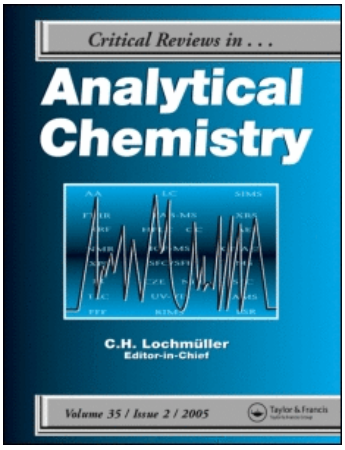

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Electrothermal Vaporization — Inductively Coupled Plasma–Mass Spectrometry (ETV-ICP-MS): A Valuable Tool for Direct Multielement Determination in Solid Samples

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ABSTRACT: Solid Sampling-Electrothermal Vaporization-Inductively Coupled Plasma-Mass Spectrometry (SS-ETV-ICP-MS) is an attractive technique for the direct simultaneous determination of trace metals in solid samples. During recent years, some important developments dealing with ETV-ICP coupling and with analyte transport efficiencies have been reported, and so SS-ETV-ICP-MS has received a renewed interest by the atomic spectroscopy community. Thus, the present review highlights the inherent capabilities of SS-ETV-ICP-MS for the simultaneous determination of trace metals. In addition, technical aspects of ETV-ICP coupling as well as more recent applications are reported. It is concluded that this technique is a powerful tool for sorting out some of the current analytical challenges, and future advances are to be expected in order to widen the field of application.

KEY WORDS: solid sampling; electrothermal vaporization; ICP-MS; trace metals; review.

I. INTRODUCTION

Electrothermal vaporization (ETV) has been studied during the last 10 years as a sample introduction technique for inductively coupled plasma (ICP) atomic emission spectrometry (AES) and mass spectrometry (MS), although analytical chemists are more familiar with the use of ETV as an atomizer source (graphite furnace) in atomic absorption spectrophotometry. Graphite furnace-atomic absorption spectrophotometry (GF-AAS) has been used for more than 25 years and has shown its great potential for the determination of trace metals at very low concentration levels in different complex matrices.[1] By the correct selection of thermal programs, the addition of matrix modifiers, etc., it is possible to generate the desired atomic vapor inside the graphite tube. However, whereas complete atomization of the analyte is mandatory in GF-AAS, it is not necessary in ETV coupled to ICP. In this case, the complete vaporization of the analyte and its efficient transport to the plasma is only necessary. Thus, ETV acts as a sample introduction system, and it can be considered an independent device of the tandem ETV-ICP.

Nowadays there is a wide variety of sample introduction devices for ICP. Liquid samples are easily introduced by pneumatic, ultrasonic, thermospray, hydraulic high pressure, as well as a variety of microflow nebulizers. Direct sample insertion devices or laser ablation can handle solid

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samples, and gases can be sampled directly after vapor generation. It is clear that ETV is able to handle any kind of the mentioned samples, and it is especially suitable for the direct analysis of solid samples,[2] making it an attractive device to be used as a sample introduction system for ICP.

ETV was coupled to ICP-AES by Nixon et al.[3] in 1974, but the popularization of this technique has been slow mainly due to the difficulties encountered using current spectrotometers for the accurate measurement of transient signals, especially when a background correction is necessary. However, after the first coupling to ICP-MS,[4] ETV as a sample introduction system for ICP has received renewed interest by the atomic spectroscopy community due to its high sensitivity compared with GF-AAS and its ability (as a fast sequential technique) to measure transient signals of different isotopes (elements) "simultaneously". The potential of this technique has been widely demonstrated in recent years; however, unfortunately, most of the applications have focused on the handling of liquid samples that can be easily introduced by commercially available (microflow) nebulizers. Thus, the aim of this paper is to highlight the inherent capabilities of solid sampling (SS)-ETV-ICP-MS for the simultaneous determination of trace metals, although some applications dealing with liquid samples are considered as some aspects (instrumental coupling, transport efficiency, etc.) are independent of the final application.

II. ETV DEVICES AND COUPLING TO ICP

An "ideal" ETV device for the direct analysis of solid samples should meet the requirements of a furnace device together with the possibility of solid sample introduction without disturbing the plasma. The sample should be completely vaporized after its introduction into the furnace, and the analyte must be transported to the plasma with minimal loses (in the furnace itself or in the connecting tubing) and separately from the rest of the volatilized matrix. Thus, as in GFAAS, an SS-ETV-ICP procedure includes different thermal steps (drying, ashing, and volatilization) in order to remove matrix components before the analyte is transferred to the plasma or to volatilize the analyte before removing the bulk sample. It is important to stress that during the drying, and especially during the ashing steps, a huge amount of matrix components are volatilized, and thus it is necessary to prevent their introduction into the plasma. On the other hand, in order to achieve an efficient analyte transport, some modifications on the ETV device should be introduced in such a way that the aerosol vapor is condensed into particles, which diminishes analyte loses in the transport tubes (a more detailed description on aerosol formation is given in the next section).

