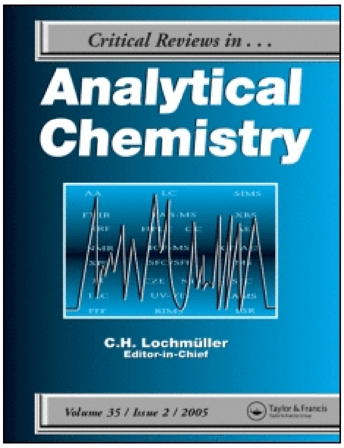

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Electrothermal Vaporization for Sample Introduction in Plasma Source Spectrometry

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ABSTRACT: Electrothermal vaporization (ETV) as a sample introduction technique for plasma source spectrometry offers several advantages over traditional solution nebulization sample introduction methods. Because volatilization of the analyte occurs in the ETV device, the plasma is not required to desolvate the sample and, therefore, the plasma has greater energy available for atomization, ionization, and excitation. The furnace also offers the ability to separate sample matrix components from the analyte of interest, which causes a reduction in interferences in the emission or mass spectrum. Both of these advantages allow for improved detectability for most elements. ETV also allows for the analysis of solid samples with minimum sample pretreatment, which broadens the numbers of samples amenable to analysis by plasma spectrometry. In the nearly 20 years that have followed the first report of ETV as a sample introduction method for plasma sources, there has been extensive research improving the design of the vaporization device, investigating matrix effects using ETV, analyzing solid samples, and coupling the devices to alternate plasma sources (other than inductively coupled plasma [ICP]). This review discusses the current state of electrothermal sample introduction for plasma source spectrometry and possible future directions of the technique.

KEY WORDS: electrothermal vaporization, inductively coupled plasma (ICP), microwave induced plasma, sample introduction.

I. INTRODUCTION

Electrothermal vaporization (ETV) as a means of sample introduction for analysis by plasma source spectrometry has been investigated by many researchers since its first report in 1974[1] as a sample introduction technique for inductively coupled plasma-atomic emission spectrometry (ICP-AES). ETV sample introduction devices have since found continued use with ICP-AES,[2–67] and have been investigated in conjunction with inductively coupled plasma-mass spectrometry (ICP-MS),[17,27,68–92] microwave inducted plasma-atomic emission spectrometry (MIP-AES),[93–109] microwave induced plasma mass spectrometry (MIP-MS),[93] direct current plasma atomic emission spectrometry (DCP-AES),[2,110–112] and capacitively coupled plasma atomic emission spectrometry (CCP-AES).[113–117] The following report details some of the work reported on the use of electrothermal vaporization sample introduction methods for inductively coupled plasma and microwave plasma spectrometric techniques. Because of minimal applications, the direct current plasma and capacitively coupled plasma will not be covered in detail in this discussion; however, a brief discussion and some references are included for completeness.

A. Plasma Types

1. Inductively Coupled Plasmas

The inductively coupled plasma has become one of the most widely used sources in atomic spectrometry. The first attempts at radiofrequency (rf) plasmas occurred in the early 1900s, how-

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ever, these plasmas could only be sustained at low pressures. The experimental difficulties associated with this undoubtedly allowed flame atomic emission techniques a greater popularity. Plasmas resembling ICPs first appeared in the early 1960s[118] and the first reports of an inductively coupled plasma for spectrochemical analysis appeared independently in 1964 and 1965.[119,120] Since that time, progress in ICP research has proceeded rapidly. One of the major areas of activity in ICP research has been in the area of sample introduction. Electrothermal vaporization is one of the techniques undergoing wide-scale investigation. An in-depth discussion of the ICP is beyond the scope of this review; however, a brief description is necessary to provide a basis from which a greater understanding of electrothermal vaporization sample introduction can be obtained.

The ICP system typically consists of a quartz torch (see Figure 1), a three-turn copper load coil, and a rf generator, often operated at a frequency of 27.1 MHz. The plasma is generated by passing the rf energy to the load coil, which forms an oscillating magnetic field. The plasma gas, typically argon, is seeded with electrons, generally by means of a tesla coil. The electrons gain energy while traveling in an annular path due to the magnetic field and collide with support gas atoms. These collisions, along with ohmic heating of the support gas, will cause further excitation of neutral atoms and more electrons and ions will be generated. This process has a cascade effect until a plasma is formed and sustained.

The processes that a sample undergoes in a typical ICP experiment are shown in Figure 2. In an ICP experiment the sample is typically in the form of a solution (or is placed into a solution form by means of sample pretreatment). This solution is introduced into the plasma as an aerosol produced in a pneumatic nebulizer or other device. This fine mist of droplets is then trans-

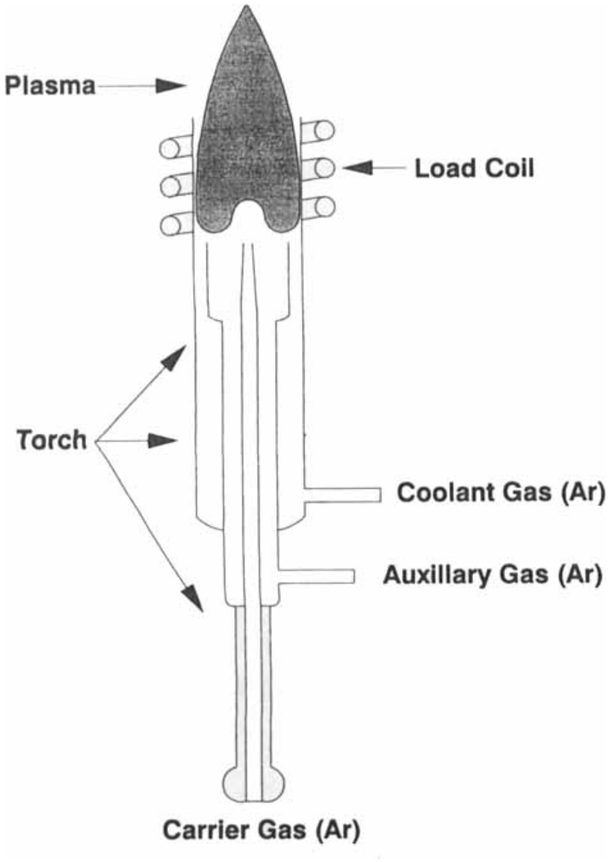

FIGURE 1. ICP torch diagram; not drawn to scale.

