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The ETV as a thermochemical reactor for ICP-MS sample introduction†‡

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Electrothermal vaporization (ETV) for sample introduction into (inductively coupled) plasmas has been explored for more than two decades, first for use with optical spectroscopy and subsequently with mass spectrometry. It is with the latter that its full potential has been appreciated *vis-à-vis* solution sample nebulization. Tandem coupling of an ETV to a plasma source elicits a number of attractive features, not least of which is the explicit use of the device as a thermochemical reactor for *in situ* pretreatment of samples. This aspect of ETV use has not yet been su ciently well explored, despite an accumulated body of literature in the related field of ETAAS, where judicious selection of thermal programs and chemical modifiers has been extensively used to minimize analytical problems. Of particular interest for ETV sample introduction is the feasibility of using classical chemical modifiers or other reagents to alter the volatility of either the analyte or the concomitant matrix, thereby permitting a thermal or temporal separation of their release from the ETV surface. This approach may alleviate space charge interference e ects, minimize polyatomic ion interferences and e ectively enhance resolution, permit direct speciation of trace element fractions in samples as well as serve as a 'crucible' for sample preparation. The literature in this field is reviewed and examples of such applications for ICP-AES and ICP-MS detection are presented.

Introduction

The term 'electrothermal vaporizer' can be used to encompass a wide range of physical platforms used for the resistive heating of a substrate upon which a (condensed phase) analyte sample has been placed such as to result in its (rapid) release into the gas phase. This process may result in the simple vaporization of the analyte and any accompanying matrix, or the partial or complete atomization of the analyte and/or matrix. Samples may be introduced in the form of solids, slurries, liquids, gases or aerosols. Although rods, boats, filaments, cups and tubes have been used as heated substrates, discussion will be essentially limited to tubular graphite furnaces, as they are the most well-characterized and provide the most controllable thermal environment when heated either longitudinally or axially.[1] Direct sample insertion (DSI) devices, while exhibiting some properties similar to ETVs, will not be considered since, despite some potential for use of modifiers to alter the chemistry of the sample and microenvironment within the vaporizer, minimal thermal control is available (determined by depth of insertion into the plasma[2]) and application requires availability of a demountable torch.

The atomic spectroscopy community is most familiar with a variant of the ETV technique pertaining to its use as an atomizer (ETA) over the past 25 years in atomic absorption spectrometry (AAS)[3] and applications of the ETV have been amply demonstrated.[4,5] The analysts' freedom to select suitable thermal programs in combination with the application of gaseous and liquid (dissolved) reagents permits wide-ranging physicochemical transformations of samples and analytes to be accomplished *in situ* (*i.e.*, selective vaporization of matrices and transformation of analyte species to other forms by application of heat, reagents or direct interaction with the substrate surface). It must be noted that the requirements for successful application of the ETV as an atomization source for AAS are distinctly di erent from the objectives set for its use as a vaporizer for sample introduction into plasma sources such as the inductively coupled and microwave induced plasmas (ICPs and MIPs). Whereas complete atomization of the sample and confinement of the atomic vapor within the high temperature observation volume is sought for AAS, it is su cient to ensure complete vaporization of the analyte species and its e cient transport from the ETV to the plasma or other observation volume used for atomic spectrometry; in principle, the two-step atomizer (cup-in-tube) may be viewed as the use of an ETV for sample introduction into an ETA.[6] Formation of gaseous analyte molecular species or the adsorption/occlusion of molecules or atoms of analyte on/in transportable (matrix) aerosol is the principal objective.[7] The ETV may thus be considered one of the constituents of a tandem source[8] in which the best characteristics of the device can be separately optimized to take advantage of its unique sample treatment capabilities in combination with those o ered by a variety of plasma sources.

An array of sample introduction techniques is currently utilized for plasma spectrochemistry.[9] Liquids are accommodated using pneumatic, ultrasonic, thermospray and hydraulic high pressure nebulizers or any of the more e cient continuous microflow nebulizers (HEN, DIHEN, MCN, DIN, OCN, *etc.*) as well as through use of direct sample insertion devices. Solids can be directly introduced (using DSI devices) as well as in the form of dry powders (using fluidized beds) or as laser ablated or spark eroded aerosols. Gases are sampled directly following vapor generation (*e.g.*, hydride formation). The ETV is unique amongst these in that this single device is able to accommodate all phases of matter: conventional dosing of microliter volumes of liquid samples, direct weighing of powders, injection of slurries of solids[10] as well as the sequestration

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of chemically and physically generated analyte vapors and aerosols[11–13] for subsequent introduction into plasmas.