The ETV devices commercially available for ICP-MS are designed for the handling of liquid samples or for their use in GFAAS.[5,6] Thus, some modifications have been proposed in the literature in order to allow the introduction of solid samples in a reproducible and easy manner without disturbing the plasma. One of the most used designs is the flowthrough type, also referred to as "boat in tube"-type furnaces, because most of them are equipped with a sample boat, and it is schematically shown in Figure 1. These furnaces were originally designed for the analysis of solids by GFAAS, and thus some modifications, such as changing the gas flows and closing the furnace by a shutter, have been made. The sample, weighed in a tared graphite boat, is introduced in the furnace through the right side, usually with the help of a pair of tweezers, enabling a reproducible positioning of the sample boat in the furnace. In addition, this procedure allows further automation by integrating a solid-sampling workstation and by incorporating a micro-balance to the system.

On the other hand, in order to form a stable aerosol, the introduction of a cold gas flow (referred to as bypass gas in Figure 1) is usually carried out. This modification was proposed by Kántor and Zaray[7] allowing sample vapor mixing with cold gas flow favoring aerosol vapor condensation into particles, which prevents them from interacting with the tubing walls. Ren and Salin[8] proposed a further furnace modification by drilling four holes in one of the graphite contact rings. With this design, when a gas flow is introduced through these holes, one fraction acts as cooling

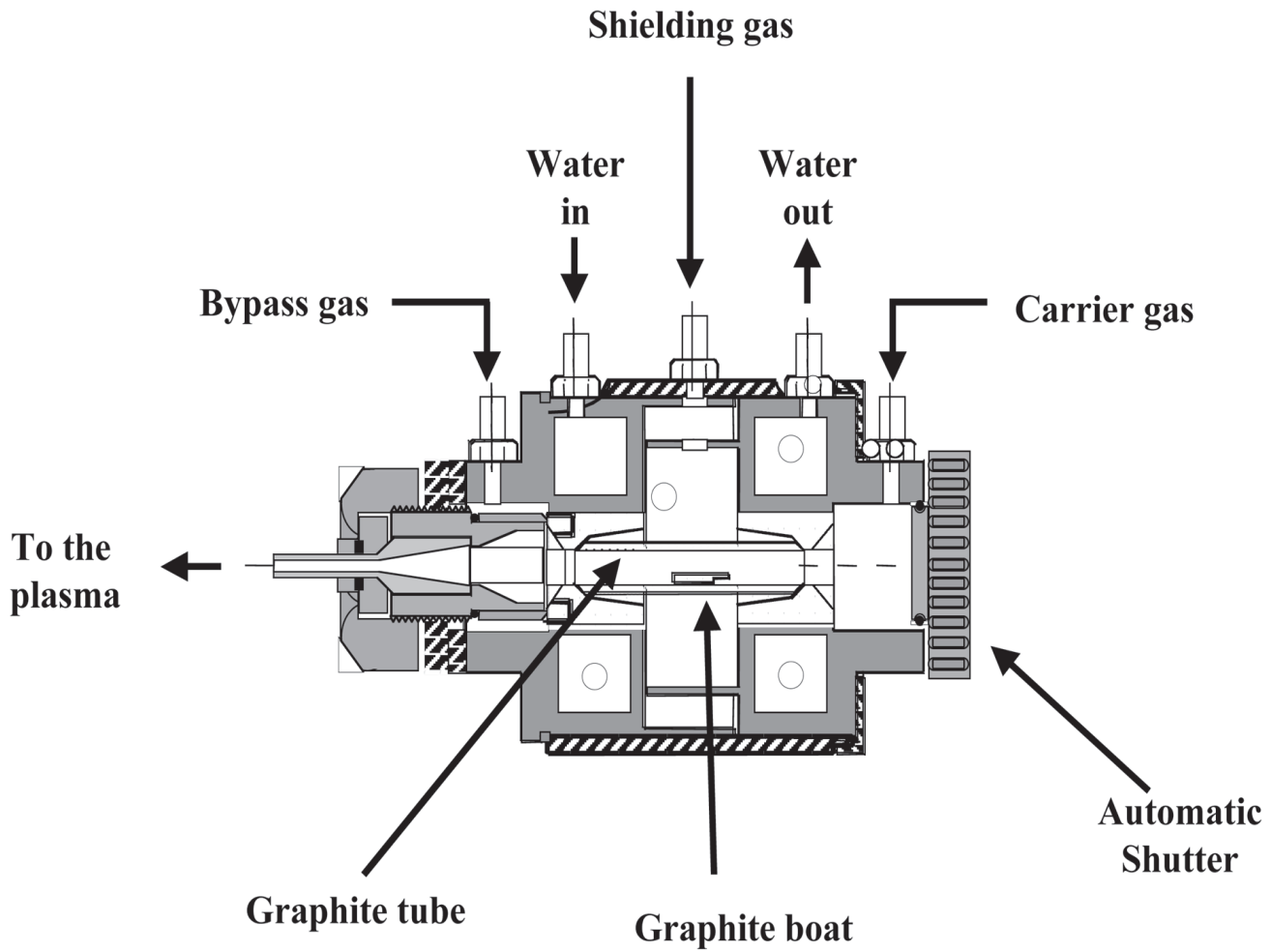

FIGURE 1. "Boat in tube" ETV design after modifications to be coupled to ICP.

