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Future of atomic spectrometry for environmental analysis[†]

Invited Lecture

R. E. Sturgeon

Institute for National Measurement Standards, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R9

Environmental analyses for trace metals are currently being driven by three major factors: the demand for more elements at lower concentration levels; the increasing interest in elemental speciation due to the issues of bioavailability and toxicity; and the greater need to minimize contamination and sample work-up as a consequence of enhanced instrumental limits of detection. These three 'tenets' are themselves tempered by the growing cost of analyses which requires reduced sample consumption and waste generation (disposal concerns). Multielemental optical and mass spectrometric techniques coupled to on-line sample preparation and direct solids analysis approaches will play a dominant role in future commercial environmental laboratories. Few, if any, cost effective alternatives are available to conduct inorganic environmental analyses, thereby assuring the continued reliance on atomic spectroscopic techniques. Prediction of specific sources and detection systems likely to be in use is less straight-forward, but it is not inconceivable that new approaches will be fostered by evolutionary rather than revolutionary processes; today's 'research' prototypes will form the basis of tomorrow's work-horse instrumentation. The current state-of-the-art is reviewed and examples of future technologies presented.

Keywords: *Environmental analysis; atomic spectrometry; sample preparation; sample introduction; future*

Global ecological problems have resulted in a growing awareness and interest in the analysis of environmental samples. The impact of the effects of trace elements in the environment on man's health has fostered development of analytical techniques and instrumentation capable of addressing these issues. Concentrations no greater than the parts per million level and, more frequently, parts per billion or less, are of concern in all phases of the environment: air, water, solid earth and the biosphere, and include indigenous metals as well as those derived from anthropogenic activities. Accurate and reliable analytical methods possessing high sensitivity and selectivity, coupled with convenience and economy, applicable to real-world samples, are required. Whereas many elemental pollutants are present in industrial sites and nearby ecosystems at levels so high that monitoring can be easily accommodated with current methodologies, to establish 'baseline' levels of many elements and to attempt to reconstruct the past natural distribution of toxic pollutants on a global scale requires state-of-the-art ultrasensitive techniques possessing detection power at the pg g^{-1} level and below, often with limited sample size.¹ In general, the low background levels in most samples necessitate extreme detection limits while the increased supply of samples urges accelerated throughput. This state can be managed by resorting to automation and use of analytical tech-

niques possessing multielement capabilities. Although numerous instrumental methods of analysis are currently available, measurements undertaken for commercial or regulatory purposes usually need to be made using either specified methods (compliance methodologies) or methods possessing specified characteristics and, as such, qualify as validated analytical procedures. Thus, although one can 'read all about it' in the most recent analytical journals, many high-power analytical techniques currently in research laboratories have not yet made their way into the hands of environmental laboratory personnel. There is a continuing need for method validation so that the reliability of derived data can be clearly demonstrated. This can only be achieved through labourious interlaboratory collaborative studies and the use of well-characterized samples and reference materials.²

Several modern analytical methods have attained the capability of measuring most elements at the ng g^{-1} level or lower. The study of the sources, transport and fate of the elements in the environment has therefore advanced accordingly. Attempts to extend these methods to significantly lower concentration limits are often fraught with problems of sampling and storage, on the one hand, and contamination from handling and reagents on the other. A symbiotic 'see-saw' relationship has evolved between advances in instrumental detection capabilities and sample pretreatment methodology; when method detection limits become bounded by reproducibility of blank measurement or high levels of contamination, new procedures are developed to extract maximum benefit from the instrumentation. Recently, this trend has essentially driven the growth of flow injection methodologies, the minimization and miniaturization of sample handling and pretreatment, and its implementation on-line to the instrument. Complex chemical processing conveniently accomplished on-line often alleviates the need for extensive and costly clean room facilities while permitting information on element speciation to be obtained with ever-smaller subsamples.

During the past decade, increasing attention has been focussed on the elucidation of the various forms of an element present in a sample.³ Metal toxicity is often related to its chemical form and, consequently, simple determination of a total content no longer provides an adequate measure for evaluation of impact on the environment, its bioavailability and toxicity. The separation and quantification of identifiable forms of an element (chemical, physical or morphological) present in a given matrix are crucial from a risk assessment perspective. When coupled to an appropriate separation technique, atomic spectrometric detectors play a major role in this field.

Discussions or musings about the 'future' of atomic spectrometry for environmental analysis must include advances in related technical areas, in addition to those of instrumentation itself. As illustrated in Fig. 1, environmental analysis is characterized by the interplay of at least three domains of activity: sample preparation, sample introduction and instrumentation.

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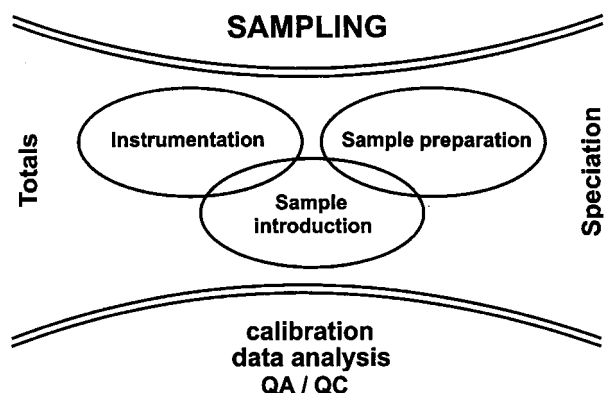


Fig. 1 Domains of activity for environmental analyses.