The advantages and disadvantages of the ETV as a sample introduction technique for plasma spectrochemistry are summarized in Table 1. The microsampling capability originally touted as a major benefit to use of the ETV has been significantly eroded in the past few years following the introduction and acceptance of numerous microflow nebulizers operating with high e ciency in the $<100\ \mu l\ min^{-1}$ flow range.[9] Nevertheless, small, discrete sample volumes can be conveniently processed with the ETV. More significantly, the ETV e ciently handles solutions containing dissolved solids, up to 100% content (*i.e.*, solids), which would plug nebulizers when continuously aspirated,[14–20] and can be directly used for the analysis of organic solvents. The e ciency[21–23] of these devices is typically in the range of 20%, well above that of conventional nebulizer sample introduction, but less than that available with microflow nebulizers. Enhanced detection power ensues,[4,5] often as a direct result of reduced solvent-related polyatomic spectral interferences (with lower oxide fractions as well) in addition to the possible sample preconcentration schemes which can be implemented with the ETV. Furthermore, and uniquely, it is possible to enhance the e ective resolution of the MS system by taking advantage of the added temporal (thermal) dimension associated with the analyte desorption event,[24] utilize the device as a digestion medium for sample pretreatment and derive speciation information. In general, sample manipulation can be minimized with this device, in that many physicochemical reactions can be implemented *in situ*.

Use of the ETV is not without significant drawbacks. The discrete nature of sampling leads to transient response, which is more di cult to quantitate precisely (5–15% RSD typical) than steady-state signals, although precision can be improved to 0.5–2% by using the isotope dilution approach[5]. The lower sample throughput (typically 20 per h) frequently unsettles users. The recent introduction of ICP-time of flight instrumentation will remove these obstacles currently associated with quadrupole based detectors, which limit acquisition to 4–5 elements per transient and restrict measures which can be taken to enhance precision. Clearly, non-volatile elements and those that are prone to formation of low volatility carbides are not optimal candidates for quantitation by this technique. The potential for severe memory e ects remains when dealing with such elements or high concentrations of matrix elements which are target analytes in subsequent samples. In general, it is expedient to have a knowledge of the chemistries prevailing in the ETV reactor in order to elicit optimal performance from this introduction technique, which likely accounts for the majority of users being those having a background in ETAAS.

Table 1 Advantages and disadvantages of the ETV for sample introduction

Advantages—
Microsampling capability
High dissolved solids samples accommodated
High sample transport e ciency
Compatible with organic solvents
Enhanced detection power
Reduced solvent spectral interferences
Reduced analyte oxide fractions
Control of matrix (space charge) interferences
Enhanced e ective resolution (added dimensionality)
Speciation capabilities
In situ sample digestion
Minimization of sample handling
Disadvantages—
Transient signals; peak duration 2–5 s
Limited to 4–5 elements per transient (scanning instruments)
Low throughput
Poor(er) precision
Limited to volatile elements/species
Memory e ects
Internal standard (carrier) needed
Method of additions often required for quantitation
Requires knowledge of chemistries in ETV reactor

Being cognizant of these limitations and shortcomings, it is useful to reflect on what the potential contributions this sample introduction technique might encompass. There is a general reluctance to use this device for routine work and, to date, most applications have (unfortunately) focussed on liquid samples, which are often best handled by the many pneumatic microsample introduction approaches already available. As noted by Montaser *et al.*,[9] '…the true strength of the ETV… is the ability to handle di cult liquid matrices (organic samples, high salt samples, radioactive and toxic materials), slurries, solids and to allow speciation studies'. While many such samples can indeed be used with the ETV, the restrictions noted above concerning formation of non-volatile species and memory e ects from carbide forming elements (*i.e.*, with radioactive elements) must be respected. ETV was first coupled to an ICP for optical emission work some 25 years ago,[25] with the first report on its application to ICP-MS in 1983.[26] Several reviews have already explored many niche applications of the ETV which illustrate some of its strengths;[4,5,27] it is the objective of this review to highlight the proficiencies of the ETV which advantageously utilize both its physical and chemical attributes to achieve unique *in situ* sample handling and pretreatment capabilities. Emphasis will be placed on thermochemical interactions of the analyte–matrix with the ETV substrate and/or added gas, liquid or solid reagents. Examples are drawn from relevant ETAAS literature which can, by extrapolation, be utilized for such tandem source applications, as well as reports directly addressing ETV sample introduction issues. Areas relating to the use of the ETV as a preconcentration cell (to enhance detection power further and minimize matrix interferences), for *in situ* sample preparation, as well as analyte speciation will also be addressed, although it is recognized that these topics strictly do not fall under the purview of the chemistry of the system. Issues relating to analyte transport e ciency and the need for physical carriers are also not considered here and the reader is referred elsewhere for a discussion of these topics.[21–23]