gas to promote aerosol formation, and the other is led through a gap between the graphite contact and the transport tube minimizing condensation in the tubing.

In our laboratory, two different designs have been used[9,10] and are shown in Figure 2. One of them (Figure 2A) includes a modified graphite contact by the production of a circular groove, and six stubs provided the flow of argon to the groove. With this design a circular flow of cool gas around the carrier gas from the tube is achieved. The alternative design (Figure 2B), developed by Perlz and Hassler,[11] made use of tubes equipped with a nozzle which are inserted into a collector tube. In this case, the bypass gas is led through the gap between the nozzle and the collector tube. In these studies, the transport efficiency of the nozzle-type tube, was superior to that of the standard tube, but the former provokes a significant tailing of transient signals. The origin of this tailing is assigned to condensation and revaporization of analytes in the nozzle tube because the temperature rise for the tip of the nozzle is delayed and might not reach the final temperature of the tube walls or of the platform.

Finally, the ETV device has to be connected to the ICP. This physical coupling is usually carried out using glass, silicon rubber, tygon, or Teflon® tubes. According to several studies,[12-14] analyte losses are kept to a minimum when the smallest tube diameter, the shortest length, and the highest possible gas flow rate are used. In general, in ETV-ICP coupling for a gas flow of 0.3 to 0.8 l/min, a tube length of 30 to 60 cm, and an inner tube diameter of 3 to 4 mm are recommended. Similar results were obtained recently by Venable and Holcombe,[15] who carried out a Monte Carlo simulation to determine the cause of signal broadening in ETV-ICP-MS. In this study, while a decrease in transfer tube radius and length reduces band broadening, a higher carrier gas flow rate (which reduced residence time in transfer line of particles) increases peak broadening. Thus, it was concluded that the parabolic flow profile generated by laminar flow of the carrier gas was the main cause of analyte dispersion.

III. AEROSOL FORMATION AND TRANSPORT EFFICIENCY

It was noticed, even in early ETV-ICP studies, that mass transport efficiency was not quantitative, and that a significant fraction of vaporized analyte did not reach the plasma. In addition, it was observed that calibration curves were not linear when the analyte was vaporized alone in solution, but they became linear after the addition of a salt.[16,17] Ediger and Beres[16] interpreted the nonlinearity of calibration curves using a theoretical model derived by Kantor.[18] Although a deep discussion on aerosol formation and mass transport process is beyond the scope of this review, the following description helps to understand some experimental aspects of ETV-ICP coupling (i.e., sample mass, carrier gas flow rate). Kantor's model[18] considers that the transport of analyte vapor from the ETV surface is dependent on the formation of stable nuclei of size exceeding a critical diameter according to the following equation:

$$d_p = 4\sigma \frac{V_m}{kT \ln S} \qquad (1)$$

where d_p is the critical diameter, σ is the surface tension of the liquid droplet, V_m is the molecular volume of the vapor species, k is the Boltzmann constant, T is the absolute temperature, and S is the saturation ratio, which gives the degree of supersaturation according to the equation:

$$S = \frac{P_{vap}}{P_s} \qquad (2)$$

where P_{vap} is the partial pressure of the vapor, and P_s is the saturation vapor pressure of the component. Thus, if at a given temperature the partial pressure of a given analyte exceeds its P_s, the vapor is supersaturated and condensation takes place. In addition, according to Eq. 1, for a given saturation ratio at a certain temperature, only those particles with a diameter equal or higher than d_p will be stable. As mentioned before, the formation of an aerosol is based on the condensation of supersaturated vapor (which is obtained when a

