JAAS

Journal of Analytical Atomic Spectrometry
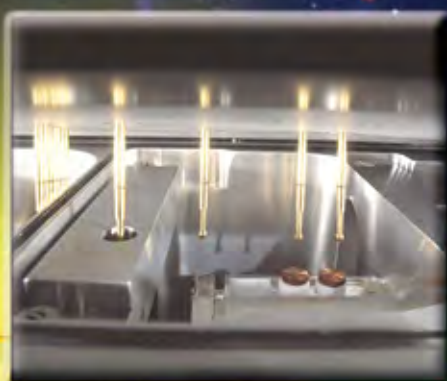
Celebrating
25 years

Atomic Spectrometry Timeline

FES

ICP/MS

ICP/OES

MS

GDS

Metallomics

AAS AFS

XRF

Future

1850 1860 1870 1880 1890 1900 1910 1920 1930 1940 1950 1960 1970 1980 1990 2000 2010 2020

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Atomic Spectrometry Updates:
A 25-year retrospective

EDITORIAL
Hill
JAAS 25th anniversary–Atomic
Spectrometry Updates

Atomic Spectrometry Updates: A 25-year retrospective†

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Members of the Atomic Spectrometry Updates Editorial Board take a look back over 25 years at how the subject of atomic spectrometry has changed, and how the review articles have developed to reflect this.

Introduction

As has been pointed out in the accompanying Editorial, the Atomic Spectrometry Update (ASU) review articles have been an integral part of the Journal of Analytical Atomic Spectrometry (*JAAS*) since the journal first appeared in 1986. In the intervening 25 years, some 150 of these articles have been published, each of which presents a critical review, written by experts, of the immediate past 12 month's (or so, one has to allow a few months for the production time of the articles) worth of critical developments (as evidenced by work reported in the primary literature) in one of the several important areas identified of interest to the readers of *JAAS*—the atomic spectrometry research community. Broadly speaking, these topics were either related to the sample type or to the instrumental technique. The sample type reviews have dealt with environmental materials (minerals, soils, waters, air), biological materials (clinical samples, foods and beverages), and industrial materials (chemicals, metals, ceramics, fuels). The instrumentation reviews have been more varied over the years reflecting the significant developments of the past 25 years. Currently, all techniques except X-ray spectrometry are covered in one ASU (though in the past there have been as many as three separate reviews covering absorption, emission and mass spectrometries). The topic of speciation now merits its own review, with the second ASU bearing this title appearing in 2010.

As may be imagined, the production to a rigorous timetable of six or seven such review articles each year is a considerable undertaking involving a large number of scientists. During the past 25 years, about 100 scientists have contributed, of whom six have co-authored 20 or more reviews. Although 25 years ago, the writers were all based in the UK, this is no longer the case, and about a dozen members of the current writing teams reside outside the UK (in half a dozen different North American and European countries). As several writers have moved institutions during their writing tenure, there are well over 100 different organizations listed as affiliations. In terms of impact, the University of Plymouth is in a league of its own, as the home of about one-third of all authors. Other notable contributions have come from the British Geological Survey, The Health and Safety Executive, The University of Surrey, The Macaulay Land Use Research Institute, and British Nuclear Fuels. A number of industrial organizations

are also prominent on this list including, ICI, Shell, Perkin Elmer, and Oxford Instruments. There is a strong Scottish connection: the contributions of several institutions in Glasgow (the Universities and Royal Infirmary) put that city into silver-medal position (behind Plymouth), and the University of Aberdeen brings a double-digit contribution to add to the contributions from "The Macaulay".

Members of the writing teams were asked to reflect on the developments they have noticed over the past 25 years, rather than the normal one year (a time period over which it is often difficult to discern any significant developments) and these reflections are what follows. The material is arranged so that sample types are dealt with first, followed by instrumentation, followed by speciation. However, as will be apparent, it is developments in instrumental capabilities that are identified as the major themes.

Environmental analysis

The initial ASU on environmental analysis, published in February 1986,[1] consisted of three review topics: air, water and soils/plants and related materials. Significantly, this initial review did not contain a section devoted to the analysis of geological materials. This was rectified to some extent in the second review with a section entitled "minerals and refractories".[2] However, it was not until the fifth ASU review published in 1990 that the relevance of geological materials to environmental analysis was established.[3] From then on, the scope of this Environmental Analysis Update has remained constant throughout all the other changes in ASU. With regard to water analysis, there are striking similarities between the review of February 1986[1] and that of February 2009.[3] From the 1986 review it was reported that "the most significant developments in the analysis of natural water samples over the past year have been primarily in the area of sample pre-treatment, particularly automated preconcentration techniques and automated hydride generation". This has been the main trend for the past 25 years, as detection limits have been forced down and more and more elements are monitored in natural waters.

Environmental materials—sample decomposition

Little has changed in terms of acid mixtures employed and the degree of total decomposition achieved. Sample preparation has always been one of the great challenges, particularly for geo-analysts, mainly because of the highly refractory nature of some

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† Each section of this Perspective has been provided by representatives of the Atomic Spectrometry Updates Topic Groups, and the introduction was authored by Julian Tyson.

mineral phases. High performance closed vessel microwave assisted digestion systems are now the norm in many trace elemental laboratories. It must be noted however that performance of such systems has taken twenty or so years to evolve to the current level of maturity. Further advances are on the way with the next generation of microwave assisted high-pressure autoclave systems, which will offer even superior performance.

Aqua regia leaching of soils remains the standard approach. Here, given that such work is generally carried out in commercial laboratories, sample throughput is a key issue and as such hot-block digestion techniques remain dominant. High sample throughputs remain an issue for microwave digestion systems. Interestingly a new focused microwave system, combining the efficiency of microwave systems with the throughput of hotblock systems, has just been commercially launched.

The emerging dominance of inductively coupled plasma-mass spectrometry (ICP-MS) as the technique of choice meant that fusions were no longer fashionable because the high dissolved solids content of the resulting solution, even after dilution, led to cone blockage. With improved tolerance to high TDS in ICP-MS, fusions procedures are now, once again, in routine use in geochemical laboratories where complete dissolutions are required. Additionally, there has been a number of innovations; modern glassy carbon crucibles contribute much lower levels of contamination than ones historically used made out of nickel or zirconium and the advent of induction based and microwave assisted fusion systems now offer a rapid heating and cooling capability in a flame free environment.

Sample separation and preconcentration

Even now, with the greatly improved sensitivity of ICP-MS, preconcentration procedures are still required for some niche trace element measurements, the classic one in the geochemical arena being fire assay for precious metals. Isotopic determinations by MC-ICP-MS are still heavily dependent on chemical separation procedures to achieve the accuracies required. Solvent extraction, with the ubiquitous MIBK, has given way to ion-exchange as the dominant separation technique, making use of a new generation of ion-exchange resins, particularly those manufactured by Eichrom™. In the air measurement arena, a fertile area of work over the last twenty-five years has been the development of gold trapping systems for the collection and preconcentration of elemental mercury vapour which have now reached a high level of maturity.

For water analysis, given the relative simplicity of the matrix and low concentrations typically found in natural waters, preconcentration techniques have extensively been used to boost method sensitivities. When this review was first written,[1] period 8-hydroxyquinoline was being reported as an attractive alternative to ion exchange or chelating resins, either immobilised on controlled pore glass or silica, in 1987 it was also noted that "the use of complexing agents immobilised on suitable substrates has continued to receive attention", a trend that has continued to the present day.[2] Co-precipitation was heavily reported and is undergoing a renaissance at the moment. By the 1988 review[4] some species specific preconcentration techniques started to appear for organotin compounds. By the 1989 review[5] the maturity of preconcentration methods employing solid support

materials was noted as the "experimental results are concerned with automation and information is presented in plenary lectures". By 1994 the use of ICP-MS was becoming more routine and many of the resins, chelating agents and precipitation techniques previously reported were being tried with ICP-MS detection, with increasing levels of automation. Flotation methods started to appear in 1998,[6] where either precipitates or metal chelates are "floated" as a surfactant foam on the surface of the sample, to separate them from the aqueous phase, these seem to be a precursor to cloud point extraction. Cloud point extraction is effectively a "green chemistry" approach as it is a solventless solvent extraction, with the solvent phase replaced by a surfactant. Its debut was in the 1999 Environmental Update[7] and it has been increasingly reported in the literature since then. Some papers report useful multi-elemental capabilities of the complexing agents used, but the literature is awash with single element methods using obscure complexing agents that do not offer any significant advantage over more established methods. There is now a continuous crossover of methods that are popular in organic analytical chemistry, two recent examples being solid phase microextraction (SPME) and stir-bar sorptive extraction that can be successfully applied to the preconcentration of organometallic species such as the organotins.[8]

In the 1992 review[9] the sampling and storage of water samples prior to analysis started to become important, especially as detection limits started to drop to trace and ultra trace levels. The solution proposed was preconcentration in the field, followed by lab analysis. In 1994[10] it was noted that there was an increase in the use of microwave digestion of waste water samples to obtain a total metal content prior to their analysis by AAS and ETAAS. The need by this time, for ultra-clean working procedures was starting to be recognised, and where available the use of portable clean laboratories and Class 100 clean rooms was starting to cast doubt on previously published data, where clean procedures were not used. In the 1998 review onwards, there was enough research in sample collection and preservation to merit its own subheading in the ASU.

Sample speciation

It is clear looking over the last 25 years that a tremendous amount of effort has been expended in elemental speciation, particularly in the soil and water arenas. Here speciation in waters of As, Cr, Hg and Sn species; Cr and Hg species in soils and more recently Se species in plant materials has predominated. Initial studies were conducted using HPLC/GC techniques coupled to vapour generation/trapping AAS and ICP-AES systems. Often, given the low concentration of total analyte in waters, speciation approaches have been coupled with separation and preconcentration procedures *i.e.*, giving rise to non-chromatographic approaches. Here a plethora of approaches have been developed! Along similar lines, operationally defined leaching procedures have been developed and sometimes reinvented as a means of assessing the form and mobility of elemental species in soils, *e.g.*, BCR type leach protocols. Here, since the procedure used defines the end result, necessary work has had to be carried out in developing appropriate certified reference soils.

In the 1986 review it was stated "progress in areas such as coupled HPLC-ICP-MS and standardisation/intercalibration is

anticipated".[1] It is pretty clear however that despite analytical efforts made to date, take up of the science by regulatory authorities to date has generally not occurred. However changes may be afoot as concerns grow over exposure to environmental sources of organometallic species. Regulatory momentum coupled with advances in commercially available and robust GC/HPLC-ICP-MS systems suggests that there may be a new dawn in environmental speciation. Two growing areas of speciation are worth noting: the speciation of mercury compounds in the atmosphere, driven largely by the availability of one particular speciation sampler/analyser system; and the use of HPLC-ICP-MS systems for the determination of marker elements such as Br, I, P, S in chemical warfare agents, haloform species and pesticides in aquatic systems.

Coupled chromatographic techniques and speciation have concentrated on the species of As, Cr, Hg and Pb and Sn, few studies using ICP-MS were reported initially, most used HPLC coupled with hydride generation AAS or ICP-OES for the determination of the species of interest. Non-chromatographic methods for elements such as Sb and Se were reported. They can be differentiated into their inorganic species, such as Se^{IV} and Se^{VI} by exploiting the pH dependence of the reduction steps required. Typically one species generates a hydride, the concentration of which is measured in the unaltered sample, then a reduction of the sample is carried out to determine the total and the higher oxidation state species concentration is deduced by difference. Throughout this 25-year review period, this technique has been the main non chromatographic speciation strategy. Much research has been directed at improving As hydride generation of the various species that As takes. Hydride trapping prior to sequential volatilization into quartz furnace AAS instrument was reported in 1989,[5] and a further refinement of cold trapping the hydrides and determining the species generated by coupled GC-AAS was reported in the same year, as was a capillary GC-AAS method for the speciation analysis of mercury. Directly coupled HPLC-ICP-MS for the determination of alkyl tin compounds was reported for the first time in the 1990 review.[3]

Speciation in water samples, however, is hampered by the low concentrations of the target analytes. It is a challenge analysing the total concentration for some elements, splitting that small signal into its constituent species makes life even more difficult. Through the 1990's, efforts were focussed on separating species and coupling chromatographic systems to detectors, the water samples that were analysed were often spiked with the species of interest. Preconcentration methods such as those mentioned earlier are required to carry out accurate speciation analysis of trace elements in natural waters. By 1996 speciation methods incorporating preconcentration methods for Sb and Hg were being reported.[11] Sulfyhydryl cotton as a solid phase for mercury species extraction was reported in 1998.[6] By 1999[7] there was a veritable explosion in speciation methods, although most were refinements of existing techniques. In this period, non metallic element speciation started to take off with methods published for the speciation analysis of I and/or Br in water. In the year 2000, capillary electrophoresis started to be coupled to ICP-MS, particularly for the separation of species of As.