Chemistry in the ETV

Reduction of matrix/spectral interferences

One of the key advantages of the ETV for sample introduction into ICP-MS instruments is the use of the device to modify the composition of the sample entering the plasma. This is most conveniently accomplished by application of judicious thermal programming. Appropriate ashing temperatures should be used to remove unwanted matrix constituents when possible along with the objective of minimal transport of matrix components to the plasma at all times, even during the high temperature clean step. In combination with suitable reagents to execute physicochemical reactions which e ect separation of the analyte from the matrix species, the ETV functions as a dynamic, albeit, highly non-uniform, thermochemical reactor. It is likely that the first reference to the ETV as a 'thermochemical reactor' was coined by Gilmutdinov *et al.*[28]

It is expedient at this point to discuss interferences and their origins. Clearly, if the response from an analyte is altered in a sample matrix compared with that from a standard, a matrix e ect is operative. The origin may lie within the ETV itself, wherein the matrix may promote the low temperature loss of

analyte (*e.g.*, as a volatile chloride) or inhibit its complete volatilization (by occlusion in a low volatility component). Sample transport e ciency from the ETV to the plasma may also be altered by the presence of the matrix, serving either to enhance (through formation of a more stable transportable aerosol) or decrease the e ciency (by formation of a reactive film on the surface of the transport tube). Once in the plasma, matrix induced signal suppressions or enhancements may originate from an alteration of the degree of ionization, or the zone of maximum ion density sampled. Within the MS interface, space charge e ects may dominate, leading to mass bias problems, especially when dealing with relatively massive ionized matrix components and low relative atomic mass analytes. Finally, spectroscopic interferences take the form of polyatomic ions, such as matrix element argides or oxides with nominally the same mass as the analyte. Although the e ects of some of these may be remediated by use of sector instruments, often the maximum resolution of 10 000 available with these machines is not su cient and semi-empirical corrections to response can be attempted. Spectroscopic interferences may, for all practical purposes, also be isobaric (*e.g.*, Cd and Sn isotopes) which would require resolving powers of 10^5 to eliminate. As most ICP-MS instruments are quadrupole based, with an e ective unit resolution, all 'spectroscopic' interferences become synonymous with 'isobaric' interferences.

Solvent removal to minimize polyatomic interferences. Simple removal of the sample solvent, typically water, can substantially alter the concentrations of oxide and hydroxide species in the plasma, thereby reducing spectral interferences from polyatomic interferences. This process is e ciently accomplished with the ETV during the sample drying stage, the e cacy of which is mirrored in the numerous e orts targeting sample desolvation for pneumatic nebulization using heated spray chambers with tandem condensers or membrane driers to remove moisture. This is particularly advantageous when applied to the determination of the rare earth elements, wherein multiple corrections for polyatomic oxides are otherwise necessitated.[29,30] The same benefits can be more e ciently realized with the ETV. Additionally, reduced solvent load alters plasma chemistry in that electron density is lowered but the excitation temperatures are increased, less power is expended in vaporizing/dissociating water and the plasma ionization characteristics are improved, thereby enhancing signal intensity.[31]

Minimizing transport of matrix components. Apart from the elimination of solvent load, sample matrix load can also be altered by one of two approaches: the sample matrix may be selectively vaporized in a separate step, prior to the vaporization and introduction of the analyte into the plasma or, in reverse fashion, the matrix is selectively removed from the ETV following early (low temperature) transfer of the analyte to the plasma. In either case, it is often not su cient to simply apply an appropriate thermal program, as the volatilities of the analyte and matrix are frequently not disparate enough to accomplish significant separation e ciently. For this reason, chemical modifiers are often utilized which react with either the analyte or the matrix components to create new compounds which enhance their volatility di erences and permit more e cient and selective vaporization of one of them. The 'art' of such applications is well developed and borrowed from the literature on ETAAS.[32–34] Unfortunately, addition of modifiers is often plagued with the adventitious introduction of concomitant analyte impurities. These increase the analytical blank and degrade the detection limit and/or create new spectral interferences *via* reaction of the relatively massive (μg scale) amounts of modifier with plasma gas species (*i.e.*, generation of argide species).[35]

Elimination of matrix components entering the plasma may not only alleviate spectral interferences as well as non-spectroscopic e ects (*e.g.*, ionization suppression from EIEs), but the matrix e ect associated with the space charge phenomenon can, in principle, also be minimized. Caution must be exercised in that space charge e ects from sample components are hopefully not replaced with an equally deleterious matrix from added modifiers. An example of this will be presented later in connection with the determination of Se in a reference sediment material.