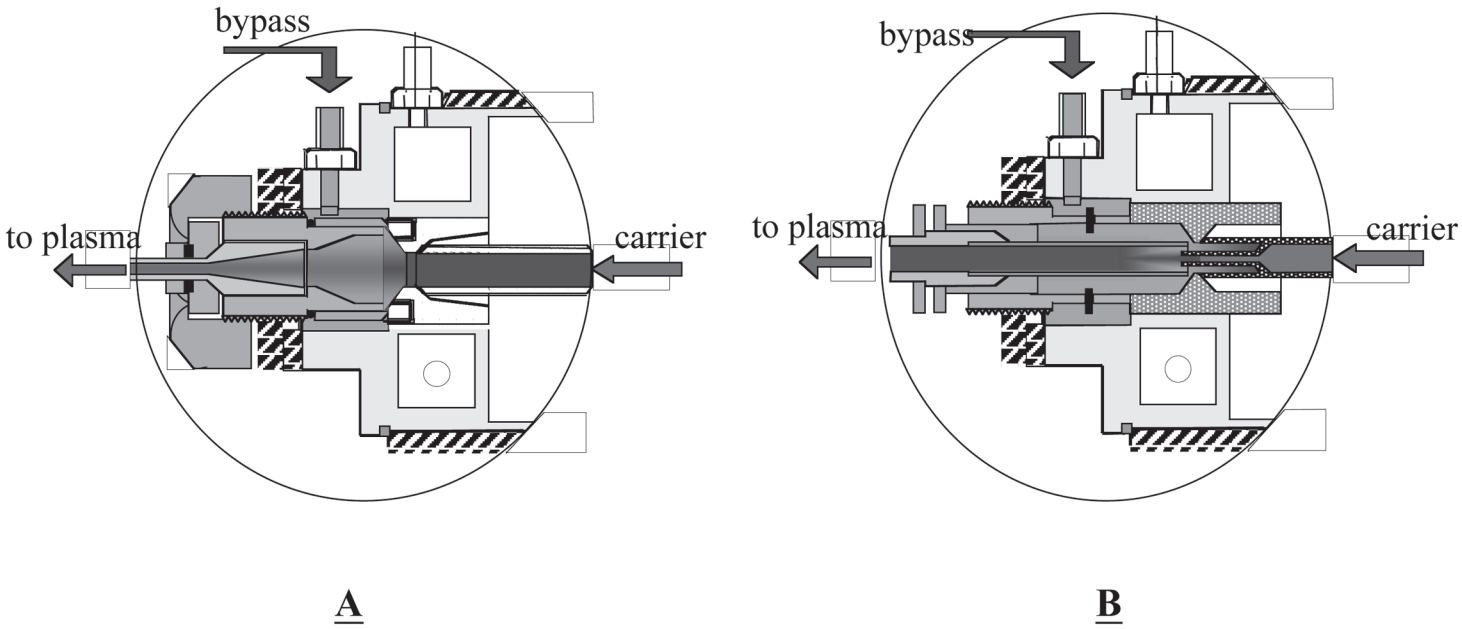

FIGURE 2. Electrothermal vaporizer with standard tube (A) and nozzle-type tube (B), and the corresponding interfaces.

saturated vapor is cooled down) on small particles, thus the introduction of a "cooling gas" at the end of the furnace enhances the supersaturation and increases the condensation of the vapor on the sites.

Once a stable nucleous is formed (according to Eq. 1), the particle grows by condensation of the vapor on it. Hence, if liquid samples are used there are not enough molecular species to act as nuclei, thus leading to nonlinear calibration curves. However, this is not a problem in ETV of solid samples because a large amount of particles are present. On the other hand, particle growth can be produced by the coagulation of particles to form a new larger particle and thus decreasing the number of fine particles. If particles grow too large, sedimentation in the transport tubes becomes important. Therefore, an optimum particle size is required.

Nucleation starts for a given analyte at its corresponding temperature of supersaturation.[18] Thus, for volatile elements, nucleation starts along the tubing, which can provoke condensation of atomic vapor on the cold transport tubes. However, for less volatile or refractory elements, high loses can be occur in the cool ends of the graphite tube. For volatile elements, loses can be minimized by cooling down the vapor in the furnace, whereas for refractory elements the introduction of gaseous (i.e., Trifluoromethane) or solid (i.e., Teflon® powder) improves their vaporization increasing the transport efficiency.

Analyte transport efficiency in ETV-ICP-MS was first reported by Park et al.[19] and since then, several different studies have been carried out using different approaches and can be categorized as:

1. Trapping the analytes from the carrier gas stream using filters and trap solutions,[20] gas-sampling bags[21] or electrostatic deposition[22] and subsequent analyte determination.
2. "Indirect methods" based on the quantification of analytes deposited in the furnace, interface, and tubing.[23,24]
3. Methods relating signal intensities obtained in ETV to signals obtained with a reference method (i.e., pneumatic nebulization of solutions).[9,25]
4. Radiotracer experiments (combining approaches 1 and 2).[26]

From these studies, with their own advantages and limitations in calculating absolute transport efficiencies, it is clear that transport efficiencies range from 10 to 35%, depending on the analyte. It is important to stress that most of these studies have been carried out using liquid standards and nuclei formation, which has a direct influence on transport efficiency (as stated previously), is disfavored regarding ETV of solid samples. Thus, transport efficiencies in ETV of solid samples should be higher, and thus, theoretically, a higher sensitivity should be obtained. However, the composition of the matrix can affect vaporization and transport processes and can reduce sensitivity drastically. Apart from theoretic considerations, it is clear that this fact has strong implications in the calibration process, as discussed in the next section.

