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

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**SUMMARY OF CONTENTS**

**Strapline:** *This review of 151 references covers developments in ‘Atomic Spectrometry’ published in the twelve months from November 2014 to November 2015 inclusive. It covers atomic emission, absorption, fluorescence and mass spectrometry, but excludes material on speciation and coupled techniques which is included in a separate review. It should be read in conjunction with the previous review1 and the other related reviews in the series.2-6 A critical approach to the selection of material has been adopted, with only novel developments in instrumentation, techniques and methodology being included. Most of the techniques discussed have reached a stage of maturity where major advances are less common, with many of the novel developments falling under the category of ‘applications’ and advances in instrumentation being confined to component parts, such as sample introduction and sample preparation systems. There have been some developments in mass spectrometry, with reports of distance of flight (DOF)-MS and zoom-TOF-MS to improve speed of data collection and resolution respectively; and further insights into space charge effects in the ICP channel and ion beam of ICP-MS. The development of components for portable systems continues to be of interest, covering areas such as plasma sources for OES, fibre-optic laser systems for LIBS, and compact components for planetary exploration. The quest for high sensitivity and precision and low noise has driven developments in MC-ISP-MS in order to improve precision of IR measurements for geochronology and other applications.*

**1. Sample Introduction**

* 1. **Liquids**

**1.1.1 Sample pre-treatment.**

* + 1. **Sample pre-treatment.**

Deng *et al*.7 have reviewed (135 references) preconcentration and separation techniques for AFS. The review covers LLE, SPE, microwave/ultrasound-assisted extraction, pressurised liquid extraction, and VG. It covers the development of the techniques and application of these methods in combination with AFS for ultra-trace determinations in liquids and solids.

* + - 1. *Solid phase extraction.* This is a mature area of research, with numerous applications utilising a wide variety of media. Traditionally, polymeric or silica based substrates have been used as the solid phase, often coated with a secondary exchange medium such as a complexing agent. More recently, natural materials have been used as the stationary phase, and are advantageous in circumstances where technical materials are expensive or difficult to source. Most separation schemes require a liquid sample to exchange with the solid phase in either a continuous flow or batch mode of operation. Hu and Chen8 reviewed the use of nanometer sized materials in SPE with detection using atomic spectrometry.

In recent years, the trend has been towards *miniaturization of instrumentation*, and SPE is no exception. Wang *et al*.9 developed a chip-based micro-SPE system coupled with ICP-MS. The PDMS chip consisted of five microextraction channels (500 x 50 µm) and eight microvalves (800 x 50 µm). Selected channels on the chip were packed with a magnetic solid phase prepared by self-assembled Fe3O4@SiO2@APTES MNPs in a magnetic field provided by permanent magnets ‘purchased from a local market’. Five sample solutions were introduced into five microextraction channels on the chip at 8 µL min−1, and then selectively eluted in 2% thiourea solution and analysed by ICP-MS. The authors used this system for the determination of Bi, Cd, Cu, Hg, Pb and Zn in cell lysate, with LODs in the range from 4.2 to 49 ng L-1.

 A similar concept was realised by Shih *et al*.10, who developed a micro-SPE system using a PMMA chip. They functionalised the inside surfaces of the channels using a 1,1-dichloroethene/1 2,2’-Azobisisobutyronitrile/ehthanol/hexane mixture which underwent a photocatalytic reaction to form highly electronegative C-Cl moieties with dipole–ion interactions. This had the effect of creating a SPE medium at the surface much like that observed on the inside of PVC capillary tubing, which has previously been used for SPE. A fully automated system operating at a flow rate of 100 µL min-1 was used to determine Cd, Co, Cu, Mn and Ni in NIST 1643e (artifcial saline water), with LODs ranging from 3.48 to 20.68 ng L-1.

A problem often encountered with SPE separations is that, in order to improve efficiency, they must be performed at elevated pressure using finely divided media. One method of reducing the back pressure, while maintaining high efficiency, is to use a *monolithic material.* Liu *et al*.11 fabricated and functionalised a monolithic capillary column with mercapto groups using cystamine dihydrochloride. They used this for the determination of Au and Pd in human urine and serum by ICP-MS, with LODs of 5.9 and 8.3 ng L-1, respectively. An enrichment factor of 10 was achieved and the sample throughput rate was 11 h-1.

*1.1.1.2 Liquid phase extraction.* The only real novel development over the last few years has been the use of ionic liquids (ILs) as an extraction medium. This topic has been reviewed 112 references) by Stanisz *et al*.12 who cover applications of dispersive, single drop and hollow fibre LPE. They include tables of applications cross-indexed by analyte, sample, type of IL and other criteria.

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*1.1.1.3 Elemental tagging.* The use of elemental tagging as a means of improving the selectivity, sensitivity and precision of biological assays has been a feature of recent reviews. Peptides and nucleic acids can be tagged using conjugating molecules that contain a metal moiety, with or without isotopic enrichment. In the former case, attachment is usually by means of conjugation with the tagging molecule, often via an antigen-antibody pair of the type typically used for immunoassay. In the latter case, a complementary nucleic acid probe contains the tagging agent. Charour *et al*.13 reviewed (164 references) the use of ICP-MS for quantification of proteins by isotope tagging. They included a useful overview of both relative and absolute quantification methods as developed mainly for MALDI-MS or ES-MS, then went on to briefly review the use of elemental tags using ICP-MS.

A major advantage of using an elemental tagging approach is that multiple analytes can be targeted simultaneously by using more than one tag per assay. For example, Zhang *et al*.14 used 4-mercaptophenylboronic acid functionalised magnetic beads to capture alpha-fetoprotein (AFP) and carcinoembryonic antigen (CEA). After blocking non-specific adsorption with skimmed milk, they added a mixture of Au and Ag nanoparticles which had been functionalised with anti-AFP and anti-CEA antibodies, respectively. The magnetic beads were then separated using a magnetic field and the Au and Ag protein-antibody complexes released using formic acid, and subsequently determined by ICP-MS. The technique yielded LODs of 0.054 and 0.086 µg L-1 for CEA and AFP, respectively, which is comparable with other ICP-MS immunoassays.

One of the problems when labelling proteins and peptides with large conjugate molecules, such as 1,4,7,10-tetraazacyclododecane-N, N’, N’’, N’’’-tetraacetic acid (DOTA), is that of achieving 100 % labelling efficiency, because of the slow reaction kinetics and steric hindrance. He *et al*.15 addressed this problem by using a two-step approach. First, the thiol group of cysteine was modified with 2-iodo-N-(prop-2-yn-yl)acetamide to create a spacer before subsequent labelling with the bulky DOTA-azide complex. Results indicated that *c.a*. 96% of detected cysteine-containing peptides were completely labelled using this approach, compared with less than 90% when other DOTA-based labelling strategies were used.

There have already been several publications on the use of *elemental tagging in conjunction with nucleic acid probes* for use in DNA assays. Hu *et al*.16 reported a novel approach using Cd quantum dots (QDs). First, they immobilised captured DNA strands on an Au disc followed by hybridisation with the target DNA (in this case an HIV fragment). This was hybridised in turn by biotin-labelled DNA, and then tagged with strepdavidin labelled CdS QD assembled SiO2 microspheres to form a ‘sandwich’. Finally, after washing with buffer and DDW, the Cd was released by dissolution in 2% (v/v) nitric acid and subsequent determination by HG-AFS. The amplification provided by the use of CdS-QD microspheres yielded an LOD of 0.8 amol L-1, with the capability to assay target DNA strands at a concentration of 1 fmol L-1. While not completely selective for the target strands, discrimination was in the order: non-complementary < three-base mismatched < two-base mismatched < one-base mismatched < complementary target.

 Deng *et al*.17 have made further advances in the method of hybridisation chain reaction (HCR) amplification of DNA by developing a non-enzymatic protocol. In this case the ‘sandwich’ was formed from an MNP-streptavidin-biotin-DNA capture probe. This was hybridised with the target DNA strand then further hybridised with a second DNA capture probe. Two hairpin DNA probes, H1 and H2 were then added, H2 being labelled with a lanthanide element. These hairpin DNA strands have matched potential energies, so that they undergo an isothermal hybridisation reaction starting at the second capture probe and then adding alternately to it in an amplification process. When the amplification was complete, magnetic separation was performed to remove excess DNA probes and H2-Ln was then released by heating at 90 °C for 20 min. Analysis was performed using ICP-MS with an estimated LOD of 300 fM.

Finally, an illustration of how the elemental tagging technique has entered the mainstream is exemplified by an article, in the *Journal of Chemical* *Education*, by Schwarz *et al*.18 In this, they described an experiment undertaken by graduate students using the metal coded affinity tag (MeCAT) procedure to quantify ovalbumin in hen egg white.

**1.1.2 Nebulisation.** The techniques of ICP-OES and ICP-MS are considered to be the most important tools in inorganic analytical chemistry. Their analytical performance has improved dramatically, since the introduction of the ICP in the 1970s, as a result of advances in RF generators, spectrometers, detectors and microelectronics. For the majority of cases, however, liquid sample introduction is still based on the pneumatic principle first described in the late 19th century. Bings *et al.*19 provide a critical review of the developments in liquid sample introduction, described by the authors as the “Achilles' heel of atomic spectrometry”.

Low cost 3D printer technology has been reported for the fast fabrication of a wide range of products. There are clear merits to the technique. Thomson has described some initial research into the use *of 3D printing for the fabrication of cyclonic spray chambers for ICP.*20 The linearity, precision and LODs obtained from the 3D printed chamber compared well with those obtained with a commercial model. The performance of subsequent prints of the same spray chamber was compared and shown to be highly reproducible. This work suggests that low-cost 3D printing techniques can be used as an inexpensive way to fabricate prototype spray chambers to accelerate the research in this area. Geertsen *et al*.21 used the 3D-printing process to produce a range of cyclonic spray chambers for ICP-AES. Three different processes, five materials and eight designs were used to produce the chambers, and their analytical performance compared with that of commercial glass and PFA chambers. LODs obtained with polymer printed chambers were comparable to those measured with the glass chamber, however, the sensitivity was lower with the 3D-printed chambers. The printed chambers allowed improvements in LODs compared to PFA chambers. At low temperature, a printed chamber’s efficiency depended on both the printing process and the manufacturing material. This work further demonstrated the advantages of 3D printing for fast prototyping of spray chambers and improvements over commercial systems.

*A novel concentric type grid nebuliser* was developed and described by Inagaki *et al.*22. The nebuliser had a grid screen (over 350 meshes per inch) set inside the nozzle which acted as both as a gas-liquid mixing filter and a gas flow damper. The liquid then broke up into small droplets by passing through the grid with low velocity. The performance of the grid nebuliser was compared with that of a number of commercially available nebulisers. The primary aerosols generated were finer and their velocities lower than those obtained with the other nebuliaers, resulting in high transport efficiency and sensitivity improvements for ICP-OES. The nebuliser also showed a good tolerance for high total dissolved solid concentrations because no clogging was observed when a saturated NaCl solution was continuously nebulised for 5 hours. The LODs obtained were better than, or similar to those of the commercial nebulisers, as was the plasma stability. Analysis of NMIJ CRM 7531-a brown rice flour resulted in values for Cd, Cu, Fe, Mn and Zn in good agreement with their certified values. The results demonstrated that the novel grid nebuliser is a useful option, especially for high dissolved solids solution analysis.