One definite trend with the commercial availability of GC-ICP-MS interfaces has been the increase in the number of GC-ICP-MS

methods produced, not only for organometallic compounds but also organophosphorus pesticides and other organic compounds,[12] containing heteroatoms that are now interference free with the advent of cell based ICP-MS instruments.

Sample introduction

Vapour generation systems continue to be used to introduce mercury and other metalloid species into atomic spectrometric instrumentation in a gaseous form. The technique provides a means of separating elements from a matrix and preconcentrating them, of minimising memory and isobaric interference effects, and presenting a sample in a suitable format for techniques such as FAFS. Vapour generation is one of the most commonly used techniques for improving detection limits, even though it is limited to the hydride forming elements and mercury. Over this review period vapour generation has been successfully coupled to virtually every kind of atomic spectroscopy instrumentation. Most articles deal with one of the following three arguments: further reduction of detection limits by using hydride trapping or amalgamation with gold (for Hg), speciation by difference by the selective reduction of higher non-hydride generating oxidation states, and the quest for conditions that allow multi-elemental hydride generation. One particular challenge has been the development of on-line reduction methods allowing rapid reduction of the species present in an HPLC, to the hydride generating oxidation state in the eluent prior to hydride generation and detection by any number of methods.

In earlier reviews, different solid sampling approaches were contemplated ranging from slurry sampling to spark emission of pressed pellets as a means of avoiding tedious sample dissolution procedures. Interest in such approaches remained with particular research groups but the lack of commercially available systems probably hindered any possible growth in their use. Furthermore it was hard to see, in many cases, beyond the use of the long established XRF technique. Likewise the development of approaches using laser induced breakdown spectroscopy (LIBS) continues to occupy the attention of a few research groups. Here steady progress is being driven by a growing understanding of the technique coupled with emergence of commercially available systems that potentially can be deployed for measurements in the field.

Because of the natural heterogeneity of geological materials, Earth scientists have always been in the vanguard of developments in laser ablation (LA). They recognised that it had the potential to provide spatially resolved data at the micrometre scale, with good multi-element sensitivity across the Periodic Table. Moreover, little or no sample preparation was required. One of the early breakthroughs, reported in 1993 by two groups conducting independent research on either side of the Atlantic, was the use of a frequency quadrupled Nd:YAG laser operating in the far ultraviolet region at 266 nm. Since then, many workers have confirmed that wavelengths in the UV are preferred over those in the IR, as the shorter wavelength radiation couples more efficiently to transparent materials, such as quartz. This results in a more controllable ablation process and a higher proportion of very small particles that can be transported to the plasma.

Developments in laser ablation in the intervening years have focused on ensuring that the particles reaching the plasma are

representative of the target material and on reducing elemental fractionation during ablation. Currently, it is thought that shorter laser pulses of femtosecond rather than nanosecond duration, may lead to both reduced fractionation and better depth resolution. Even though standards with a wider range of matrix composition are still required, laser ablation ICP-MS is now employed on a routine basis in many geoanalytical laboratories worldwide for bulk and spot analysis. Applications such as the multi-element analysis of single fluid inclusions have opened up a whole new approach to studies of the chemistry of fluids in the Earth's crust and formation of ore deposits.

Instrumentation

A transition from FAAS to ICP-AES as a workhorse in environmental laboratories in the 1980's was driven by a commercial necessity for higher sample throughputs with a greater degree of automation. By the early 1990's many water laboratories migrated to ICP-MS as the technique promised to offer the throughput capabilities of ICP-AES coupled with the sensitivities of ETAAS. The greater sensitivity offered by ICP-MS, compared to that of ICP-AES, led to its rapid acceptance by the Earth science community. Indeed, some of the leading practitioners of the technique worked in geochemical laboratories. Data on suites of geochemically important elements, such as the REEs, were now obtainable with detection limits superior to those of ICP-AES, and without the need for time-consuming separation from the matrix.

Atomic absorption and fluorescence methods

The main trend in water analysis has been the gradual decline and replacement of FAAS with ICP-AES, and the rise and fall of ETAAS in the face of competition from ICP-MS. AAS is still heavily used throughout the world due to its low relative cost and usefulness for cross-checking results from other instruments. Most of the advances now are front-end modifications; advances in the instruments themselves seem to be mostly increased computerisation with automatic set-up of conditions.

In the 1986 review[1] there was a lot of interest in electrothermal atomisation atomic absorption spectroscopy (ETAAS), the stabilised temperature platforms with Zeeman background correction and matrix modification allowed the direct determination of several elements in seawater. Over the years the sensitivity of FAAS has been improved by various groups by the use of atom trapping techniques such as slotted quartz tubes for the analysis of various elements in drinking water. Vapour generation techniques were also widely used with both FAAS and ETAAS instruments. The minimisation of matrix interferences for furnace instruments using matrix modifiers was thoroughly investigated as was the use of the Zeeman effect for background correction. Of particular interest was the search for a universal matrix modifier or the comparison wall, platform or graphite probe atomisation techniques. A preconcentration method that has attracted a lot of interest that is specific to ETAAS is the use of tungsten wire for preconcentration of metals prior to analysis. One of the limiting factors for AAS is that it is essentially mono-elemental, attempts have been made to create fast sequential instruments to speed analysis[9] or perform simultaneous multi-element ETAAS.[7] Occasionally truly novel applications/modifications are reported, the use of tuned laser diodes as light sources for isotope dilution AAS was one that particularly stood out.[8]

Atomic fluorescence was predominantly used as a detection method for Hg after cold vapour generation. Occasionally laser excited atomic fluorescence spectroscopy (LEAFS) was reported for ultra trace analyses, such as the detection of Pb in ice cores.[9,13] The capability of ICP-atomic fluorescence spectroscopy was also still being investigated, a technique that has virtually died out.

Atomic emission spectroscopy—ICP-AES

In the 1986 review,[1] it was noted that "few papers either of an applied or fundamental nature have been published and this is an indication of the growing maturity of plasma emission methodology". In 1987, it was noted that "inductively coupled plasma atomic emission spectroscopy retains a dominant position in water analysis". Gaseous evolution formed the basis of most of the new methods reported. Simplex optimization was used to find the best conditions for the simultaneous determination of As, Sb and Se by hydride generation ICP-AES, dissolved organic carbon (DOC) was determined after conversion to CO_2 in a heated quartz tube filled with copper oxide, the generation of H_2S was exploited to determine sulfide in natural waters.

For most of the review period, the vast majority of the papers have reported "front end" innovations, to improve the inherent sensitivity of the instrument using flow injection, preconcentration or vapour generation techniques. Some of the more important innovations include the cyclonic or centrifugal spray chamber as it was originally called and the re-introduction of the ultrasonic nebuliser[3] and the use of continuous hydride generation simultaneously with conventional nebulisation to add As, Se and Sb to an analytical suite of elements.[10] Dual view instruments were reported in the 1999 review,[7] as was the use of heated spray chamber desolvation systems and the use of microconcentric nebulisers. A genuine leap forward in the speed, flexibility and utility of ICP-AES occurred when manufacturers adopted Echelle spectrometers and coupled them with array detectors.[14] DCP-AES, still being used in 1987, has died out.

Atomic emission spectroscopy—MIP-AES

In 1986, a new argon-fed toroidal microwave induced plasma (MIP) was reported for the analysis of trace elements in water, snow and ice using pneumatic nebulisation.[1] An MIP-AES instrument was also evaluated for the determination of Hg by cold vapour generation and gold trapping prior to detection for the ultra trace analysis of lake water samples.[2] Helium MIP-AES instruments evolved to become more utilized as a detector for GC and GC-MIP-AES methods for Sn and Pb speciation were reported in the 1994 review.[10] In the 1997 review[15] more applications for GC-MIP-AES were noted than for ICP-OES, it was used for the simultaneous determination of organotin, organolead and organomercury, the detection of volatile S compounds and the determination of C and S in organophosphorus pesticides. Atmospheric pressure MIP-AES was shown to be useful for halide analysis.[7] This was expanded to absorbable organically bound elements such as Br, Cl, F, I, P, and S in water samples after

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J. Anal. At. Spectrom., 2010, **25**, 1546–1566 | 1549

thermal desorption and MIP-AES detection. Sadly MIP-AES instrumentation is no longer available commercially.

By far the most important advance in water analysis over the 25 year review period has been the development of ICP-MS from a research curiosity to a robust, precise and sensitive analytical tool that now can detect most elements in fresh and drinking waters without any sample pretreatment. In the 1986 review, the advantages of ICP-MS were being extolled at conferences but it was noted that "a more comprehensive review of this powerful technique must await more complete studies than those so far reported". By 1987, matrix separation using 8-hydroxyquinoline-modified silica columns had already been evaluated for seawater analysis and standard additions, external calibration and isotope dilution had been assessed as potential calibration techniques. The literature explosion was noted in the 1989 review[5] of methods using preconcentration techniques with Chelex-100 or other chelating solid phases for seawater matrix removal and analyte preconcentration, as well as for preconcentrating trace elements in rainwater. Routine methods for the elemental analysis of drinking water were published and this was the year when it was noted "a definite trend in water analysis towards the application of ICP-MS." By the early 1990's, the capability of ICP-MS as an element specific HPLC detector was being increasingly exploited for speciation analysis. By 1993, NIST had published version 4 of a protocol for the determination of trace elements in waters and wastes by ICP-MS.[13] Sensitivity improvements were gained using similar strategies to those employed with ICP-AES, such as the use of ultrasonic nebulisers. Sensitivity improvements due to instrument design were obtained when sector field mass spectrometers were used with the ICP atom source. The high sensitivity of these instruments was exploited for the determination of REE in river water.

Accelerated developments in ICP-MS instrumentation were apparent in the 1999 review[7] with the development of the plasma optical emission mass spectrometer POEMS instrument that could simultaneously carry out EPA methods 200.7 and 200.8, this was also the year of the "cold plasma" that improved the LODs for the light elements. Microconcentric nebulisers were used in combination with ICP-sector field-MS (ICP-SF-MS) to improve detection limits and reduce sample consumption. This combination was further improved when a heated desolvation unit was used, allowing elements to be detected in Antarctic snow and ice, something that previously required preconcentration. In the 2000 review,[16] the first collision cell instrument with a hexapole cell was described, however the boom in the literature of the use of these instruments occurred during the period covered by the 2003 review,[17] and by the 2005 review,[12] a themed issue of *JAAS* focussing on the use of collision and reaction cell techniques in atomic mass spectrometry has appeared.

Early claims, mainly by instrument manufacturers, that the ICP-MS technique was capable of yielding elemental data on both trace elements and major constituents were somewhat premature. However, once detectors with an extended dynamic range—employing both analogue and pulse-counting modes—were developed, count rates over nine or so orders of magnitude became possible. It was now possible to dilute samples so that the major elements fall within the analogue calibration range, while good detection limits were maintained for trace elements in pulse counting mode.

Isobaric interferences remained an issue, however, and necessitated the development and frequent checking of computer algorithms to correct for interferences from major element polyatomic ions, particularly on trace elements with an m/z of <80. Many analysts also modified their dissolution protocols, sometimes detrimentally, in order to produce a final solution in dilute nitric acid because of the contribution of other mineral acids to the formation of significant polyatomic interferences. Resolution, (pun intended), was on hand with the development of collision and reaction cells to reduce such isobaric interferences. Initially, cell equipped systems were often used as single element detectors for key elements, such as As and Se, but with improvements in cell construction and better appreciation of the physical and chemical principles involved, collision and reaction cells are now widely applicable for multielement analysis. An additional benefit has been that analysts have been able to use appropriate acid mixtures for sample decomposition without compromise.