During the ashing and vaporization process, a huge amount of matrix components is released from the furnace to the plasma. This affects not only the analyte transport but also the sensitivity (and selectivity) of its determination. It has been widely reported that matrix components can cause nonspectroscopic interferences, resulting in analyte signal enhancement or suppression, and thus it is desirable that analytes reach the plasma before or after matrix volatilization. Selective matrix (or analyte) volatilization, possible for liquid samples if analyte and matrix elements have very different volatility, is not easily achievable when solid samples are to be analyzed because some reactions with matrix components may occur, completely changing the vaporization characteristics. However, the change of vaporization conditions and mechanisms can be carried out in a controlled manner by using matrix modifiers. Matrix modifiers, studied extensively in GFAAS, may be added to the sample to promote matrix vaporization, leaving the analyte in the furnace or the analyte can be turned into a more volatile chemical form. Within the second alternative, and also to minimize differences in vaporization of dissimilar matrices, halogenating reagents (gaseous and solids) have been mainly used. This technique was introduced by Kirkbright and Snook[27] using a

halocarbon/argon (0.1% of CHF_3 or CCl_4) mixture to facilitate vaporization of Zr, B, Cr, Mo, and W from solutions and since then halocarbon modifiers have been applied successfully to promote vaporization of less volatile elements.[6] Other matrix modifiers used in ETV-ICP have been complexing reagents (i.e., 8-hydroxiquinoline for V[28] and Cr[29] determination, citric acid for early volatilization of Se[30]), organometallic reagents,[31,32] or the use of oxygen for *in situ* sample decomposition of biological samples before analyte vaporization,[33] among others. A review by Sturgeon and Lam,[34] including references on the applicability of chemical modifiers and the use of ETV as a thermochemical reactor, is recommended for further information.

IV. CALIBRATION

In ETV-ICP-MS, as in other techniques for the direct analysis of solid samples, calibration is a difficult task. Calibrants with a matrix similar to the samples to be analyzed are not always available, and, on the other hand, enhancement or suppression of signals processes differ from one matrix to another, thus making it difficult to use one calibration method for a given analyte in any kind of sample. Thus, it is important to test the performance of any calibration method carefully in order to guarantee the accuracy of the obtained quantitative results.

The different calibration methods used in ETV-ICP-MS are external calibration with aqueous solutions or solid samples (certified reference materials, CRMs), use of internal standards, single or multiple standard additions, and isotope dilution.

A. External Calibration with Aqueous Solutions

This method of calibration is well known and easy to carry out but only in a few cases[35,36] it has been used with success. As was stated in Section III (aerosol formation and transport efficiency), calibration graphs using aqueous solutions are not linear because particles able to transport the analyte to the plasma are not present. However, after the addition of salts calibration graphs become linear as suitable amount of nuclei are formed during vaporization. This "standard modification" has been mostly carried out by adding NaCl,[37] diluted metal free-sea water,[36] and palladium,[38] among others.[34] It is clear that although transport efficiencies of calibrants and samples may not be different using this approach, matrix effects cannot be suppressed (or compensated), and thus other alternative calibration methods have to be used.

B. External Calibration with Solid (Reference Materials)

In the early days of ETV-ICP-MS, it was concluded by Wang et al.[39] that external calibration with a CRM of similar composition to the sample and analyte concentration level should be used in order to obtain maximum accuracy. This conclusion has been confirmed over the years, although this approach includes some drawbacks. ETV-ICP-MS using CRMs as calibrants cannot be considered an independent technique because it uses a certified value based on the results obtained by other laboratories using different techniques. Moreover, the uncertainty of a certified analyte content is larger than that in an aqueous solution, hence higher contributions from calibration to the overall uncertainty must be expected. In addition, it has been demonstrated that the use of an internal standard is also necessary to get accurate results.[35,40] Finally, the main drawback, even nowadays, is that appropriate reference materials for all kinds of samples are not available.

C. Internal Standard Addition

Internal standard addition cannot be considered a calibration method but a complement to external calibration using aqueous standards or CRMs. It has been indicated that matrix components can modify plasma conditions, and thus enhancement or suppression of analyte signals may occur. By using an internal standard, an ac-

ceptable correction can be made allowing even the use of aqueous standards.[35] However, the selection of an appropriate internal standard is not easily achievable. An internal standard should fulfill the following conditions: (1) it should show a chemistry as similar as possible to that of the analyte element; (2) the mass number of the internal standard should be close to that of the analyte; and (3) it should be present in the sample at negligible concentration levels. Obviously, an "ideal" internal standard does not exist, particularly in multielement analysis, but its use can help to solve some calibration problems as has been demonstrated in several publications.[2,35,40,43]

In order to circumvent some of the mentioned conditions that an internal standard should fulfill, Vanhaecke et al.[42] proposed the use of the argon dimmer as internal standard, and as a diagnosis tool for matrix effects in analyte response, for the determination of As in Sea Lettuce (BCR CRM 279), although, from our point of view, this tool has not been completely exploited yet.