Makonnen *et al*.23 used an *infrared-heated sample introduction system with a PN* for ICP-OES. The aerosol generated by a Burgener parallel-flow nebuliser was heated to 230 °C using a ceramic IR heater. Under optimum conditions, and compared to PN alone at room temperature, a 6-fold improvement in sensitivity and a 4-7 fold improvement in LOD was obtained for 38 elements. The improvement was found to be more significant for ionic rather than atomic emission lines. Plasma robustness also increased significantly over room temperature PN. In addition, these improvements in analytical performance were observed using a sample introduction rate over 10 times lower than room temperature PN.

*A valve-based droplet direct injection system* was evaluated by Shigeta *et al*.24. In this system, the sample solution was directly injected as a single droplet or a series of droplets into the ICP. The droplet volume could be controlled across a range of droplet sizes and the system could be applied to the direct injection of cells contained in a droplet. The droplet system was optimised and LODs for Mg Na, and Sr were 56.5, 20.3 and 20.6 pg, respectively. A single droplet containing yeast cells was directly introduced into ICP and an emission profile for Na measured with a satisfactory SNR.

**1.1.3 Glow discharge.** *A liquid sampling atmospheric pressure GD microplasma* was evaluated with regard to its spectrochemical robustness, for use as a miniaturised OES source, by Manard *et al*.25 The plasma *Texc*, *Tion* and Mg ion:atom ratios were measured for a range of analytes, including transition metals, easily ionised elements (group I), and elements with low second ionisation potentials (group II). The plasma characteristics were unchanged throughout the introduction of 11 different matrix elements at concentrations of 500 µg mL-1, indicating relative immunity to spectrochemical matrix effects. The lack of appreciable perturbation in excitation/ionisation conditions observed was reflected in the fact that no changes to the intensities of the probe Mg species were observed at matrix loadings of up to 1000 µg mL-1 of Ba. The results indicated that the LS-AP-GD could be used as an OES source for the analysis of diverse aqueous samples without appreciable spectroscopic matrix effects. The authors noted, however, that potential physical matrix effects including vapourisation effects must be evaluated.

The same LS-AP-GD was also assessed as *an ionisation source for elemental MS analysis*.26, 27 Operating parameters, including the sheath/cooling gas flow rate, discharge current, liquid flow rate, and the distance between the plasma and the sampling cone of the mass spectrometer were discussed. The intensity of the atomic ions, levels of spectral background, the signal-to-background ratios, and the atomic-to-oxide/hydroxide adduct ratios were monitored in order to obtain a fundamental understanding of how each parameter affected the performance of the source and also the inter-parametric effects. The results indicate that the discharge current and the liquid sampling flow rates were the key aspects that controlled the spectral composition. LODs were calculated using the SBR-RSDB (signal-to-background ratio/relative standard deviation of the background) approach under optimised conditions. The LODs for test elements Ag, Cs, La, Ni and Pb ranged from 15 to 400 ng mL-1 for 10 µL injections, with absolute mass values from 0.2 to 4 ng. In a third publication, the versatile LS-AP-DG was assessed as *an ionisation source for metal speciation* in a preliminary study using uranyl-ion acetate as the test system.28 Molecular mass spectra could be obtained from the same source by simple modification of the sustaining electrolyte solution. Chemical information on the degree of acetate complexation of uranyl ion (UO22+) was assessed as a function of pH on the spectral abundance of three metallic species. The application of the LS-AP-GD to both atomic mass spectra and structurally significant spectra for organometallic complexes is a unique and potentially powerful combination.

**1.2. Vapour generation**

There have been several developments in *VG using various forms of plasmas*. Li *et al*.29 developed a system whereby a single drop was suspended between a stainless steel tube and a tungsten electrode. A GD was generated upon application of 60 V at 20 kHz, using an ozone generator power supply, resulting in generation of volatile Cd and Zn species which were swept away in an Ar-H2 gas stream for analysis by AFS, ICP-AES or ICP-MS. The authors concluded that the majority of Cd species were either free atoms, whereas Zn was generated as the hydride, and speculated that the mechanism of formation involved reducing species such as H• radicals and electrons arising from dissociation of H2O and H2 by the plasma. They ruled out GD sputtering by observing an analytical signal for Cd in the absence of a flame in AFS. The LODs were 0.2 pg for Cd and 2 pg for Zn, respectively, using a sample size of 20 µL. Efficiency of vapour generation was estimated to be between 80 and 90%, which is much better than conventional CVG. A similar system was investigated by Zhu *et al.,*30 this time using a DBD plasma in the presence of hydrogen, for the determination of Zn by AFS. They obtained an LOD of 0.2 µg L-1 and found that there were no matrix effects provided that any interfering ions were kept below concentrations of between 1 and 10 mg L-1.

Clearly, the aforementioned techniques are ideal for a portable AFS instrument because they do not require the usual array of chemicals for reduction. A more complex use of GD generation was reported by Zheng *et al*.31, who used a similar d.c. GD plasma generation setup to the one described by Li *et al*.29, to generate Hg vapour in a continuous stream. The carrier gas containing the generated Hg was then directed onto the surface of a graphite sheet where it was pre-concentrated for subsequent analysis by LIBS. They achieved an LOD of 0.36 mg L-1using the Hg(I) line at 253.65 nm, which doesn’t seem worth the extra effort.

*Photochemical vapour generation* has attracted a significant amount of interest recently, with a variety of simple organic acids being used to facilitate PVG *via* a free radical mechanism in the presence of UV radiation. Several modifications to the basic setup has been made in order to improve efficiency, usually involving some sort of catalyst or surface reaction. To this end, Gao *et al*.32 investigated the effect of adding a variety of transition metal ions to the PVG reaction with formic, acetic and propionic acids, for the generation of volatile Pb species. They found that Ni2+ and Co2+ caused the greatest enhancement using 5 % formic acid, even in the presence of Cu2+at a concentration of 5 µg g-1. Using MC-ICP-MS, they obtained method LOD of 0.005 ng g−1 in 5% formic acid and 3.0 μg g−1 Ni2+ which were 16-fold lower than the author’s previously reported LODs using HG-AFS (0.08 ng g−1), but comparable to HG-ICP-MS (0.003 ng g−1). Taking this a step further, Jia *et al*.33 used the metal organic framework CAU-1 (i.e. Al4(OH)2(OCH3)4(H2N–BDC)3) to aid in the PVG of SeVI with detection using AFS. They prepared a suspension containing SeVI, HCOOH (10%, v/v) and CAU-1 nanoparticles which was was pumped into a coiled quartz tube (250mmin length and 3.0mmi.d.) wrapped around a UV lamp. An LOD of 0.04 ppb was quoted by the authors, who also speculated on the mechanism of action of the catalyst.

 Another way of improving PVG efficiency is to increase the flux of UV radiation to the reaction cell. Sturgeon34 has reported using a 19 W, 0.72 mL volume UV lamp to provide deep UV radiation at 185 nm. This was coupled with a glass, thin film gas-liquid separator and ICP-TOF-MS for the PVG and detection of methyl bromide. Generation of the volatile bromine species, from bromide and bromate ions in 2 % acetic acid, was enhanced by the presence of 3000 µg mL-1 NH4Cl. The flow rate was 3.3 mL min-1, resulting in a radiation time of 13 s in the flow-through system, with generation efficiency of 95 %. The LOD was 0.14 ng mL-1 using ICP-TOF-MS detection and the method was validated by analysis of several CRMS. One unresolved problem, however, was the unequal generation efficiency of the Br- and BrO3- ions, which was not ameliorated by any of the usual redox approaches prior to the PVG step. In a subsequent paper35 the same set-up was used for PVG of volatile species from SbIII, SbV and trimethyltantimony(V)dibromine. In this case, the generation efficiency of the various Sb species was equivalent when using a mixture of 5% (v/v) formic and 15% acetic acids (v/v) as the reductant, with a method LOD of 0.0006 ng g−1. Interference free determinations were possible using ICP-MS when by the methods of standard additions and ID-MS. An identical design of photorector was used by Duan *et al*.36 for the PVG of Sn in the presence of 0.8% acetic acid, with LOQ of 0.02 µg L-1 using ICP-MS. Research in this area suggests that PVG is a highly efficient method of vapour generation for certain analytes, though matrix effects have yet to be fully evaluated to test the analytical utility of the technique for real samples.

*Catalytic additives* *to enhance CVG* were utilised by Arslan *et al*.37 to enhance the CVG of Cd. They optimised the CVG process to achieve enhancement in Cd signal by 40-fold, with 3% (m/v) NaBH4 and {4% (v/v) HCl + 0.03 M TiIII + 0.16 M KCN}, and 35-fold using 3% (m/v) NaBH4 and {2% (v/v) HNO3 + 0.03 M TiIV + 0.16 M KCN}. Experiments strongly suggested that it was the catalytic effect of the Ti addition, rather than complexation with CN-, that caused the improved CVG reaction, provided that the reagents were mixed prior to mixing the NaBH4 reductant. The LODs were 3.2 ng L−1 and 6.4 ng L−1 for TiIII and TiIV respectively, which were blank limited by the reagents. The matrix elements CoII, CrIII, CuII, FeIII, MnII, NiII and ZnII did not cause any appreciable suppression up to a concentration of 1.0 μg mL−1,andmethod validation by analysis of several fish shellfish samples yielded recoveries between 95 and 105% for DOLT-4, and 91 and 98% for SRM2976.

**1.3 Solids**

**1.3.1 Direct methods**

*1.3.1.1 Glow discharge.* A special JAAS issue was devoted to the second International Glow Discharge Spectroscopy Symposium with invited submissions on the topic.38, 39

A measurement model based on the use of a pin-cell GD-MS *for the assignment of purity of high-purity metals* was described by Sturgeon *et al*.40. By determining the impurity mass fractions of all additional elements present in the sample, including non-metals and gases, a mass balance calculation was carried out. This resulted in a primary method with direct traceability to the SI system of units. The major source of uncertainty in the traceability chain stemmed from the need to adjust the measured quantity values of each impurity element by a relative sensitivity factor derived from *ab initio* calculations. This was then and validated by analysis of CRMs. The authors suggested that the proposed method was sufficiently well understood that a measurement equation could be developed for which all parameters are measured in terms of SI units; that all contributions to uncertainty can be quantitatively evaluated; and that the performance of GD-MS in comparisons of trace elements in complex metal matrices is in conformance with claimed capabilities. The results obtained from a range of instrument calibration scenarios were presented with a view to extending discussion of the approach within the metrological community.

A review on recent work and developments in GD at atmospheric pressure, when used as a source for OES and MS, was provided by Broekaert and Reinsberg41. Diagnostics and analytical features of the DC GDs at atmospheric pressure, with conductive solid electrodes, liquid cathodes and flowing afterglow sources were described. Possibilities for the introduction of analytes in solution, in the gaseous state and direct solid sampling were discussed.

The analytical capabilities of a GD *as a secondary source for excitation/ionisation* of the material provided by LA have been compared to conventional LIBS by de Vega *et al.*42 The analytical advantages offered by LA-GD stem from the ability to independently optimise the sampling and excitation processes, resulting in reduced matrix dependence, greater precision and sensitivity than encountered using LIBS. An ablation chamber that includes two electrodes to generate the GD discharge has been built and evaluated in comparison to LIBS. Improved LODs, calibration linearity and lower matrix effects were recorded with the LA-GD coupled system, compared with LIBS analysis, in the analysis of conducting reference materials, glass and fluorine pellets.