The dash to ICP-MS has not however consigned FAAS, ETAAS and ICP-AES to museums. For laboratories undertaking analysis of environmental matrices where only a couple of elements are required, such techniques remain competitive. They are also still widely used in developing nations. A renaissance of sorts did occur in the mid 1990's with the availability of solid-state detector equipped ICP-AES systems. Here the ability to perform measurements using multiple emission lines contrasted with the isobaric issues experienced with ICP-MS systems available at that time. More recently, the availability of AAS systems similarly equipped with solid-state detector systems may result in a similar renaissance of this particular technique.

Single collector magnetic sector ICP-MS instruments were designed to offer greater sensitivity than quadrupole-based systems. When they became available commercially in 1989, their use tended to be restricted to facilities where applications in which high mass resolution or enhanced sensitivity were essential requirements. In the intervening years, the use of such instruments has generally not spread to other environmental laboratories, partly due to cost considerations but mostly because the needs of these laboratories were satisfied by the performance of quadrupole-based systems.

For isotope geologists, the real advance was the introduction of multiple collector instruments. These offered truly simultaneous measurements of ions with a precision that rivalled or exceeded that achieved by thermal ionisation mass spectrometry (TIMS). Furthermore, the plasma source is capable of ionising geochemically-important elements that are difficult or impossible to measure by TIMS. From the early days of this technique, applications in geochemistry and cosmology drove many of the developments. In a relatively short time, MC-ICP-MS has come to dominate methodologies for isotope ratio determinations for radiogenic elements employed in geochronology and associated studies. In addition, access to the technique has considerably expanded our knowledge of the stable isotope composition of a much wider range of elements in geological systems, including Ca, Cu, Fe, Ge, Mg, Mo, Si, Tl and Zn, than hitherto possible.

The potential of laser ablation coupled to MC-ICP-MS was recognised during the early stages of its development in the early 1990's. It opened up the possibility of *in situ* isotope ratio determinations with minimal preparation. Preliminary studies

demonstrated reproducibility comparable with ion microprobe measurements and a precision rivalling that of TIMS. Early instruments relied on the use of Faraday cups for ion detection. Once one or more electron multipliers were included in the detector assemblies, much weaker ion beams could be counted, allowing low and high abundance ions to be determined simultaneously. Since then, the use of LA-MC-ICP-MS in geoscience applications has grown exponentially as the number of isotopic systems studied has expanded.

Laser induced breakdown spectroscopy (LIBS) has recently been reported to have been trialled at deep ocean pressures for the bulk analysis of seawater, opening the possibility of *in situ* analysis of hydrothermal vent plumes.[18] Micro-LIBS combined with LIFS has been used to measure Pb in drinking water,[19] although probably not needed for a routine analysis that is readily carried out by other methods.

XRF techniques are widely used in geochemical laboratories for major and minor elemental analysis, *i.e.*, down to 0.1% (m/m). Developments in energy dispersive systems with polarised optics over the last ten or so years has enabled trace elements, *i.e.*, around 0.01% (m/m) or lower to be measured. The application of XRF systems to the analysis of liquids typically involves some kind of preconcentration technique, such as co-precipitation,[4] or immobilisation of the analytes onto a solid support such as a filter[20] or solid phase extraction disks.[12] Sometimes preconcentration is not necessary, wavelength dispersive X-ray fluorescence was described for the routine determination of F in waste water.[5] However due to the sensitivity problems encountered typically most water analyses are carried out by total reflection X-ray fluorescence (TXRF), which was first reported as applied to natural waters in the 1990 review.[3] Portable XRF is often touted as a possible solution to the difficulties in the preservation of samples, by carrying out analyses in the field. A specific filter for heavy metals combined with such an instrument was found to be ideal for on-site screening of liquid pollutants.[16] A portable TXRF instrument was reported in the 2005 review.[12] A Micro-XRF spectrometer with a customised temperature controlled sample holder was used for the non-destructive analysis of ice samples from Antarctica, a considerable advantage given the effort that goes into the collection of these precious samples.[21]

Vapour generation is one of the most commonly used techniques for improving detection limits, even though it is limited to the hydride-forming elements and Hg. Over this review period, it has been successfully coupled to virtually every kind of atomic spectrometry instrumentation. Most articles deal with one of the following three topics: further decrease of detection limits by using hydride trapping or amalgamation with gold (for Hg), speciation by difference by the selective reduction of higher non-hydride generating oxidation states, and the quest for conditions that allow multi-elemental hydride generation. One particular challenge has been the development of on-line reduction methods allowing rapid reduction of the species separated by HPLC to the hydride-generating oxidation state in the eluent prior to hydride generation and detection.

Developments in air measurements have shown that bulk compositional data alone are not sufficient for toxicological investigations or source apportionment studies. Furthermore, the transient nature of many pollution episodes requires the development and deployment of real-time analysers in the field.

Instruments that can sample and interrogate single particles with respect to size, number, volume and chemical composition are being developed as we enter the 'Age of the Nanoparticle' with its funding gravy train. Real-time measurements of inorganic gases are now common. The growing use of field-deployable ion-chromatographic and optical systems for the determination of the ionic and carbon content of airborne particles are also noteworthy developments. The determination of the trace metal content of such particles in real time remains elusive, but a promising development is a combined airsampler/XRF spectrometer with the ability to provide hourly data at low ng m^{-3} concentrations.

External assurance control and reference materials

Currently, there is a greater appreciation of the importance of metrology in analytical chemistry with many environmental laboratories accredited to international standards such as ISO 17025. A key conformity requirement is that such laboratories should take part in appropriate proficiency testing schemes. Many such schemes now exist for water and soil analysis, provided by both the public and private sectors. Similar developments can be seen within the geochemical arena where an important development was the launch in 1996 of GeoPT, a scheme designed to assess the performance of laboratories that analyse silicate rocks.

Historically, programmes to characterise such materials were often organised, at a national or European Commission level, by inviting laboratories to contribute data. Now, however, financial recoveries, if not returns, are required when developing reference materials. Finding volunteer laboratories is also a challenge. A trend that is likely to continue is the provision by certain proficiency testing providers of surplus test samples as reference materials for every day use.

Clinical and biological materials

The development of more sensitive and versatile techniques for measurement of trace elements in the analysis of clinical and biological materials has enabled the determination of a wider range of elements and hence has led to new applications, for example, the determination of wear metals in prostheses. Clinical interest in some elements has grown while for others, such as aluminium, their importance has waned. Recent emphasis on speciation of elements has been enabled by the coupling of sensitive element-specific detectors with separation techniques. Advances made in separation techniques and molecular detection have been embraced in the development of these coupled techniques.

This section concentrates on three major stories that we have been following in writing these updates. They are:

1. The developments in ICP-MS and the impact this has made on the analysis of trace elements in biological material.

2. The painstaking work that went into improving the accuracy and sensitivity of the determination of selenium in biological materials and then in tackling the speciation of this element.

3. Lead, the element that never went away. 25 years ago, exposure to lead had already been drastically reduced but

subsequent interest in lead never waned, helped by some interesting developments in methodology.

Development of ICP-MS

A major development has to be the move away from measurement techniques based on AAS to methods based on ICP-MS. The technique was originally described in 1981 by Date and Gray[22] and immediately created considerable interest in the analytical fraternity, who were impressed at the possibilities but sceptical about the chances of this technique ever getting off the ground. After all, it was a combination of two technologies that were at the time notoriously unreliable. However, inductively-coupled plasmas became much more reliable, as significant resources were put into their development particularly for ICP-AES, although the mass spectrometer, with its associated vacuum system, remained troublesome and early adopters using this instrument for routine analysis found that they really needed two instruments, as the downtime of an individual instrument was excessive.

In our first Update[23] in 1986, we recorded that ICP-MS had yet to make an impact on clinical and biological analyses, the only report being a conference paper on the analysis of oyster tissue. However, there were a considerable number of papers describing the use of ICP-AES, mainly for soft and hard tissues. By 1988, we wrote about several conference presentations but there were still no published papers to review. In the following year, there were 8 published papers and 15 conference reports.

In the early years, multielement applications of ICP-MS became less popular as many isobaric and matrix interferences compromised accuracy. Instead, workers were concentrating on other benefits of ICP-MS and applying them to single-element analysis. An ICP-mass spectrometer was shown to be a useful (but perhaps expensive) detector for HPLC in speciation. Dean et al.[24] in 1987 showed how such a system could be used to detect metalloprotein species. Inductively-coupled plasma MS was also being applied to stable isotope studies of the metabolism of minerals and trace elements (e.g. Janghorbani et al.[25]) and to the determination of Pb isotopes in blood (e.g. Delves[26]). The isobaric interferences are insignificant at $m/z > 80$, so that ICP-MS became a good method to determine heavy elements, especially those that were difficult to determine by existing techniques. Igarishi et al.[27] showed that ICP-MS could be used for the determination of Th and U in biological materials. Matrix interferences were still present but could be overcome by using an internal standard similar in mass (^{209}Bi). In our 1996 Update,[8] we noted that 52% of the papers covered in that review year related to single element applications, often in speciation studies, 34% on multielement determinations and 14% on stable isotope studies. Although true multielement analysis was proving difficult, it was possible to explore the potential for determining relevant groups of elements. For example, Nixon and Moyer[28] developed a method for the routine analysis of whole blood and urine for the toxic elements As, Cd, Pb and Tl. There was also interest developing around this time in multielement speciation. Feldmann[29] coupled ion chromatography to both a conductivity detector and an ICP-mass spectrometer and was able to monitor the anions PO_4^{3-}, Br^-, Cl^-, NO_3, SO_4^{2-}, AsO_3^-, AsO_4^-, SeO_3^- and SeO_4^- in urine. Later, as we covered in our 2000 Update,[30]

there was a lot of interest in a new coupling for speciation—capillary electrophoresis with ICP-MS. The interface was important, requiring a low consumption nebuliser, a low volume spray chamber, and additional gas flow to avoid suction on the capillary (e.g., Van Holderbeke et al.[31]).

An appreciation of the possibilities and problems of multi-element analysis can be obtained by studying the paper of Vandecasteele et al.,[32] originally presented as an invited lecture at the 1993 European Winter Conference on Plasma Spectrochemistry in Spain. They had developed a method to determine trace and ultratrace elements in serum, particularly with the objective of establishing reference ranges for the more difficult elements and to characterize a second generation RM. Samples were diluted 1 + 4 with 0.14 M HNO_3 and matrix interferences were overcome by internal standards. Many approaches were tried in the early 90s to overcome isobaric interferences—hydride generation for As and Se,[33] prior separation by chromatography either off-line[34] or on-line,[35] and addition of gases such as CH_4[36] or N_2[37] to the nebulizer gas. The advent of commercially-available, high-resolution ICP-mass spectrometers gave another tool to combat interferences. Moens et al.[38] demonstrated this in the determination of V, Fe, Cu, Zn and Ag in human serum with this instrument. The LODs possible with this technique were 10–100 times better than with a quadrupole ICP-mass spectrometer and they concluded that ways of reducing blanks and combating memory effects would be necessary to exploit the greater sensitivity of high-resolution ICP-MS. The high sensitivity of the instrument in low resolution mode was exploited by Begerow et al.[39] to measure physiological concentrations of Pt in urine (<8 ng L^{-1}). The resolution from interferences in high resolution mode was exploited by Sturup et al.[40] in stable isotope studies to determine ^{44}Ca : ^{43}Ca and ^{42}Ca : ^{43}Ca ratios in human urine. Such was the developing interest in high-resolution ICP-MS that a themed issue of JAAS in April 2000[41] highlighted this technique. The editors of that issue, Jakubowski and Moens, recommended that this new technique should be called ICP-sector field MS (ICP-SF-MS). It was clear from the papers on multielement analysis of human body fluids that the analysis might need to be run at least twice at different resolutions to get results. Low resolution offered high sensitivity but isobaric interferences remained. Many of the interferences were resolved at medium resolution giving good accuracy, but for As high resolution was necessary (e.g., Begerow).[42]

By 1998, quadrupole ICP-MS was becoming more widely used for routine multielement analysis in clinical laboratories. In our Update for that year,[43] we covered conference presentations detailing the experience of laboratories in the US and Canada. The new sector field instruments were expensive, but, around the same time, developments in the less expensive ICP quadrupole mass spectrometers ensured continuing interest in these instruments. Manufacturers were offering instruments with reaction cells that allowed the incorporation of gases such as CH_4 to control interferences. The first paper we covered in our Updates using this innovation was that of Sloth and Larsen[44] who showed that, with CH_4 introduced into the dynamic reaction cell, it was possible to achieve an almost interference-free determination of ^{80}Se in the speciation of selenoamino acids separated by HPLC. Later, St. Remy et al.[45] used H_2 in an octopole reaction cell to minimize interferences in the determination of essential and toxic

elements in acid digests of premature human milk. The cell was effective in removing polyatomic interferences at ^{52}Cr, $^{54,57}Fe$ and $^{77,78}Se$ lines but problems remained for ^{56}Fe and ^{63}Cu. In a comparison with ICP-SF-MS, the researchers stated that the LODs were similar for this kind of matrix but the sector field instrument could not resolve the Ar–Ar+ interference on Se, so that a minor isotope of Se (^{82}Se) had to be monitored with an LOD an order of magnitude worse than with the reaction cell method. It is now clear that the reaction cell has been very effective in reducing polyatomic interferences and has greatly improved the ability of the quadrupole ICP mass spectrometer to act as a routine multielement analyser in clinical laboratories.