Additional constituents of this picture include the aspects of calibration, data reduction and analysis and an effective quality assurance (QA)/quality control (QC) program. Sampling (and sample preservation and storage) protocols should also be well-appreciated in the context of environmental analysis. Suffice it to say that, '... unless the complete history of a sample is known with certainty, the analyst is well advised not to spend his time analysing it'.⁴ Although the importance of competent sampling, subsampling, storage and preservation protocols, as well as QA issues, are well-appreciated in the context of environmental analysis, these are not addressed in this article and the reader should consult the appropriate literature on these subjects. As quality aspects are so inextricably interwoven with actual measurements, modern instruments are often supplied with software driven user calibration protocols which support in-house QA programs. Quality control is focussing on completing a task right the first time and verifying that the system of controls (sample receipt, handling, storage, security, chain-of-custody, document control, standards, traceability, calibration protocols, method validation, data review/assessment/rejection and reporting) is being effectively used. Tutorial treatment of these aspects can be found in the excellent reviews by Uriano,⁵ Mesley *et al.*⁶ and Taylor and Stanley.⁷

A cursory examination of current literature⁸ reveals that environmental analyses are primarily driven by three major factors, as summarized in Table 1: the demand for more elements at lower concentration levels; the increasing interest in elemental speciation due to the issues of bioavailability and toxicity; and the greater need to minimize contamination and sample work up as a consequence of enhanced instrumental limits of detection. These three 'tenets' are tempered by the growing cost of analyses, which mandates reduced sample consumption and waste generation (disposal concerns) and, in themselves, form a pronouncement for future activities in the environmental analysis arena. Although one must be careful about making predictions, especially about the future; as they may solicit derision, it is nevertheless the aim of this 'review' to attempt a future perspective of this discipline. Of the several approaches that can be used to project the future,⁹ the easiest is to track current trends and extrapolate them. This is the strategy used here since, in general, developments in instrumentation have been incremental or evolutionary, rather than

Table 1 'The Three Tenets'

More elements sought at lower concentrations
Total element determinations becoming less relevant → speciation
Greater need to minimize contamination as a consequence of enhanced instrumental LODs
Reduced waste production—reagent consumption

revolutionary, with innovative breakthroughs occasionally occurring by exception. Future instrumentation will more likely be driven by need, with effort made to focus on application (of available instrumentation) to specific determinations rather than finding applications for new techniques. Literature cited herein is not intended to be comprehensive, but has been selected with a view to environmental relevance, a pertinent review or seminal topic paper, or for potential application. Apologies are expressed to those whose publications have been overlooked inadvertently, or by choice due to the above constraints.

THE PRESENT

A profusion of instrumental approaches has been brought to bear on environmental analysis problems. Of available atomic spectrometric techniques, these include: flame atomic absorption spectrometry (FAAS), graphite furnace or electrothermal vaporization AAS (GF- or ETAAS), inductively coupled plasma atomic emission (ICP-AES) and mass spectrometries (ICP-MS), X-ray and total reflection X-ray fluorescence techniques (TXRF), atomic fluorescence spectrometry (AFS), microwave-induced plasma source (MIP) AES and MS, laser induced breakdown spectroscopy (LIBS), laser excited atomic fluorescence (LEAFS) and glow discharge (GD, both dc and rf) AES and MS. At the risk of offending a large group of environmental analytical spectroscopists, and to limit coverage to a manageable level, some of the more esoteric but often widely applied instrumental methods not included in this discussion comprise secondary ionization and sputter neutral MS (SIMS and SNMS), laser microprobe (LAMMA) and proton induced X-ray emission (PIXE), extended X-ray absorption fine structure (EXAFS) for solids speciation, accelerator MS (AMS) and neutron activation (NAA and INAA) analysis techniques. The reader is directed to some recent relevant reviews in the areas of NAA and environmental materials,^{10,11} AMS in environmental geoscience,¹² applications of synchrotron X-ray sources¹³ and speciation by EXAFS.¹⁴ Some typical characteristics of the 'core' analytical techniques that comprise the focus of this discussion are summarized in Table 2. With the exceptions of LIBS and LEAFS, currently all are widely utilized in environmental studies but presently no single technique appears to be capable of addressing all analytical needs. Whereas the estimated detection limits presented are often in the ng ml^{-1} range or lower, these data pertain to matrix free solutions containing only the analyte of interest. Real sample matrices may give rise to a plethora of potential problems, often associated with high dissolved solids content, including suppression of sensitivity, increased background levels and spectral interferences. The practical consequence is that, if the effects cannot be remedied by simple dilution, matrix separation and concentration of the analyte(s) becomes necessary. This is often the case, in any event, as many samples from uncontaminated sources contain analytes of interest at concentration levels which challenge the best instrumental limits of detection. Sample preparation techniques range from little or none, for direct analysis of aerosols and solids [by ETV,^{15,16} XRF,¹⁷⁻¹⁹ continuous emission monitoring (CEM^{20,21})] or simple aspiration and dispensing of liquids into atomic spectrometric sources, to elementary dilution of liquids with ultrapure water or application of digestion,²²⁻²⁵ dissolution,²⁶⁻²⁸ separation/concentration²⁹⁻³¹ and derivatization³²⁻³⁶ schemes for treating liquid and solid matrices. Sample introduction techniques for aerosols and vapours include direct presentation to the instrument (CEM,^{20,21} XRF¹⁷⁻¹⁹ and ETV^{15,16}) or transfer of the analytes to a solution (following elution from adsorbents or digestion/dissolution of filter media) for introduction *via* a number of avenues, comprising ETV,^{37,38} thermospray,^{39,40}

Table 2 Instrumental techniques

Technique	Detection limit (ppb)	Multielement	Selectivity	Matrix interferences	Maximum matrix concentration (%)	Precision (%)	Accuracy
ETAAS	10 ⁻² -1	(No)	Good	Small	≤100	0.5-5	Good
FAAS	1-10 ³	(No)	Good	Small	1-10	0.1-1	Good
ICP-AES	10 ⁻² -10	Yes	Moderate	Moderate	1-2	0.3-2	Moderate
ICP-MS	10 ⁻³ -1	Yes	Good ^a	Moderate	<0.5	1-2	Good
TXRF	10 ⁻² -1	Yes	Good	Moderate	<0.5	2-5	Good
LIBS	10 ² -10 ³	Yes	Moderate	Moderate	≤100	1-10	Moderate
ET-LEAFS	10 ⁻⁵ -10	No	Excellent	Small	≤100	3-5	Good

^a Isotope selectivity.

