ) for the $^{235}U/^{238}U$ ratio was achieved. Each study defined a reproducibility window between 0.5% and 2% as the state of the art for $^{235}U/^{238}U$ determinations on individual particles, setting the analytical benchmark for nuclear forensic methods in the future.

Efforts to measure $^{236}U/^{238}U$ in samples with ultra-low ^{236}U have been advanced by Tanimizu *et al.*[151] using tandem Q-ICP-MS/MS. A key feature of this analysis was the oxidation of U in the reaction cell between the tandem quadrupoles. In this reaction only 1% of the UH^+ was converted to UOH^+. The reduction in $^{235}UOH^+$ production enabled $^{236}U^{16}O^+/^{238}U^{16}O^+$ to be measured down to 10^{-9}, which approaches the analytical LOD of TIMS.

As with many isotope systems reviewed, the common aim is to increase sensitivity, reduce background interference and improve precision of analysis, ultimately to enable IR measurement of ever smaller quantities. One requirement in the nuclear field is the monitoring of humans, particularly if exposed to anthropogenic sources of uranium in their occupation, or as a result of proximity to a nuclear installation. Arnason *et al.*[152] took on the challenge of measuring <40 pg mL^{-1} of uranium isotopes in urine. Solid phase extraction of the urine matrix followed by U isolation using a double-washed UTEVA resin minimised the blanks to <0.3 pg, *i.e.*, ~1%. Based on a urine sample of as little as 1 mL and ≥50 pg U, the $^{235}U/^{238}U$ ratio was measured within 2% (2σ), which is a useful level of detection for monitoring.

Where the quantity of uranium is not restricted, $^{235}U/^{238}U$ can be determined by more conventional mass spectrometric techniques. Mathew *et al.*[153] used sample loads of 1 to 2 μg U to assess the total evaporation TIMS method. One finding was that the mass bias, assessed by various U standards, was consistent within individual analytical turrets (batches), but variable between turrets. Using these standard-based 'external' estimates of the mass bias resulted in precision better than 0.04% (2σ) for the $^{235}U/^{238}U$ ratio, which approaches the precision attainable by U double spike analysis. However, this external method could not detect if an individual sample had incomplete matrix separation, which may influence the degree of mass bias.

4.4 Stable isotope fractionation

Investigations into stable isotope fractionation of heavy elements has been the focus of a number of studies. Ohno and Hirata[154] have investigated the variation of Ce and Nd isotopes in natural geological reference materials. Interestingly, carbonate standards were found to have significantly higher Ce and Nd isotope ratios compared to igneous and other sedimentary rocks. However, no difference in the amount of isotopic fractionation was found between the two elements, implying that this fractionation is independent of changes in redox state.

Pramann *et al.*[155] have investigated a potential source of "broadband" interference across the Si mass spectrum in MC-ICP-MS. This took the form of a broad raised background centred at ^{29}Si–^{30}Si, present in NaOH-containing solutions but absent from KOH solutions. It appeared that this interference was detector specific because it was not observed in the central Faraday cup, only in the high- and low-mass Faraday arrays. The logical conclusion is that the interference, which significantly degrades Si isotope ratios, was caused by ion scattering in the presence of high sodium concentration. Absence of the interference from the centre Faraday was most likely related to this detector's position in a shielded location offset behind the main high-low Faraday array.

As often happens with analytical developments, sometimes two papers on essentially the same technique emerge simultaneously. Yang *et al.*[156] and Sanchez-Lorda *et al.*[157] are an example of such. Elements with relatively similar ionization efficiencies can experience similar levels of instrumental mass bias. For elements with different efficiencies, such as Hf and Yb, mass bias interrelationship can be formulated during, or prior to, the measurement. Hence, it is a logical progression to examine if elemental concentration ratios and isotope ratios can be measured within an individual multicollector analysis. In both of the aforementioned papers MC-ICP-MS was trialled for the measurement of $^{143}Nd/^{144}Nd$ in the same run as $^{147}Sm/^{144}Nd$. These ratios are of particular interest because they form the basis of Sm-Nd geochronology, and because they are preferably measured from the same dissolution and chemical separation. Conventional analysis of the Sm-Nd system is by TIMS or MC-ICP-MS and requires IDA to determine the concentration ratio and chemical separation of Sm from Nd. Both studies used Nd isotopic standards doped with variable amounts of Sm to replicate the likely natural range of Sm/Nd, and formulated a relationship between the exponential mass bias coefficients to correct the isobaric ^{144}Sm interference. Reported errors on $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ were similar for the two studies, and were roughly equivalent to measurements made by conventional methods. Sanchez-Lorda *et al.*[157] reported that $^{147}Sm/^{144}Nd$ reproducibility ranged from 0.2% to 0.7%, which is slightly higher than for IDA measurements. A significant difference in the papers is that these workers also included a new methodology to isolate the rare earths from the matrix elements prior to the combined-run $^{143}Nd/^{144}Nd$, $^{147}Sm/^{144}Nd$ MS analysis.