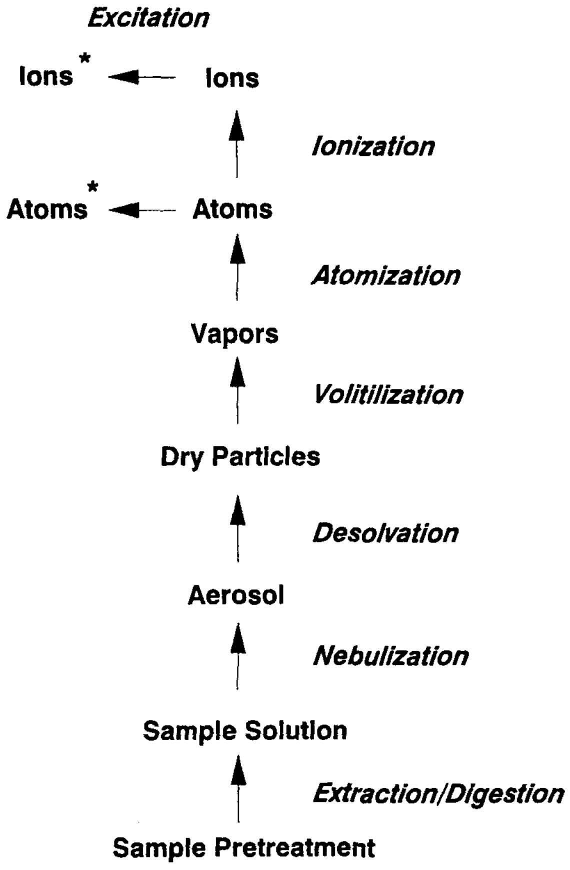

FIGURE 2. Representation of the processes occurring in a plasma.

ported to the plasma by a carrier gas. Once the aerosol enters the plasma it is desolvated, vaporized, atomized, excited, and ionized. The final stages provide excited atoms or ions for optical or mass spectrometric detection.

2. Microwave Induced Plasmas

The other commonly utilized plasma for elemental analysis is the microwave-induced plasma. The MIP was first studied as a source for atomic emission analysis in the late 1950s.[121] Although the MIP has been studied for approximately the same period of time as the ICP, it has not been developed and commercialized to the same extent. This is primarily due to the less robust nature of the plasma and difficulties encountered when introducing solutions into the plasma. Because of this, it has been used primarily as a complementary technique for elements difficult to detect with an ICP (such as the halogens). The primary application of the MIP has been as a gas chromatographic detector; however, other methods of sample introduction, primarily gaseous sample techniques, have found significant use.

The most common type of MIP system consists of a discharge tube placed in the center of a resonant cavity (Beenakker TM_{010}). The cavity is connected to a microwave generator via a coaxial cable. A diagram of such an instrument is shown in Figure 3. The plasma, typically formed from helium gas, is generated in the resonant cavity. Electrons seeded into the discharge tube, through a tesla coil or other device, interact with the electromagnetic field formed in the cavity. These electrons oscillate at the magnetic field frequency and are accelerated and collide with each other and neutral atoms. A cascade effect is generated by this process, similar to an ICP, and an MIP is formed. This process generates sufficient energy to maintain the plasma, atomize and/or ionize, and excite the analytes.

Other types of MIPs have been studied for analytical use. One of these plasmas involves the use of a tantalum electrode placed at the center of the discharge tube. This electrode is coupled to the microwave oscillator through a wave guide and the plasma is formed at the tip of the electrode. Another alternative apparatus involves a surface-wave device (surfatron). This device utilizes a resonant cavity and shapes the axial electric field so that its radial intensity is greatest at the dielectric-plasma boundary near the center of the plasma system.[122]

The sample being analyzed undergoes the same series of events that occur in an ICP. However, gaseous sample introduction methods (such as

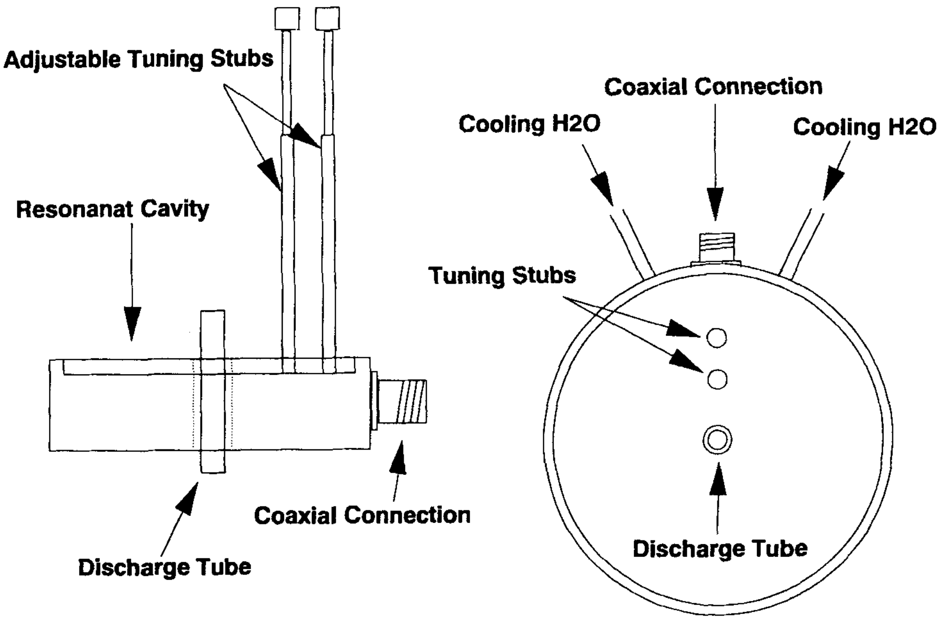

FIGURE 3. Schematic diagram of a Beenakker TM_{010} microwave cavity.

gas chromatography [GC]) are generally employed with MIPs due to the less robust nature of the plasma when compared with an ICP. This allows for removal of the desolvation step in the sample excitation/ionization process, which consumes a great deal of energy. Because ETV is capable of desolvating and vaporizing samples in the solution (as well as solid form), it is well suited for coupling to MIPs and helps extend the number of sample types available for analysis by MIP-spectrometry.