electrospray^{41,42}/ionspray,⁴³ vapour generation^{32,44,45} and pneumatic (concentric, cross-flow, Babington and frit) or ultrasonic nebulization⁴⁶ in combination with a spray chamber or any of the more efficient continuous microflow-scale nebulizers (*i.e.*, the micro-ultrasonic nebulizer, μ -USN;⁴⁷ the microconcentric nebulizer, MCN;⁴⁸ the high efficiency nebulizer, HEN;⁴⁹ the direct injection nebulizer, DIN;⁵⁰ the oscillating concentric nebulizer, OCN;⁵¹ the hydraulic high pressure nebulizer, HHPN;⁵² or the single bore pneumatic high pressure nebulizer, SBHPPN⁵³) and the monodisperse dried microparticulate injector (MDMI).⁵⁴ Solids have been introduced into sources by way of a simple pressed disk (for GDs⁵⁵⁻⁵⁷), by direct sample insertion (DSI) into plasmas,⁵⁸ dry powder introduction into plasmas,⁵⁹ by spark and laser ablation techniques (SA^{60,61} and LA⁶²⁻⁶⁶), slurry sampling of milled powders⁶⁷⁻⁶⁹ and ETV vaporization of solids,^{70,71} slurries of solids^{72,73} or aerosol deposits.⁷⁴

As noted earlier, however, environmental analytical laboratories are often constrained to utilize compliance methodologies (such as those of the US EPA, Occupational Safety and Health Administration, various national Department of the Environment organizations) as analytical protocols are largely driven by regulation and require use of specific procedures approved by the relevant regulatory agency. As such, measurements need to be made using validated methods⁷⁵ having specified accuracy and precision, ruggedness, operating range, selectivity, susceptibility to interferences and limits of detection and determination. Thus, promising new instrumentation, sample preparation techniques and sample introduction methodologies currently on the forefront of research are often excluded from use in the environmental laboratory routine. Laser and spark ablation, direct sample insertion, electrothermal vaporization, direct powder sampling and slurry sample introduction techniques are (can) not (be) utilized. Similarly, instrumentation for the continuous monitoring of fugitive hazardous air pollutant metals²⁰ is not yet widely supported. Few (*e.g.*, standardized soil leach tests), if any, speciation methodologies are validated⁷⁶ and, perhaps precisely for this reason, the field is rapidly advancing in this sphere. Development of new methodologies and improvement of existing techniques for regulatory elemental determinations in environmental matrices constitutes a major challenge for analytical chemists. Since validation of procedures proceeds through intercomparison exercises,⁷⁷ wherein the 'old' is pitted against the 'new', it is not uncommon that slow dissemination of this information leads to the large delays experienced between introduction of techniques and their acceptance.

THE FUTURE

Based on the perceived needs presented in Table 1, it is possible to extrapolate activities in many areas, as the fields are sufficiently well-established at present to estimate what their capacities will be in a few years. In general, a higher level of integration of the entire analytical operation will occur, as

sample preparation, introduction and detection are melded into what can be called the 'intelligent' instrument. Enhanced element throughput will be realized through increased use of multielement instrumental approaches, such as continuum source AAS, XRF and TXRF, LIBS, plasma source AES and MS, as well as a rejuvenation of the dc arc, since array spectrometers can be used for simultaneous multiline detection using time- and wavelength-integrated intensities and possess powerful multicomponent spectral deconvolution software. Automation of many routine sample preparation tasks can be anticipated. Enhanced limits of detection can be achieved with direct solids (*e.g.*, LA) and slurry sampling approaches as well as through more extensive use of on-line chemical manifolds and FI techniques to minimize sample contamination and perform matrix separation-analyte concentration functions. Alternative plasma sources, including non-ambient pressure He plasmas, may find more extensive application. Speciation measurements will become more prevalent and readily implemented as a consequence of the multidimensionality afforded from tandem and combined sources, on-line chemical manifolds and increased availability of reference materials certified for species content.⁷⁸ Sample consumption and minimization of waste will be addressed through FI and on-line sample preparation techniques, direct analysis of solids, enhanced field testing operations and the advent of nanotechnology in miniaturizing many fluidic laboratory functions. These possibilities are summarized in Table 3.

In light of these forecasts, it is expedient to examine the state-of-the-art in selected areas of atomic spectrometric research in an effort to shed more light on these possible near-future developments. Hieftje⁷⁹⁻⁸¹ and Tölg⁸² have earlier addressed similar issues, with emphasis on the development of new sources for plasma spectrochemical instrumentation and challenges in trace element analysis, respectively. A blend of

Table 3 Future considerations

More elements, faster:	Automation/intelligence Multielement instrumentation Faster sample preparation (solids)
Enhanced LODs:	On-line chemical manifolds Alternative plasmas Multidimensionality
Sample/waste minimization:	FI On-line physical/chemical manipulation Solids/slurry techniques Nanotechnology Field testing
Speciation:	Multidimensionality On-line physical/chemical manifolds Alternative plasmas Reference materials

these two approaches will be attempted here. In all likelihood, analytical atomic spectrometry for environmental analysis will, as noted earlier, be need-driven rather than technique driven. Available instrumentation is, for the most part, sufficiently powerful to address environmental issues; it remains to find ways to apply this instrumentation to specific problems.

Future sample preparation—introduction

Since the preparation of samples is often dictated by the form in which they can be presented to the instrument, no attempt will be made to discuss these two functions separately in a rigorous manner. Much of what follows is based on the assumption that research-laboratory based sample preparation—introduction techniques currently identified as promising will undergo validation and acceptance into the environmental analytical laboratory.

Currently, aerosol and gaseous samples are collected by filtration or adsorption techniques and analysed principally by non-destructive NAA and XRF¹⁸ procedures, or by solubilization of filters or elution of material from adsorbents prior to instrumental analysis. Attempts to obtain (near) real-time monitoring of hazardous air pollutant metals have resulted in the successful development of a mobile Ar-ICP based continuous emission monitor (Thermo Jarrell Ash) which utilizes air as the central sample stream and nebulized standards for calibration purposes.^{20,21} An electrothermal atomizer employing electrostatic precipitation accumulation of aerosol on the surface of the heated graphite tube has been shown to be useful for the determination of Pb in air, without the need for calibration standards when operated in the AAS mode.¹⁵ This methodology has been extended to other elements and permits field samples to be acquired with the loaded tubes returned to the (mobile) laboratory for analysis with a time resolution of hours.⁸³ This approach would not likely compete with the multielement real-time use of the CEM detailed above, especially in light of the fact that the CEM currently possesses sufficient detection power to meet legislative emission control monitoring levels.