Recent improvements in sample introduction and plasma sampling have produced a step-change in the sensitivity of ICP systems. Using a PFA microflow nebulizer, desolvator and X-skimmer/Jet-sampler cones, Huang *et al.*[158] sought to precisely determine Nd isotope ratios for ng levels of analyte using MC-

ICP-MS. They achieved a sensitivity of >2000 V per μg mL^{-1} for Nd. At this elevated level of detection, a 2.5 ng mL^{-1} solution produces a 1 V signal for ^{146}Nd (∼1×10^{-11}A ion current). The analysis of small volume samples (0.5 mL) containing 0.5 ng of Nd resulted in a ^{143}Nd/^{144}Nd ratio for the JNdi-1 standard of 0.512101 ± 0.000029 (2σ, $n = 6$). With 5 ng of Nd the errors were reduced to 0.512124 ± 0.000010 which is comparable to typical long-term reproducibility statistics for NdO^+ measurements by TIMS. Huang *et al.*[158] have used this advance in sensitivity to evaluate the potential for this method to tackle Nd isotope determinations on seawater. Using a 5 km seawater sampling station off Bermuda as a trial for the method, the results were comparable to previously achieved Nd isotopic profiles.

4.5 Laser ablation isotope analysis

In situ analysis of materials by LA continues improve with respect to the precision of IR measurements. Chen *et al.*[159] used a fs-laser in combination with MC-ICP-MS to examine the Pb isotope ratios in copper-based coins. Due to its high Pb content bronze is an idea material for this type of analysis. The reported precision of <60 ppm (1σ) for ^{208}Pb/^{204}Pb approached the level achievable by solution analysis. However, the key result of the study was the ability to rapidly discriminate between coins of different dynasties and detect heterogeneity of metal sources within an individual dynastic currency. This is quite interesting from an archaeological perspective but also has implications for the forensic analysis of ballistics and discrimination of other metal components.

The IRA of Pb by LA-MC-ICP-MS was also tackled in a study by Darling *et al.*[160] who compared the results from direct measurement with samples where Pb was chromatographically separated from the matrix. A suite of samples from the Sudbury impact structure, in particular the included sulfide minerals chalcophyrite, pentlandite, pyrite and pyrrhotite, were the focus of the study. Encouragingly, the Pb isotope ratios generated by the direct sampling and by chemical isolation of Pb were within analytical uncertainty, typically 0.1% (2σ) for ^{206}Pb/^{204}Pb. This was achieved despite bias corrections being made to non-matrix matched external standard measurements. Common problems encountered with sulfide mineral analysis are the isobaric and molecular interferences from oxides, argades and sulfides of Re, Os, Pt and the rare-earth elements. However, by restricting oxide production to <0.5%, and monitoring the ^{205}Tl/^{203}Tl ratio, it was concluded that these isobaric interferences did not influence the measured Pb isotope ratios. An interesting facet of the results is that analyses from each sample, including the solution analyses, formed linear arrays in Pb-isotope space (*e.g.*, ^{207}Pb/^{204}Pb – ^{206}Pb/^{204}Pb). This suggests a isochronous relationship, and helps define the initial (at formation) isotope ratios across the spectrum of samples studied.

A major issue encountered in LA analysis is concentration calibration. This has often been addresses by normalising analyte signals to other elements of known concentration, or by the co-introduction of a calibrated spike solution. The best accuracy can be achieved using IDA, which Claverie *et al.*[161] demonstrated using a spinning platform within the ablation cell. Sample material and an isotope spike in solid form were located adjacent to each other on the sample holder, such that fast rotation (∼2000 rpm) of the sample under the laser resulted in a quasi-simultaneous ablation of the spike and sample. Initial trials also included the addition of a Gd spike to both sample and reference materials to correct for any differences in the ablation rate caused by position or material properties.

In some instances, *e.g.*, for large samples, it is not appropriate to undertake laser ablation in a standard ablation cell. Dorta *et al.*[62] experimented with fs-LA of samples in air, followed by conversion to an argon carrier in a gas exchange device, and introduction to a MC-ICP-MS instrument. Results for Hf, Pb, and Zn isotopes were comparable with air sampling and a conventional He atmosphere ablation cell. Single shot analyses produced an acceptable level of precision for archaeological applications.