From the early 1990s, laser ablation ICP-MS was being explored for the determination of a range of elements in biological samples. For example, Denoyer[46] pressed solid materials into pellets with a binding agent. Semi-quantitative analysis was possible with results on RMs accurate to within 20–40% when internal standardization was used. Later, the technique was applied to speciation in human serum by two-dimensional gel electrophoresis (for example, Nielsen et al.).[47] The distribution of the metals in the gel could be measured using laser ablation and the proteins could be identified by staining. Laser ablation has also been applied by Watling[48] to produce 'fingerprints' of cannabis samples from Western Australia in order to identify the source of the cannabis.

Essential elements

Work on Cu and Zn continues, but although there is more data and the technical possibilities are greater, clinically there has been little change in how these elements are perceived. Studies of the elements Mn and Cr, deemed to be essential, have also benefited from improvements in measurement technology but there is still no convincing evidence for their essentiality. There is much more evidence for their toxicity. For example, Mn was added to intravenous feeding regimens with a trace element additive, that probably contained too much Mn. Brain damage was demonstrated and now patients need to be monitored for blood Mn.[49]

The essential element of interest and promise has been Se. 25 years ago, the methods available were based on ETAAS, HGAAS and molecular fluorimetry. The thrust of research then was to improve the sensitivity and accuracy of the former two methods. An IUPAC interlaboratory comparison[50] published in 1986 showed that HGAAS results were lower results than those of ETAAS. Welz et al.[51] showed that the digestion conditions were critical and it was necessary to add $HClO_4$. The improved digestion conditions were evaluated in a further interlaboratory trial[52,53] and shown to give satisfactory results.

The modifier originally used in the determination of Se by ETAAS was nickel, but a number of studies subsequently showed the benefits of using platinum group elements. Palladium was the most often used, either on its own or combined with $Mg(NO_3)_2$. Schlemmer and Welz[54] in an important development, advocated $Pd/Mg(NO_3)_2$ as a universal modifier. A problem with determination by ETAAS was error in correction for the background from iron or phosphorus when a D_2-based correction system was used, as shown by Neve and Molle.[55] They recommended Zeeman-effect background correction, as did many

others. However, other workers (e.g., Sampson[56]) found ways round the background correction errors and showed that the cheaper D_2- based system could still give accurate results. As was later shown by Radziuk and Thomassen,[57] there is still spectral interference from phosphate in Zeeman-effect background correction and this is better controlled by choice of type and amount of modifier.

In our 1991 Update,[58] we noted the impact that automation by FI was having on HGAAS methodology (for example, McLaughlin et al.[59] and the determination of Se by Guo et al.).[60] A simplified measurement system, based on non-dispersive AFS, was developed by D'Ulivo et al.[61] Hydride generation proved to be a suitable interface for determination of Se by ICP-MS, as it enhanced sample transport efficiency and removed a number of interferences.[62]

By 1996, a growing awareness in Se speciation was apparent. Combinations of HPLC with ICP-MS or ETAAS were being developed to measure Se species in dietary components and in clinical and biological samples. For example, Crews et al.[63] developed an isotope ratio HPLC-ICP-MS method to separate Se-methionine, Se-cysteine, selenite and selenate. The distribution of Se in human serum was studied by Harrison et al.[64] using separation by affinity chromatography and determination of Se in the fractions by ETAAS. Of the total Se, 53% was reported to be bound to selenoprotein P, 39% as glutathione peroxidase and 9% bound to albumin. There was also the question of how these different Se species affected measurement of total Se in methods commonly used at the time. Johannessen et al.[65] compared the efficacy of various modifiers in ETAAS for the thermal stabilization of selenite, selenate, Se-methionine and trimethyselenium and found incomplete stabilization of the latter by commonly-used modifiers. Attention also turned to the speciation of Se in urine which was proving more difficult as the concentrations of the species were so low. Studies by Gammelgard et al. in 2000[66,67] produced a successful method to separate species and showed the kind of results that could be obtained on urine samples. In the following years, more and more Se-containing species were identified. For example, Gammelgard's group[68] isolated a Se metabolite from urine samples from volunteers given a Se supplement and, using atmospheric pressure chemical ionisation MS, identified it as a selenosugar, methyl n-acetylseleno-hexosamine. Thereafter, the story of Se speciation gets even more complex and it is better to consult a review (e.g., Dumont et al.,[69] Pedrero and Madrid[70]). The complexity of the techniques used in speciation, the need for preservation of species and the complexity of the results obtained is one reason why the separate Update on speciation, which first appeared in 2009, was commissioned.[71]

By the 1999[72] and 2000[30] Updates, it was evident that we were seeing ICP-MS methods for routine determination of Se in serum that were intended to replace ETAAS methodology. For example, Delves and co-workers[73,74] overcame interference from Ar by using 1% butanol as the diluent. This also was found to increase the sensitivity. Blockage of the cones was prevented by the addition of Triton X-100 and EDTA to the diluent. The method was applied to the determination of Se in serum, whole blood and erythrocytes. With the advent of reaction cells in ICP-MS, another option for controlling interferences was feasible. Reyes et al.[75] used H_2 as the reaction gas to reduce interferences

from Ar in the determination of Se isotopes, and improve LODs. Other gases that work as well or better are D_2,[76] Xe[77] and CH_4.[78]

Supplementation of the diet with selenium was being considered by government organisations in areas where the intake was insufficient. In our 1993 Update, we covered an important study by Moser-Veillon *et al.*[79] in which GC-MS was used with isotope dilution to study the absorption of Se in lactating and non-lactating women. Using two stable isotopes of selenium, ^{74}Se and ^{76}Se as tags, they found that absorption of Se as selenomethionine was higher than as selenite. In Finland, Se had been added to fertilizer and in 1998, Wang *et al.*[80] reported that serum Se levels in young adults had increased over 5 years from a mean of 1.04 μmol L^{-1} to 1.59 μmol L^{-1}, while in children it had risen from 0.87 μmol L^{-1} to 1.31 μmol L^{-1}. The hope here was that Se supplementation would reduce cardiovascular disease, but a more important prospect loomed which would spawn a number of large-scale studies. This was the prevention of prostate cancer. The kind of study which led to this "gold rush" is illustrated by the results of Brooks *et al.*[81] in 2001 who found, in a case control study of 148 elderly men, that low plasma Se concentrations were associated with a 4–5 fold increased risk of prostate cancer. This supported the findings of Clark *et al.*[82] in 1998 that a daily supplement of 200 μg Se was associated with a 63% reduction in the incidence of prostate cancer. Sadly, the lead investigator in this study, Larry Clark, subsequently died of prostate cancer, and, unfortunately for the rest of the world, the results to date of studies that followed seem to indicate that supplementation with Se does not prevent prostate cancer.

Lead

Exposure to lead is now much less than it used to be. Lead concentrations have been decreased in water, paint, petrol and, more recently, in solder. Nevertheless, over the past 25 years, interest in lead measurement and studies has not diminished.

Part of the reason has been the need to chronicle the fall in blood lead concentrations in the population and to examine the possible effects of lower lead exposure. To achieve this, accurate and more sensitive methods were necessary. Most have been based on ETAAS, mainly using the stabilised temperature platform furnace approach, which became the standard. An early landmark development was that of Shuttler and Delves[83] who produced a method suitable for epidemiological studies. They used a diluent containing NH_3, $NH_4H_2PO_4$ and $(NH_4)_2H_2EDTA$ and added O_2 at the ashing stage. Many similar methods followed, the main differences being in the use of alternative platinum group modifiers. An interesting development reported in the 1996,[84] 1997[85] and 1999[72] Updates was the low-cost portable instrument using tungsten coil atomisers, for the mass screening of children for lead exposure in the US.

It is often said that there is nothing new, just new people rediscovering old ideas. So it seemed with the idea of using blood spots on filter paper for the determination of blood lead in children. The technique had been investigated in the 1970's, particularly at the Health and Safety Laboratory, UK, and many problems, particularly the contamination of the blood spots, resulted in its rejection in later studies. In 1995, Verebey *et al.*[86] described their method using finger-tip capillary sampling onto filter paper which we covered in 1996.[84] In the 1998 review,[43] we

referred to the vigorous correspondence which ensued between Verebey and Delves.[87–90] Delves[87] argued that the comparison data published by Verebey *et al.*[86] showed a positive bias by this collection technique that made it unreliable for screening childhood exposure to Pb. It gave false positive values and high imprecisions of up to 40% RSD at 10 μg dL^{-1}. Verebey[88] maintained that modern conditions allowed the collection of filter paper samples without sample contamination and that false positives were no higher than with other collection techniques. Despite this controversy, papers still appear using this technique. In the 2004 Update,[91] we included the work of Shen and colleagues[92] in a study of blood lead levels in Chinese schoolchildren, in which they claimed good agreement between the blood spot technique and venous sampling. In the 2008 Update,[93] we mentioned a paper in which LA-ICP-TOF-MS was used to measure total Pb and Pb isotope ratios in discs punched from blood spots. The isotope ratios were used to identify extraneous contamination. The same approach was again featured in the 2010 Update;[94] the researchers' description of the method as "simple" was considered inappropriate.

Another active research area has been the measurement of plasma or serum Pb. As the concentration is less than 0.5% of that in whole blood, very good sensitivity is needed, such as that provided by ICP-SF-MS. However, great care has to be taken with sampling, as studies by Smith *et al.*[95] showed. Serum collected by an ultraclean method gave 0.4% of the whole blood concentration but the concentration increased if the blood was allowed to stand 1 h before centrifugation. Plasma contained the same concentration of Pb but was unaffected by standing; EDTA blood was completely unsuitable because of the chelation of Pb from the blood cells. A later study by Manton *et al.*[96] found a linear relationship between plasma and whole blood Pb up to whole blood concentrations of 60 μg L^{-1}. They found serum Pb was 0.24% of total blood Pb, lower than previous findings. In their study of 154 adults with a history of Pb exposure, Barbosa *et al.*[97] showed a curvilinear relationship between plasma Pb (range 0.02–2.9 μg L^{-1}) and blood Pb (range 10–428 μg L^{-1}).

Interest in lead studies has increased as there are now two new tools to study lead exposure—identification of the source of lead exposure through lead isotope studies and *in vivo* measurement of bone lead concentrations.