Although solution nebulization or sample aliquoting are the most common methods for introducing samples into atomic spectrometers, they exhibit several shortcomings, not the least of which is the time necessary to digest and solubilize solid samples. In light of this, there is a growing interest in the development of introduction methods for solid samples, including direct solid and powder sampling techniques, slurry sampling, spark erosion and laser ablation.^{66,84} Traditionally, the difficulties in accepting these alternative sample introduction techniques have been associated with the calibration of the instrument response, sample homogeneity and the accuracy and precision attainable. The limitations of slurry sample introduction into plasmas have most recently been addressed by Ebdon *et al.*⁶⁸ An appreciation for their occurrence, minimization and control would serve to alleviate these concerns in many cases, leading to a broader acceptance of these approaches. This technique is particularly attractive as it is simple to implement, is inexpensive and requires little instrument modification. Slurry sample introduction with the electrothermal atomizer for AAS detection is less subject to significant particle size effects and offers a long residence time with corresponding high atomization efficiency.⁷² Of all of the slurry sampling techniques, those associated with use of the ETV have been evaluated most thoroughly *via* international collaborative studies⁷² and thus have the most likely opportunity for acceptance as official methodology. Automated injection of slurry samples into flowing streams has also been demonstrated.⁶⁹

Conventional laser ablation of solid samples and *in situ* laser ablation ICP are currently popular techniques by virtue of the availability of high-power Nd:YAG laser sources operating in

the IR (1064 nm, or frequency quadrupled outputs) and excimer UV lasers with output at 308 nm (the latter are preferable from the view of minimization of selective volatilization and enhanced ablation efficiency⁸⁵) coupled with the possibility of microanalysis with sub-mm resolution. Fractional ablation and matrix-related variations in ablation efficiency must be overcome if quantitative data are desired. The availability of array spectrometers will foster increased use of this sample introduction approach for plasmas^{86,87} as a consequence of the enhanced precision and more reliable recording of transient information. Similarly, renewed interest in the dc arc spectrographic analysis of solids is bound to increase as a consequence of their coupling to solid-state multichannel detection systems based on array spectrometers.⁸⁸ Advances made in the areas of matrix effect correction⁸⁹ through normalization of signal intensity using an acoustic pulse from the plasma (related to the mass of matrix ablated) along with temperature normalization, calculated from the ratio of two lines of a fixed element, allows for a multi-matrix calibration curve yielding a few per cent. accuracy. Calibration procedures based on the simultaneous introduction of dried solution aerosols along with the laser aerosol serve to enhance the reliability of data for ICP-MS applications.⁹⁰ Even if all problems are not solved in the near term, efficient application of the technique for environmental analysis may prove expedient for rapid site mapping and sample screening.

Without doubt, the greatest impact on sample processing and introduction for atomic spectrometry has derived from the fields of FI technology⁹¹ and microwave radiation.²⁶ Flow injection has, and will, continued to revolutionize the treatment and presentation of samples to spectrometers, permitting the direct processing of solids and other complex samples,⁹² on-line matrix separation, analyte preconcentration, isotope dilution spiking and vapour generation as well as various pretreatment scenarios, including dilutions, digestions and dissolutions.^{93,94} Savings in time, reagents, sample and the need for expensive clean facilities have been realized, commensurate with enhancements in precision and detection power. There is no reason not to believe that future applications of these techniques will proliferate. The desire to process samples in an FI format has also fostered further commercial development of sample introduction devices, in particular, the variety of pneumatic nebulizers which handle low-flow, low-volume samples. The microconcentric nebulizer is currently most attractive for such applications as a consequence of its high efficiency, low-flow and normal pressure operation.^{48,95} Further refinements in spray chambers and nebulizers to promote higher efficiency and faster washout and equilibration times will emerge which will also serve to enhance throughput.

The application of microwave radiation to analytical and environmental chemistry has been equally significant.²⁶ Microwave assisted techniques have revolutionized the procedures by which samples are treated, including all-manner of acidic dissolutions at ambient pressure,⁹⁶ low pressure,⁹⁷ very high pressure²⁸ and in continuous flowing streams;²⁷ on-line microwave assisted digestions²⁵ and, more recently, species selective extractions and derivatizations.^{34,35,98} Apart from those scenarios where samples are manipulated in an automated fashion in flowing streams, robotic systems may be utilized to enhance throughput of discrete processing modes further.^{99,100} These trends will continue in the future, with instruments providing safer, cheaper, cleaner, more chemically resistant digestion vessels with higher pressure options, more precise control of applied powers and developed temperatures and closer integration of such systems in on-line configurations with atomic spectroscopic instrumentation.

Future instrumentation

Enhanced throughput will clearly be achieved by more frequent use of techniques that efficiently generate multielement infor-

mation, such as emission and mass spectrometries. Clever source and detector designs also permit conventional single element at-a-time AAS to enjoy multielement capability. Thus, array-based high-resolution spectrometers^{101,102} have revolutionized the measurement of optical intensity and implementation of multicomponent spectral deconvolution, thereby rejuvenating interest in classical dc arc 'spectrography',⁸⁸ facilitating the development of multielement continuum source atomic absorption,^{103,104} and fostering further maturation of alternative sample introduction techniques. In this connection, such spectrometers can be used to improve the precision of LA-solid sampling ICP-AES⁸⁶ approaches and permit full advantage of solution FI,¹⁰⁵ *in situ* LA,⁶² introduction of dried microparticulate samples^{106,107} and ETV-derived aerosols³⁷ for the registration of transient multielement information with enhanced sampling efficiency. Inexpensive, fast electronic spectrometers based on acousto-optic tunable filter technology¹⁰⁸⁻¹¹⁰ may also become available. These have the advantage of providing a compact, rugged design with wide tuning range, reasonable bandwidth and high-speed (μ s) random or sequential wavelength access. They can perform as either a monochromator or polychromator. Currently, access to the UV spectral regions is limited as further developments in birefringent crystals are awaited.