Dating minerals by LA-MC-ICP-MS continues to evolve. Cottle *et al.*[162] employed a single-shot method with modified data reduction and error propagation routines for U–Pb dating of zircon and monazite. The method effectively integrated the total signal for each isotope, such that only a single isotope ratio was generated instead of a series of measured values. Key advantages of this method are that it counters any IR bias resulting from signal decay or response-time offsets caused by differences between Faraday and ion counting detectors. The method generated accurate and reproducible ages for standard zircons and monazites relatively rapidly, being around 6 times faster than conventional LA-ICP-MS. Probably the most appropriate application is where an age population is required amongst a large number of zircons. Examples of this include identification of age grouping of grains in detrital sediments and in screening zircon populations prior to more detailed age-selective analysis.

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.

8-HQ	8-Hydroxyquinoline
a.c.	Alternating current
AA	Atomic absorption
AAS	Atomic absorption spectrometry
AIP	Atom-imprinted polymer
ASE	Amplified spontaneous emission
CID	Collision induced dissociation
CRDS	Cavity ringdown spectroscopy
CRM	Certified reference materials
CVG	Chemical vapour generation
DBD	Dielectric barrier discharge
DLLME	Dispersive liquid–liquid microextraction
DDTC	Diethyldithiocarbamate
DLAAS	Diode laser atomic absorption spectroscopy
DMA	Dimethylarsenic (include oxidation state if known)
DOF-MS	Distance-of-flight mass spectrometry

DRC	Dynamic reaction cell
EDXRF	Energy dispersive X-ray fluorescence
EPA	Environmental protection agency
ES	Electrospray
ESI-MS	Electrospray ionization mass spectrometry
ETV-ICP-MS	Electrothermal vapourization inductively coupled plasma mass spectrometry
FAAS	Flame atomic absorption spectrometry
FFF	Field flow fractionation
FI	Flow injection
GC-MS	Gas chromatography mass spectrometry
GD	Glow discharge
GD-MS	Glow discharge mass spectrometry
GE	Gel electrophoresis
GF	Graphite furnace
HG	Hydride generation
HPLC	High performance liquid chromatography
ICP	Inductively coupled plasma
ICP-AES	Inductively coupled plasma atomic emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-MS/MS	Inductively coupled plasma mass spectrometry/mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
ID	Isotope dilution
IDA	Isotope dilution analysis
IDMS	Isotope dilution mass spectrometry
IIP	Ion-imprinted polymer
IL	Ionic liquid
IR	Isotope ratio
IRA	Isotope ratio analysis
LA	Laser ablation
LA-ICP-MS	Laser ablation inductively coupled plasma mass spectrometry
LAMIS	Laser ablation molecular isotopic spectrometry
LC	Liquid chromatography
LC-MRM-MS	Liquid chromatography multiple reaction monitoring mass spectrometry
LEP	Liquid electrode plasma
LIBS	Laser induced breakdown spectroscopy
LLE	Liquid–liquid extraction
LLLME	Liquid–liquid–liquid microextraction
LOD	Limit of detection
LOV	Lab-on-a-valve
LPME	Liquid phase microextraction
MC-ICP-MS	Multicollector inductively coupled plasma mass spectrometry
MCP	Microchannel plate
MDG	Monodisperse microdroplet generator
MeCat	Metal coded affinity tag
MeSeCys	Methylselenocysteine
MIP	Microwave induced plasma
MNP	Magnetic nano-particle
MS	Mass spectrometry
NE-LIBS	Nanoparticles enhanced LIBS
NIST	National institute of standards and technology
NP	Nano-particle
NTV	Near torch vapourization
OES	Optical emission spectroscopy
PDMS	Polydimethylsiloxane
PFA	Perfluoroalkyl
QMS	Quadrupole mass spectrometry
Q-ICP-MS	Quadrupole inductively couple plasma mass spectrometry
qPCR	Quantitative polymerase chain reaction
r.f.	Radio frequency
REE	Rare earth element
RSD	Relative standard deviation
SC-GD	Solution-cathode glow discharge
SDS-PAGE	Sodium dodecyl sulfate polyacrylamide gel electrophoresis
SeCys2	Selenocystine
SeEt	Selenoethionine
SeMet	Selenomethionine
SF-ICP-MS	Sector field inductively coupled plasma mass spectrometry
SF-MS	Sector field mass spectrometry
SIMS	Secondary ion mass spectrometry
SPE	Solid phase extraction
SPME	Solid phase micro-extraction
TEM	Transmission electron microscopy
TOF-MS	Time-of-flight mass spectrometry
UV-vis	Ultraviolet-visible spectrophotometry.

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