The work of Delves and Campbell[98] on a method to determine total Pb and isotope ratios in blood by ICP-MS was covered in the 1988[99] and 1989[100] Updates. They detected clear differences in the ratios for three UK towns. However the identification of the source of lead exposure is not always easy, as was shown in a later study by Viczian *et al.*[101] in 1990, but clearly the technique had potential.

Perhaps the most important development in this field over the 25 years has been the ability to measure bone Pb by *in vivo* XRF. Previously bone stores could only be determined at autopsy. An interesting example of this was the determination of high concentrations of Pb in the bones of members of the 1845 Franklin Arctic Expedition,[102] which were ascribed to the crudely soldered cans in which their food was preserved. For children, there was always the possibility to determine Pb in deciduous teeth (see, for example the work of Keating *et al.*[103]). However in 1989,[102] we covered the work of Chettle *et al.*[104] who described their method for the determination of Pb in tibia by non-invasive

XRF. In 1992, they published the results of a study of Pb in the tibia of occupationally-exposed workers[105] and compared the results to blood lead measurements. This study showed the improved precision they had achieved over a similar study five years earlier. It then became an important tool to use in any study of lead exposure, and in 2002,[106] we covered two large-scale studies[107,108] in the US which had used this technique. An important study by Needleman *et al.*[109] indicated a relationship between delinquency and lead exposure. Using *in vivo* K-line XRF measurements, they showed that tibia Pb in 194 delinquent youths (11.0 ± 32.7 µg g^{-1}) was significantly higher than in 146 non-delinquent youths (1.5 ± 32.1 µg g^{-1}). Chettle published two reviews in 2005[110] and 2008[111] that outlined developments in this methodology and its application.

As many recent studies have shown subtle effects of lead exposure, interest in lead studies and in methods for the determination of lead in clinical samples will continue for the near future.

Food

It is tempting to say little has changed in food analysis. Unlike the situation for the pharmaceuticals or chemicals industry, there are not the discoveries that bring new drugs, polymers, catalysts, and agrochemicals to the market with the associated needs for new methods of analysis. None the less, issue of adulteration, organic and genetically modified produce, and of large scale populations afflicted by contaminated water, drive developments in chemical measurement as well as attracting the attention of national media. The elements that were toxic—As, Cd, Hg, Pb—remain so, as do the elements essential to human health and nutrition. Instrumental developments, particularly the growth of inorganic mass spectrometry and hyphenated techniques have allowed the analyst to characterise more elements at greater sensitivity. Increased computing power has enabled chemometric techniques to be developed that allow enforcement laboratories and brand owners to check the authenticity of their raw materials and finished products.

Sample preparation

There have been many developments in sample preparation procedures. Direct solid sampling was initially of interest. The 1988 review[112] noting "The one application area which has grown in popularity almost exponentially over the past few years is the direct analysis of solids, slurries or suspensions". Methods typically involved direct insertion of fresh or dried samples into an ETAA spectrometer (86/1764, 86/1765). By 1991, the ASU was reporting the demise of solid sampling and the growth of slurry approaches, which were seen as more practical. Slurry application papers continued to appear over a number of years, with studies discussing issues such as the value of air-ashing in ETAAS (91/6), calibration (91/2220), the potential of FI systems for directly coupling on-line digestions with AAS (92/4636) and the application of ultrasound (94/2886). In recent years, the numbers of such reports have declined, presumably in part due to the rise of affordable microwave systems. Accessories available with ICP-MS, such as laser ablation and ETV have lead to a slight revival in interest in solid sampling recently.

Sample dissolution was historically achieved through wet or dry ashing with oxidising acids. In 1989 the ASU noted "papers received this year tend to suggest that the method of wet digestion in a microwave oven is superior to either of the traditional approaches". Nikdel and Temelli (88/1232) listed the advantages of microwave-assisted digestion of citrus juice samples as "rapid dissolution, complete digestion, sample integrity, minimal reagent use, lower reagent blank, simultaneous multiple sample digestion and finally possible automation." In the intervening years, most, if not all, of these benefits have been demonstrated, and the automated equipment has been widely adopted. A recent development is the recognition of the merits of alkaline digestion.[113]

When the available instrument lacks the required sensitivity for a particular analysis, there is a need for enrichment/pre-concentration. Many inventive approaches have been developed often involving chelation extraction, with APDC or DDC, solid-phase extraction, with Amberlite (95/3102), Dowex, or activated C,[114] or cryogenic trapping, which is especially useful for speciation.[115] Frequently FI systems have been utilised, in some cases to miniaturise[116] the process and reduce reagent requirements, in others to allow the use of in-line reactors.[117] A relatively recent innovation has been cloud point extraction using non-ionic surfactants. Exotic variations on the preconcentration theme have included the use of fungi immobilised on sand,[118] a Pb^{2+} templated polymer for Pb in tap and seawater,[119] and a minicolumn packed with polyurethane foam loaded with 2-(2-benzothiazolylazo)-2-p-cresol.[120] A method for determining methylmercury using headspace preconcentration of the hydride vapour in a single drop containing Pd^{II} or Pt^{IV} was developed by Gil *et al.*[121]

Elements of interest and their species

To illustrate how interest in elements has changed, the following Table 1 shows, in descending order, the five most studied elements in foods in 1986, 1987, 2008 and 2009.

In the first two and the last two ASUs, Cd, Hg and Pb have been in the top 5 elements of interest, and As was in three of the issues, demonstrating that it has been toxicity, rather than the nutrient status, that has motivated developments in the application of analytical atomic spectrometry. Associated with this, many of the studies of As, Hg and more recently, of Se, have been about speciation. Indeed, the very first ASU noted that "Some interest in speciation was evident with the publication of recommendations from the Trace Element Speciation in Foodstuffs Sub-committee of the Analytical Methods Committee of the Royal Society of Chemistry (S/926). This Sub-Committee proposed that "enzyme digestion at body temperature should be

Table 1

Top 5 elements

1986	1987	2008	2009
Hg	Pb	Se	Hg
Pb	As	As	Se
Se	Cd	Hg	Pb
Ca	Hg	Cd	Cd
As, Cd (joint)	Cu	Pb	Zn

used for fractionation studies." In the 2009 ASU, multiple examples of enzyme-assisted extraction were noted.[122,123,124]

Over a period of 25 years interest in certain elements inevitably waxes and wanes. In the late 1980's the ASU reported a number of studies focussing on Al, with interest in the relatively high concentrations in tea leaves (89/480) and also possible migration from Al cookware (89/18790, 90/391). This growth in interest was associated with the unfortunate dumping of 20 tonnes of $Al_2(SO_4)_3$, accidentally released into the public water supply of Camelford, UK, and speculation that Al was a causative factor in Alzheimer's disease (90/C4035). In 1992, the ASU reviewers prophetically wrote "Lack of verification of the findings by other workers could raise serious doubts about the implication of Al in this disease." The lack of verification did subsequently lead to decreased research in this area, and in the 1995 ASU review,[125] the decline in Al and the rise to pre-eminence of Se was highlighted. The growth in interest in Se has largely been driven by the need to understand its species and their clinical benefit. Serendipitously the need to speciate Se has coincided with the emergence of MS techniques that, *via* electrospray or other devices, can be relatively easily coupled to chromatographic techniques. The first publication of separation, quantification and, structure elucidation *via* MS, was published in 1999.[126] As early as 2003, MS speciation for a range of elements was being reviewed.[127] Sn also had a period of topicality, associated with the development of methods to determine TBT and associated species.

Interest in As is in part due to the wide range of As species toxicity. However, a more tragic reason is that many of the years of *JAAS* have overlapped with the catastrophic As contamination of drinking water in parts of India and Bangladesh. Papers reporting this appeared in the 1996 ASU, Chakraborti and colleagues (95/3698) reporting the "districts affected have an area of 34000 km² and hold a population of 30 million people". Sadly, reports have continued to the present day.

Progress with analytical techniques

During the last 25 years there have been many instrumental developments—the slotted tube atom retarder for AAS, transversely heated ETAAS, integrated platforms, and portable XRF, but possibly the two most important and enduring for food analysis have been the growth of inorganic mass spectrometry and advances in computing power. The latter has lead to improved data manipulation and diagnostics, the former to multielement and isotopic analysis. The first applications of ICP-MS were reported in the 1989 ASU.[112] Beauchemin *et al.* determined 13 trace elements in marine biological RMs and, of considerable future significance, Dean *et al.* determined Pb in milk powder, including the Pb isotope ratios. The potential of combining elemental data with computing power started to become apparent in the 1991 ASU when the first characterisation studies were reported. Favretto *et al.* used principal component analysis to classify polluted and unpolluted mussels. Fruit juices were investigated with regard to the differences in method of processing and in the country of origin. Similarly, analysis of some 50 inorganic components of wine by ICP-AES allowed grape type and the origin of wines to be defined and assisted in helping to assign a vintage year. The approach helped both authenticate and detect adulteration of high value food and beverages. Schwartz and Hecking determined the geographic origin of orange juice, pistachio and macadamia nuts and Martin *et al.* reported multivariate analysis and chemometric approaches to discriminate between Arabica and Robusta coffee varieties.[128] Continued development of MS instruments has maintained their dominant position in many applications. The 1999 ASU[129] notes "that more laboratories now have double focusing magnetic sector ICP-MS." Other relevant developments have included coupling of ETV and LA to ICP-MS, which has lead to further interest in solid analysis, and collision cells for reducing polyatomic interferences. The sensitivity and selectivity of MS techniques has accelerated the demise of others and in recent years, reports featuring DCP, MIP, NAA and SIMS are virtually non-existent. However, despite predictions of its demise, AAS has continued in its role as analytical workhorse. It is currently used to measure Na, due to the interest in the link between dietary salt and hypertension.

Applications

Over 25 years some of the more interesting and/or unusual applications include comparisons of organic and conventionally reared food,[130] the potential to utilise genetically modified plants for phytoremediation,[131] As, Cd and Pb contamination of 80 year old cherry preserves, the nutritional status of penguin liver and kidney,[132] risks associated with the use of lead shot in the slaughter of poultry,[133] Si contamination of human milk from silicone implants,[134] Cu, Fe and Zn content of the dangerous sounding Venezuelan beverage "Cocuy de Penca Firewater",[135] evaluation of the risks from both Pb and the ethanol in illegal moonshine[136] and, finally, well water from Japan which appeared to have been contaminated with residues from chemical warfare agents.[137]

Industrial Analysis

Although "Industrial Analysis" as a title for an ASU review first appeared in 1989, the review was based on a similar range of topics presented in previous ASU publications. It is noticeable that many of the overall topics of interest have remained the same over the 25 year period of ASU publications, with only changes of emphasis on specific analytes or occasionally a subtle change of the focus of the study. For instance, what was, initially, used as a simple quality control technique to determine the overall composition of a sample or the concentration of contaminants, has increasingly found a second function of trying to elucidate mechanistic aspects of processes, *e.g.*, how a particular catalyst works or why one semiconductor works better than another. It is also noticeable that it is becoming increasingly difficult to segregate individual topic sections, since many materials could equally be classed in more than one category. An example includes CERMETS, which are composites of a ceramic and a metal that may be used in the electronics industry. Such samples could easily be discussed in any one (or more) of these sections.

There have been many advances over the period with the use of hand-held or portable devices proving invaluable to the industrial analytical chemist. Monitoring samples at the production line is far more cost effective than taking samples to a laboratory

and then performing analyses off-line. This is because analysis at the production line enables faulty samples to be identified rapidly and remedial action taken almost immediately. The alternative is to take sub-samples from a batch, transport them to a laboratory, complete an analysis and then discovering that the entire batch of samples has the same fault. Savings in terms of both time and money are therefore obtainable using this new style of instrumentation. Instrumentation such as the portable XRF or LIBS devices are therefore extremely useful additions to an analyst's arsenal.