Faster sample processing is often limited by the speed of sample preparation. As noted above, instrumental techniques having solid sampling capabilities will enhance both detection power (through elimination of dilution steps during digestion and by virtually eliminating the methodological blank contamination) and sample throughput. One such candidate is LIBS.^{111,112} LIBS allows real-time *in situ* measurements of trace elements in solids,¹¹³ liquids^{114,115} and aerosol¹¹⁶ samples, can be configured as a site-portable instrument¹¹⁷ and possesses sufficient sensitivity to be of use for conventional laboratory or field screening operations. The instrumentation is fairly rugged and requires little maintenance compared with most other laser-based spectrometers. Problems associated with working in air at atmospheric pressure (increased background and molecular band emission) may be alleviated through use of spatially and temporally resolved measurements using gated charge-coupled devices for detection,¹¹⁸ thereby enhancing applicability to environmental scenarios. Recently, Xu *et al.*¹¹⁹ suggested that it is possible to determine absolute concentrations of analytes using LIBS by processing single shot data to compensate for intrinsic fluctuations in laser events, eliminating the need for a reference component and enhancing performance ten-fold.

X-ray spectrometric methods based on total reflection geometry (TXRF) have gained widespread strength in the past decade; this trend will likely continue due to the detection power (2–10 pg, 100 pg ml⁻¹ relative), quasi matrix-independent calibration (internal standard), multielement capability and non-destructive nature¹²⁰ of this methodology. When combined with appropriate sample decomposition/digestion techniques, samples from virtually all phases of the environment can be analysed using TXRF.¹²¹ Exploitation of energy dispersive XRF techniques offers considerable potential for further developments in the field of trace and microanalysis of environmental materials with the application of brighter X-ray sources and standardized sample preparation methodologies. Minimal sample preparation (*e.g.*, blending with activated alumina) has been used for the determination of toxic elements in liquid hazardous waste, industrial waste solvents, sewage sludge, liquified waste fuels, paints and inorganic pigments in liquid form, electroplating solutions and waste oils.¹²² Such simple sample preparation techniques may also extend the applications of field-portable XRF instrumentation.

Developments in plasma source mass spectrometry are likely the most eagerly awaited.^{80,81} Apart from enhancements which

may be forthcoming in ion-optic throughput, the ability to measure virtually simultaneously a full spectrum of all ions in a very short time period with enhanced ion transmission is the promise of time-of-flight based instrumentation,^{123,124} as opposed to currently used quadrupole filters. The former will likely prevail over ion trap and Fourier transform ion cyclotron mass spectrometric approaches because of cost, simplicity and dynamic range.¹²⁵ Such conditions are favourable for advantageous use of internal standardization (and isotope dilution calibration) to enhance measurement precision and for the more reliable measurement of multielement information generated from transient sources such as LA, FI and ETV. Additionally, the virtually unlimited upper mass range of such systems endears them to speciation applications where parent molecular ions and fragmentation products are of equal or more interest than elemental ion intensities, even if chromatography is employed prior to the source.¹²⁶ Although resolving power (currently 1600–2000) is substantially improved over quadrupole devices,¹²⁶ it is not yet sufficient to remove many common polyatomic isobaric overlaps experienced in ICP-MS. Despite such shortcomings, it remains more cost effective than magnetic sector instruments, which compromise sensitivity for resolution.^{127,128} In this respect, it is of interest to note the recent report¹²⁹ on the design and performance of a plasma source mass *spectrograph* for true simultaneous multielement detection. Promising performance criteria could be met with the exception of resolution, owing to poor peak shape in the multichannel-plate array detector. As there is no need to pulse ions into this mass analyser, a much higher duty factor for sample use can be realized with this approach. Ying and Douglas have recently reported on the operation of a quadrupole mass filter in the 'second' stability region, obtaining resolution at half-height of up to 9000.¹³⁰ Sensitivity is degraded (100-fold) in this mode, similar to that of sector-based instruments. A continuum background of 1000 s⁻¹ currently plagues this instrument but no attempts have been made to reduce this. Recent instrument developments and analytical applications of ICP-MS have been reviewed by Jakubowski and Stuewer.¹³¹ Incorporation of a collision cell (CID) in the ion optics train, as available with the ICP-HEX-MS system from Micromass, should substantially reduce the resolution requirements needed to avoid many common polyatomic isobaric interferences without sacrificing sensitivity.

Use of microwave and glow discharge (GD) devices for environmental analysis, either in AES or MS formats, will likely remain peripheral in terms of total impact on sample load.¹³²⁻¹³⁴ These techniques have recently been reviewed by Winefordner and co-workers.^{134,135} Although the GD presents a very versatile source, in that rf sputtering eliminates the need for a conductive sample,⁵⁵ and introduction of liquids (*via* a particle beam interface¹³⁶) as well as gases¹³⁷ has been demonstrated, it is most likely that it, and the MIP,¹³⁸ will find only limited niche usage in connection with speciation applications. Exciting new prospects are arising in the area of rf GDMS for GC detection of elemental species.¹³⁹

Forecasts suggesting an enhanced role for lasers in optical (for AAS, LEAFS) and mass spectrometry [resonance ionization (RI), multiphoton ionization (MPI), laser enhanced ionization (LEI), field ionization] instrumentation have been made for many years, all suitably contingent upon availability of cheap, tunable, powerful laser sources which access the UV. Significant advances have been achieved with semiconductor lasers and diode-pumped laser systems in recent years such that robust, solid-state benchtop systems can now be made readily available as turnkey systems.^{140,141} However, for access to the deeper UV, where most optical transitions of interest to analytical spectroscopists occur, frequency doubling and quadrupling is still required with consequent loss of intensity necessary to achieve optical saturation (*e.g.*, for

LEAFS¹⁴²) with pumped tunable dye lasers. Recently, solid-state laser systems based on optical parametric oscillators (OPO) have become commercially available and characterized for use with LEAFS.¹⁴³ These devices can be tuned over wide wavelength ranges with efficient output for effective frequency doubling applications to 220 nm. Zhou *et al.*¹⁴³ reported the 'rapid' (4.5 h) sequential multielement determination of five analytes in a river sediment by flame LEAFS. Momentous advances have also been noted in diode laser technology, to the point where simple diode laser source-based AAS instrumentation could become routine^{144,145} ('blue' diode lasers have become commercially available which can be frequency doubled into the far UV for stable AAS work and LaserSpec Analytik, Munich, Germany, now markets a laser diode-based ETAAS- and FAAS instrument as well as a diode source compatible with existing AAS instruments). However, it may now prove even more difficult for such techniques to compete. Continuum source wavelength- and time-integrated AAS using high-resolution array-based spectrometers^{103,104} will likely become available and, although they would undoubtedly be more complex optically, wavelength range would not be an issue. Interestingly, the lower detection limits that can be attained with diode laser source AAS^{140,144,145} may help sustain continued use of FAAS as a cost effective viable alternative to plasma source multielement instrumentation, especially with a multielement DL-AAS approach,¹⁴⁵ as it is already estimated that until 8–14 elements are to be determined, FAAS is currently competitive with more expensive techniques in terms of productivity.¹⁴⁶