B. Detection Schemes

1. Atomic Emission Detection

AES is the most commonly utilized of the plasma spectrometric techniques, and several companies currently market commercial ICP emission systems. Although no general-purpose MIP-AES systems are commercially available, an MIP emission detector for gas chromatography is on the market. A schematic diagram of a typical ICP-AES instrument is shown in Figure 4. An MIP-AES system is similar to ICP-AES and only differs by the plasma formation system.

Light emitted from the relaxation of the excited state atoms (or ions) is focused onto an entrance slit of a monochromator by means of a lens or mirror. The radiation then travels to a diffraction grating where the light is dispersed, the wavelengths of the lines present in the spectrum are characteristic of the element(s) contained in the sample. A selected wavelength, characteristic of the element of interest, is then sampled by the exit slit of the monochromator. The intensity of the radiation emitted with this particular wavelength is then detected by a photomultiplier tube.

AES provides a convenient method of quantitatively determining the elemental composition of a sample. With solution nebulization sample introduction, detection limits in the subparts per million range are typical. The optical emission instrument can provide simultaneous multielement information when the previously described monochromator is replaced by a polychrometer. Disadvantages of atomic emission stem from the complex spectra obtained; each element typically has many lines associated with its presence. Complicated spectra can lead to overlap of analytical lines and difficulties assigning a peak to a particular element.

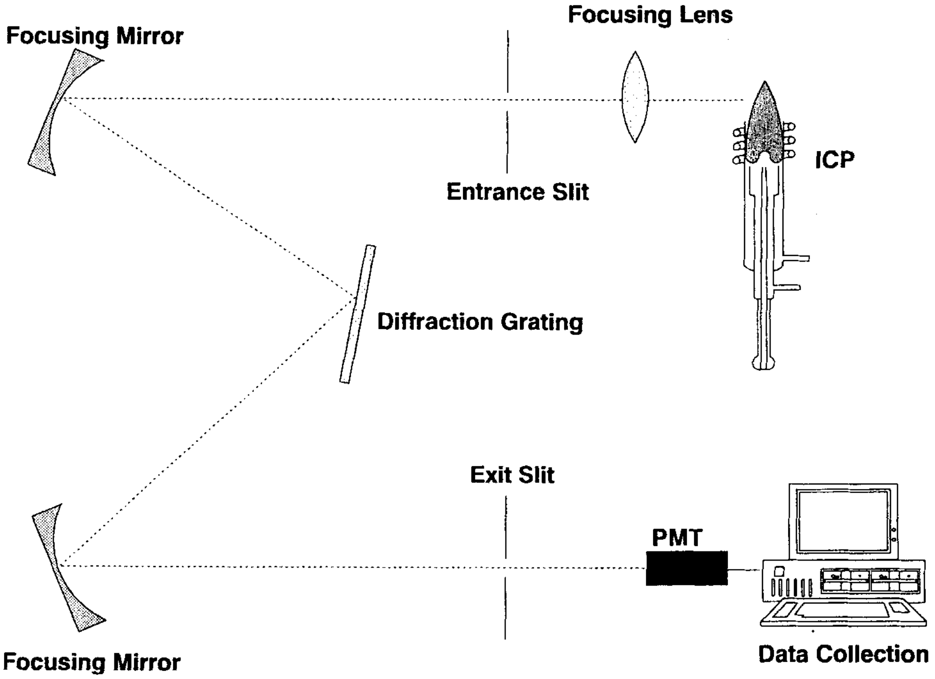

FIGURE 4. Diagram of a typical ICP-AES instrument.

Other spectral interferences may result from molecular bands originating from the sample solution, plasma gases, and atmospheric gases.

2. *Mass Spectrometric Detection*

Mass spectrometry, while commonly used in organic analysis, has only recently become an important tool for atomic spectroscopy. Currently, ICP-MS instruments are commercially available from several vendors, and the number of companies offering these systems is on the rise. The first ICP-MS coupling was reported in the late 1970s.[123] Research on MIP-MS coupling is still in its infancy. However, it does offer potential as a complementary source to ICP-MS. This is due primarily to the ability to analyze elements that are difficult to ionize with an argon ICP. The energy available from a helium MIP is greater and allows for ionization of elements with high ionization potentials, such as halogens. As with the organic MS, plasma-MS is based on detecting the analyte of interest in an ionic form. In plasma-MS the analyte ions are generally metal ions (or other elemental ions) that are produced by introducing the sample into the plasma. These ions are extracted into the mass spectrometer through a differentially pumped interface. The ions are then separated by a mass filter (such as a quadrapole) and detected by an electron multiplier tube. A schematic diagram of a VG PlasmaQuad ICP-MS instrument is shown in Figure 5. MIP-MS is accomplished by replacing the torch box in Figure 5 with the microwave cavity and discharge tube.

Plasma-MS has several advantages over AES systems. Primarily, these are its excellent sensitivity, selectivity, and capability for isotope determinations. Detection limits with ICP-MS are typically two to three orders of magnitude better than those obtained with ICP-AES, and the elemental spectra are also much simpler. This allows for greater detectability and certainty in assigning peaks. Because the instrument is also capable of measuring isotope ratios, isotope dilution analyses are possible. The disadvantages of plasma-MS stem from its greater cost and instrument complexity. Finally, the largest experimental difficulty encountered with plasma source MS stems from isobaric interferences arising from polyatomic species involving materials in the sample matrix and/or plasma gas.