Figure 3 shows the ^{206}Pb, $^{80}Ar_2^+$, and $^{206}Pb/^{80}Ar_2^+$ ratio signals for a river sediment candidate reference material (BCR 280R) and the corresponding derived sample mass response curves.[41] It is clear that linearity of sample mass response curve is obtained when $^{206}Pb/^{80}Ar_2^+$ ratio signal was used, that is, using the argon dimmer as internal standard. As shown in Figure 3A, matrix constituents produce an enhancement of argon dimmer and ^{206}Pb signals making important (in terms of peak area measurement) the second and third broad peaks. However, if the ^{206}Pb signal is corrected by the use of argon dimmer signal (Figure 3C), the contributions of the third peak (and in some extent of the second peak) to the overall peak area become negligible, and a linear mass response curve is obtained. Similar results[41] were obtained in our laboratory for ^{58}Ni, ^{63}Cu, ^{82}Se, ^{114}Cd, ^{120}Sn, ^{121}Sb, ^{202}Hg, and ^{205}Tl, in the same reference material BCR 280R covering a wide range of atomic masses and volatility characteristics. These results clearly show the potential of the argon dimmer use as internal standard, and further research should be done covering other elements and samples.

D. Standard Addition

This calibration methodology, widely used in other analytical techniques, was evaluated by Vanhaecke et al.[35] in the determination of arsenic in standard reference materials of plant origin by SS-ETV-ICP-MS. These authors noticed that when liquid As spikes were added after solid sample loading into the boat, the shape of the $^{75}As^+$ profile was altered, which meant that As coming from the spike contributed in a different manner than As from the solid sample. However, when liquid As spikes were previously added (and dried using an IR lamp) before solid sample loading the shape of the signal profile was not altered. Standard addition in SS-ETV-ICP-MS has been studied extensively by the same research group[40,42,44-47] obtaining similar conclusions, and thus liquid spikes addition before solid sample loading is recommended. It is important to point out that this methodology can be performed by using a single standard addition if the absolute analyte amount added is as close as possible to that present in the sample.

A variation of this methodology is the so-called "generalized simplified standard addition method", where the addition and sample mass are varied and a plane is fitted to the signal responses. Subsequently, analyte concentration is determined from the three fitted parameters of the plane. Using this approach, instrument drift occurring during long procedures could be corrected.[48]

E. Isotope Dilution

Isotope dilution mass spectrometry (IDMS) has been defined as a technique capable of providing improved accuracy and precision over alternative ICP-MS methods.[49,50] This technique is based on the addition of an isotopically enriched material that acts as the "ideal" internal standard. Obviously, the application of this technique requires that more than one isotope of the analyte occurs in nature and that the selected isotopes are free of interferences. These requirements limit its applicability and its use in SS-ETV-ICP-MS has been scarce so far.[51-53]