**1.3.2 Indirect methods.**

*1.3.2.1 Laser ablation.* The main analytical problem in solid sample quantitative analyses by LA-ICP-MS is the calibration step. Problems arise from non-stoichiometric effects during vapourisation, transport of ablated aerosols, atomisation, and ionisation in the plasma. These effects, known as *elemental fractionation,* are mainly sample matrix dependent and have resulted in a need for matrix matched samples, preparation of which is difficult and time-consuming. A review by Miliszkiewicz *et al*.43 summarises recent calibration approaches and related standards preparation techniques for the analysis of various solid materials by LA-ICP-MS. The use of reference glasses, solution based standards, synthetic standards based on the main sample matrix component or powdered matrix CRMs, matrix-matched standards based on spiked sample materials, and non-matrix-matched standards, for calibration were discussed. Isotope dilution methods and signal normalisation protocols used in order to improve precision were also considered.

A number of approaches to the study of elemental fractionation in LA have been reported over the time period covered by this review. *Characterisation of the emitted plasma plume using OES* can be used to identify the sources of elemental fractionation in LA. LaHaye *et al*. 44 applied this approach to the fs-LA-ICP-MS analysis of a brass sample. Plume parameters of *Te* and density were estimated and correlated with ICP-MS signal characteristics, to offer insight into how laser ablation plume parameters are related to LA-ICP-MS results. The hydrodynamic expansion features of fs-LA sample introduction plumes were evaluated using shadowgraphy (an optical method that reveals non-uniformities in transparent media) and time-and spectrally-resolved fast-gated photography. Results showed dissimilarities in the expansion features exhibited by Cu(I) and Zn(I). Good correlation was noted between the ICP-MS signal intensities and characteristic parameters of the sample introduction plumes. However, the crater formation during single spot ablation caused significant changes in line emission intensities despite constant estimated temperature and density values.

The source and degree of elemental fractionation in LA-ICP-MS were also investigated by Luo *et al*.45. The ICP-induced fractionation behaviour of 63 elements was studied using a local aerosol extraction strategy with a 193 nm excimer LA system for sampling. The sampling distance between the ablation site and the gas outlet nozzle tip positively correlated with the size of the LA-produced aerosol particles or agglomerates. At a low makeup gas flow rate of 0.6 L min-1 (hot plasma conditions), the increase in the size of aerosol agglomerates or particles, due to the increased sampling distance from 1 mm to 10 mm, did not affect the ionisation efficiency of the sample aerosol in the ICP. In contrast, at a high makeup gas flow rate of 0.9 L min-1, the normalised signal intensities of the elements significantly differed when the sampling distance increased from 1 mm to 10 mm. Results obtained demonstrated that changes in the size of aerosol particles or agglomerates under given conditions did not affect the transport efficiency of aerosol particles but did affect the vapourisation of aerosol particles in the ICP. The mass load effect was more significant in the presence of large amounts of large aerosol particles and agglomerates, which caused reduction in the vapourisation of aerosol particles. Results also show that the sample position in the normal ablation cell affected the size of laser ablation produced aerosol particles or agglomerates. The high velocity of the carrier gas flow rate on the ablation site facilitated the production of small aerosol agglomerates or particles. Conclusions from the work described suggest that hot plasma conditions and high carrier gas flow rate on the ablation site are required to reduce ICP-induced fractionation.

To elucidate the mechanisms of elemental fractionation observed in LA-ICP-MS the relative intensities of 34 elements, normalised against a Ca internal standard, were measured every minute during a 10-min laser ablation of NIST 610 glass standard.46 Temporal changes in the fractionation index (FI) were obtained by dividing the relative intensity at every minute by that of the first minute. The particles generated by laser ablation were collected on a filter every minute, and they were observed using scanning electron microscopy to investigate changes in the upper size range of particles. Large variations among the larger particles were observed using single-site mode and under 1.0 mm defocus conditions. The 34 measured elements were classified into two groups, depending on their observed FI variation. The FI variation was explained by elemental behaviour due to changes in the large size of ablated particles introduced into the ICP.

Sheheen *et al*.47 investigated elemental fractionation and ICP-MS signal response for two different pulse width laser beams originating from the same laser system. Femtosecond and picosecond laser beams at pulse widths of 130 fs and 110 ps, respectively, and a wavelength of 785 nm, were used to ablate NIST 610 synthetic glass and SRM 1107 Naval Brass B at the same spot for 800 to 1000 laser pulses at different repetition rates (5 to 50 Hz). It was found that elemental fractionation was dependent on repetition rate and showed a trend with fs laser ablation opposite to that observed in ps laser ablation for most measured isotopes. ICP-MS signal intensity was higher in fs than ps LA-ICP-MS in both SRMs when ablation was conducted under the same fluence and repetition rate. The differences in signal intensity were partly related to differences in particle size distribution between particles generated by the different laser pulses and the consequent differences in transport and ionisation efficiencies. The main reason for the higher signal intensity resulting from fs laser pulses was related to the larger crater sizes compared to those created during ps laser ablation. Elemental ratios measured were found to change with the number of laser pulses with data points being more scattered in ps than fs laser pulses. Reproducibility of replicate measurements of signal intensities, fractionation and elemental ratios was found to be better for fs-LA-ICP-MS (RSD -3 to 6%) than ps-LA-ICP-MS (RSD -7 to 11%).

*Low-dispersion LA has been combined with ICP-TOF-MS* to provide full-spectrum elemental imaging at high lateral resolution and fast image-acquisition speeds by Gundlach-Graham *et al*.48 The low-dispersion LA cell described was capable of delivering 99% of the total LA signal within 9 ms, and the prototype TOF-MS instrument enabled simultaneous and representative determination of all elemental ions from these fast-transient ablation events. This fast ablated-aerosol transport eliminated the effects of pulse-to-pulse mixing at laser-pulse repetition rates up to 100 Hz. Additionally, by boosting the instantaneous concentration of LA aerosol into the ICP with the use of a low-dispersion ablation cell, signal-to-noise ratios, and thus LODs, were improved for all measured isotopes; the lowest LODs were in the single digit ppm for a single-shot LA signal from a 10-μm diameter laser spot. Significantly, high-sensitivity, multielement and single-shot-resolved detection enabled the use of small LA spot sizes to improve lateral resolution and the development of single-shot quantitative imaging, while also maintaining fast image-acquisition speeds. Simultaneous elemental imaging of major and minor constituents in an Opalinus clay-rock sample at a 1.5 μm laser-spot diameter and quantitative imaging of a multidomain Pallasite meteorite at a 10 μm LA-spot size were demonstrated.

ICP-distance of flight (DOF)-MS is well suited for the analysis of laser-generated aerosols because it offers both high-speed mass analysis and simultaneous multi-elemental detection. Gundlach-Graham *et al*.49 evaluated the analytical performance of an LA-ICP-DOF-MS, equipped with a microchannel plate-based imaging detector, for the measurement of steady-state LA signals, as well as transient signals produced from single LA events. Steady-state detection limits were 1 μg g-1, and absolute single-pulse LA detection limits were 200 fg for uranium; the system was capable of performing time-resolved single-pulse LA analysis. Simultaneous multi-elemental detection resulted in good shot-to-shot reproducibility of 6% RSD, and isotope-ratio precision of 0.3% RSD with a 10 s integration time.

A double-pulse LA sampling system has been proposed for minimally destructive multi-element analysis.50 The performance of a 266 to 213 nm double-pulse scheme was compared with that of a single 266 nm pulse scheme. The initial laser pulse at 266 nm ablated a mica sample and 10 ns later the second pulse, at 213 nm and 64 mJ cm-2, orthogonally intercepted the gas plume to enhance the analyte signal. Emissions from Al, Mg, Na and Si were simultaneously observed. At low 266 nm laser fluence, when only sub-ng of sample mass was removed, the signal enhancement by the 213 nm pulse was especially apparent. The minimum detectable amount of Al was about 24 fmol compared with around 100 times that mass if the sample was analysed using the 266 nm pulse alone. The minimum detectable mass for the other analytes was also reduced by about two orders of magnitude when the second pulse at 213 nm was introduced, thereby resulting in a significant improvement in LODs when using the double-pulse approach.

For LA-ICP-MS imaging experiments - as well as other techniques used for elemental or molecular mapping – it is of vital importance that the measured distribution agrees with the actual distribution. Conventionally, experimental conditions have been chosen so that washout effects and signal carry-over are minimised by scanning the sample surface very slowly. As a result, measurement times become very long and obtaining well resolved images requires acquisition times of several hours up to more than one day. In order to reduce scan times without compromising image quality, Bonta *et al*.51 proposed the use of a metric to compare the measured elemental distribution with their actual distribution based on a sample with visually distinguishable features. The approach allowed quantitative determination of the image quality, enabled comparison of multiple measurement conditions and was used for method optimisation.

A novel procedure, based on the use of a 1030 nm fs LA device operating at a high repetition rate (30 000 Hz) and coupled to a sector field-ICP-MS, was applied to the direct analysis of dried blood spots.52 The technique allowed the complete ablation of a dried blood spot sample in 200 s (for samples of 5 μL). Integration of the complete signal obtained, and the use of Pt as an internal standard (which can be added to the clinical filter paper prior to the blood deposition, allowing effective unsupervised sample collection), permitted obtaining an analytical response that is independent of the particular characteristics of every sample. An analytical method was developed for the direct determination of several elements (Cd, Co, Cu and Pb) in four blood reference materials and three real samples, providing accurate results in all cases, at concentration levels ranging from 0.1 to hundreds of μg L-1. Detection limits of 0.043 (Cd), 0.42 (Co), 0.54 (Cu), and 0.040 (Pb) μg L-1 were achieved, and precision values in the range 3 and 9% RSD. The potential to couple the LA device simultaneously to a multicollector-ICP-MS and a sector field-ICP-M spectrometer by split-flow was also demonstrated, allowing both elemental (Co, Cu, Cd and Pb) and isotopic (Cu isotopic composition) information to be collected from every sample, therefore maximising the information that can be drawn from a single dried blood spot specimen. The authors noted that the drawback to the method at this stage is the internal precision δ65Cu measurements (approx. 1500 ppm), and variation between samples. This clearly needs further investigation before the potentially useful approach can be extended.

*1.2.2.2 Thermal vapourisation.*Resano *et al*.53 provided a tutorial review of the literature devoted to direct sample analysis using HR-GF-CS-AAS in an attempt to provide guidelines on the critical issues in method development. The authors discussed the advantages and limitations of the technique, emphasising the benefits for direct analysis of solid samples, slurries and complex liquid samples. Compared with line source AAS, CS-AAS offers: (i) improved detection and correction for spectral interferences; (ii) the option to adjust the sensitivity to the analyte content; (iii) strategies to minimise matrix effects and calibrate with aqueous standard solutions; and (iv) the possibility to carry out multi-element analysis.

A novel approach to direct solid sample analysis by HR-CS-GF-AAS using thermoplastic starch platforms for the determination of Mo and V was proposed by Colares *et al*.54 The platform was prepared from a mixture of commercial corn starch (28% amylase and 72% amylopectin), with sorbitol as the plasticiser in a 70:30 mass-based ratio. Use of the starch platforms has been shown to increase the lifetime of the graphite tube significantly and result in much less pronounced tailing of the absorbance signals of refractory elements such as Mo and V. This makes it possible to reduce atomisation and cleaning times, compared to the use of a conventional graphite platform. Memory effects were significantly reduced using the starch-based platform, resulting in improved precision. The LOD and characteristic mass were determined to be 25 pg and 7 pg for Mo, and 130 pg and 18 pg for V, respectively. The accuracy was confirmed by successful analysis of a series of CRMs, including bovine liver, beef liver, rice flour and urban dust for Mo, and coal, urban dust, lichen and particulate matter for V.