The relatively new technique of LIBS, although in use in the 1980s, has become a very popular choice of analytical technique in recent years. As well as being relatively non-destructive, making it an ideal choice for precious, historical or archaeological samples, it may also be used to obtain both molecular and atomic information. The technique also has the advantage that it may be used in a stand-off fashion enabling the rapid identification of plastic materials or for the identification of explosives from a safe distance.[138]

The other area in which interest has increased is that of chemometric analysis. Many years ago, chemometrics were used either to "correct" the data when the "wrong answer" was obtained or to try and optimise the operating conditions. Since then, far more powerful packages have been developed that enable the more rapid optimisation of experimental protocols as well as obtaining the maximum amount of information from the experimental data. Using software packages such as Principle Components Analysis, it is possible to characterise groupings of elements in samples and this has enabled archaeologists to determine the origin of ceramics and glasses, and hence potential trade-routes or to identify different manufacturing techniques.[139] The same approach is used in the forensic science industry to differentiate between different glasses or different gunshot residues.

There have been changes in use of instrumentation. Arc/spark technologies, commonplace 20–30 years ago especially in the ferrous metals industry, are now very little use for research. They have been replaced by LIBS, glow discharge and even laser ablation. This latter sample introduction system has been increasing in popularity recently because of the advent of shorter duration laser pulses (nanosecond or even femtosecond) that lead to improved sampling. Shaheen and co-workers recently used such a sampling system to determine a total of 63 major, minor and trace elements that ranged in mass from Li up to U in the materials NIST 610, 612 and 614, as well as some USGS materials.[140] Using Ca-43 as an internal standard and the NIST 612 as the external calibrant, the researchers managed to correct for matrix effects, drift and the amount of sample ablated. Accurate data were obtained (agreement to within 10% of certified or previously published data), with a precision of better than 10% RSD for most elements. Fractionation for most elements was found to be minimal. This compares somewhat favourably with the problems of LA sample introduction discussed in a review by Darke and Tyson from 1993 that included the calibration and standardization of the analyses.[141] Certainly, in the 1980s and 1990s it was concluded that calibration should be achieved using materials as closely matched to the samples as possible. If this was not possible, then the results could usually be classed, at best, as semi-quantitative. The advances in laser

technology have also decreased the crater (*i.e.*, the damage). Again, this would be advantageous for many sample types.

From the individual sample standpoint, there have been several new sample types that need to be reviewed. Over the last few years, nano-technology has expanded hugely, with nano-particles being used for things as diverse as catalysts, sunscreen lotions, delivery vehicles for drugs, and electronics. Similarly, the analysis and depth-profiling of thin films has also increased in recent years. The analysis of surfaces has traditionally used techniques such as the various forms of electron microscopy and SIMS. However, nowadays there are several variants of SIMS as well as numerous versions of XRF (micro-XRF, glancing incident XRF (GIXRF)[142] and grazing exit micro XRF (GE-MXRF)[143] that also fulfil this role. In addition, other X-ray based techniques, such as angle resolved X-ray photoelectron spectroscopy (ARXPS), near-edge X-ray absorption fine structure (NEXAFS) and TXRF have also found usage. Depth-profiling may be achieved by an assortment of techniques, including laser ablation or glow discharge followed by atomic spectrometric measurement, SIMS, ToF-SIMS and secondary neutral mass spectrometry (SNMS). The ever-decreasing size of semiconductor components has pushed SIMS to unprecedented degrees of depth resolution. The needs of the semiconductor industry are the main driving force behind the commercial development of instrumentation with lower LODs.

The analysis of petroleum products and fuels has remained an important area of research, even though there has been a change of emphasis in some of the analytes determined. In the 1980s, many cars still ran on leaded fuel and hence the determination of Pb in gasoline was common, often with relatively simple AAS-instrumentation. Although the determination of metals is still commonplace for these sample types, more sensitive instrumentation is required. The analyte under most scrutiny at present is S. There has been a desire to decrease the amount of this element in fuels for many years and so increasingly low LODs are required to be able to determine it accurately. It is also worth noting that the determination of S in diesel can be used for forensic purposes. Tax-free diesel contains the dye coumarin, which can be removed using sulfuric acid. The S to C ratio, determined by GC-AED can show if there has been illegal removal of the dye from the diesel.[144]

The determination of wear metals in lubricating oils continues to be popular. The ASU review from 1991 identified the problem of particle sizes greater than a few micrometres not travelling from the nebuliser to the plasma during ICP analysis. Hence, unless steps to counter this were taken, inaccurate results were obtained. It is interesting to note that in the most recent Industrial ASU, there was a report of a comparison of different sample preparation methods for the analysis of lubricating oils.[145] There are now assorted "alternative" fuels, such as gasohols and biodiesels to be analysed. The poisoning of catalytic converters by P from oil additives such as zinc dialkyldithiophosphate (ZDDP), must be monitored.

The subject of organic materials has diversified over the years. Materials now included in this section include leather, paper, paints, drugs and various others as well as the traditional organic chemicals and solvents. The introduction of organic solvents to plasma-based instrumentation was problematic for many years. This was because the increased solvent vapour loading tended to

extinguish the plasma. Modern instruments cope with organic solvents far more readily. Many ICP-OES instruments can handle 80–100% methanol, whereas previously, 30–50% was the limit. Modern ICP-MS instruments may also cope with the solvents more readily, but often the addition of oxygen or air to prevent soot deposition on sample interface cones and/or the lens stack is still required. The introduction of solvents is facilitated further by specialised nebuliser and spray chamber assemblies that may be chilled to decrease the solvent loading and may also have a very low sample uptake rate. Since modern instruments tend to have better sensitivity and better stability, many organic solvents may be analysed directly. Previously, it was often necessary to perform lengthy preconcentration/matrix elimination protocols, which tended to use far more of the sample. Atomic spectrometric analysis of drugs has moved on from simple quality control measures, although this is performed as a matter of routine. This is one of the areas where the application of atomic spectrometry can yield useful information. As an example, high resolution ICP-MS has found usage for the detection of counterfeit drugs.[146] The development of high resolution ICP-mass spectrometry instruments has therefore aided analytical chemists, because not only do they determine analytes with fewer interferences, the multi-collector instruments have sufficiently good precision on the isotopic ratio measurements to differentiate sources of materials.

The inorganic and acids section of the review continues to discuss inorganic chemicals, but also encompasses materials such as cements and concretes, new matrix modifiers used for ETAAS and the production of relevant certified or standard reference materials.

The nuclear industry has continued to be a keen user of atomic spectrometric instrumentation. This may be for something as simple as measuring the purity of the yellow cake ore through to measuring environmental contaminants, *e.g.*, from the Palomares or Thule incidents. More recently, the determination of depleted U in the environment or in clinical samples has become a popular analysis. The topic of nuclear forensics is also increasing in research popularity as scientists strive to identify the origin of nuclear isotopes. For example, Mayer and co-workers[147] discussed how nuclear forensics provides clues on the origin and intended use of nuclear or other radioactive material involved in illicit incidents. They also provide a brief description of the nuclear forensic methodology and describe in detail the challenges associated with age determination of plutonium materials. The nuclear analyst is also assisted by some of the lesser used atomic spectrometric techniques, such as resonance ionization mass spectrometry (RIMS), which has been used since the mid 1980s for determining Pu isotopic information, accelerator mass spectrometry (measuring Pu isotopes since the 1990s) and thermal ionization mass spectrometry (TIMS) that has been measuring nuclear materials for several decades. The use of magnetic sector ICP-MS instrumentation has also been increasing in recent years, presumably because of the relative rapidity compared with some other techniques.

Instrumental development

A good place to start with a retrospective of instrumental developments is to look back at what the state-of-the-art was twenty five years ago, as this summary from the first 'Instrumentation' ASU[148] illustrates:

'The ASU review in this issue describes the progress made in the last 12 months in the development of instrumentation for atomic spectroscopy. There has been considerable interest in the use of echelle spectrometers in ICP-OES to provide sufficiently high resolution to alleviate the worst effects of spectral interferences. One of the most significant advances in the area of high-resolution spectroscopy has been the application of Fourier transform spectrometers in ICP-OES since this approach also provides the analyst with information from the entire spectrum. Inductively coupled plasma mass spectrometry is clearly becoming established as a trace analysis technique. Consequently, there has been a more realistic appraisal of the advantages and limitations of the technique with respect to interference effects, although it is evident that the optimum instrumental configuration has yet to be established. Lasers have featured prominently as light sources for AFS and have been used with flame, ICP and electrothermal atomisers for extremely sensitive measurement of a range of elements. Laser ablation has attracted considerable attention as an alternative method of sample introduction to the ICP, as has electrothermal vaporisation, and consequently spectrometers have been modified to accommodate the transient signals thus produced. In AAS, there has been increasing use of continuum light sources which allow the possibility of simultaneous multielement analysis. The development of constant temperature type electrothermal atomisers continues to be an area of substantial activity, but no such system has yet been introduced on a commercial basis. The enormous impact of microcomputers on all aspects of instrumentation for atomic spectroscopy hardly needs to be highlighted, and considerable research effort is being expended in this area, particularly by instrument manufacturers.'

John Marshall, 1986

Now compare this with the latest summary from the latest ASU, which relates to instrumental developments:[149]

This is the second iteration of this review covering developments in 'Atomic Spectrometry'. It covers atomic emission, absorption, fluorescence and mass spectrometry, but excludes material on speciation and coupled techniques, which is included in a separate review. It should be read in conjunction with the other related reviews in the series. A critical approach to the selection of material has been adopted, with only novel developments in instrumentation, techniques and methodology being included. Most techniques have reached a level of maturity that precludes the emergence of 'stand-out' new developments. It is noteworthy that there are very few novel publications in sections on chemometrics, fundamental studies, or direct solids analysis. Sample introduction continues to generate a steady stream of research outputs, but these are mainly derivative and focused on applications. The advent of SF-ICP-MS is becoming widely adopted as a reliable technique for IR measurements, so this had been the main growth area. Likewise, the use of femtosecond UV lasers has now entered the mainstream for geological applications.

E. Hywel Evans, 2010

Although all of the threads of instrumental development can be followed in the ASUs, the highlights are as follows:

Inductively coupled plasma atomic emission spectrometry was well established 25 years ago, and echelle spectrometers were already being investigated as a means of getting higher resolution;

however, their full utility would not be realised until the advent of charge transfer device (CTD) detectors[150,151] that made possible simultaneous measurement of a large number of analytical lines, with the added benefits of monitoring multiple analytes in transient signals and make use of much more data for chemometric applications. It is worth noting that, probably as a result of the aforementioned developments, Fourier transform spectrometers mentioned in the 1986 ASU never really took off. Axial viewing of the plasma in ICP-AES, while studied as early as 1979,[152] waited another sixteen years to enter the mainstream, and now most instrument manufacturers offer both radial and axial viewing options.

Inductively coupled plasma mass spectrometry had burst onto the scene only a few years prior to the first publication of *JAAS*,[153–159] but it was already becoming an established technique. Problems with interferences would eventually be largely solved by instrumental developments such as cool plasmas,[160] collision/reaction cells[161,162] and, for the more well-heeled, sector field, SF-ICP-MS.[165] Indeed, SF-ICP-MS is now used extensively for quick and precise isotope ratio measurements, and is rapidly replacing thermal ionisation mass spectrometry (TIMS) as the method of choice in geological applications.[164] Other types of mass analyser, such as time-of-flight (TOF),[165] and ion traps[166] have not become firmly established. Recent developments in array detectors may have further applications with SF-ICP-MS instruments.[167]

Alternative plasma sources, in particular microwave induced plasmas, have a long history of use in conjunction with gas chromatography and atomic emission detection.[168–171] Subsequently they have been used as ion sources for mass spectrometry,[172,173] in particular for use as chromatographic detectors for speciation analysis.[174]

Accelerator mass spectrometry was used for elemental analysis as far back as 1989[175] and has recently become popular for isotopic analysis of a limited number of elements, principally because the size and complexity of such instruments has been much reduced. However, it remains to be seen whether this technique will eventually enter the mainstream.