C. Electrothermal Vaporization Sample Introduction

Plasma spectrometry, despite many advantages, suffers from a major drawback: the lack of an "ideal" sample introduction method.[124] The need

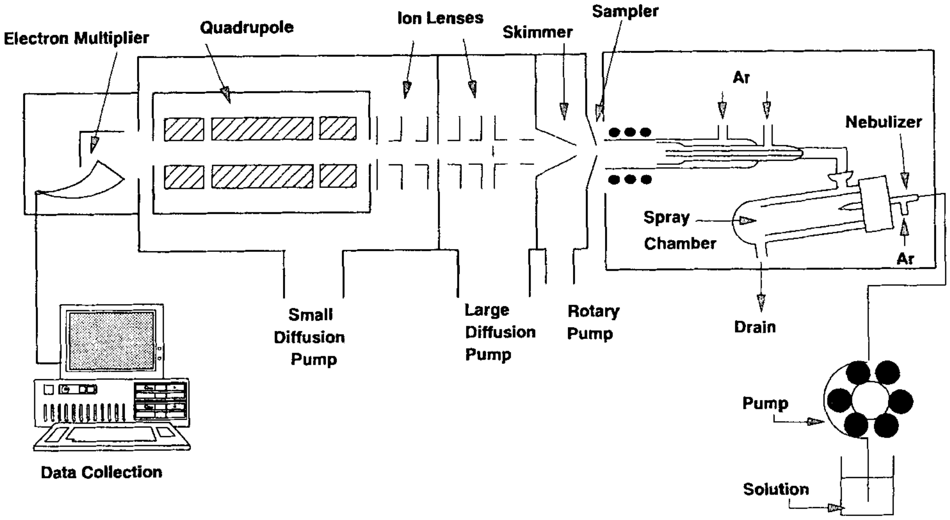

FIGURE 5. VG PlasmaQuad ICP-MS instrument.

for an "ideal" sample introduction technique can be stated as follows: (1) a highly efficient method of introducing the sample into the plasma; (2) the ability to utilize small volume samples; (3) tolerance for complex matrix "real word" samples; (4) amenity to samples in solid, liquid, and gas phases, which minimize sample pretreatment.

Electrothermal vaporization (ETV) as a sample introduction technique offers some distinct advantages over conventional methods of sample introduction, such as solution nebulization, and meets several of the criteria for an "ideal" detector. These advantages primarily arise from the gaseous nature of the sample emitted from the ETV device. The most universal advantage is the improved transport efficiency achieved. With solution nebulization transport efficiencies of less than 2% are typical,[124] while ETV sample introduction has transport efficiencies on the order of 20 to 80%. Greater transport efficiencies allow for better detectability because a larger portion of the sample reaches the plasma. The gaseous nature of the sample also adds to the sensitivity of the technique because the plasma is not required to desolvate or vaporize the sample, as well as atomize, ionize, and excite the analyte. This adds to the efficiency of ionization, for an MS detector, and excitation, for an AES detector. Desolvation and vaporization of the analyte in the ETV system point out one of the main differences of using an ETV system for sample introduction and performing an analysis by graphite furnace atomic absorption spectrometry (GFAAS). In the GFAAS technique, the furnace is required not only to desolvate and vaporize the sample, but also for atomization of the analyte of interest. Because partial atomization is achieved with the ETV method, the sensitivity of the plasma technique is further enhanced. However, the selection of the vaporization temperature (atomization temperature) is not as critical in ETV as it is in GFAAS.

Additional advantages come from the ability of the electrothermal vaporizer to be programmed; sample matrix constituents can therefore be removed with careful selection of drying and ashing temperatures. This is beneficial to both AES and MS detection methods, because it removes some of the potential interfering species prior to vaporization of the analyte and introduction into the plasma. Removal of these species allows for determination of elements difficult with solution nebulization, due to interferences from solution- or matrix-related species. Other matrix removal advantages include the reduction of nonspectroscopic interferences from high salt content samples. Because, through matrix modifiers and drying and ashing the sample, the salt can be removed from the sample prior to volatilization of the analyte of interest, these effects will be greatly reduced. High dissolved solid content samples can also cause problems with the performance of the nebulizer. If high salt or other solid content samples are nebulized utilizing a pneumatic nebulizer, the nebulizer can become clogged. When utilizing mass spectrometric detection the difficulties with clogging are extended to include the sampler and skimmer orifices.

ETV is also ideally suited for analysis of samples that are volume limited. Sample amounts required for analysis by ETV plasma spectrometry are less than 10 μl, while for solution nebulization volumes on the order of 1 ml are required. This is particularly important when analyzing biological samples and many environmental samples where sample amount is limited. Another sample handling advantage of ETV is the ability to analyze solid samples directly. As indicated in Figure 2, a sample pretreatment step is usually required for analysis of solid samples; this may involve digestion or extraction of the sample. However, these techniques may introduce contaminants into the sample and also involve dilution of the sample, therefore reducing the ability to determine low amounts of elements present.

Disadvantages of ETV as a sample introduction technique for plasma spectrometry also exist. First, the ETV system generates a signal that is transient in nature. This makes it difficult to obtain multielement determinations, or isotope ratios for mass spectrometry because of the low duty cycle for a given element. A second common difficulty with ETV is poor reproducibility (typically around 10% relative standard deviation). Inconsistent sample insertion, irreproducibile vaporization of the sample from the furnace, platform, or filament surface, formation of molecular species involving the furnace material, and overall higher cost and complexity when compared with solution nebulization techniques are also disadvantages.

II. FURNACE DESIGN CONSIDERATIONS

Before discussing in greater detail the research that is currently being performed on the use of ETV for sample introduction into plasmas, it is useful to understand the type of instrumentation that is currently being used in this field. Many reported instrument designs are modifications of existing instruments used for atomic absorption techniques. Modifications reported to date have attempted to maximize analyte transport efficiency from the furnace to the plasma. Other workers have designed systems especially for use as sample introduction devices. Both of these applications have definite advantages and the "ideal" ETV device may ultimately be a hybrid of the two.