Enhanced detection power

As noted in Table 1, commensurate with increased elemental coverage, enhanced detection power (lower LODs) is sought. Several approaches can be taken to enhance this figure of merit: those related to sample introduction and processing have been discussed earlier. Brighter and more stable sources contribute to enhanced LODs with LEAFS, hence the drive to implement diode lasers with this technique, as noted earlier. Lower background intensities translate into improved LODs in optical emission spectrometry. Axial viewing of an ICP discharge improves the efficiency of observation of the central channel containing the sample (extended pathlength) and avoids the surrounding intense Ar plasma (lower background). Although 5–10-fold improvements in LOD are often claimed, Dubuisson *et al.*¹⁴⁷ have demonstrated that this figure is typically in the range 2–3, but with matrix effects being no more severe than with radial viewing of the same plasma. Modern, commercial ICP-AES spectrometers and sample introduction systems can now reach the 1 ng ml⁻¹ level for difficult elements (*e.g.*, Pb³⁹) and lower (10 pg ml⁻¹ for Fe^{39,147}).

Developments in the area of plasma discharges in gases other than Ar have been of on-going interest. In particular, He enhances the degrees of ionization of a number of hard-to-ionize elements and, because it is essentially monoisotopic and occurs at low masses, polyatomic isobaric overlaps are less severe. Nam *et al.*¹⁴⁸ have reported on the successful operation of a He-ICP-MS system which permits, for example, direct, interference-free detection of Fe and K. Although there was evidence of a secondary discharge in the extraction interface, it is anticipated that this will be resolved with suitable load coil matching circuitry. It remains to explore the performance of this system with complex sample matrices; if successful, the He plasma may likely find widespread usage for niche problems only, considering current domination of the field by, and entrenchment of, the Ar ICP.

Operating discharges at reduced pressure also serves to diminish background intensity in optical emission because of the decreased frequency of recombination events (hence,

decreased recombination continuum). Commensurate with this is a loss of thermal capacity and decreased ability to volatilize and atomize aerosols and dissociate polyatomic species, making the discharge more difficult to operate. Nevertheless, tandem source arrangements can be used to take advantage of excitation-ionization events in such systems, as evidenced by the recent application of an rf GD device for elemental speciation.¹³⁹ Proliferation of reduced pressure discharges will not be widespread as a result of their more complex hardware, but specific niche applications, as in the case of generation of speciation information, may become attractive. Enhancing the LODs with plasma source MS will be accomplished with the design of more efficient analyte transfer through both the skimmer and ion optics.⁸⁰ Sampling low-pressure discharges can effectively accomplish this but at the cost of reduced applicability.

Intelligent systems

Every generation of instrument has been more highly automated than its predecessor and there is no reason to believe that this trend will not continue to hold for the foreseeable future. Additionally, instrumentation will likely become more 'intelligent'; software on many instruments currently permits automatic optimization of measurement parameters to obtain maximum S/N on samples (*e.g.*, torch positioning and ETV thermal program), self-diagnostics and feedback represent a small additional step. Analytical results are already capable of being monitored and flagged for a variety of problems. By integrating the instrument with the sample preparation methodology, an intelligent device will be able to reprocess a flagged sample to implement on-line, real-time adaptive optimization.¹⁴⁹ Simple measures, such as sample dilution in an appropriate manifold if it is over-range (the correct degree of dilution being automatically determined by a feedback process to maintain optimum S/N and S/B or blank), concentration of a sample by processing an aliquot through a chemfold, or automatic matrix separation if it is deemed that targeted concomitant levels of potential interferents are too high. The possibilities for such intelligent feedback actions are manifold when multidimensional instrumentation is contemplated, as on-line sample preparation is coupled into both the source and detection systems wherein parameters, specific to each component and common to the synergy of the entire assembly, can be independently optimized. Intelligent instrumentation and enhanced software control will also allow manufacturers of successful instruments to penetrate niches and make it possible for relatively unsophisticated operators to perform well.

Multidimensionality

All current sources used for atomic spectrometry have deficiencies and often fall far short of possessing all of the ideal attributes desired.⁷⁹ Tandem sources have been implemented in an effort to realize these ideal capabilities,¹⁵⁰ wherein two separately operable sources are coupled to take advantage of the optimum attributes of each. For the purposes of this discussion, and to extend the concept of multidimensionality, the strict definition¹⁵⁰ of a tandem source is relaxed to include hyphenated techniques. In this respect, the delineation between sample preparation-introduction and the term tandem source is lost, as the former may be used to impart multidimensionality to a system. Extracting speciation information from samples utilizing hyphenated techniques, as discussed earlier, may be considered an example of enhanced multidimensionality. Speciation studies utilizing element specific atomic spectroscopic techniques for detection of chromatographic events, as discussed earlier, may be considered examples of enhancing

the dimensionality of an analytical system. The added variable of analyte retention time augments the usual two-dimensional intensity–time signal resolved by the source–detector, providing enhanced selectivity and confidence in the identification of element response by comparison with chromatographed standards. A particularly powerful example of the attributes of multidimensionality is the use of a tandem source comprising an electrothermal vaporizer for sample introduction into an ICP-TOFMS.¹²⁵ The characteristic appearance temperatures of several elements (Cd, In and Sn) were used to advantage to separate them temporally when they would otherwise exhibit mutual (isotopic) isobaric interference. Attempting this by mass spectrometry alone would have demanded unattainable resolution with the system used. A similar example utilized the different vaporization characteristics of inorganic and organic mercury species to permit their first-order separation and quantitation in biological materials by ETV-ICP-MS techniques.¹⁵¹ Multidimensionality may also be interpreted from the viewpoint of modularization of an instrument,⁸⁰ where, for example, a given source could be coupled to a variety of sample introduction systems, such as LA, SA, FI-PN, vapour generation, ETV, DSI, GC, LC-PN, in the case of an ICP; or a specific detection system, such as a mass spectrometer, could be configured to accept ions from several sources, such as the ICP, GD and ES/IS (electrospray/ion spray) or used in both an optical and mass spectrometric mode.¹⁵² Such ‘generic’, modular instrumentation would prove to be very flexible, cost effective and extremely useful for analytical problem solving in non-routine environments. The current similarity of API (atmospheric pressure ionization) MS hardware utilized with ES/IS for molecular detection/identification and their (simpler) elemental MS counterparts bodes well for development of a universal interface and detector, to be used with both approaches, as has recently been demonstrated.¹²⁶