As noted earlier, refractory elements, and those that interact at high temperature with graphite to form non-volatile carbides, are troublesome for ETV sample introduction, resulting in non-quantitative release from the ETV or excessively broad 'transients' having degraded precision of measurement. Similarly, such matrix species may be di cult to remove from the device and create problems for subsequent determinations. This dilemma is not unique to tandem source ETV, having been earlier encountered with ETAAS and even dc arc emission spectrography. As a consequence, several approaches have been adopted which take advantage of the chemistry which can be used at elevated temperature to create conditions within the ETV which enhance the volatility of the sample and/or analyte, including the introduction of halogenation and complexation reagents.[36–47] Ng and Caruso[38] reported on the use of a 7% (m/v) solution of NH_4Cl to facilitate the vaporization of Zr, U, V and Cr from a graphite cup by preferential *in situ* formation of the volatile chlorides. Similarly, Matousek and Powell[36] utilized direct injection of chlorine gas (50 μl) into the furnace during the high temperature vaporization stage to achieve e cient removal of refractory carbide residues. This provided an alternative to halocarbon purging.[47] Huang *et al.*[37] added a 1.8% slurry of PTFE directly to dosed samples and, by charring the sample at 450 °C, e ected decomposition of the PTFE to liberate fluorine which subsequently attacked the sample matrix and enhanced the volatility of the analyte.

A variation of this approach was used to separate As[39] and Si[40] selectively from sample matrices by the addition of an aliquot of 3% (m/v) NaF solution to a mixture of the sample and H_2SO_4. The heat of the reaction was su cient to volatilize AsF_3 and SiF_4 from the medium for transport to an ICP (for AES detection). Although the reaction was conducted in a separate PTFE reservoir, extrapolation of this approach to ETV-ICP-MS is straightforward.

Kumamaru and co-workers advantageously utilized the ETV as a thermochemical reactor to undertake *in situ* alkylation reactions.[42–44] Following the dosing of the liquid sample and application of a drying stage to remove all water, the residue was reacted with a solution of ethylmagnesium bromide in tetrahydrofuran to permit release of the volatile diethylberyllium at temperatures as low as 600 °C.[42] Similar approaches also permitted the formation and volatilization of dibutylzinc at 250–450 °C[43] following *in situ* butylation with butyllithium and the volatilization of ethylgallium at 600 °C[44] by reaction with ethylmagnesium bromide. In each case, quantitative release of the analyte could be achieved, permitting its complete separation from the matrix. Low temperature vaporization (900 °C) of the 8-hydroxyquinolate complex of V[45] and Cr (950 °C)[46] was used to facilitate determination of these elements in rock, steel and aluminium samples following addition of 10 μl of a 0.2 M solution of reagent to the sample in the furnace. Although the above studies were conducted with an ETV-ICP-AES system, these approaches are clearly amenable to operation with ICP-MS. Indeed, Byrne *et al.*[41] also reported on the *in situ* formation of a volatile 8-hydroxyquinolate complex of Cr for ETV-ICP-MS analysis which enhanced the limit of detection 20-fold compared with vaporization without the reagent. This was ascribed to a lowering of the required vaporization temperature (to 1800 °C) which

minimized the release of carbon into the ICP, thereby decreasing the intensity of the polyatomic $^{12}C^{40}Ar^+$ species interfering with the measurement of the principal Cr isotope.

Altering release of volatile elements. Separation of relatively volatile analytes from matrices of similar volatility presents a di cult challenge, as exemplified by the determination of elements such as Zn and Cd in seawater. The massive amount of salts that co-volatilize with these elements create not only excessive space charge problems, which virtually suppress the analyte ion signal,[48,49] but can interfere with the measurement of other analytes (*e.g.*, As) due to formation of polyatomic species ($^{40}Ar^{35}Cl^+$).

Two approaches to this problem arise: stabilization of the analyte with use of a classical modifier, such as reduced palladium, while attempting to volatilize the major fraction of matrix selectively, or formation of a more volatile complex of the analyte which permits its selective low temperature release. An example of the former is the work of Grégoire and Ballinas[48] who utilized Pd and Mg to stabilize As while treating the sample with NH_4NO_3 (to form NH_4Cl) in an e ort to volatilize as much chloride (in the form of NH_4Cl) as possible at 1000 °C prior to the determination of As in seawater (to minimize $^{40}Ar^{35}Cl^+$ polyatomic interference).