A. Modification of Graphite Furnace Atomic Absorption Instruments

A schematic diagram of a modified Perkin-Elmer graphite furnace is shown in Figure 6. This type of system is well understood for atomic absorption, and research is currently underway for determining if absolute (calibrationless) analyses are possible with such a system for GFAAS.[125-127] With the wealth of information available suggesting vaporization/atomization mechanisms occurring in the furnace, the vaporization process of the analyte in the furnace should be well characterized. Difficulties with this design include the lack of a gas flow for transporting the vaporized material to the plasma. Because the furnace is designed for static vaporization (the analyte remains in the furnace during analysis), the design requires modification to sweep the material from the furnace to the plasma. Another difficulty with such a design is the method of introducing the sample into the furnace. In GFAAS the sample is generally introduced through a hole in the side of the graphite tube. For use as a plasma sample introduction apparatus, this hole needs to be plugged or tubes without the hole need to be used.

One of the most commonly modified furnaces used as an ETV sample introduction device is the Perkin-Elmer HGA series graphite furnace.[30,37,62,65,71,77,93,97] A number of different models have been adapted for use in plasma sample introduction applications, including the HGA 74, 300, 500, and 2200 systems. A second, commonly modified furnace is manufactured by Varian.[24,51,61,67,95,104] However, modifications to furnaces from a number of other manufacturers

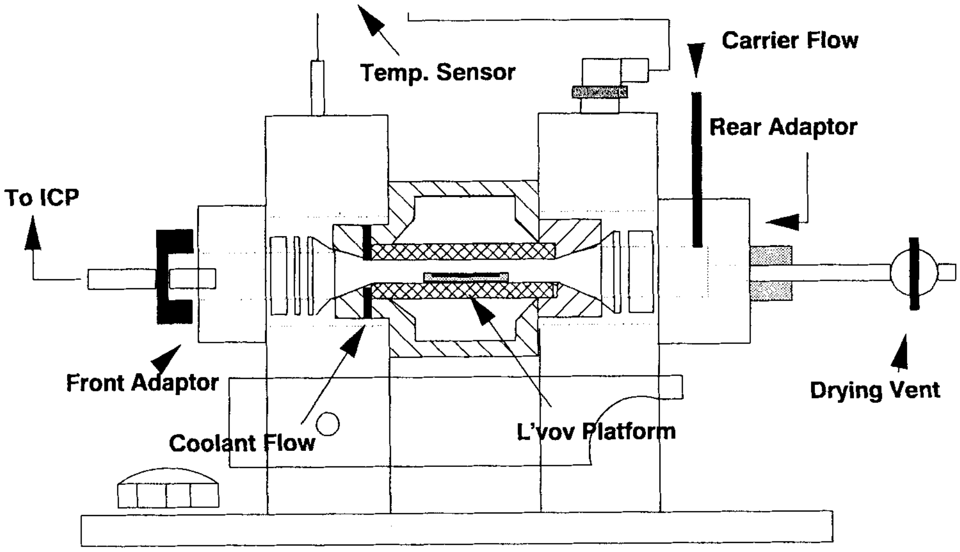

FIGURE 6. Modified Perkin-Elmer HGA 300 graphite furnace for ICP sample introduction. (Reproduced from Carey, J.M. et al. Spectrochim. Acta. 1991, *46B*, **1711**. With permission from Pergamon Press, Ltd.)

have also been described.[5,12,50,90] These modified instruments have been used with both inductively coupled plasmas and microwave induced plasmas. A number of different approaches have been taken to improve transport efficiency. The two main approaches can be divided broadly into placing the furnace as close to the base of the torch as possible (minimizing the transfer distance) and minimizing sample condensation and adhesion to transfer line walls. While each of these methods has been investigated with the different instrument types, for ease of comparison only the Perkin-Elmer furnace modifications are covered here.

Minimizing the distance between the furnace outlet and the plasma has been the most common method of attempting to improve the transport efficiency of the sample introduction method while interfacing the ETV furnace to the plasma system. This method allows for the transfer of material into the plasma while the atomic vapor is still hot. Condensation on the transfer line walls is minimized in this configuration because the distance traveled by the vapor is minimal. Disadvantages of the design are the often complex modifications necessary to facilitate interfacing to the plasma torch and difficulties in switching to different sample introduction methods. For axially mounted torches, such as those found in ICP-MS and MIP systems, the furnace is often maintained in the horizontal position, typical of the configuration for AA measurements.[93] For ICP-AES measurements the furnace has been interfaced in a vertical manner (on its side) so that the position of one of the windows for AA is connected to the torch base.[37] The windows for AA measurements are replaced to facilitate coupling with the plasma torch at one end and introduction of the carrier gas flow and/or sample introduction at the other end.

Modifications performed on a HGA-500 graphite furnace to facilitate interfacing to an axially mounted MIP system[93] are illustrated in Figure 7. While complicated, this arrangement does indicate the modification difficulties necessary for this type of interfacing. Not only are the modifications complex, but the integrated design of the system makes switching to other methods of sample introduction difficult. This could be a major disadvantage when comparisons to other sample introduction methods are made or if other sample introduction techniques are used in conjunction with ETV. Despite these modifications, this design is efficient and causes the vaporization of the sample to occur at the plasma. This does not allow for recondensation of the sample during transfer to the plasma, leading to transport efficiencies near the theoretical value of 100%. However, no actual determination of the transport efficiency was reported.

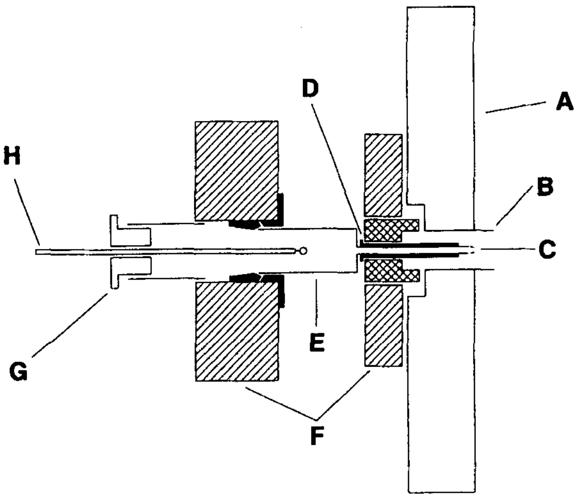

FIGURE 7. Integrated Perkin-Elmer HGA 500 graphite furnace MIP system: (A) microwave cavity, (B) quartz containment tube, (C) tantalum tip, (D) brass contact, (E) graphite injector tube, (F) furnace electrodes, (G) guide, (H) ceramic rod with tungsten loop. (Reproduced from Evans, E. H. et al. Appl. Spectrosc. 1991, *45,* **1478**. With permission from The Society for Applied Spectroscopy.)