A novel coupling of TLC to diode laser thermal vapourisation (DL-TV)-ICP-MS was suggested by Bednarik *et al.* 55. The substrate was the cellulose stationary phase on aluminum-backed TLC sheets overprinted with black ink to absorb laser light. The experimental arrangement is relatively low cost, consisting of an 808 nm 1.2 W continuous-wave IR DL attached to a syringe pump serving as the movable stage. Using a glass tubular cell, the entire length of a TLC separation channel was scanned. The 8-cm long lanes were scanned in around 35 s. The TLC-DL-TV-ICP-MS coupling was demonstrated via the separation of four cobalamins (hydroxo-, adenosyl-, cyano-, and methylcobalamin) with LODs of around 2 pg and RSDs of around 15% for each individual species.

**2. Instrumentation, Fundamentals and Chemometrics**

**2.1 Instrumentation**

A field of research which has attracted much attention over the last few years is the development of miniature atom cells for AES and MS. In principle, it is a trivial matter to generate miniature plasmas which are capable of ionising and exciting atoms and molecules. However, there are practical problems which must be overcome in order that they are viable sources for atomic spectroscopy, namely: miniaturisation of the power source; robustness and reproducibility of the plasma; and sample introduction. Ironically, it is often the case that engineered solutions to these problems result in complete instruments which are anything but miniature.

One way of overcoming the ‘sample introduction problem’ is to do away with it entirely, as is the case with ambient desorption-ionisation MS (ADI-MS). In this type of source a microplasma (which can be generated in a variety of ways) is directed at an angle to the sample such that the afterglow interacts with the surface of the sample to cause desorption, then ionisation of the desorbed molecules. Storey *et al*.56 investigated a flowing atmospheric pressure afterglow (FAPA) source contained in a quartz tube (9mm i.d., 12 mm o.d.) sealed around a concentric tungsten pin cathode and capillary anode (stainless steel, 2.5 cm long, 3.3 mm o.d., 1.5 mm i.d.). The discharge was operated in helium at a flow rate of 0.75 L min-1 and a maximum current of 30 mA, with a separate DC potential of 88 V applied to the capillary anode. Whole coffee beans were analysed by being moved around in the afterglow on a translational stage, and the molecular fragment ions generated in this way were detected using TOF-MS. The same group also investigated using the afterglow of a microstrip MIP as an ADI source57 but few results were presented other than to say that the (M+H)+ ion for acetaminophen was observed.

Horvati *et al*.58 overviewed (60 references) the various types of microplasma used for ADI-MS, then reviewed fundamentals of DBD-type sources. They concluded that DBD sources can be operated in either ‘homogeneous’ or ‘filamentary’ modes by increasing the applied voltage above certain threshold value. The two modes had, respectively, *Trot* of 293 K and 500 K, with Penning and charge transfer ionisation processes dominating, respectively. The argument that the authors focus on is ‘what is better for efficient soft ionisation’, however, there is clearly potential for both of them to be developed as a universal ‘tuneable’ ion source for MS. Hence, more papers in the atomic spectrometry literature on this topic may be forthcoming. Yu *et al*.59 also reviewed (50 references) the use of the DBD, but for AES rather than MS. They focussed on the use of various sample introduction methods, including nebulisation, ETA and VG.

An alternative approach to avoiding sample introduction altogether is to generate the plasma inside the sample itself, as is the case with the liquid electrode microplasma (LEP). Kohara *et al*.60 followed up on their previous work by using an hourglass capillary in which to generate the microplasma. The capillary was made of silica, was only 50 µm wide at the narrowest part and the plasma was generated by applying a pulsed DC voltage across two Pt electrodes, at the capillary ends. Samples containing trace metals were introduced using a syringe pump and the resultant atomic emission was relayed to a CCD spectrometer both by fibre optic and lens arrangements. With this set-up they achieved LODs ranging from 1 µg L-1 for Li to 306 µg L-1for V.

The quest for *improved detection limits* is continual and reduction in instrumental noise is one way of doing this. Axner *et al*.61 have developed a technique called noise-immune cavity-enhanced analytical atomic spectrometry (NICE-AAS). The instrument is based on a combination of frequency modulation spectroscopy (FMS) for reduction of noise and cavity enhancement (CE) to maximise interaction between the light and the sample, which is already used in an established technique called NICE-OHMS (optical heterodyne molecular spectroscopy) for detection of molecular compounds in gas phase. The paper described the technique and the underlying theory in some detail which cannot be done justice in a review article, so the interested reader is directed there. However, the authors concluded that, in the absence of spectral interferences or contamination, detection of Hg down to 10 zg cm-3 (25 atoms cm-3) and Na atomised in a GF down to 50 zg mL-1 in a 10 µL liquid sample (15 atoms) should theoretically be possible. The authors conceded that there were some technical considerations, such as the selection of appropriate lasers to cover possible transitions in the visible and UV, and that the relatively large bandwidths of absorption profiles at atmospheric pressure require RF components and detectors with bandwidths in the GHz range. However, they also point out that there are solutions available.

 *Improved resolution* also falls into the category of a never ending quest. Dennis *et al*.62 investigated the performance of a zoom-TOF-MS instrument, based on a combination of constant momentum acceleration (CMA) and constant energy acceleration (CEA)-TOF-MS. Higher resolution for a target m/z range was achieved by adjusting the acceleration, reflectron and ion optics conditions in a TOF-MS instrument with orthogonal-acceleration geometry, a total field-free distance of 43 cm, and a DC-GD ionisation source. An improvement in resolution of 1.6 times compared to CEA-TOF-MS was achieved (maximum FWHM resolution of 2550 compared with 1610 CEA) without degradation in S/N ratio.

**2.2 Fundamentals**

**2.2.1 Fundamental constants**

Fundamental data is constantly being updated and, as usual, a smattering of papers in the astrophysics field, which might be of interest to atomic spectroscopists, are worth mentioning for reference purposes. Radiative lifetimes are generally measured using LIF to derive oscillator strengths and transition probabilities. Hartog *et al*.63 determined radiative lifetimes of 72 odd-parity levels of La(I), ranging in energy from 15031 to 32140 cm−1, and transition probabilities of 315 atomic lines. In a separate paper, the same group reported64 the radiative lifetimes of 31 even-parity levels of Fe(I), ranging from 45061 to 56842 cm-1, and oscillator strengths for 203 atomic lines. Both studies were performed using LIF on a slow atomic beam. Shang *et al*.65 reported radiative lifetimes for 32 excited levels of Mn(I) (45,754.27 to 54,950.81 cm-1) and for 17 excited levels of Ni (I) (28,578.018 to 50,851.199 cm-1), using time-resolved LIF in a laser-induced plasma, some for the first time.

An ongoing effort by the international scientific community has been *the accurate measurement of* *Avogadro’s constant* using pure crystals of silicon – the purpose of which is to redefine the mole and kilogram. The kilogram remains the only base unit defined by a physical artefact, a 90% Pt – 10% Ir alloy cylinder stored at the BIPM near Paris, from which many other SI units are derived. If the mass were to change so would all these units, hence the requirement for redefinition based on an exact value of a fundamental constant. The method adopted has been to synthesise two 1 kg single-crystal Si spheres, designated S5 and S8, from isotopically enriched Si (0.999 96 28Si). By determining the mass, volume, lattice parameter of the unit cell and the molar mass of each sphere, the Avogadro constant NA can be determined. In practice, the absolute isotopic composition of the Si is measured to derive the amount-of-substance fractions which are multiplied by the well-known relative atomic masses of 28Si, 29Si and 30Si respectively. Vocke *et al*.66 determined the absolute molar mass of a 28Si enriched crystal produced by the International Avogadro Coordination (AVO28). They used TMAH to dissolve two 200 mg pairs of AVO28 samples (which was a departure from the usual method of NaOH dissolution) and MC-ICP-MS to measure the Si isotope ratios at high resolution. In this case a narrower slit (16 µm versus 25 µm) resolved 29Si from 28Si1H , a between-sample cleaning regime was used and two sets of mass bias correction solutions were also analysed. Using this data they derived a value for the Avogadro constant (NA = 6.022 140 76(19)×1023 mol−1) and the Planck constant (h = 6.626 070 17(21) × 10−34 J s). They also detected a small variability in the Si isotopic composition of the material, but not so large as to have a significant effect on the overall uncertainty.

**2.2.2 Diagnostics**

*2.2.2.1 Plasmas. Diagnostic studies of ion generation and sampling in ICP-MS* have yielded some interesting insights over the last couple of review periods, in particular the distribution of analyte and interfering species in the ion beam. Continuing in this vein, Moses *et al*.67 used LIF to study the spatial distribution of Ba(II), Ca(II) and Sc(II) fluorescence in a 10 mm long volume, from the end of the torch to less than 0.1mm in front of the sampling cone. They did this for ICP-MS with both LA and solution nebulisation (SN). High resolution images were thus obtained as a function of the carrier gas flow rate, with and without the addition of helium. Aerosols produced by LA resulted in ions formed further upstream in the plasma, with a broader axial distribution and narrower radial distribution, compared to SN, presumably reflecting the respective effects of larger particle size with LA and aerosol desolvation with SN. The addition of He to the nebuliser gas flow led to ionisation further upstream, possibly explained by fewer large particles transported to the ICP, and increased gas-kinetic temperature. In a complementary paper, Kivel *et al*.68 reported on an *in situ* study of the radial isotopic composition of the ion beam extracted from an HR-ICP-MS instrument. They achieved this by incorporating an aperture plate, variable between 0.5-6.0 mm diameter, at the base of the extraction lens. Using this set-up they observed *radial dependence of the isotopic composition for Cd and Pb*, but not B, with a trend towards smaller beam diameters for higher masses. They also found that the beam width at the extraction lens aperture was almost identical to the aperture diameter in the standard instrument, thus concluding that space-charge effects and energy-selective ion transmission are of minor importance for mass discrimination once the ion beam is formed.

 Further back in the ion sampling process, Luo *et al*.45 studied elemental fractionation in a LA-ICP-MS ablation cell by varying the distance between the ablation spot of a 193 nm excimer laser and the gas outlet. The point of extraction was through a 0.6 mm i.d. outlet which was directly in line-of-sight with the 2 mm i.d. gas inlet, with constant He carrier gas flow, of 0.65 L min-1, plus variable make-up gas flow. They found that larger aerosol particles, formed in the low gas-velocity zone of the ablation cell away from the inlet-outlet axis, were not completely vapourised in the ICP. This resulted in depletion of refractory elements and an increase in mass-induced matrix effects.

*Excitation mechanisms in plasmas* have long been a favourite topic for study. Following on from their previous work, Weiss *et al*.69 published a useful review of the *application of transition rate (TR) diagrams* to analytical GD-AES. Such diagrams are useful when considering radiative de-excitation processes in non-dense plasmas such as the GD. A TR diagram consists of plots of radiative population and depopulation rates as a function of energy level relative to the ground state. If the lifetime of the upper state of an emission line is limited by radiative decay, then the rate of collisional excitation will be equal to the difference between its rates of radiative excitation and de-excitation. In order to properly construct a TR diagram it is necessary to examine as wide a wavelength range as possible in order to: capture the important emission lines, e.g. in the vacuum UV; resolve all analytical lines of interest; and correct for wavelength specific variation in intensities. In the paper, TR diagrams for Cu(II), Mn(II) and Fe(II) in argon and neon discharges were reviewed and compared. A major conclusion was that asymmetric charge transfer (ACT) reactions, between neutral atoms and ions of the discharge gas, were found to dominate the excitation of ionic spectra in the GD, at least for the elements studied. The TR approach revealed that the ionic emission spectrum resulted from a complex interaction of major ionisation mechanisms. As a consequence the authors warn of the dangers of studying LTE conditions using a limited set of lines, and of the same element under different excitation conditions. The same group has reported separately on the application of this technique for the study of excitation of Cu and Fe lines in argon and neon GDs.70, 71

An alternative method for the determination of *ne* has been proposed by Yubero *et al*.72 using the difference in width of the Hα and Hβ Balmer lines. The method does not require knowledge of the Tgas or the Van der Waals broadening of the line by assuming that the Stark profiles can be approximated to a Lorentz function. Measurement of *ne* in an atmospheric argon MIP yielded values between 1.4 x 1014 and 3.5 x 1014 cm-3.