Fig. 1 illustrates transient signals for As obtained for a similar situation encountered in our own laboratory. Despite use of an Ni modifier to enhance the thermal stability of As, and in addition to the introduction of NH_4NO_3 coupled with a pyrolysis temperature of 1100 °C, the signal for As is significantly suppressed in a neat sample of 20 µl of seawater (NASS-4 reference material). Additionally, it is clear that complete removal of the chloride fraction of the matrix is unsuccessful, as the recorded $^{40}Ar^{37}Cl^+$ reveals that ^{75}As would also be compromised by overlap with more abundant $^{40}Ar^{35}Cl^+$. Based on earlier reports that use of EDTA or organic diacids, such as ascorbic or citric acid, is useful for facilitating early release of volatile elements from saline media,[50–52] experiments were conducted to address the e cacy of this approach for the direct determination of As in seawater. Further, as it is well-known that environmental samples may contain As in several di erent chemical forms, *i.e.*, monomethylated and dimethylated species, arsenocholine and arsenosugars[53–55] (arsenobetaine has not been reported in seawater, rather a halogenated betaine-like species), which may have di erent volatility and chemistry for interaction with Pd or Ni modifiers,[56] it was deemed appropriate to ensure that all forms of As likely to be present in the sample be first converted to a common (inorganic) form. This was conveniently achieved *in situ* by undertaking oxidation of the sample at 500 °C while admitting a 200 ml min^{-1} flow of air into the ETV. If this oxidative conversion is not completed, use of ascorbic acid alone results in the loss of a fraction of the total As at temperatures as low as 200 °C. Following completion of the oxidation step, ascorbic acid modifier was then added to promote early release of As and the sample vaporized at a relatively low temperature of 500 °C (using a ramped heating of 300 °C s^{-1}). Fig. 2 illustrates the recorded transient along with that for $^{40}Ar^{37}Cl^+$. It is clear that nearly complete separation of the As from the matrix has now been achieved and there is insignificant 'isobaric' correction required for interference from $^{40}Ar^{35}Cl^+$. Total As in this sample was determined by the method of additions to yield 2.0 ± 0.3 ($n = 26$) ng ml^{-1} as compared with 1.69 ± 0.09 ng ml^{-1} obtained by hydride generation ETAAS following photo-oxidation of the sample. A limit of detection for As was estimated to be 7.5 ng l^{-1} with a sample throughput of 15 per h.

A further example of the utility of the ETV to function as a thermochemical reactor can be illustrated by the direct determination of Cd in seawater.[57] Fig. 3A shows transients for release of 100 pg of Cd from a standard 1% (v/v) solution of HNO_3 using a maximum power heating mode for the ETV (approximate heating rate of 1800 °C s^{-1}). Fig. 3B presents a trace for the release of 100 pg Cd in the presence of 0.2 mg EDTA when using a ramped heating of the ETV (1000 °C s^{-1}). The integrated intensities for traces A and B are, within experimental uncertainty, the same. Fig. 3C presents a trace for the ramped atomization of 200 pg Cd without EDTA, from which it is clear that the integrated intensity for the ^{111}Cd is less than 1% of its response in the presence of EDTA. Atomic absorption spectrometry was used to show that the Cd was likely released at approximately 700 °C in the form of a cold vapor from samples treated with EDTA.

Chapple and Byrne[49] adopted a di erent approach to the problem in that multiple additions of HNO_3 were made to the sample in combination with pyrolysis at 1200 °C in an e ort to remove the salt matrix from seawater samples. Volatile elements were lost in the process and only Co, Cu, Mn, Ni and V could subsequently be quantitated.

A further example of the utility of the ETV functioning as a reactor for *in situ* sample processing is the thermal generation of a volatile complex of Se by reaction with added citric acid to promote its quantitative and early release from a matrix of digested sediment.[58] Atomic absorption spectrometry was subsequently used to show that the Se volatilized as a molecular complex from the sample at temperatures below 600 °C (*i.e.*, no atomic absorption was registered). Fig. 4 illustrates typical Se signal transients generated in the absence and presence of added citric acid. Although sensitivity is enhanced more than 50-fold, the depression evident in the tail of the signal in the presence of citric acid is a consequence of the concurrent release of excess modifier from the ETV. This space charge interference, which likely occurs throughout the entire vaporiz-