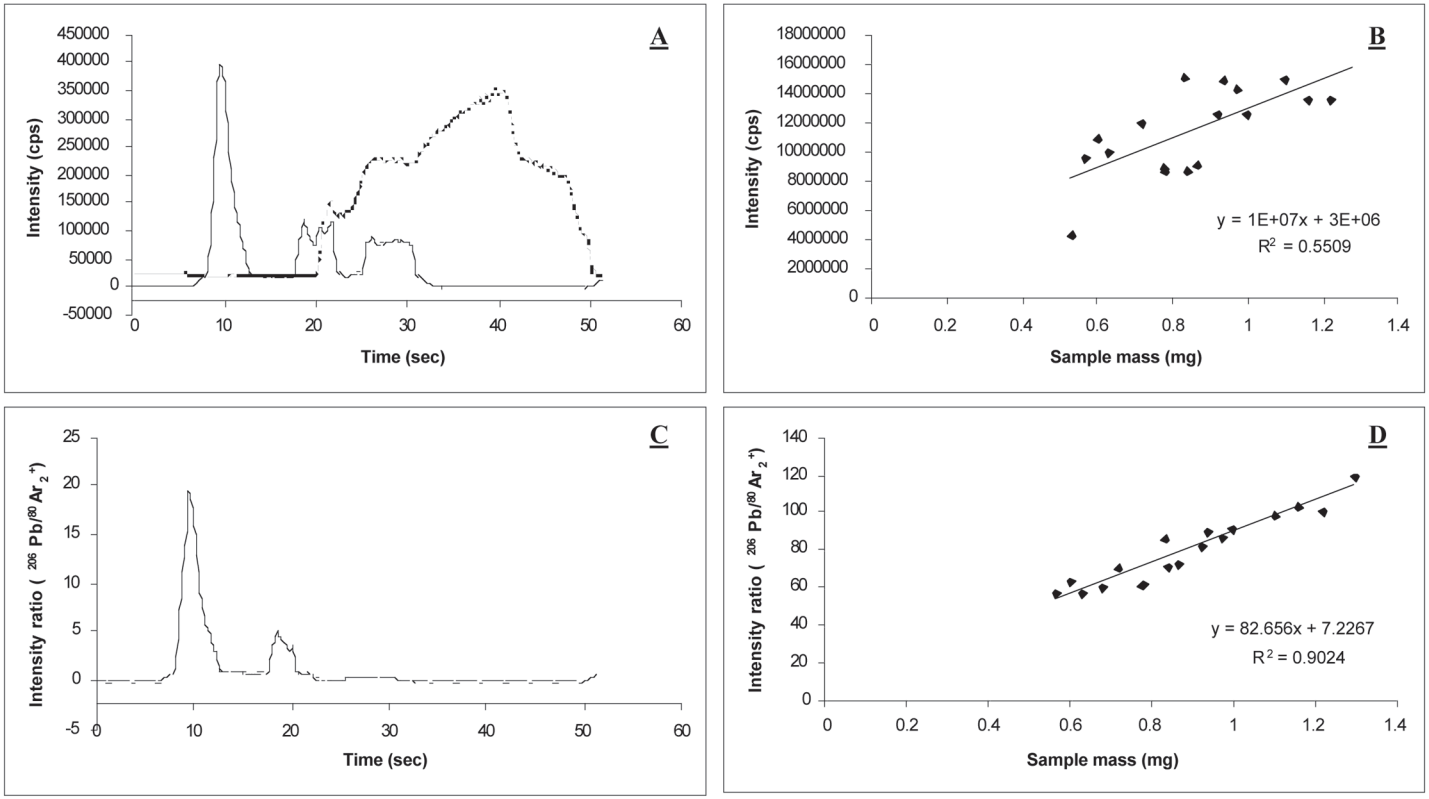

FIGURE 3. ETV-ICP-MS signal profiles and sample mass response curves for river sediment candidate reference material BCR 280R: (A) ^{206}Pb (solid line) and $^{80}Ar_2^+$ (dashed line) signal profiles; (B) Sample mass response curve for ^{206}Pb (signal intensity vs. sample mass analyzed); (C) $^{206}Pb/^{80}Ar_2^+$ ratio signal profile; (D) Sample mass response curve for $^{206}Pb/^{80}Ar_2^+$ (signal intensity vs. sample mass analyzed).

From the comments included in this section, it can be concluded that the different calibration strategies used in SS-ETV-ICP-MS allow the acquisition of accurate and precise results in the determination of trace metals in different kinds of samples. However, as a given calibration method can work better than others, comparison of the performance of the different methodologies should be carried out.

V. APPLICATIONS

There are currently over 100 published papers on applications of ETV-ICP-MS, but, unfortunately, only the applications shown in Table 1 deal with the direct analysis of solid samples. Most of the published papers are devoted to the determination of trace metals in liquid samples, solid samples after digestion by traditional techniques or slurries that, from our point of view, do not reflect the full potential of ETV-ICP-MS. As shown in Table 1, SS-ETV-ICP-MS has been used to analyze several elements in different (and complex) samples, such as alloys, sediments, sludges, plastics, etc., and the different calibration strategies to be used in routine analysis are well documented. Thus, the direct analysis of solid samples by ETV-ICP-MS, without any sample pretreatment, become a more popular technique in the near future.

It is important to point out that it is rather surprising that around 50% of the papers on SS-ETV-ICP-MS deal with the determination of only 1 element, 30% describe the determination of 2 to 4 elements, and only 20% report the determination of a larger number of elements. A possible reason, as stated by Vanhaecke et al.,[58] is the rather limited suitability of the quadrupole filter (the most commonly used in ICP-MS instrumentation) to deal with transient signals. From this point of view, it is clear that there is a maximum number of elements (isotopes) that can be monitored simultaneously, but it is unclear just what is this limit. Resano et al.[61] carried out a systematic study of the number of mass-to-charge ratios that could be "simultaneously" monitored in ETV-ICP-MS quadrupole-based instruments without negatively affecting the precision, the sensitivity, and detection limits. From this study, it was concluded that it was possible to monitor more than 20 elements for a standard peak width of 1.5 to 2 s. Recently, Venable et al.[62] reported a mathematical solution and an experimental procedure for calculating the maximum number of transient signals that can be monitored in ETV-quadrupole-based ICP-MS. In this case, the theory was validated, and it was concluded that 21 masses (or up to 68 by increasing the signal width from 0.25 to 1.5 s) could be accurately determined from a single ETV run. Thus, it is clear that the multielement capabilities of ETV-ICP-MS quadrupole-based systems have been underestimated, although, taking into account that ETV is not equally suited for all elements, the real limit is set by the furnace behavior of the analytes and the matrix.