*Multiple dimensional modelling* has been a favourite topic of research over the years because the radial and axial inhomogeneity of many analytical plasmas requires more than simple line-of-sight optical probing. Nagulin *et al*.73 developed a four-dimensional model (spatial plus time) of an argon ICP torch using computational fluid dynamics software. The model took into account the nonstationary nature of the plasma and the physical processes taking place in it. Significantly, they confirmed the veracity of the model with empirical evidence obtained using Schlieren spectroscopy and smoke visualisation. Taken together, the model and empirical evidence revealed a number of effects which probably resulted from peculiarities of the gas flow - such as reverse gas flow, the formation of separated plasmoids, plasma pulsation and rotation. The images in the paper reveal an inhomogeneous and turbulent system which is a nice visual representation of many of the inconsistencies observed by analytical spectroscopists over the years.

*Ambient desorption ionisation (ADI) sources* have increased in popularity over the last five years. Although not strictly sources used for atomic spectroscopy they share many of the same characteristics, and applications are finding their way into the literature. Reininger *et al*.74 compared the number densities of He 2s 3S1 metastable species in a high frequency DBD, a low temperature plasma (LTP) and two atmospheric pressure, AC and DC, GDs. Laser AAS was performed on the He 2s 3S1–2p 3P0, 2s 3S1–2p 3P1, and 2s 3S1–2p 3P2 transitions at 1082.9091140 nm, 1083.0250105 nm, and 1083.0339773 nm respectively. Number densities of these species were found to be 1.39 × 1012 cm−3 and 0.011 × 1012 cm−3 in the plasma plumes downstream of their capillary exits, for the DBD and the LTP respectively. In the two GDs studied, densities of 0.58 × 1012 cm−3 and 0.97 × 1012 cm−3 were measured in the interelectrode regions of the AC and DC GDs, respectively. The authors pointed out that the levels of He metastable species measured were similar to the levels of impurities found in high purity helium gas used for this type of application. Hence, impurities in the gas rather than differences in atmospheric conditions are likely to be the reason why variability is observed between ADI sources used in different labs.

If confidence in your LODs is important to you, then a quick read of the paper by Wysoczanski and Voigtman75 is in order. They emphasise that ‘obtaining unbiased detection limits is not abstruse and need not be mathematically complicated’ but then go on to make it seem quite complicated indeed.

*2.2.2.2 Graphite furnaces***.** A number of models describing *convective and diffusive vapour transport* have been combined to calculate sensitivities (characteristic mass) for a range of analytes in GF-AAS.76 The developed model encompassed the influence of forced convection (from the internal gas mini-flow) combined with the concentration diffusion of the analyte atoms on the residence time in a standard THFA. Several relationships for the diffusional and convectional residence times were studied and compared, including factors that accounted for the effects of the sample/platform dimension and the dosing hole. The model approaches were applied to calculations of characteristic masses of Ag, As, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, V and Zn. Characteristic masses were also determined experimentally using a THFA operated either under stopped, or mini-flow (50 cm3 min-1) of the internal sheath gas during atomisation. The theoretical and experimental ratios of characteristic mass for mini-flow:stop-flow conditions were found to be similar for each analyte. Fairly good agreement was also found between calculated and experimental values, indicating the potential of the approach for evaluating the performance of a given GF-AAS instrument.

Sapphire is presented as a high temperature and corrosion resistant atomiser material for AAS. Musil *et al*.77 studied the atomisation and *in situ* collection of volatile Ag species using a sapphire atomiser. A modular atomiser design was employed which allowed measurements in two modes: (i) on-line atomisation and (ii) *in situ* collection (directly in the optical tube) by using excess oxygen over hydrogen in the carrier gas during the trapping step and *vice versa* in the volatilisation step. Compared with quartz atomisers, the sapphire tube atomiser provided a significantly increased lifetime as well as improved collection repeatability. *In situ* collection of Ag in the sapphire tube was greater than 90% and the LODs in the on-line atomisation and *in situ* collection modes, respectively, were 1.2 ng mL-1 and 0.15 ng mL-1. A sapphire atomiser has been suggested78 for the in-atomiser preconcentration of volatile Au species because results from another study suggest that this is not possible with a quartz version.

**2.2.3 Interferences**

*Elimination of spectroscopic interferences in Q-ICP-MS using a collision/reaction cell (CRC)* is now commonplace. Instruments generally come equipped with an extra quadrupole-, hexapole- or octopole-containing cell that can be pressurised with a reactive gas. Interference removal is effected by either selective reaction of the reactive gas (e.g. H2, O2, NH3) with the analyte and/or interfering ion(s), or by collisions of the ions with a non-reactive gas (e.g., He). Both of these processes can be combined with kinetic energy discrimination (KED) to filter interfering ions. More recently, ICP-MS instruments have come equipped with a triple quadrupole, so-called ICP-MS/MS. In this arrangement a third quadrupole is used to isolate ions of a specific *m/z* prior to introduction into the CRC, so that reactions can be more tightly controlled. A useful tutorial review (55 references) by Balcaen *et al*.79 describes these options, their mode of operation, types of reaction gas and mechanisms, and applications. The review includes a useful table which collates the key research papers cross-indexed with analyte, reaction gas and application. A more theoretical review (25 references) by Yamada80 focussed specifically on KED. The review goes into some detail based on a hard sphere collision model, and describes how ions are transmitted (or not) based on their ability to surmount the energy barrier downstream of the collision cell. One particularly useful aspect of the review is that it is largely uses theory from gas kinetics which will be familiar to the average undergraduate chemistry student, so that even this reviewer could understand it!

In order to make an informed choice about the appropriate reaction gas for elimination of an interference it is useful to know the rate constants for a range of potential reactions. Gray and Olesik81 studied reactions of neutral gases with Ar+ and Ar2+ in a collision/reaction in order to elucidate how the decrease in ICP-MS ion signals observed is correlated to kinetic rate constants of ion-molecule reactions. They calculated the rate of effusion of the gas from the reaction cell in order to estimate the neutral gas pressure inside the cell and measured ion signals at different gas pressures. This allowed them to use ICP-MS and first order kinetics to estimate the rate constants for a number of reactions for which data was only previously obtainable using selected ion flow tube (SIFT) MS. In this way, kinetic rate constants were determined for reactions between Ar+ and Ar2+, and CH3F reaction gas, as 9.59 × 10−10 and 1.03 × 10−9 cm3 molecule−1 s−1, respectively. In another paper82 on the same topic the authors studied the effectiveness of thirteen collision/reaction gases for reducing interferences caused by ArAr+,Ar2H+, Ar2H2+, SeH+, BrH+ and ArCl+ on Se+ isotopes. They concluded that N2, CO and Ar reacted rapidly with ArAr+, ArArH+, ArCl+ and BrH+, but not with Se+. Experiments using CH4 and CD4 found that H-atom transfer from CH4 to Se+ resulted in the formation of SeH+. Other reaction gases such as NH3, N2O, O2, CH3F and C2H6 reacted variably with Se+ to form Se-containing reaction product ions; Ne did not react with ArCl+; and Xe and SF6 caused large decreases in the Se+ signals due to scattering losses.

*Non-spectroscopic interferences in ICP-AES* present a problem for the analysis of any sample with significant matrix content. Many different approaches have been used to circumvent them, the simplest of which is dilution. In order to expedite this, Cheung *et al*.83 developed a gradient dilution approach using a HPLC pump prior to the nebuliser to perform on-line mixing of the sample solution and diluent. During the linear dilution process signals from two emission lines were ratioed. A ratio which remained constant with dilution indicated the absence of a matrix interference and the point on the dilution profile where the ratio stabilised indicated the optimal dilution factor to correct the interference. This method was used to identify and overcome *matrix interferences caused by organic solvents* such as xylene, which is typically used as a diluent for wear oils and other types of organic samples. Both plasma-based and sample introduction matrix effects were investigated by studying 400 ppm K in pure xylene and xylene with 10% toluene, respectively. These solution were subject to gradient dilution while monitoring Zn(I):Cu(I) and Mg(II):Mg(I) line ratios. The effect of added K was clearly identified but the effect of toluene was too small to be clearly flagged. In a follow-up paper84 the same authors took their procedure a step further by combining the gradient dilution approach with previous research by the same group into spatial emission profiles (as discussed in ASU Review J. Anal. At. Spectrom., 2014, 29, 773–794 ) which were used to identify matrix interferences in end-on ICP-AES. While successful, the authors acknowledged that this approach is time consuming, with each gradient dilution taking 30 minutes, and the dilution factor of 1:100 is limited by the pump. Nevertheless, the approach could one day result in a fully automated, ‘intelligent’ system for the analysis of complex samples.

**2.3 Chemometrics**

There has been a paucity of novel developments in chemometrics over the last few years, and this year is no exception. However, given *the importance of instrumental calibration* to the final result, it is worth highlighting several papers dedicated to this topic. Badocco *et al*.85 used a statistical model to identify the major factors contributing to the variance in the determination of metals in drinking water using ICP-MS. Using a factorial approach, they identified that the main contributions to variance were instrumental errors and operating conditions. The former error was typically random, and the latter systematic at each concentration level but random among concentration levels. The conclusion resulting from this was that a two-component variance regression should be used to keep these two components separated. In a further paper,86 the authors applied this approach to the determination of LOD and found that the two-component variance regression resulted in LODs that were larger than those obtained using a one-component variance regression. The importance of calibration was also highlighted in a report by Clough *et al.*87, who produced an uncertainty budget for FI-ICP-MS analysis of metals in seawater. They found that the major contributors to uncertainty were the precision of the peak area measurement and the uncertainty associated with the slope of the calibration curve. While these types of study may seem unnecessarily pedantic they are important in the context of obtaining comparable and traceable data.

In a more practical development, Jones *et al*.88 reported on a ‘standard dilution analysis approach’ which utilised a single standard and an internal standard diluted with the sample. When applied to ICP-AES, the method involved gradual dilution of a solution containing 50% sample and 50% standard with a second solution containing 50% sample and 50% blank. This effectively dynamically mimics a standard additions method. A major advantage is that it simultaneously corrects for matrix effects and for fluctuations in signal. The technique shares some similarities with a method developed some years ago to simplify the calculation of uncertainty budgets (S. Merson and P. Evans, J. Anal. At. Spectrom., 2003, 18(4), 372).

1. **Laser-based atomic spectrometry**

Key fundamental studies and instrumental developments (published in 2015) in laser-based atomic spectrometry are highlighted in this section. Progress in this area during the previous years can be followed here1. Atomic spectrometry techniques where the laser is used as either an intense energy source or a source of precise wavelength (e.g. LIBS and LIF) are considered. However, studies related to LA-ICP-MS/AES, and to the use of lasers for fundamental studies of the properties of atoms or for thin film deposition are not reviewed.

**3.1 Laser induced breakdown spectroscopy (LIBS)**

LIBS is highlighted as one of the most important widespread 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 it does not cover detailed applications. Further information can be found in a critical review of recent progress in analytical LIBS, which includes instrumental progress, trends in data evaluation, and prominent applications recently reported by Galbács89.