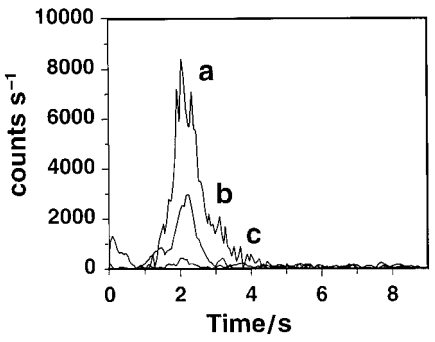

Fig. 1 Signal transients for As using ETV-ICP-MS sample introduction. a 20 pg As standard, 300 °C pyrolysis temperature; b 20 µl sample of seawater (NASS-4, equivalent to approximately 40 pg As) spiked with 5 µg Ni and 10 µg NH_4NO_3 modifiers, 1100 °C pyrolysis temperature; and c trace for $^{40}Ar^{37}Cl^+$.

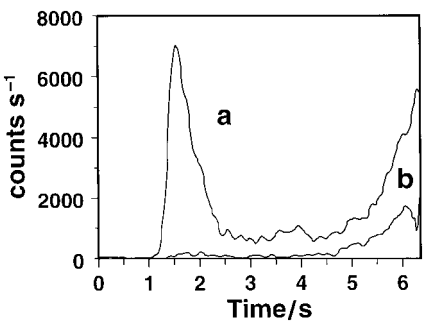

Fig. 2 Signal profiles for As and background in NASS-4 seawater for ETV sample introduction following air oxidation, addition of ascorbic acid, pyrolysis at 400 °C and ramped atomization (5 s) to 1400 °C, 2 s read delay. a ^{75}As; and b $^{40}Ar^{37}Cl^+$.

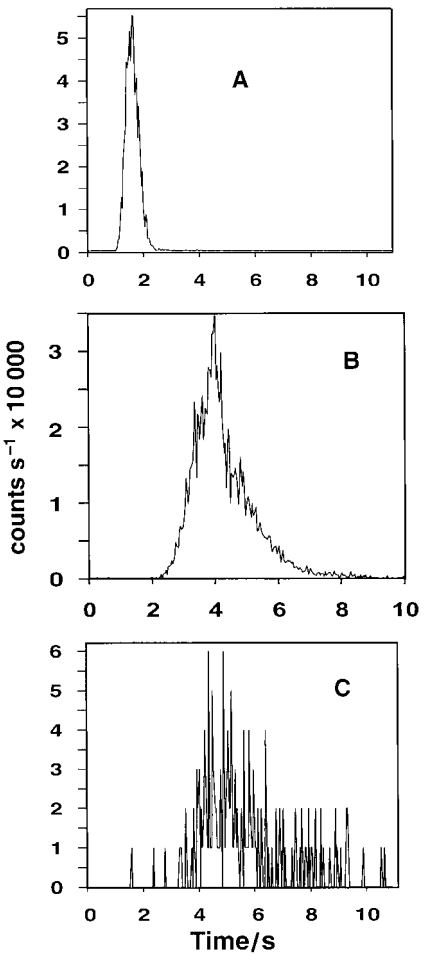

Fig. 3 Signal profiles for ^{111}Cd with ETV sample introduction, 350 °C pyrolysis. A, 100 pg Cd with maximum power heating to 1900 °C; B, 100 pg Cd with 0.2 mg EDTA, ramped heating at 1000 °C s^{-1}; and C, 200 pg Cd, no modifier, ramped heating at 1000 °C s^{-1}.

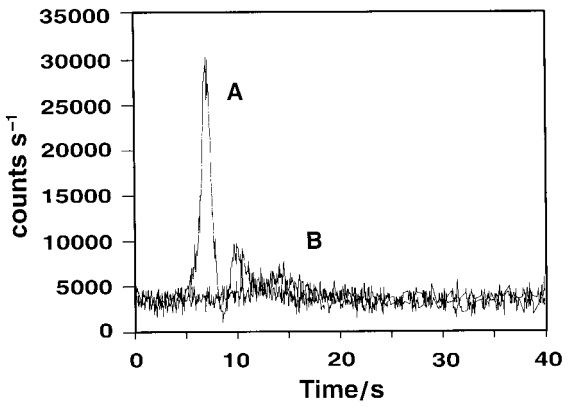

Fig. 4 Signal profiles for ^{78}Se with (trace A, 50 pg Se) and without (trace B, 500 pg Se) citric acid. 'Pyrolysis' temperature of 120 °C, ramped (20 s) atomization to 2600 °C.

ation event, noticeably compromised the ^{77}Se:^{82}Se ratio but permitted the determination of ultra-trace concentration (50 ng g^{-1}) of Se in a sediment by the method of additions.[58]