Direct solids analysis using glow discharge, arc and spark atomic emission spectrometry had been around for a long while prior to 1986, however, the reintroduction of radio-frequency (RF) GD-MS[176] made possible the direct analysis of non-conducting samples without the need for mixing with a conducting medium. Electrothermal vaporization and laser ablation are mentioned in 1986 as alternative methods of sample introduction into the ICP.[177,178] Of these, only the latter has really carved a place for itself, particularly coupled with ICP-MS for geological applications, and more so since the advent of the new generation of UV lasers.[179]

LIBS has seen rapid growth over the last decade or so. In LIBS, a laser is used as an energy source and focused in a high-energy pulse on to a small area to ablate (vaporize) a volume of sample (micro sampling). The laser energy may also be used to generate a plasma and excite the emission spectrum of analyte atoms. Recently, the commercial availability of diode, nano-second, and femtosecond lasers have allowed rapid development of this area. The use of lasers as excitation sources has not seen rapid growth; techniques such as laser induced fluorescence, cavity ringdown spectroscopy, laser atomic absorption

spectrometry, and laser enhanced ionisation still occupying niche areas. The potential promise of low cost laser excitation using tuneable diode lasers has yet to be realised in routine application.

Speciation analysis, utilizing a separation step (chromatographic or otherwise) coupled with atomic absorption, emission, fluorescence and mass spectrometry came on the scene in the 1980s[180,181] and now warrants its own ASU review![182] The coupling of liquid chromatography (LC) with ICP-MS has been a major success story, particularly for the speciation of As, Hg, Pb Se, and Sn, in environmental samples and, more recently, for metallomic studies, a field which now has a dedicated journal. The applications in metallomics have been driven by the low limits of detection, quantification of multiple species, and the ability to undertake isotope tracer studies. The other success has been gas chromatography (GC) coupled with MIP-AES, particularly in the petrochemical industry, largely due to the success of the GC-AED instrument.

Sample introduction methods have remained fairly unchanged, with variations on the pneumatic nebuliser still predominating. Vapour generation has expanded to include more elements than the traditional metalloids,[183] and has been successfully coupled with AFS to provide a relatively simple and robust detector for on-line and lab-based determinations of selected elements.[184] Flow injection analysis is now routinely used as a method of sample introduction and lends itself to on-line sample preparation methods utilising ion exchange and chelating columns used for pre-concentration or matrix removal. Microwave digestion is now commonly used for sample dissolution.

In conclusion, it seems that the majority of advances in instrumentation had their roots at the very inception of *JAAS* and ASU, the most universally significant being the advent of SF-ICP-MS and array detectors for ICP-AES.

X-Ray fluorescence (and MS)

Andrew Ellis writes about his ASU Topic Group *modus operandi*:

The first XRF ASU in 1988 was a combined review with Mass Spectrometry in order to ensure there was enough material of interest to readers. The topic group editor for this, the first new review to be included in ASU, was Allan Ure with John Williams and myself as the new writers. John was in the vanguard of ICP-MS and I was asked to take care of the XRF section of this combined Update. As novice writers, we were fortunate to have the talented, experienced leadership of Allan, who took care of the core MS section. Allan's knowledge of his subject was, of course, profound, as was his knowledge of every detail of the Writer's Handbook to which he adhered with an almost religious fervour—or at least it felt like that to John and me. Our initial attempts to construct incisive, succinct technical commentary with the necessary structure and terminology (not forgetting that all-important key phrase at the start of the paragraph) were greeted with little enthusiasm by our mentor. Little by little though we learned the craft as each sentence and paragraph was painstakingly demolished and reconstructed into a proper ASU. For the second review, Allan was replaced as the writer of the core MS section by Jeff Bacon, a colleague of Allan's at the Macaulay Institute, whom Allan had recruited. In order to ensure we continued on the straight and narrow literary track, Allan remained as the referee for the MS/XRF ASU and

continued his tuition that year as we prepared the material. The Topic Group meeting that second year was in a corridor at the side of the bar at the BNASS meeting and the three new writers have clear in our memory the chink of glasses from the surroundings while we sat in a huddle with Allan, each having their own paragraphs meticulously and heavily adjusted by the master. The meeting reconvened the next day after a late, challenging and fairly dry first session but by the end of the second session we had learned much and would go on to remember the rigour and dedication that was expected of an ASU writer.

Although Allan did not join us for subsequent Topic Group meetings, we adopted the same rigour and process of meeting for as long as it took to dissemble and re-craft each other's sections until we had a consistent article of which we could be proud and, we hoped, so could our Referee. The process took 2 days in those early years and was made the more interesting for two years as we met in the very creative atmosphere of the groaning watermill that John lived in near Epsom. The distribution of the source material in the early years is shown in Table 2.

Although conference papers have now gone from our repertoire, without them the ICP-MS part of the review would have been very thin in the first two years! As Topic Group editor, I had the "advantage", as it was described by the General Editor, of being able to see ALL the references that went into the ASU system, which numbered some thousands at the time. Every month a plain brown envelope would arrive, brim full of sheets of CA Selects, Analytical Abstracts pages (typically 12 to a page and completely randomized) and other papers. The XRF, Inorganic MS and ICP-MS items were then cut out by hand, put in separate piles and made ready for the writing cycle. Any attempt to carry out this cutting and sorting operation with a window open or in the presence of my 4 year old daughter resulted in the inevitable but tedious game of "hunt the abstracts". Further removal of duplicates and photocopying for the writing team made the whole process particularly onerous and very difficult to transfer to others once they heard what was involved! At least with Web of Science and the current process, the Topic Group Editor can open a window when working and does not develop "abstract cutter's thumb"! By 1996 the combined review had become too big and was split into separate reviews. Recently, as atomic MS has matured, relevant material is now covered in the Instrumentation ASU and in the Speciation ASU.

The XRF technique has developed to analyse more elements at lower concentration levels from an increasing range of configurations to suit a wide budget range. Whilst XRF is known as a "non-destructive" technique, analysts have reported a plethora of methods to ensure that the sample is representative and prepare an aliquot for analysis. With maturity, it is inevitable that the application sections of our XRF Review have expanded. Sophisticated data handling programmes offered by the instrument manufacturers take the technique to routine laboratory analysts, who may not experience the excitement felt by earlier workers.

In the area of instrumentation, EDXRF technologies have seen dramatic changes over the past 25 years, particularly in the detection systems used. In 1985, most EDXRF systems were floor-standing or needed substantial benches and the detector was a bulky lithium-drifted Si(Li) detector that required cooling with liquid nitrogen (LN). Such detectors, equipped with a Dewar of 7 to 25 litre capacity, required regular topping up with LN, which ranged from a chore, through a hazard, to passing entertainment when a new practitioner poured LN onto a benchtop unit at shoulder height and received a refreshing chill to the lower body. Start-up times were a matter of hours and failure to keep a system cool often resulted in an expensive and lengthy repair at a distant facility. Those detectors were, however, very good spectroscopy devices with good X-ray stopping power, energy resolution as low as 140 eV for premium systems at low count rates (<5 kcps) but often in the 170 to 200 eV range for practical purposes. Nowadays, the Peltier-cooled Si PIN or Si Drift detector (SDD) is most commonly used. Such detectors are the size of a matchbox, require only electrical power and are ready to use in a couple of minutes. In addition to these huge strides in operational simplicity, the modern SDD offers an excellent energy resolution of <130 eV energy resolution at count rates of at least 50 kcps and is even now to be found in the latest models of handheld EDXRF system.

Excitation in EDXRF has also seen substantial changes and where most compact systems of 25 years ago used radioisotope sources for excitation; most systems nowadays employ compact, low-power X-ray tubes that require no liquid cooling and can operate at voltages up to 50 kV. The latest hand held (HHXRF) systems are equipped with very compact, light and frugal X-ray sources that are still able to deliver 50 kV and 50 μA. Equally impressive on the benchtop has been the deployment of polarized X-ray excitation and Cartesian geometry using X-ray sources delivering only 50 W of beam power. Such systems yield XRF spectra with extremely low background and have improved EDXRF detection limits by at least one order of magnitude for several key applications. In particular, detection limits for S in road fuels of <1 ppm are the norm and environmental solid samples such as soils and plastics can be measured with straightforward sample preparation and detection limits in the sub-ppm range for many important analytes.

As with consumer computing systems, the strides in computer power have been truly staggering in the past quarter century. In the 1980's laboratory computers were necessary for EDXRF systems, particularly, and those systems were typically using 8 inch floppy disks for data storage (128 Kb) and CPU memory of perhaps 32 Kb. Needless to say, the analytical software was limited and the user interfaces non-existent or challenging. Since that time, desktop computing power has grown massively, as expected from Moore's Law, and the use of Fundamental Parameter (FP) computations has transformed XRF analytical software. Massive on-line disk storage, fast CPU's and staggering amounts of RAM have brought real-time FP analysis to most modern XRF systems and this capability is particularly valuable for the analysis of unknown samples for which Reference Materials and calibration samples are unavailable.

Table 2

Year	1988	1989	1990	1991	1992
Total Papers	235	502	779	393	976
%Conf	41%	15%	7%	15%	3%
%MS	22%	42%	53%	44%	49%
%ICP-MS	44%	15%	9%	15%	14%
%XRF	34%	43%	39%	41%	36%

When you combine all of the above massive strides, we now have available to us a 2 kg handheld EDXRF system with a 50 kV X-ray tube, a 130 eV SDD X-ray detector that performs a measurement and FP calculations for complex samples in a total time of less than 5 s. Such performance represents a very considerable advance from that of the days when steel samples were sent to the lab for Mo and Co determinations whose results "should be back in a week"!

Twenty-five years ago, hand-held XRF instrumentation was at a relatively early stage of development and generally reliant on instrumentation that incorporated radioactive excitation sources. Indeed, rather than hand-held, some forms of instrumentation can best be described as 'luggable'. The present author well recalls the realisation for the need to incorporate a small sack trolley as an essential hand held XRF accessory for the *in situ* measurements of rock outcrops in the field. In addition, early forms of instrumentation sometimes had limited computing power and relied on pre-analysed site-specific calibration samples to overcome limited matrix correction computing capability. This is an area where instrumentation has been revolutionised by developments in the miniaturisation in electronic circuitry, the consequential substantial enhancement in computing power and especially the development of the low power miniature X-ray tube. These developments justify a progression in descriptive terminology from 'luggable' to 'portable' to 'hand-held' to 'point and analyse'. The growth of HHXRF has indeed been staggering in the past decade, with several thousand units per year being sold in recent years. One application area that has seen a tremendous bulge in the past decade and for which HHXRF has been widely deployed, has been that of RoHS determinations in all types of electronics. Despite the absence of any standard analytical methods, the number of EDXRF systems sold into this application segment is far in excess of 10,000 in the period 2003–2009.

One of the remarkable aspects of the use of XRF in geological applications is the way the technique has sustained its role in the routine analysis of silicate rocks usually for geochemical research applications over the last 25 years, despite the sustained onslaught and implementation of ICP-MS techniques. Although the advantages in sensitivity and detection limits that have led to the widespread use of ICP-MS for the determination of a wide range of trace elements, XRF retains a distinctive role in the routine measurement of the major elements and a range of trace elements (notably Rb, Sr, Nb, Zr, Y) some of which present challenges to alternative techniques that depend on solution chemistry. The last 25 years has also seen a trend in the increasing use of ED-XRF technologies in geological applications, not least because the development of innovative polarised excitation geometries has significantly boosted trace element detection limit performance.

Twenty five years ago, interest in XRF applications to archaeology and cultural heritage samples was often limited and based on the application of conventional techniques developed originally for the analysis of geological or metallurgical materials. Sometimes, this approach depended on destructive analysis (from the point of view of the need to crush the sample). The widespread adoption of EDXRF over this period significantly extended the range of materials characterised by this technique, in part taking advantage of the lower potential for low power X-ray tubes so not damaging delicate samples. These studies were often still dependent on the need to take the sample to the XRF laboratory, a significant restriction in many applications. Over the last 25 years, however, a number of pioneering laboratories started to take the XRF to the artefact, sometimes on the basis of the building of bespoke instrumentation from individual components. However, we are now seeing a quiet revolution in the widespread use of true handheld XRF instrumentation as a must-have component in the investigation of a huge range of artefact types. Sometimes results are used in provenancing studies, to detect forgeries, and to understand manufacturing/fabrication processes. This revolution in handheld XRF is leading to the application to a much wider range of sample types, where the advantages of field analysis and the instant availability of data can be exploited. Examples include lead in paint, contaminated soil, metal sorting and recycling, health and safety, mining and mineral exploration. Often these applications are backed up by the need to collect and submit samples for conventional laboratory analysis, although in a much more informed and efficient way than if the hand-held XRF investigator had to rely on a conventional sampling and analysis programme.