**3.1.1 Fundamental studies.** During the review period several reports of *methods to measure and predict laser-induced plasma dynamics* were published. For instance, determination of temporal variations in temperature and electron density in laser-induced plasmas, due to the presence of multi-element aerosol particles, was investigated by Asgill *et al*.90. Changes in the temperature profile of particle-derived analyte species, mainly observed within the first 20–40 μs of plasma lifetime, confirmed the effect of local perturbation of plasma properties. A strong equilibrium was found to exist between the gaseous species. The authors claimed that within a laser-induced plasma there are finite rates of heat and mass transfer, which significantly contribute to the observed matrix effects in LIBS analysis, and which are contrary to the assumption of rapid dissociation and diffusion processes.

Morel *et al*. 91 developed a spherical layer plasma model to investigate the dynamics of a femtosecond/picosecond laser-induced aluminum plasma in a nitrogen background gas. They used, an upgraded collisional–radiative model (CoRaM-Al), involving 250 levels of Al, Al+ and Al2+, implemented in spherical computational fluid dynamics code to predict the dynamics from plasma instigation to extinction. The model was applied to a test case (Al surface ablated by using a 30 ps, 10 mJ Nd:YAG laser pulse at 532 nm.) A strong expansion phase, where the plasma strongly lost energy through radiative recombination, was initially measured. After several tens of ns a shock layer was found to compress the Al plasma, increasing its temperature to values close to 9000 K. Subsequent relaxation took place accompanied by slowly decreasing temperature. In this case, plasma lifetime was calculated to be about 4 × 10−5 s. The model will be further improved by considering traces of light elements within the sample (e.g. determination of deuterium and tritium in the plasma facing components of fusion reactors.)

LIBS investigations dealing with molecular emission bands (e.g. analysis of explosives, determination of isotopic ratios by LAMIS, etc.) require theoretical models to calculate their emission spectra or to infer important parameters. For instance, *molecular transitions of selected diatomic molecules*, including AlO, C2, CN and TiO, were accurately computed by Parigger *et al*.92. Their computational procedure could be used to theoretically predict the diatomic spectra, given knowledge of parameters such as the temperature of the diatomic transitions, or to infer information from experimentally measured spectra (using a fitting algorithm). Programs and data files were provided for LIBS investigations dealing with these diatomic molecules. Gaft *et al*.93 studied and interpreted LIBS emission of complex molecules that combine boron, oxygen and alkaline-earth elements. They observed that boron combines with Ca, Mg, and Sr and O to form molecules of boron-bearing minerals (e.g. CaBO2, MgBO2 and SrBO2 type) with strong and characteristic band emission. These molecular bands dominated the plasma emission after a very long delay time (> 30 μs).

Femtosecond LIBS reduces the thermal effects during laser–matter interactions, allowing the formation of a crater whose size is close to the limit of diffraction. Threshold fluence value for plasma formation was determined during femtosecond single-shot laser ablation on different pure metallic samples and alloys, using optical emission spectroscopy, by López-Claros *et al*.94 A correlation was observed between fluence threshold and work function of pure metals, evidencing the importance of the surface electron excitation in the femtosecond laser–matter interaction. Moreover, the same fluence threshold was measured for the different elements in the pure metals and in the alloys, resulting in a matrix independent value. It was postulated that elemental fractionation during the ablation process might occur close to threshold fluence value due to selective ablation of elements with slightly different threshold fluences.

A new method for quantitative elemental analysis by LIBS, based on generalised curves of growth (Cσ graphs), was proposed and successfully tested by Aragón *et al*.95. Cσ graphs played a role similar to that of calibration curves in conventional quantitative LIBS. However, in this case it was not necessary to separately calibrate each element as several elements could be included in the same plot. The method comprised an initial procedure for characterisation plus two alternative procedures for analysis, resulting in relative and absolute concentrations, respectively. A homogeneous double model of the plasma was used to describe line emission from neutral atoms and singly-charged ions employing different parameters, while the equation of radiative transfer was integrated over a single homogeneous region. As the homogeneous double model is only a convenient simplified approximation of the complex distribution of parameters in the plasma, a criterion based on a model limit was used to discard data described wrongly by the model. An improved method for calibration free (CF)-LIBS quantitative analysis, based on the use of an internal reference conjugated with an external standard, was proposed by Dong *et al*.96. Spectral intensities of atom and ion lines were corrected to compensate for self-absorption effects using an iterative, internal reference line (free from self-absorption) procedure. Moreover, an accurate evaluation of the plasma temperature was performed using a matrix-matched standard sample along with a genetic algorithm and an iterative procedure. The modified CF-LIBS method was claimed to show more precise results than classical CF-LIBS for the quantitative analysis of aluminum-bronze alloys. A quantitative LIBS method, based on adaptive selection of analytical lines and a relevance vector machine, was developed by Yang *et al*.97. Candidate analytical lines were automatically selected, based on the built-in geometric features of the spectral data (e.g. FWHM, spectral intensity) in order to overcome the drawback of high dependency on *a priori* knowledge. The developed quantitative method provided a confidence interval of the predicted concentrations which could be related to the degree of noise and uncertainty hidden in the spectral data. This method was applied to the analysis of 23 high-alloy steel samples, and yielded analytical results which were better than those obtained using partial least squares regression, artificial neural networks and standard support vector machine. Zhang *et al*.98 also developed a new software method based on wavelet threshold denoising (WTD), to minimise the noise and increase the SNR in LIBS emission spectra. Entropy analysis was used to select the optimal decomposition level, which is a parameter that strongly influences the effectiveness of WTD. It was claimed that using this method, fluctuations of spectral line intensities could be largely reduced, and higher slopes and improved correlation coefficients of calibration curves could be obtained.

**3.1.2 Instrumentation.** Development of *fibre-based portable LIBS* systems are of great interest for different kind of applications. For instance, a fiber-optics based remote LIBS instrument was designed for the analysis of submerged materials in a real underwater archeological site by Guirado *et al*.99. This LIBS prototype allowed multi-pulse excitation, which increased the laser transmission efficiency to 74%, through a 55-m long optical fiber. As a result, LIBS emission intensity was enhanced by a factor of 15 compared to the value obtained using single-pulse at the same irradiance. It was claimed that this prototype might allow the analysis of a broader range of materials, including marble, ceramics and concrete.

Parker *et al*.100 investigated a 100 m cavity femtosecond Yb fibre oscillator working at 2 MHz for use in LIBS. The ablation threshold of Cu using the Yb fiber oscillator system was measured to be five times lower compared with the amplified Ti:sapphire system. This effect was attributed to the formation of nanostructures on the surface of the sample. Acquisition of femtosecond LIBS spectra was achieved in a new regime of MHz repetition rates combined with laser pulses of ~320 nJ. This device could be further developed into a compact, fiber-based portable LIBS system, taking advantage of the benefits of ultrafast pulses and high repetition rates.

A single-beam-splitting LIBS, where an individual ns laser pulse is split into two sub-pulses using a beam splitter, was developed by Xu *et al*.101 for field applications. Delay between pulses (~ ps) was much shorter than in conventional double pulsed (DP)-LIBS (~ µs). Nevertheless, this set-up was considered advantageous for low-cost field applications while maintaining the main advantages of conventional dual-pulse LIBS. Signal enhancement, compared to single pulse LIBS, was observed at low laser pulse energy and was attributed to effective pulse–plasma energetic coupling and shock front's attenuation. Femtosecond-DP-LIBS, using an individual laser pulse, was also investigated in a collinear geometry by Shen *et al*.102 The authors concluded that signal enhancement was correlated with the increase of the electron temperature.

The analytical capabilities of mid-infrared (2.05 µm) and near-infrared (800nm) femtosecond LIBS were compared for the analysis of copper by Hartig *et al*.103 Experimental analysis and theoretical modeling showed that lower plasma temperature and shorter plasma lifetime, which results in lower continuum emission and less fraction of laser energy absorbed, was obtained using mid-infrared femtosecond LIBS. As a result of this study, it was claimed that mid-infrared femtosecond LIBS improved the SBR by about 50% for Cu(I) emission lines, but decreased the SNR by 40%.

**3.1.3 Novel LIBS approaches.** LIBS shows great analytical potential when operated not only at atmospheric pressure but also at low pressure conditions. For instance, Cho *et al*. 104 investigated LIBS capabilities for future explorations of the Moon and Mars. In particular, the development of an *in-situ* isochron-based K-Ar dating instrument, combining LIBS and QMS, was investigated. Accurate determination of K, which is considered the bottle-neck of K-Ar dating, was required. The K LIBS emission signal at 769.89 nm was measured and normalised using O emission at 777 nm to allow a power-law calibration function for K. The authors concluded, bearing in mind that Ar could be measured with only 15% error using QMS, that the level of precision achieved in age determination will greatly improve Martian geochronology. All LIBS measurements were conducted using an instrument constructed from components of the same type that were carried in previous planetary missions (*e.g.* a compact spectrometer with a moderate wavelength resolution and without a gate delay or intensifier). Kim *et al*.105 investigated the use of magnetic fields to enhance the laser-induced plasma emission at low pressure. A Nd:YAG laser was used for the ablation of metal samples, using different laser energies (e.g. 30 and 140 mJ/pulse), pressure conditions (between 760 and 10 torr), and applied magnetic fields (e.g. between 0.1 and 0.5 T). The application of the external magnetic field at low pressure resulted in the enhancement of the electron density and ablated mass, and in the decrease of the expansion instability responsible for faster electron recombination. Application of a non-uniform magnetic field may provide a deeper understanding of the plasma to enable control for further spectral enhancement.

Hyphenated techniques based on LIBS are employed to improve the analysis of trace elements. For instance, LIBS combined with Solution Cathode Glow Discharge (SCGD) was used to determine trace mercury in an aqueous solution by Zheng *et al*.31. The aqueous solution was converted into mercury vapour using a closed SCGD. Air flow containing this Hg vapour was introduced to a gas-liquid separator for pre-concentration then injected onto a graphite sheet. LIBS analysis was performed on the surface of the graphite sheet where the Hg vapour was adsorbed. The spectral line of Hg(I) at 253.65 nm was selected for the analysis with a resulting LOD of 0.36 mg L-1. Another approach to the analysis of liquid samples was reported by Aguirre *et al*.,106 who used LIBS detection preceded by a single drop microextraction procedure for analyte enrichment. Ammonium pyrrolidinedithiocarbamate chelates were extracted into a small volume of toluene and dried on an aluminium substrate. The LODs for several analytes were improved by a factor of 2.5 compared to direct LIBS.

 Yin *et al.*107 improved the signal stability of LIBS analysis of gaseous samples by using a bowl-shaped confinement to stabilise the core of the LIBS plasma. This confined the plasma energy to a more restricted area. The RSDs for nitrogen and oxygen were ~ 3% and 4%, respectively.

**3.2 Laser-induced fluorescence (LIF).**

Miyabe *et al*.108 employed laser-induced fluorescence imaging spectroscopy to investigate the dynamic behavior of an ablation plume in ambient gas. A plasma plume, produced by a 2nd harmonic Nd:YAG laser, was intersected with a sheet-shaped UV beam from a dye laser. Time-resolved fluorescence images were then acquired with an intensified CCD camera at various delay times. Ablated ground state species were observed to accumulate in a hemispherical layer between the plume and the ambient gas. Ground state atoms in this layer were claimed to be produced through ion–electron recombination and subsequent relaxation. Moreover, the size of the inner cavity, containing a reduced density of ablated species and formed near the center of the plume, increased with decreasing mass of the ambient gas. The knowledge obtained in this study was considered to be of importance for optimising experimental conditions in Laser Ablation Atomic Absorption and LIBS analyses.