Apart from the direct minimization of some polyatomic interferences by judicious use of thermal programming and *in situ* thermochemical reactions with suitable reagents, as described above, the ETV also o ers the advantage of an added dimensionality to the analysis. Temporal release of analytes from the surface of the ETV can be used to advantage to e ect a chromatographic separation of the various species desorbing from the graphite surface. A particularly powerful example of the attributes of this added dimensionality is the use of ETV for sample introduction into an ICP-TOF-MS instrument.[24] The characteristic appearance temperatures of several elements (Cd, Sn and In) were used to separate the signals temporally when they would otherwise exhibit mutual (isobaric) interference. Attempting this by mass spectrometry alone would have demanded unattainable resolution with the system used (90–100 k).

In situ speciation

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.[59] In addition to valence state speciation information, identification of organometallic species (of As, Se, Sn, Hg and Pb) has been most actively pursued. Although numerous tandem source approaches have been utilized relying on the chromatographic characteristics of the temporally- or volume-resolved response from atomic detectors to identify the species detected,[59,60] little has been accomplished with use of the ETV. While admittedly the examples which follow could be, in some cases, more easily addressed with other techniques, they nonetheless provide evidence of the capabilities of the ETV in this area of study.

Richner and Wunderli[61] used the ETV to e ect a thermal separation of inorganic chlorine from its more volatile forms associated with polychlorinated biphenyls, enabling quantitation of the latter in waste oils by ICP-MS. Organochlorine could be removed from the sample aliquot by heating the ETV to 400 °C, whereas the inorganic fraction was removed by heating to 2650 °C.

Discrimination of the inorganic fraction from total mercury present in biological tissue was reported by Willie *et al.*[62] and provided an elegant example of the use of the ETV as a thermochemical reactor for *in situ* sample pretreatment and speciation. The integrity of the species was preserved by solubilization of the tissue with tetramethylammonium hydroxide (TMAH). For the determination of total mercury, sample aliquots were simply dried and vaporized into the plasma. For the selective determination of inorganic mercury, iodoacetic acid, sodium thiosulfate and acetic acid were added to the sample, cleaving the methylmercury from the tissue. Volatile methylmercury iodide so formed was released during the sample drying stage (120 °C), leaving only inorganic mercury to be quantitated by the method of additions.

Other, less quantitative, speciation schemes for the determination of the various forms of mercury present in soils and sediments rely on simple thermal distillation or pyrolysis of a sample (2 mg) by heating at 0.5 °C s^{-1} and sweeping the evolved gas into a quartz tube for AAS detection.[63,64] The same can be conveniently accomplished with the ETV, wherein the vapors are swept to the ICP torch. Calibration is achieved with use of standard reference soils. This is clearly likely to provide a qualitative approach to this problem, as otherwise the standard soils themselves must be certified for speciation content.

Arpadjan and Krivan[65] quantitatively achieved *in situ* separation of Cr^{III} from Cr^{VI} using the heated graphite furnace to initiate reaction of samples (water and urine) with a mixture of TMAH, methanol, sodium acetate and trifluoroacetylacetone (TFA). The TFA complex of Cr^{III} was removed from the cell by heating to 400–1200 °C (300 s heating at 400 °C), after which the Cr^{VI} was volatilized by heating to 2600 °C. Extrapolation of the procedure to ETV-ICP-MS detection remains to be verified in light of the problems which arise from $^{52}ArC^{+}$. However, the methodology reported by Byrne

et al.[41] and Tao and Kumamaru[46] may likely be utilized to circumvent this problem by release of Cr^{VI} at low temperature.

A similar approach to the ultra-trace di erential determination of As^{V} and As^{III} in aqueous environmental samples was reported by Chen *et al.*[66] When the graphite surface of the ETV was modified by high temperature impregnation with zirconium, it was possible to volatilize As^{III} selectively in the form of the chloride by addition of 9 M HCl to the sample and heating to 400 °C. The As^{V} was retained in the tube to temperatures up to 1400 °C by interaction with the surface. The method of additions was used for quantitation. At this temperature, most of the chloride has been removed from the furnace and spectral interference from $^{40}Ar^{35}Cl^{+}$ should be negligible.

In situ sample preparation

The ETV has also been used as an e cient medium for solid sample digestion. The relatively inert, high purity graphite substrate and programmable temperature may be used to process samples *in situ* more e ciently than o -line bulk processing. An example of this is reported by Okamoto *et al.*,[67] wherein a weighed, powdered botanical sample was mixed with ammonium phosphate (modifier) and placed into an ETV device. TMAH was added to e ect an *in situ* wet digestion at 150 °C. Ashing of the sample at 1000 °C removed the bulk of the matrix and the Cd analyte was then volatilized into a plasma by heating to 2500 °C. The most remarkable feature of the technique was that both sample decomposition and vaporization were accomplished using the same vessel.