Speciation

It is appropriate at this juncture to address speciation, as significant advances in this domain have been realized as a result of application of hyphenated techniques and multidimensional instrumentation to this issue; in particular, the marriage of various chromatographies and atomic spectrometry has proven indispensable.^{138,139,153–158} The answers to questions relating to toxicity, bioavailability and transport processes are highly dependent on an element’s form and can only be ascertained by acquiring quantitative species-specific information. In addition to valence state speciation information, which can often be obtained through simple chemical manipulation of the sample with reagents (*e.g.*, Cr^{III} versus Cr^{VI}), identification of organometallic species of As, Sn, Hg, Pb and Se has been most actively pursued. Elegant combinations of state-of-the-art tandem techniques have been employed,^{51,159,160} but in all cases have relied on the chromatographic characteristics of the temporally- or volume-resolved response from atomic detectors to identify the species observed. Apart from the assumption that complete resolution of any possible co-eluting species has been achieved, this approach requires standards be available for each species examined and that they suffer no matrix induced shifts in retention time compared with those in the standard substance calibration mixture. This presents a fatal obstacle in the event that an uncharacterized element peak appears in the chromatogram with no retention time match with a known standard. Since no molecular information is available from conventional plasma sources, structural information is lost and identification is impossible. Recent work with multidimensional instrumentation has rectified this problem by a combination of liquid chromatography with electrospray/ion spray sources for measurement of fragment ion patterns, generating (potentially

near simultaneous) structural information which can be used to deduce species identity in the absence of standards.^{41,43,126,161,162} ‘Dual mode’ analysis, achieved by judicious selection of operating conditions in the API source interface, permits elemental atomic and molecular information to be obtained on the same sample.¹²⁶ Low pressure, low power, conventional elemental atomic spectrometers have also shown promise for providing molecular and atomic speciation information^{139,163} when operated in a ‘dual’ power mode. Introduction of GC elements into a low power (30 W) rf GD¹³⁹ device or low power (45 W), low pressure (1 Torr; 1 Torr = 133.322 Pa) ICP discharge¹⁶³ have been used to obtain molecular information from fragment ions and elemental verification from elemental ions for organotin and -lead species. Future speciation methodologies will benefit from approaches such as these and further support the need for multidimensional instrumentation which possesses synergism. It is also clear that enhanced availability of reference materials certified for their elemental speciation content will be required to promote such activities and support acceptance of the data generated.^{78,163–165}

Field portability

Cost projections for environmental restoration are enormous for North America and they may be larger for the former East Bloc nations. Faster and less expensive approaches to the problems of environmental characterization are required. One means of meeting these goals is the more effective use of on-site field sampling and testing. Field screening is most effective in situations where the immediate availability of results will affect the cost, progress or safety of site operations. Additionally, with prudent use of screening, it is estimated that the cost of environmental testing can be reduced 50% or more.¹⁶⁶ Field screening can be used to analyse the nature, extent and magnitude of contamination at a site, indicating if targeted analytes are present above or below a preset concentration threshold. Although such an approach would not replace the need for fixed laboratory-based methods, the need for such testing would be reduced and restricted to samples identified as contaminated. Additionally, sample integrity could be more easily maintained.

Two approaches have been taken to implement field testing: use of specifically designed field portable instrumentation and the assembly of a mobile laboratory comprising conventional instrumentation. Whereas there is a variety of instrumentation that can be taken into the field for detection and quantitation of volatile molecular compounds, including portable GC and GC-MS devices and even a TOF-based battery powered MS with a membrane inlet,¹⁶⁷ the same cannot be said for the elemental analysis sector. To date, only field portable energy dispersive, radioisotope-excited XRF equipment with Si(Li) or HgI₂ detectors have been widely used and evaluated for *in situ* analysis of such samples as contaminated soils and silicate rocks.^{168–170} Empirical calibration based on a suite of synthetically prepared calibration samples or a set of analysed site-specific samples can be undertaken. High *Z* elements have LODs in the range of tens of mg kg⁻¹ whereas those for lighter elements may range up to 1000 mg kg⁻¹. A mobile laboratory containing an ICP-MS was recently evaluated for performance against fixed laboratory EDXRF and ETAAS/ICP-AES methodologies and found to be useful for the rapid screening of environmental samples in the field.¹⁷¹ The need for additional, more sensitive field-portable instrumentation will become more acute as the costs and expansion of remediation increase. Currently, field-portable ETV-AAS units are available based on low-power tungsten furnaces.¹⁷² Portable LIBS-based instrumentation is also likely to proliferate¹¹⁷ as it is an excellent candidate for *in situ* site characterizations as remote sensing is possible *via* fibre optic interfaces. Robust, solid-state

electronic spectrometers, such as those based on AOTF or array technology, can be coupled with multiple diode laser sources or a continuum source for multielement AAS, or ICP sources for AES measurements in mobile laboratories. Additionally, use of field sampling operations which also achieve a first-order sample pretreatment, such as matrix separation or concentration of the analyte, as described earlier, should become more widespread. The complexity of operations that can now be achieved with on-line FI chemofolds obviates the need for clean room facilities in many instances and enhances the prospects of undertaking analytical operations on site.

Although laboratory-based instrumentation provides more precise and accurate analytical data than most field methods, field analytical chemistry has significantly increased over the past few years and will continue to grow as a result of the promise of reduced cost and potential of real-time decisions.