**4 Isotope Analysis**

In the past year, advances in instrumental design mean that some features are now must-have options when specifying a mass spectrometer purchase for use in IRMS. One such feature of newer ICP-MS instruments is a high-sensitivity interface with modified sampling and skimming cones. This has increased instrument sensitivity, hence reducing the amount of analyte required for a given level of precision. Another advance is the addition of high-impedance resistors fitted to Faraday detectors. These reduce the baseline noise of the detector, thereby enhancing precision when measuring small ion beams (<1 x 10-12A). A number of studies reviewed here utilise these new current-to-voltage convertors and the results are now translating into significant advances in precision when measuring high-magnitude isotope ratios. However, combining traditional resistors (1011 Ω) with new variants (1012 Ω and 1013 Ω) has required additional calibration to produce concordant isotope ratios.

**4.1 Reviews**

*Nuclear safeguarding* is an expanding field requiring the use of a range of isotope ratio mass spectrometry systems. Boulyga *et al.*109 provided a review of the key techniques and applications. TIMS, MC-ICP-MS and SIMS were each defined as having advantages for U and Pu analysis depending on the vagaries of particular polyatomic and isobaric interferences. One important issue is the current unavailability of a suitable CRM for QA of isotope ratio measurements in uranium particles. The review also defined a technical wish-list for a potential ‘universal detection system’ in a mass spectrometer, including a 16 cup array comprising both Faraday and ion counting detectors, each channel equipped with an energy filter to improve abundance sensitivity.

Gentile *et al.*110 provided a comprehensive review of the use of *stable isotope ratio mass spectrometry in forensic science*. These workers compiled and assessed the use of δ13C, δ15N, δ18O and δ2H to discriminate between the provenances of illicit drugs, explosives and human remains. One issue highlighted is the need for a coordinated international database of the key analytical information. Further improvements in the precision of δ15N were also achieved by Lott *et al.*111, who used a thermal decomposition method with an elemental analyser/ isotope ratio mass spectrometer that improved the recovery of nitrogen from organic and inorganic materials.

*Geochronological analytical methods* involving the U-Th-Pb system were reviewed by Schaltegger *et al.*112. These authors provided a useful comparison of the pros and cons of the three analytical tools used: TIMS, SIMS and LA-ICP-MS. An additional aim was to guide scientists with particular geochronological or geochemical questions towards the most suitable technique. Particularly good examples were presented including: the effects of 230Th and 231Pa on the precision of dating young samples; age and compositional zonation of zircons; and the timescales of crystal fractionation during the evolution of magma bodies.

**4.2 Isotope Dilution Analysis (IDA)**

Feng and Wang113 provided an assessment of in-line mixing devices used to combine laser ablated product with a 207Pb spike, prior to measurement of *Pb concentration by isotope dilution ICP-MS*. Analysis of NIST glasses demonstrated that Pb isotope ratios measured on the combined aerosols from a membrane desolvator and laser ablation were most stable when mixing was completed in a spherical chamber with a sphere-centred exit nozzle. Results for NIST 610 Pb (426 µg g-1) were found to be in good agreement with the certified values. Fernández *et al.*114 used a similar laser-nebuliser combination to measure Pb, Rb and Sr concentrations in NIST 610, 612 and 614 by ID-MS. However, these workers used a *double ID protocol* where the concentration was calculated by combining the analyses of an ablated sample-isotope spike mixture and an ablated certified standard-isotope spike mix. This method benefitted from being able to determine all parameters, other than the mass fraction of the solid standard, during the analytical protocol.

Wang *et al.*115 used ID-ICP-MS to determine Ag, Ba, Bi, Cd, Cu, Cu, In, Mo, Sm, Tl and W in six reference materials and four carbonaceous chondrites. They also determined S, Se and Te and produced accurate results despite the volatility of these elements. This was ascribed to the closed system, pressure bomb dissolution procedure. Khan *et al.*116 described a method for ID-ICP-MS analysis of Zn. This compared analysis both with and without matrix separation and examined the role of doubly-charged Ba ions interfering with the measurement of Zn isotopes.

Instrumental *mass bias caused by matrix differences* was investigated by Pak.117 It was found that the Cd isotope concentration determined by IDA had errors up to 1.5% in the presence of a U matrix. Mass bias during ID-ICP-MS analysis was also the subject of a study by Teran-Baamonde *et al.*118 The authors used a least squares fit of the measured and theoretical ratios of several poly-isotopic systems (Cd, Cr and Nd). Resultant plots for different forms of mass fractionation correction (exponential, linear and power) provided a visual indication of the most suitable correction procedure for the analytical system.

**4.3 Isotope Ratio Analysis (IRA)**

**4.3.1 New developments.** Isotope analysis is driven forward by instrument manufacturers and users striving for ever-higher levels of sensitivity from their mass spectrometers. However, the consequences of metaphorically “turning up the wick” are not always fully considered. In this respect, Albarede *et al.*119 investigated how *increased ion transmission affects mass fractionation* using the latest MC-ICP-MS instrument. The authors documented a reduction in the amount of mass fractionation with increased efficiency of ion transfer, which if extrapolated to 100% transmission, would result in zero fractionation (i.e. β = 0). As they noted, full-transmission instruments may not be available anytime soon, but the effects of reduced mass fractionation on correction systematics need review. It was found that fractionation followed an exponential law and could be expressed as a function of ion transmission.

Doherty120 examined some of the reasons why Pb isotopes corrected using *Tl-spiking can produce anomalous and inaccurate results*. Determinate errors were identified as relating to variable instrument drift, and as a result of proportional errors from horizontal offset effects and differences in response surface curvatures. A sequential correction procedure involving a mass fractionation – instrument drift – proportional error was proposed.

Taylor *et al.*121 provided an assessment of the realistic levels of precision that can be determined by different *mass fractionation correction procedures* used for Pb isotope measurement. Comparisons were made between the conventional TIMS-based sample fractionation = standard fractionation, Tl-spiking, double/triple (poly) spiking and ICP-based sample-standard bracketing. This provided a basis for assessing which method produced an appropriate level of precision for a particular task. In addition, measurements of the Pb isotope ratio standards were compiled and an updated average NIST SRM 981using poly-spike determinations was presented. Future enhancement in the precision of Pb isotope measurement in the form of ultra-high precision was show to be possible by averaging multiple measurements and by utilising high impedance amplifiers. This latter development was examined by Klaver *et al*.122 who used a *1013 Ω-equipped Faraday* to measure the minor 204Pb isotope alongside regular 1011 Ω detectors for the more abundant Pb isotopes on TIMS. Pb loads of 5 ng were run using this amplifier array and compared with 75 ng loads measured using exclusively 1011 Ω. Results indicated that 5 ng samples produced isotope ratios equivalent to the larger loads, with external reproducibility of 20xPb:204Pb ratios around 2 times greater than the 75 ng loads, but still less than +/-0.002 on 206Pb:204Pb.

The use of high impedance resistors for Pb isotope measurement were also considered by Gourgiotis *et al.123* Their study examined the effects of transient signal measurement on 1011 Ω and 1012 Ω resistors. The 1012 Ω variant was found to have a slower response time, which was reflected as a drift in isotope ratios. This drift was corrected successfully by an internal signal synchronisation according to the method of Gourgiotis *et al.124.*  Further application of 1012 Ω resistors on Faraday detectors for *measuring low-levels of Pb by TIMS* was examined by Sarkar *et al.*125. In this study the performance of the high impedance resistors was compared with multiple ion counting detection on the same instrument. It was found that for loads in the range from 10 to 100 pg Pb, 1012 Ω equipped Faradays performed best, while the ion counting was superior at quantities less than 10 pg Pb.

In this atomic spectrometry update in 2014126 we described the ongoing experimentation with high impedance resistors. It is clear from the activity of scientists in this review that direct applications using Faraday collectors with1012 Ω and 1013 Ω based outputs are now filtering through to publication. An example of this was published by Koornneef *et al.127* who examined Sr and Nd isotopes in melt inclusions by TIMS. Normal procedures for melt inclusion isotope analysis use a laser ablation system in conjunction with MC-ICP-MS. However, in this analysis olivine crystals containing the melt inclusions were separated from the volcanic rock matrix and dissolved using standard HF-HNO3 dissolution. The authors assumed that the olivine itself contained undetectable quantities of Nd and Sr, and made no contribution to the analysis; all of the contribution of these elements coming from inclusions within the olivine. Nd isotopes measured from these olivine dissolutions indicated that the precision of the 1013 Ω-based Faradays is sufficient to produce useful geochemical inferences about the evolution of the magmatic system.

*High-precision Sr isotope ratio measurement by MC-ICP-MS* is hindered by isobaric Kr interference on 86Sr. To improve Sr isotope measurements, Konter *et al.*128 provided a novel correction procedure to combine the Kr correction with the mass fractionation correction. This involved equating the relationship between the 84Sr:88Sr and 86Sr:88Sr ratios in respect of the 84Kr and 86Kr interferences. Results indicated a long-term precision of +/-16 x 10-6 for 87Sr:86Sr, providing that standard values are normalised on a daily basis. As this correction method is completed within-run it has the potential to be utilised for LA Sr isotope determination. Isotope measurement of Sr using a more traditional TIMS was assessed as a method for screening natural water samples by Li *et al.*129 This study trialled measurement using two Faraday collectors equipped with 1012 Ω resistors receiving the 86Sr and 87Sr beams and suppressed Rb interference by careful pre-heating of the loaded Re filaments. As samples were run without chemical purification, minimising correction for Rb interference was key. Additionally, the method used Sr loads of 2-4 ng, making the typical precision on the water samples of +/- 28 x 10-6 for 87Sr:86Sr highly commendable.

*Uncertainties in isotopic reference materials* and multi-element tracers was comprehensively evaluated by Mclean *et al.*130 The paper focussed on the traceability of the calibration of a Pb-U isotopic tracer, based on gravimetrically determined Pb and U reference materials. Overall improvement of the assumed tracer calibration uncertainty was reduced from 1000 ppm to 300 ppm. The importance of this study relates to the need for valid uncertainty propagation in U-Pb geochronology: a technique underpinning the calibration of geologic time. Zhao *et al.*131 examined the UPb ages of zircons from the high-U Douzhashan Granite in China. Zircons in this granite also have appropriately high U content, and this provided the subject of an interesting analytical comparison. The authors measured the zircon U-Pb age by both SHRIMP and LA-ICP-MS and found that the SHRIMP produced discordant 206Pb/238U ages when the zircon spot contained >10,000 ppm U. In contrast, the LA-ICP-MS analysis resulted in a coherent age across the spectrum of U concentrations. The discordance of the SHRIMP data was ascribed to a high-U matrix effect.

Improvement of *in-situ Nd isotope determinations by LA-MC-ICP-MS* was the focus of a study by Xu *et al.*132 This work utilised a ‘Jet’ sample cone and ‘X’ skimmer cone at the plasma interface and compared these to a standard cone set-up. Nitrogen addition to the central gas flow was found to be critical in terms of sensitivity but perhaps more importantly in terms of the stability and conformity of the mass bias. Results for a number of glass standards and mineral standards such as monazite, titanite and apatite were presented and gave values and reproducibility for 143Nd:144Nd that approached measurements made using solution MC-ICP-MS.