Advances in X-ray optics have given the analyst smaller beams with higher spatial resolution. With the number of Synchrotrons increasing worldwide, SR systems coupled to μ-XRF configurations now benefit from beam sizes in the range below 1 μm and down to 10 nm. New detectors enable the processing of higher count rates thereby providing lower detection limits. The combination of various techniques at one beamline now bestows comprehensive characterization of samples. SR in combination with X-ray absorption spectroscopy has transformed chemical speciation from the adventurous exploits of the few to valuable data for the many.

Total reflection XRF (TXRF) has proved to be a boom for the semiconductor industry where wafer surface characterisation is commonplace. In recent years TXRF instrumentation now includes portable systems that extend applications out into the field. Grazing incidence systems (GI-XRF) enable comprehensive depth profiling and thin film characterization whereas the grazing emission (GE-XRF) combination offers the user spatial resolution and nanometre depth information. The powerful combination of TXRF using SR as the excitation source offers lower detection limits that have proved especially interesting in aerosol analysis. The SR-TXRF-XANES configuration offers direct sampling in a short time on only small amounts of sample and gives new insights for environmental applications. The literature also reflects the increasing use of imaging techniques that provide either 2D or 3D mapping facilities for a range of applications.

However XRF innovation and developments continue with *in vivo* bone measurements and bio-monitoring featuring in the literature. Certified reference materials (CRMs), quality managements systems and efforts to demonstrate traceability have become essential tools in the analyst's armoury. Societal interests include rapid throughput screening for combinatorial materials, the development of new materials and products exploiting nanotechnology and support for those tested by increasingly stringent environmental and industrial legislation.

Elemental speciation

Determination of the different individual chemical species that comprise the total concentration of a given metal(loid) in

a sample has collectively been referred to as: elemental; chemical; or metal speciation.[185] It is defined by IUPAC[186] as: the "distribution of an element amongst defined chemical species in a system" and speciation analysis as the "analytical activities of identifying and/or measuring the quantities of one or more individual chemical species in a sample". In practice, one of the most important characteristics of speciation analysis stems from the fact that the total concentration of the metal(loid) being studied can be measured very accurately using well validated instrumental methods. This gives a very powerful means to determine whether the analytical approach being used is providing reliable results, because the combined concentration of all the individual species in an extract of the sample must be equivalent to the total concentration of the element determined in that extract. Any significant difference between the two values being indicative of a systematic error in the analysis.

Speciation analysis was an established technique 25 years ago.[187] The hyphenation of chromatography to an element-specific detector (ESD) had been developed and applied to the measurement of the chemical species of As, Cr, Hg, Pb, Se and Sn. The coupling of gas chromatography (GC) and high performance liquid chromatography (HPLC) to AAS, FPD, ICP and ICP-MS had all been demonstrated. Identification of the elemental species relied on the availability of a characterised and chemically pure standard, so that retention time matching, under different chromatographic conditions, could be used.

Methods based on atomic spectrometry

Investigation of metal(loid) speciation using the hyphenation of GC[188] or HPLC[189] to an ESD was first carried out in the late 1970s and early 1980s. Refinement of the approach over time has lead to other separation methods, such as CE and supercritical fluid chromatography (SFC) being coupled to various different detectors, most notably ICP-MS. Early reviews of the use of different separation approaches coupled to ESD or MS included the use of GC[190] HPLC[191] and SFC.[192] Element-specific detectors such as ICP-MS or a technique based on AAS or AFS are used in speciation analysis because of their: analyte specificity; provision of quantitative data using elemental standards; and their potential to provide suitable LODs for environmental and biological sample analysis. In practice however, AAS is generally not sensitive enough without vapour generation to be used for real samples and AFS, whilst offering suitable LODs for speciation studies, is limited to those elements which form stable hydrides or elemental species. ICP-MS provides the most versatile detection system for elemental speciation analysis because it can be coupled to numerous different chromatography techniques, delivers suitable detection limits and offers multi-elemental and isotopic analysis.

Speciation analysis by chemical vapour generation

The generation of volatile analyte derivatives as a component of speciation analysis has been extensively and increasingly reported over the past 25 years. There are essentially two major themes: (1) different chemical species can be determined based on changes in the conditions of the vapour generation reaction, and (2) CVG is the interface between a separation stage and a measurement stage. A minor theme is based on the conversion of the various analyte species to volatile derivatives followed by separation of the derivatives prior to measurement. Twenty–five years ago, interest in CVG was in full swing with publications running at about 40 per year eventually rising to about 80 per year by about 1997. Speciation involving CVG is a more recent research activity, at least as evidenced by the appearance of publications with relevant keywords in the title, with publications only rising above 1 or 2 per year up to 1992 to the present rate of about 23 per year. Though such trends are often difficult to discern, it appears that the rate of publications in both areas (CVG and speciation with CVG) has levelled off, or even in the case of CVG, declined in the last 5–6 years.

The first strategy outlined above is really only applicable to simple mixtures, such as those containing (1) inorganic and methylated arsenicals, or (2) inorganic and methylmercury. As many species of the elements in question do not react with any known reagent to form a volatile derivative, their presence can only deduced by subtracting the sum of the concentration of the element due to the presence of the various vapour-forming species from the total element concentration. While not a very satisfactory speciation strategy, many researchers sometimes justify the approach on the basis that, for example in the case of arsenic, only the toxic forms are "borohydride active."

Hydride transfer from borohydride is not the only way in which volatile derivatives may be formed: there is a continued, but low-level, interest in electrochemical generation. Again, speciation based on reaction conditions is possible, but seems even less useful than the various homogeneous reaction possibilities.

Given the uncertainties over the nature of the generation of volatile derivatives, the most promising aspect of CVG in speciation analysis is as the interface between a liquid chromatographic separation and an element-specific detector. There are two challenges for such post-column reaction schemes: (1) the conversion of eluted species to a common precursor and (2) the additional broadening of the peaks. These problems would appear to be tractable for HPLC separations, but rather intractable in the case of capillary electrophoresis. The first challenge is usually approached by oxidative degradation involving one or more of the following: a strong oxidant, heat, UV light, ultrasound, or microwave radiation. The second challenge is approached by exploiting the hydrodynamics arising from gas-segmentation and tight coiling. Such an interface can go a long way to off-setting the inherent dilution of the HPLC separation by increasing the useful analyte mass flux. The benefits of AFS detection for arsenic speciation probably stems from the performance, comparable to that of HPLC-ICP-MS, which may be obtained from HPLC-HG-AFS.

The future of CVG in speciation analysis lies with further developments in interfacing high performance separation with element-specific detection. The recent reports of CVG when analyte solutions, containing low molecular-weight carboxylic acids, are irradiated with UV light seem particularly promising in this regard.

The role of molecular mass spectrometry

Although hyphenated ICP-MS techniques have dominated the area of elemental speciation, it is recognised that the approach

has limitations,[193] one of the main being that it fails to provide direct structural information for the characterisation of novel species. Thus, molecular mass spectrometric techniques, which were used with great success for characterization of organic molecules and biomolecules, were from the late 80's explored for their potential in speciation analyses. Techniques including fast-atom bombardment, thermospray and desorption chemical ionization MS have been used with varying degrees of success for speciation analysis of non-volatile species.[194] Electrospray ionization MS (ESMS) was shown to be superior to other ionization sources due to its direct and efficient generation of gas-phase ions of inorganic, organometallic and organometalloid compounds,[195] large biomolecules and non-covalent biomolecular complexes; thus allowing for the study of non-covalent metal–biomolecule interactions.[196] Since the mid 90's ESMS has been applied with great success for element speciation analyses within the research areas of environmental chemistry, health and nutrition and bio-inorganic chemistry[197] and has contributed to the identification and characterisation of a large number of metallothioneins, phytochelatins and anthropogenic contaminants[198] and other elemental species in biochemistry.[199]

The use of the different operational modes of ESMS: elemental mode (source collision-induced dissociation (SCID)), molecular mode (MS of protonated molecule ions) and tandem MS mode (product ion scan of the collision-induced dissociation (CID) products of the protonated molecule ion), are discussed in a review by Chassaigne et al.[199] The speciation strategies involve stand-alone direct infusion ESMS and ESMS coupled with an on-line separation technique, but often ESMS complements an element-specific detector such as ICP-MS,[200] which quantifies the elemental species while ESMS delivers the molecular information. Rosen and Hieftje[197] briefly review ICP-MS and ESMS instrumentation applied to speciation analysis.

Although ESMS suffers from lack of selectivity and sensitivity because of high backgrounds, comparable sensitivity to ICP-MS can be obtained when operated in the selected reaction monitoring (SRM) mode as demonstrated for more than 20 organo-arsenic species.[201] Matrix assisted laser desorption ionization (MALDI) has been applied as an alternative to ESMS for molecular weight determination in situations where matrix effects were deemed to be a problem.[202] However, MALDI has been applied less frequently because its coupling to separation techniques such as HPLC and CE is not as straightforward since the sample must be immobilized and because non-covalent bounds are destroyed due to the use of acidic matrices.[203] The potential of ICP-MS, ESMS, and MALDI-MS for bio-inorganic speciation analysis is compared in a review by Lobinski et al.[203]

Today HPLC-ESMS and tandem MS have been implemented in many laboratories as routine techniques complementary to HPLC-ICP-MS for the confirmation of known species or for the identification of unknown species in solution. A similar complementary role in speciation studies of volatile or derivatised volatile compounds is served by GC-MS. The liquid flow rate regimes of ICP-MS and ESMS are such that little compromise occurs when the two are used simultaneously. Hansen et al.[204] first reported the simultaneous ICP-MS and ESMS detection, by splitting the flow of their LC system post column (1 part into the ICP and 4 parts into the ES). In 1998, Houk[205] declared that the two types of ion source readily can be combined to provide both selective elemental analysis and molecular identification and during the last decade, researchers have developed a "dual source" instrument which combines an ICP source and an ES source with a single time-of-flight mass spectrometer (TOF-MS).[206]

Methods for quantification

Isotope dilution mass spectrometry (IDMS) is regarded as a definitive analytical technique[207] and, provided that certain criteria are met,[208] is ideally suited to speciation analysis. Iodine speciation in natural waters, by two different IDMS approaches, species specific for iodine and iodate and species unspecific for unknown organo-iodine species with detection limits of 0.5–20 and 0.7–1.4 ng ml^{-1} respectively, was undertaken by Heumann et al.[209] The ability of IDMS to overcome matrix effects, as concentrations are determined by isotope ratio measurements rather than total analyte signals, was demonstrated for lead speciation.[210] Conventional external calibration gave an erroneous result whilst the result obtained by species specific HPLC-IDMS was in good agreement with the 'true' value.

One of the key criteria for speciation analysis is that the target analyte remains unaltered during sample preparation and measurement. The use of isotopically labelled compounds highlighted species transformations during mercury,[211–215] chromium[218] and tin[217] sample preparation procedures with strategies developed to either negate or quantify any species transformation that occurred. Subsequently, it was also shown that complete analyte extraction is not necessary for accurate results to be obtained by IDMS[218,219] allowing 'milder' sample preparation techniques to be utilised. Rodríguez-González et al. have published a comprehensive review of IDMS for elemental speciation,[220] with a follow up paper covering advances in elemental speciation by IDMS over the past 5 years.[221]

IDMS is also ideally suited for the calculation of uncertainty budgets and has been used for the certification of various reference materials and for inter laboratory comparisons, particularly involving National Measurement Institutes. These activities have been comprehensively reviewed by Vogl[222] and are also covered in ref. 200 and 201. The question arises as to whether IDMS will become a routine method outside of reference and research laboratories. This is unlikely until there is a greater legislative requirement for elemental speciation measurements.[223]

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J. Anal. At. Spectrom., 2010, **25**, 1546–1566 | 1563

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