A special application of SS-ETV-ICP-MS is the multielement micro-homogeneity assessment of reference materials, because this technique combines the rapidity and reliability of electrothermal vaporization with a sensitive simultaneous determination of several elements. Moreover, it uses small sample portions (1 mg or less), which is suitable for obtaining data calculation of recommended minimum sample masses.[63] Our group, at the Institute for Reference Materials and Measurements, has successfully used this approach in homogeneity studies of candidate reference materials.[10,41] However, it is important to stress that during these studies a downward drift in the instrument sensitivity was detected. Possible reasons for this drift might be deposits on the sampling and skimmer cones and on the ion lens of the mass spectrometer.[10,57] In order to improve instrumental stability, which is necessary in homogeneity studies, the method has been modified by including a period of nebulization of an aqueous standard solution between ETV runs. In this manner, although the loss of sensitivity could not be prevented during long-term studies (each series consisted of approximately 60 replicates), the rates of sensitivity loss for ETV measurements and for standard solutions agreed well, making the corresponding signals ratio suitable for assessing homogeneity. Means of suppressing or correcting for sensitivity drift are under investigation in our laboratory, including, for example, the measurement of well-characterized reference

TABLE 1
Applications on Solid Sampling ETV-ICP-MS

Elements	Matrix	Calibration	Reference
Pb, Zn, As, Cd	Total diet. Coal fly ash.	Liquid standards, solid standards and standard addition.	[39]
As	Reference Materials of plant origin.	Liquid standards, solid standards and standard addition.	[35]
As	Sea lettuce reference material.	Single standard addition and internal standard.	[42]
Se, As	Sea lettuce and estuarine sediment reference materials.	Single standard addition and internal standard addition.	[40]
Cd	Reference materials of plant, soil and sediment origin.	Solid standards, generalized simplified standard addition and multiple standard addition.	[48]
Cd, Se	Reference materials of different origin. Tobacco (Cd).	Isotope dilution.	[51]
Pb, Ag, Cd, Tl	Atmospheric particles.	Liquid standards.	[54]
Bi, Pb, Te	Nickel alloys	Liquid standards.	[36]
Cr, Fe, Mn, Cu, Zn, Sr, Cd, Sb, Ba, Pb	Airborne particles	Liquid standards (dried aerosol).	[55]
Au, Bi, Cd, Pb, Sb, Sn, Zn	Silver alloys	Solid standard.	[56]
Pd	Solid plastic material (aliphatic polyketone).	Single standard addition and internal standard addition.	[46]
Hg	Sludge	Solid standards.	[45]
Ru	Photographic materials.	Single standard addition and internal standard addition.	[44]
Pb	Biological samples.	Liquid standards.	[57]
Co, Mn, P, Ti	Polyethyleneterephtalate	Liquid standards, solid standards and single standard addition.	[47]
Al, Ba, Cd, Cu, Mn, Pb, Ti	Polyethylene	Liquid standards and single standard addition.	[58]
S	Bisphenol A	Liquid standards.	[59]
Al, Mg, Mn, Ni, Sb, Ti, Zr	Thermographic material	Liquid standards.	[60]
Tl	Human scalp hair	Isotope dilution.	[52]
Se	Bands of gel containing Se-proteins.	Internal standard.	[43]
Methyl-Hg and inorganic Hg	Biological materials	Isotope dilution.	[53]

materials before and after a series of ETV runs, as well as reducing transport efficiency preventing damage of the cones of the instrument.

VI. CONCLUSIONS AND FUTURE TRENDS

SS-ETV-ICP-MS can be considered as a powerful analytical tool for the direct determination of several analytes simultaneously in solid samples. Sample treatment is not required minimizing contamination and/or losses of analytes and reducing the overall costs of the analysis.

During recent years there have been important developments for the selective vaporization of different analytes as well as improvements in transport efficiencies by the correct selection of chemical modifiers. However, as stated by Grégoire and Sturgeon,[20] some particles are too

large to be completely decomposed and ionized in the argon plasma and so selective loses of these particles may be a benefit for ETV-ICP-MS applications, especially those dealing with long-term studies (i.e., homogeneity studies of reference materials).

It is clear, from the Applications section, that SS-ETV-ICP-MS has not been fully exploited yet, although, from our point of view, this technique will be successfully employed in a great variety of fields. These fields of application include analytical control in industrial production, analysis of foodstuffs, analysis of high-purity materials for technological use and homogeneity testing, and production control of reference materials, among others.

Finally, SS-ETV-ICP-MS has not to be considered as competitive to other techniques (i.e., laser ablation) but as a complementary technique to overcome current analytical challenges.

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