A further example of the use of the ETV for *in situ* sample decomposition is the simple oxygen ashing of biological materials that can be achieved during slurry or solid sampling of tissues, wherein the organic matrix can be eliminated by thermally treating the sample at 600–800 °C in the presence of air.[68,69] Any oxidative destruction of the pyrolytic graphite coating that may arise as a result of using the higher temperatures likely does not impact on the ICP-MS response as significantly as with ETAAS since only volatilization of the sample is sought. More recently,[70] it has been suggested that this process may also facilitate analyte transport to the ICP as a consequence of reproducible formation of carbonaceous aerosol species (from partial oxidative destruction of the tube surface) serving as transport nuclei.

In situ preconcentration

The ETV functions e ciently for handling the e uents (concentrates) from flow injection manifolds[71,72] and is thus able to embrace all of the same advantages which accrue when these systems are interfaced to any atomic spectrometric detection system. In this respect, the ETV serves in a passive mode for tandem source sample introduction.

Apart from this obvious application, the ETV itself can function in a more proactive mode, wherein it may serve as an e cient preconcentration cell for liquids and gases to enhance relative detection power. The simplest approach in this direction is the use of spray deposition for sample dosing into the ETV.[73] Typically limited to 20–50 μl sample aliquots when pipetted, this volume may be e ectively increased to several hundred μl by spray deposition of the sample directly into a preheated ETV (typically 160 °C) using a standard pneumatic nebulizer wherein the aerosol is simultaneously desolvated and adsorbed onto the wall of the ETV. Relative detection limits can be enhanced 10-fold with ideal samples.

Similar in concept is the use of the ETV to sequester the volatile forms of elements generated in chemical manifolds, thereby providing enhancements in relative detection limits by factors in excess of 1000-fold compared with solution phase analysis. This methodology has recently been reviewed.[11] Although the principal application has been directed to the *in situ* trapping of hydride forming elements,[74] a number of volatile trace element compounds can be targeted for such application, including phosphorus,[75] sulfur[76] and several transition metals, *i.e.*, Cd,[77] Cu[78], Ni[79] and Pb[80]. Additionally, the ETV may be conveniently used as a preconcentration cell for the collection of aerosol particulates[81] using electrostatic deposition techniques. This approach has also been successfully demonstrated for the collection of the volatile hydrides of As, Se and Sb.[13]

The ETV may also function as the cathode of an electrochemical cell, thereby permitting the deposition of electroactive analytes from solution onto its surface.[82] *In situ* matrix elimination for aqueous samples, with potentially quantitative electrodeposition of trace elements within 60 s using 20–40 mA currents, can be achieved. As an example, the deposition process was automated to include application of a modifier reagent using a Pt/Ir autosampler (anode) and, in conjunction with a rinse cycle for removal of the electrolysed sample, >99.5% of a 0.5 M NaCl matrix was eliminated. The advantage of this approach to minimization of space charge matrix interferences is clear, as is extrapolation of the technique to the potential speciation of the di erent electroactive forms of elements.

Conclusion

The full potential of ETV sample introduction for tandem source ICP-MS remains to be explored and exploited. The microenvironment of the ETV is convenient for use of the cell as a thermochemical reactor for the pretreatment of samples which cannot be easily handled by other means in the laboratory. The ease with which solid (as slurry), liquid and gaseous reagents can be admixed with the sample in this graphite thermochemical reactor is attractive. The precise programming of the temperature in this environment opens the door for sample pretreatment with the aim of synthesis of volatile analyte complexes, elimination of matrix components, selective vaporization of analyte species and simple decomposition of complex materials. Each of these scenarios serves to enhance the performance of the analytical technique by minimizing sample preparation time, reducing or removing matrix-induced polyatomic interferences and space charge e ects and enhancing the relative limit of detection. Clearly, optimum benefit from these accomplishments will accrue from use of TOF instrumentation to take advantage of the 'simultaneous' registration of multielement information. It should be evident from the foregoing that ETV satisfies more than just a niche end use for relatively simple and e cient transfer of analyte to the plasma. ETV should not be viewed as competitive to other high e ciency microsample liquid introduction techniques, or in relation to laser ablation for solid sampling devices or hyphenated chromatographic approaches for speciation, but rather as a complementary methodology in the arsenal of problem solving approaches.

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