Interfacing the ETV furnace to the plasma in this manner[93] is particularly efficient for an MIP system because it allows for the direct incorporation of a tantalum tipped injection tube.[93] Injection tubes with tantalum tips ensure the formation of a power-efficient, annular plasma, with a central channel for the analyte and carrier gas to pass through. Because this system is mounted in an axial manner, it is feasible to utilize such a design for both emission and mass spectrometric detection. The integrated furnace design utilizes a tungsten loop mounted on a ceramic rod that facilitates insertion into the furnace tube. Difficulties encountered with such a method of sample introduction include irreproducible positioning of the loop in the furnace, different temperatures at the sample, and difficulties in maintaining the sample drop on the loop. Another problem with the tungsten loop design is oxidation of the loop after several firings of the furnace. This limits the use of high vaporization temperatures and therefore the furnace's utility for the determination of low-volatility elements. This particular design seems to be an excellent method for interfacing to an MIP because well-defined sample introduction methods for the technique have not been established. A modified version of the system for ICP work, however, would probably not be as useful because there are well-defined sample introduction methods that one may wish to use in conjunction with ETV, and the integrated design of this instrument would hinder the switch over.

Matusiewicz et al.[37] have reported the interface of a HGA-500 graphite furnace to an ICP mounted in a vertical manner for AES measurements. In this configuration the windows normally present for GFAAS determinations are replaced with custom adaptors constructed from PTFE (polytetrafluororethylene). One of these adaptors is used to couple the furnace to the base of the ICP torch, giving a distance of approximately 17 cm between the sample and the torch base. The other adaptor is used to introduce the carrier gas into the furnace. This particular design is not as complicated as the design described above by Evans and co-workers.[93] Despite the relative simplicity of the design, this particular instrument would not appear to be as efficient as the ETV-MIP system. The primary reason for this expectation is the distance inherent in the design of the ICP torch: the length of the injector tube. The effect of distance from the sample position in the graphite furnace to the ICP load coil was investigated, and the S/N (signal-to-noise ratio) was found to decrease with increasing transport distance.

This system[37] has a rather complex method of sample introduction because the furnace is turned on its side. The normal sample introduction orifice in the graphite tube was plugged with graphite. A new hole, or slot, was then cut in the graphite tube to facilitate insertion of a graphite rod containing the sample. The graphite rod used has a depression made in it to hold the sample (similar to the depression in a L'vov platform). Once the sample is placed into the hole, the graphite rod is inserted to a position approximately in the center of the furnace tube. While this system sounds simple enough, positioning the graphite rod is crucial in obtaining even sample heating. Another drawback of the carbon rod sample holder is the relatively large mass of the system. Because the sample position in the furnace determines the temperature of the sample, this is a tedious procedure to assure acceptable reproducibility. The relatively high mass of the sample holder may cause a temperature at the sample that is much lower than that of the furnace and will likely cause a decrease in sample temperature response to a heating gradient. Finally, inserting the rod into the furnace will partially obstruct the carrier gas flow, causing turbulence, which may result in further condensation losses on the injector tube walls.

The geometry of the sample insertion device also was varied.[37] In addition to the graphite rod design, the use of a graphite platform was investigated. The platform was found to be unsuitable for this particular design, due to diffusion of the sample to the edge of the platform and the furnace tube wall coating. Additionally, machining of the rectangular holes in the furnace tube was decidedly more difficult than a round hole for the graphite rod. Unlike the tungsten loop sample insertion device, graphite cuvettes showed no significant degradation over time, until approximately 100 firings had been performed. A disadvantage of the graphite material is the formation of carbides with certain elements that degrade the volatilization of the analyte (particularly for elements such as arsenic). The formation of these refractory carbides can be reduced significantly through the use of pyrolytically coated graphite, as is common in GFAAS. While this furnace provides a reasonable approach to coupling of ETV and ICP, the necessary modifications and modification of the ICP sample introduction system do not seem to be acceptable and other avenues will provide greater potential applicability.

The second design theory that has been applied to the modification of a commercial graphite furnace for sample introduction for plasma spectroscopy is to immediately condense the atomic vapor into clusters of atoms prior to transporting them to the plasma.[71,77] This theory is based on considerations that have been addressed in the construction of furnaces specifically designed for use as electrothermal vaporizers coupled to plasma spectrometric systems. A typical diagram of these furnaces is shown in Figure 6.

The formation of microparticles is achieved through the introduction of a coolant flow through four holes at the exit of the furnace (just prior to the front adaptor). This coolant gas is introduced perpendicular to the flow of the analyte from the furnace. A sheet of gas is formed from this that causes rapid condensation of hot atomic vapor, and subsequent formation of clusters of atoms. These atom clusters are then able to travel through the transfer line with minimal condensation losses. This system has the advantage that the distance traveled by the analyte has little effect, because no losses from the condensation of the analyte should occur. Interfacing the furnace to the plasma torch is therefore a trivial task and requires only connecting a length of tubing via a ball joint (or other connection device) to the base of the torch. An additional advantage is that the modifications per-formed on the graphite furnace are relatively straightforward.

Results in both reports[71,77] indicated that the system successfully increases transport efficiency of the analyte from the furnace to the plasma. However, neither report presents any indication of the actual transport efficiency. It was demonstrated that optimizing the coolant gas flow was critical to achieve optimum performance. Another interesting finding was that optimum condition for the coolant gas is interrelated to the carrier gas flow. Although this was not performed, a simplex, or other multivariable optimization method may be suited for these types of intercorrelated variables. The performance of the system also indicated that furnace conditions (vaporization temperature, etc.) are similar to those used for the analysis of a given element by STPF (stabilized temperature platform furnace) conditions in GFAAS. This finding is to be expected because the configuration of the system is similar to that of the original graphite furnace for AA and allows the user to take advantage of the wealth of knowledge available from the atomic absorption literature.