Nanotechnology

Microscale chemistry could reduce the volume of reagents, consumption of sample and generation of waste (and thereby cost of disposal) by several orders of magnitude. Miniaturization of instrumentation (microanalysis systems) compliments this drive. Advances are currently being made from both perspectives.¹⁷³⁻¹⁷⁹ Solid phase microextraction techniques¹⁷⁶ present unique opportunities for minimization of reagents and waste in a number of analytical processes and can result in superior method performance. The recent demonstrations of the ability to utilize electrokinetic transport of fluids (electroosmotic flow) in microfabricated channels to perform capillary electrophoresis¹⁸⁰ and the coupling of electrospray direct from the planar ends of such microchip devices^{174,175} with MS instrumentation are examples which serve to point the way of the future. It is a small leap of the imagination to consider the development of complete sample handling systems based on FI techniques working in this manner¹⁸¹ which are on-line to present instrumentation. Solenoid inkjet valves could be used as micro dispensers or autosamplers feeding such chip-based chemical processors.¹⁸² The fact that miniaturized chips would be coupled to full-sized spectrometers should not detract from this profitability. Additional microscale chemical manipulations have been performed using single drop solvent extractions¹⁷⁷ and acoustically levitated droplets for contactless handling of liquids undergoing such processes as analyte enrichment by evaporation, liquid-liquid solvent extraction and solvent exchange.¹⁷⁸ Indeed, a significant amount of analytical chemistry can be performed within the confines of a liquid drop.¹⁸³⁻¹⁸⁵ Optical trapping techniques have been used to separate and direct selectively ultrasmall samples into (such) carrier streams.¹⁷⁹ With the mating of these sampling techniques to the microcapabilities of on-chip technology described above, one can envision a complete microchemical system for fluid handling, the output of which could be directed to an intelligent multidimensional spectrometer.

CONCLUSIONS

The attributes of an ideal instrument for atomic spectrometry suitable for environmental analysis are presented in Table 4. It is assumed at this point that the reader has a full appreciation for the inclusion of the various features and no further discussion is warranted. It is clear that there is presently no single source instrument that possesses all of these features and likely one will never exist. So, what does the future hold for atomic spectrometry and environmental analysis? A number of potential points are summarized in Table 5. Clearly, the higher detection power and richer information base generated with

Table 4 Ideal instrument for environmental analysis

Accepts all samples
 Simultaneous multielement capability
 No matrix interferences—absolute analysis
 Atomic/isotopic/molecular information
 High dynamic range (>9 orders)
 Lower LODs (more sensitive)
 Microsampling capabilities
 Precise
 Fast
 Intelligent/automated
 Inexpensive
 Field portable
 Multidimensional

Table 5 The future ...

More atomic mass spectrometry with:
 —Higher resolution capabilities
 —Simultaneous detection
 —Multifunctional sources (atomic/molecular information)
 —Intelligent
 More multidimensionality through tandem sources
 More speciation information
 More on-line/in-line sample processing
 More field sampling and use of portable devices
 More laser-based instrumentation
 More nanotechnology

mass spectrometry will tend to drive the user market in this direction. Increased resolution and simultaneous detection can be achieved with TOF systems. These devices will likely remain more cost effective for atomic spectrometry than magnetic sector instruments. Although the latter provide high resolution,^{127,128} it is possible that developments in CID¹⁸⁶ may alleviate many of the polyatomic isobaric interferences currently problematic with ICP sources and multidimensional approaches will serve to further reduce these conflicts.

The demand for more speciation information will continue to increase, with multifunctional sources serving to meet the challenges. Enhanced use of on-line and in-line sample processing will be evident as FI technology becomes more clearly integrated into the primary instrumentation and under the control of its parent software. Cost effective measures will have to be implemented in order to control the increase in monitoring likely to be in demand; this aspect will be addressed through enhanced use of mobile laboratory instrumentation, continuous emission monitors and the development of more field portable devices. The performance of commercially available laser-diode based instrumentation¹⁴⁵ will be carefully monitored. Nanotechnology will continue to grow in diversity and demonstrated potential but its application to environmental elemental analysis is likely more than a decade away.

A more realistic assessment of the near-term future for the environmental analysis sector is a growth in the use of multielement detection techniques, likely based on ICP-AES with array-based spectrometers and ICP-MS with increased resolution capabilities, whether these are derived from TOF-based detection systems or from as yet unknown hardware arrangements. Large laboratories with significant sample loads and suitable support facilities will have use for ICP-MS capabilities and also likely have available ICP-AES and (multielement continuum source) ETAAS instrumentation to choose the best technique for a particular analysis. For most laboratories, ICP-AES will remain the technique of choice, as many elements that were previously only quantifiable using ETAAS techniques can now be routinely accessed with cost effective state-of-the-

art ICP-AES instrumentation. Furthermore, current developments in the field of multicomponent analysis now permit fast and quantitative analysis of all analytes by ICP-AES without the need for prior knowledge of sample composition or the selection of lines and suitable background correction points.¹⁸⁷ Spectral fitting algorithms developed for use with quadrupole ICP-MS may likewise significantly reduce interferences from polyatomic ions with this technique.¹⁸⁸

Two additional factors arise in closing discussion: the methodological blank and the 'value' of the data produced. Current instrumentation is already capable of providing 'instrumental' detection limits far superior to method detection limits for many elements, owing to our inability to control contamination and, hence, the method blank. It is to be hoped that widespread use of FI techniques and, ultimately, perhaps nanotechnology for sample handling, will help alleviate this particular problem, leaving the second point to be addressed. This pertains to the question, 'do we really want to know?' It is reasonable to question how far it is necessary to push detection power before losing connection with impact on the environment. Certainly, enhanced detection power (absolute) is a prerequisite to working with small samples and is complementary to the thrust toward microanalysis capabilities with attendant reduced consumption and waste generation. However, regulatory agencies often base acceptable limits of hazardous substances on current detection capabilities, without further criteria. This serves to increase the costs of analysis. 'When we can spot a single atom and a single molecule, we will have reached ultimate confusion. As long as we have lunatic legislation, we must be very cautious with numbers.'¹⁸⁹

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