The absolute isotopic composition of Yb has been re-evaluated by Wang *et al.*133 using MC-ICP-MS. This was achieved using synthetic mixtures of four key isotopes of Yb with >99.99% purity and calibrated using rigorous metrological validation. The result was a CRM that can be used as a δYb = 0 reference material.

**4.3.2 Geological studies.** Chang *et al.*134 have advanced *Sr isotope analysis of basaltic glass by laser ablation* MC-ICP-MS. Combined use of 1012 Ω resistors on Faraday detectors and careful calibration of Kr baselines and Rb isobaric interference enabled 2 s.d. measurement precision of +/- 0.0002 on 87Sr:86Sr using ~100µm diameter ablation pits. This should considerably improve the potential for isotopic investigations of crystal-bound melt inclusions.

Evans *et al.*135 developed an *in situ* technique for (U-Th-Sm):He and U:Pb double dating of zircon grains. This utilised a 193 nm ArF excimer laser system combined with Q-ICP-MS and He mass spectrometry. An initial pit was ablated to extract He and its volume calculated. A second smaller pit was ablated within the first, and the U-Th-Sm and isotopics determined on the material ablated.

Kimura *et al.*136 coupled a 266/200 femtosecond LA system to MC-ICP-MS to measure *U-Pb ages of zircon and monazite crystals*. The results indicated a ~0.5% age error, which was attributed to the use of high-gain amplifiers equipped with 1012 Ω resistors on Faraday detectors for the 207Pb:206Pb and 206Pb:238U. This method achieved an age precision similar to that of SHRIMP, but still required an analytical spot size of around ten times larger. Laser ablation MC-ICP-MS was also applied to *in situ* *boron isotope ratio measurement* by Lin *et al.*137 This study used a ‘Jet’ sample cone and ‘X’ skimmer cone combination with between 2 and 4 mL min-1 of N2 addition to the carrier gas. Reference minerals and standard glasses were analysed and produced a factor between 2 and10 improvement in the precision of 11B:10B with δ 11B +/- 1 at 2 s.d.

Isotopic analysis of most *metals in seawater* can be challenging, but an examination of Pb isotopes in a water column depth-profile by Paul138 used a double spike procedure to ensure accurate measurement. This involved the extraction of around 10 ng of Pb from ~2 L of seawater samples and resulted in reproducibility of ~1000 ppm on 206Pb:204Pb using 2 ng Pb.

*Chlorine isotope measurements by MC-ICP-MS* have potential difficulties in the form of interference corrections. Toyama *et al.*139 addressed this by measuring Cl isotopes using LA of either halite or AgCl precipitate. The benefit of, LA sample introduction is that it significantly reduces levels of correction required by interference from 36Ar1H+. Results of rock standards had an internal precision of +/- ~0.15 δ 37Cl and external 2 s.d. of better than +/- 0.4 δ 37Cl. This discriminated clearly between the two Japanese volcanic rock standards JB-1a and JB-3, producing δ 37Cl values of -0.97 and +0.25, respectively.

**4.3.3 Stable isotope tracer studies.** An *et al.*140 refined a method for *purification of low-Mg samples* prior to Mg isotope ratio determination, which involved adding a trace amount of HF to the eluent. Results demonstrated that external precision was better than +/- 0.05 ppt for δ 26Mg.

In order to improve the potential for the use of *tungsten as a stable isotope tracer* of geological processes Breton and Quitté141 developed a new separation procedure which achieved quantitative W recovery. W isotopes were measured using MC-ICP-MS and an internal mass fractionation normalisation from 178Hf:179Hf. Results of the analysis of geological rock standards indicated that differences of ~0.5 δ 183W184W between the peridotite rock standard PCC-1 and the andesite rock standard AGV-1 could be clearly resolved given the reproducibility of +/-0.08 δ183W184W.

Okabayashi *et al.*142 developed a *micro-electrothermal vapourisation device* to improve the precision of isotope ratio measurements on ng quantities of W. This method employed a heated Re-filament held in an Ar–He gas flow coupled with an MC-ICP-MS instrument. It was concluded from this development that the electrothermal vapourisation induced a Rayleigh law mass fractionation rather than the exponential law associated with the solution nebuliation technique. Using this form of correction it was apparent that there is the potential for precise, low level W measurement.

*Stable Nickel isotope measurement* was considered by Chernonozhkin *et al.*143 who developed a three-stage separation procedure that minimised on-column mass fractionation and spectral interferences. Results indicated that δ XXNi:58Ni ratios could be reproduced to better than 0.02 per amu.

A practical method for *Mo isotope analysis by MC-ICP-MS* using a 97Mo–100Mo double spike was presented by Skierszkan *et al.*144 This study focussed on the implementation of the technique for the measurement of environmental samples and resulted in long-term reproducibility of +/- 0.05‰ for δ 98Mo:95Mo on seawater and rock standards. Acceptable tolerance on this level of double spike precision was achieved when spike:sample molar ratios were between 0.4 and 0.8.

A number of studies examined the *measurement of lithium isotopes* by methods other than MC-ICP-MS. Yin *et al.*145, 146 used phase-conjugate degenerate four-wave mixing to selectively analyse 6Li and 7Li resulting in precision of <+/- 0.03% on a Li standard with LOD of approximately 10 ng. As a low-cost alternative to MC-ICP-MS, Zolfonoun.147 measured Li isotopes by ICP-OES, which demonstrated its potential as a measurement protocol in the nuclear industry. This is possible because the isotopic emission lines of light elements can be resolved relatively easily with a standard spectrometer.

**4.3.4 Isotopic fingerprinting.** Analysis of *microscopic nuclear materials* may benefit from a study by Duffin *et al.*148 who generated a revised set of uranium isotope ratios for NIST glass reference materials (NIST 610, 612, 614 and 616). Data from solution mass spectrometry was compared with LA-MC-ICP-MS and indicated that small-scale isotopic heterogeneity existed within the individual glass standards. This was proposed to be related to the mixture of natural and depleted uranium used in the manufacture of the standards. Low concentrations of U were also measured for isotope ratios by Quemet *et al.*149 using TIMS. This study compared combinations of a secondary electron multiplier (EM), multiple continuous dynode electron multipliers and Faraday cups in the detection array. Peak-jump EM produced the most reproducible 238U:235U ratios for sample loads of between 50 and 250 ng, and multiple Faraday cup measurements were better for greater U loads.

*Biogenic standards* were the subject of a study by Durisova *et al.*150 Nine biogenic NIST CRMs were measured for Pb isotopes using three ICP-based mass spectrometers. Data indicated that chromatographic separation to remove the biological matrix did not benefit the accuracy of the Pb isotope ratios, but did improve the internal measurement precision.

Gueguen *et al.*151 investigated the potential for liquid chromatography sample introduction to MC-ICP-MS to facilitate rapid measurement of *Nd isotope ratio measurement*. This is important in the validation codes associated with irradiated nuclear fuel samples. Their approach utilised an on-line or “intra injection” sample-standard bracketing to accommodate the mass fractionation, and assessed the effects of Faraday collector time-lag in response to signal drift.

**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.

|  |  |
| --- | --- |
| 3D | three dimensional |
| ADI | ambient desorption ionisation |
| AA | atomic absorption |
| AAS | atomic absorption spectrometry |
| AES | atomic emission spectrometry |
| AF | atomic fluorescence |
| AFS | atomic fluorescence spectrometry |
| BCR | community bureau of reference |
| CCD | charge coupled detector |
| CCP | capacitively coupled plasma |
| CRM | certified reference material |
| CRS | cavity ringdown spectroscopy |
| CS | continuum source |
| CV | cold vapour |
| CVG | chemical vapour generation |
| DBD | dielectric barrier discharge |
| DC | direct current |
| DDW | distilled deionised water |
| DL | diode laser |
| DLTV | diode laser thermal vapourisation |
| DOTA | 1,4,7,10-tetraazacyclo-dodecane N,N′,N″,N′′′-tetra acetic acid |
| ES-MS | electrospray mass spectrometry |
| ETV | electrothermal vapourisation |
| ETV-AAS | electrothermal vapourisation atomic absorption spectrometry |
| ETV-ICP-MS | electrothermal vapourisation inductively coupled plasma mass spectrometry |
| EVG | electrochemical vapour generation |
| FAPA | flowing atmospheric pressure afterglow |
| FI | flow injection |
| FWHM | full width at half maximum |
| GD | glow discharge |
| GD-AES | glow discharge atomic emission spectrometry |
| GD-MS | glow discharge mass spectrometry |
| GF-AAS | graphite furnace atomic absorption spectrometry |
| HPLC-ICP-MS | high performance liquid chromatography inductively coupled plasma mass spectrometry |
| HG-AFS | hydride generation atomic fluorescence spectrometry |
| HR | high resolution |
| ICP | inductively coupled plasma |
| ICP-AES | inductively coupled plasma atomic emission spectrometry |
| ICP-MS | inductively coupled plasma mass spectrometry |
| ICP-MS/MS | triple quadrupole inductively coupled plasma mass spectrometry |
| ICP-OES | inductively coupled plasma optical emission spectrometry  |
| ICP-QMS | inductively coupled plasma quadrupole mass spectrometry |
| ICP-TOF-MS | inductively coupled plasma time-of-flight mass spectrometry |
| ID | isotope dilution |
| IDA | isotope dilution analysis |
| ID-ICP-MS | isotope dilution inductively coupled plasma mass spectrometry |
| ID-MS | isotope dilution mass spectrometry |
| IL | ionic liquid |
| IRMS | isotope ratio mass spectrometry |
| LA | laser ablation |
| LA-ICP-MS | laser ablation inductively coupled plasma mass spectrometry |
| LA-MC-ICP-MS  | laser ablation multicollector inductively coupled plasma mass spectrometry |
| LAMIS | laser ablation molecular isotopic spectrometry |
| LC | liquid chromatography |
| LIBS | laser induced breakdown spectroscopy |
| LEP | liquid electrode microplasma |
| LIF | laser induced fluorescence |
| LOD | limit of detection |
| LTP | low temperature plasma |
| MALDI | matrix-assisted laser desorption ionisation |
| MC-ICP-MS | multicollector inductively coupled plasma mass spectrometry |
| MIP | microwave induced plasma |
| MNP | magnetic nano-particle |
| NA | Avogadro’s number |
| Nd:YAG | neodymium doped:yttrium aluminum garnet  |
| ne | electron number density |
| NIST | National Institute of Standards and Technology |
| NP | nano-particles |
| od | outer diameter |
| PFA | Perfluoroalkyl |
| PLS | partial least squares |
| PN | pneumatic nebuliser |
| ppb | parts per billion (10-9) |
| ppm | parts per million (10-6) |
| ppq | parts per quadrillion (10-15) |
| ppt | parts per trillion (10-12) |
| PVG | photochemical vapour generation |
| Q | Quadrupole |
| RF | Radiofrequency |
| RSD | relative standard deviation |
| RVM | relevance vector machine |
| SIMS | secondary ion mass spectrometry |
| SBR | signal-to-background ratio |
| SCGD | solution cathode glow discharge |
| SHRIMP | sensitive high mass resolution ion microprobe |
| SNR | signal-to-noise ratio |
| SPME | solid phase microextraction |
| Te | electron temperature |
| Tgas | gas temperature |
| THFA | transversely heated furnace atomiser |
| TIMS | thermal ionization mass spectrometry |
| Tion | ionization temperature |
| TLC | thin layer chromatography |
| TOF | time-of-flight |
| TP-LIF | two photon laser induced fluorescence |
| TV | thermal vapourisation |
| UV | Ultraviolet |
| VG | vapour generation |
| WTD | wavelet threshold denoising |

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