Two different sample introduction methods have been reported with this design. One involves the use of a tantalum loop for sample deposition and subsequent insertion into the furnace.[77] The second method involves the use of a L'vov platform in a manner similar to that used in GFAAS.[71] Both methods have advantages and disadvantages. Inserting the tantalum loop reduces the possibility of forming refractory carbides that hinder volatilization; however, impurities in the tantalum can lead to increased background levels. The same problem encountered by Evans and co-workers[93] with oxidation of the loop after a given number of firings can also be detrimental to this type of work. Finally, the reproducibility of the system was found to be limited to the ability to position the loop precisely in the furnace at the sample position from run to run. A L'vov platform provides for even heating of the sample and for more reproducible positioning of the sample in the furnace. While the formation of refractory carbides with elements present in the sample can be a problem with using the graphite platform, the use of pyrolytically coated graphite can significantly reduce this difficulty. This method suffers from difficulties in placing the sample on the platform because the sample introduction orifice in the graphite tube for AA has been plugged. With both methods, the rear adaptor in Figure 6 was removed and the sample either placed on the tungsten loop or the pipet is inserted into the furnace and the sample deposited on the platform. This was described correctly as a tedious and undesirable procedure. Despite difficulties with introducing the sample into the furnace, this approach seems to be viable and warrants further study.

B. Furnaces Specifically Designed for Plasma Sample Introduction

While there has been some success in modifying commercially available furnaces, perhaps the most promising method of producing electrothermal vaporization devices for sample introduction purposes is to design an apparatus specifically for this purpose. This approach has been undertaken by numerous workers, with good results. The advantage of such a system is found in the ability to construct an instrument to optimize analyte transport efficiency while still offering good vaporization properties. Similar approaches to optimize transport efficiency have been taken to those utilized with existing instrumentation. There have been many varying designs of thermal vaporizers for sample introduction uses. A few selected reports will be reviewed, the reader is referred to the references for additional furnace designs.

The system, on which the modifications described above for a HGA 300 graphite furnace[71,77] were based, utilizes the formation of microparticles for increasing transport efficiency.[89] This design utilizes a glass globe similar to that shown in Figure 8. In the system, the glass envelope is sealed to a metallic base via an o-ring. The clusters of atoms are formed in the approximately 5-ml volume that is enclosed in the furnace, providing sufficient room for condensation of the analyte without contacting the glass walls or the transfer line to the ICP. A theoretical approach was taken in determining the volume of the system. By solving the convective heat transfer equation it was determined that 5 ml should allow for sufficient condensation of the analyte. Microparticles are then transported to the plasma by an argon carrier gas flow introduced into the furnace tangentially that helps keep the atomic vapor and microparticles centered and off the glass and transfer line walls.

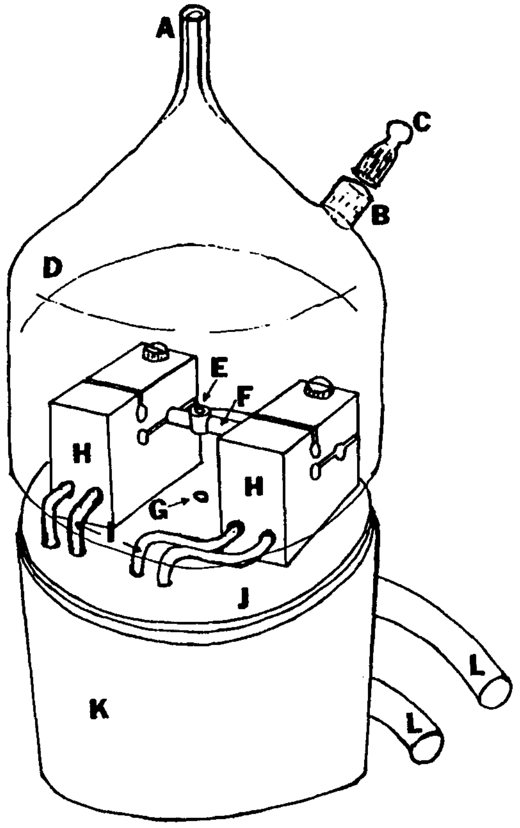

FIGURE 8. Carbon cup sample vaporization device: (A) sample and Ar carrier gas inlet to the plasma torch, (B) sample injection port, (C) ground glass stopper, (D) glass dome, (E) carbon cup, (F) support electrodes, (G) argon inlet port, (H) fixed support stainless steel blocks, (I) water cooling system, (J) Teflon base, (K) aluminum base, (L) power cable. (Reproduced from Ng, K.C.; Caruso, J. A. *Appl. Spectrosc.* 1985, *39*, **719**. With permission from The Society for Applied Spectroscopy.)

By solving for the vapor-phase diffusion coefficient under a variety of conditions, the authors illustrated the difficulties of vapor transport without accompanying condensation of the hot atomic vapor. For a transport distance of 10 cm (tubing diameter 5 mm and flow of 1 l/min), 90% of the sample should be lost to condensation on the transfer line walls. Transport efficiency of the system was tested using a mass balance experiment. In this particular report the analyte was trapped on a cotton filter and the material collected was then analyzed to determine the recovery. The average recovery for the instrument was 94%, including material recovered on the glass walls and in the transfer line. Analyte transport efficiency should be roughly equal to the amount of material trapped in the cotton filter. The average value here was 84%. This value is clearly superior to the calculated value of 10% for a system with no provisions for condensation of the material into microparticles.

The sample in this instrument was vaporized from a rhenium filament. However, at vaporization temperatures of 1800°C or greater the loss of rhenium from evaporation was sufficient to cause severe plasma loading effects. For use at these high temperatures, a graphite filament was recommended. The primary reason for not using a graphite filament from the outset was not discussed; however, the availability of the material seems to be a determining factor. Rhenium was chosen over other metals for several reasons: (1) it has a high melting point; (2) it maintains its ductibility; (3) it resists carbide formation (an advantage over graphite); and (4) it is relatively nonreactive with water vapor. Disadvantages, besides the plasma loading effects, include: (1) relatively high reactivity with matrix and sample constituents; and (2) a high vapor pressure that (as previously mentioned) limits the range of temperatures applicable. The sample is introduced into the furnace by removing the glass dome and pipeting a microliter amount of solution directly on the filament. This necessitates the use of an auxiliary argon gas flow to the plasma when the furnace is open. This design seems to be a useful one that deserves further study.

A furnace that has been designed specifically for use as a sample introduction device for MIP source spectrometry has been described by Hanamura et al.[107] This particular system is unique in that the sample is heated in a quartz crucible rather than a metal or graphite holder. This may offer advantages by reducing contamination from the sample holder surface because no metal is present, and it may also reduce the formation of refractory carbides that degrade analyte volatilization. Disadvantages of such a material would include the relatively low melting point, contamination from silicon and other materials present in the quartz, and the relatively slow heating response of quartz compared with metals and graphite. For purposes of the study presented in this report, these disadvantages were not of major consequence because a slow heating rate was used to attempt to provide some speciation information from the differing volatilities of the compounds. Another portion of the report involved the direct analysis of solid biological compounds. Despite the relatively high temperatures usually expected for such an analysis, this study only utilized a maximum temperature of 500°C. This result was acceptable because the elements being measured had high volatilities (C, H, N, O, and Hg). For use as a routine sample introduction source, this type of material for the sample holder seems to be unsatisfactory.

The sample was transported to the plasma through a transport line by a carrier gas that is matched to the plasma gas (He, Ar, or N_2 in this work[106]). The carrier was introduced into the "cylindrical" shaped furnace through the bottom, and as the sample was heated, the carrier gas flowed past the indented top of the quartz crucible, causing the carrier gas to carry the volatile components to the plasma. While the length of the transfer line was not reported, this method of transporting the sample to the plasma would seem inefficient because there were no precautions taken to prevent vapor condensation during transport. An integrated furnace MIP torch design, similar to that reported by Evans et al.,[93] would be applicable to this particular furnace design and should also be relatively easy to implement. This method should also improve the transient signal peaks obtained during the temperature ramp because dead volume is minimized. For this particular application the method of forming microparticles, described by Park et al.,[89] would not be applicable, because the peak shape would be degraded by the large dead volume of the glass envelope. While the application described in this report is interesting and the design described was demonstrated to be suitable for this purpose, it does not seem feasible for general use.

An interesting method aimed at decreasing instrument complexity and maximizing flexibility for switching to different sample introduction techniques has been reported for ICP-AES.[49] This system incorporates a tantalum boat, which acts as the heating element, mounted in a glass tube by two brass supports. Power is supplied to the tantalum boat by means of a commercial power supply manufactured by Varian. The vapor produced from heating the boat is swept to the plasma by means of a carrier flow of argon introduced into the ETV apparatus through the bottom of the glass tube. Interfacing the furnace and ICP torch is performed in the same manner as a spray chamber used with pneumatic nebulization, namely, through the use of a glass ball joint. Sample is introduced into the furnace through a sidearm on the glass tube flow cell. The system provides a transport distance of roughly 30 cm from the tantalum boat to the load coils of the ICP apparatus.

The glass flow cell system[49] seems to provide for improved transport efficiency by shortening the transport distance of the analyte vapor. This should be an effective design for accomplishing this; however, there could be condensation losses in the ICP torch. Switching to other methods of sample introduction with this system should be relatively easy, because no modification of the torch or torch box is required to include the furnace, and no complicated means of connecting the torch and furnace is required. This switchover potential is an advantage compared with some of the designs described above that utilize short transfer distances. A possible disadvantage of the system, in terms of sample transport, is that no consideration was made of the gas flow patterns in the flow cell and how efficiently the analyte vapor is swept into the ICP torch.

The method of sample introduction in this furnace,[49] while simple to perform, leaves something to be desired. While no mention was made of this being performed in the article, it would seem necessary to close the sample introduction side arm prior to vaporizing the sample from the boat. If this was not done, some analyte vapor may have been lost rather than transported to the plasma. However, if a means of effectively plugging this hole prior to vaporizing the analyte was found, this would be a suitable method of depositing the sample on the heating element. A final possibility associated with this furnace is the difficulty with the glass used in its construction. While the glass does not come in contact with the heating element itself, it is in contact with the brass supports through which the power supply is connected to the tantalum boat. Apparently no difficulties were encountered during this particular study; however, at high vaporization temperatures it appears that the glass melting could be a problem. Further work on optimizing this furnace design seems warranted, particularly in the areas of measuring and improving the transport efficiency of the system. Additionally, the investigation of additional furnace and heating element materials needs to be performed. Finally, improvements in the method of sample introduction into the furnace need to be made. While the furnace described seems intriguing, little or no optimization of its design was reported (this was not the focus of the article), but the design offers some advantages that warrant further investigation.

Despite nearly 20 years of investigation and design improvements, there is still not an "ideal" ETV sample introduction system. However, there have been significant improvements in the approaches taken to improve system transport efficiency. Perhaps in the near future, as ETV devices continue to become more commercially available, increased use of the method will spur further development of the "ideal" furnace. This type of system would allow taking advantage of the wealth of information available from GFAAS, yet still take into account the fact that sample introduction is not a static technique and transport as well as vaporization phenomena need to be explored.

III. ETV-ICP-MS

ICP-MS is rapidly becoming a method of choice for elemental analysis due to the advantages mentioned previously over traditional atomic emission methods. Due to ever-growing concerns about the environment, the need for even lower detection limits for elements increases. This has led to the further development of plasma-source mass spectrometric methods of analysis, specifically ICP-MS. One of the major areas of growth for ICP-MS research is in the area of sample introduction. One of the promising sample introduction methods for ICP-MS is ETV. A wide variety of elements have been investigated for analysis by ETV-ICP-MS. The elements determined by ETV-ICP-MS, ranges of detection limits reported, and references for each element are shown in Table 1. No attempt has been made in constructing this table to note the sample matrix in which the detection limit was determined, this may lead to higher detection limits for elements in more complex matrices. In addition, no compensation was made for the calculation method used (e.g., 3 σ vs. 2 σ).

A. Matrix Effects

One of the major areas of work in ETV-ICP-MS, and also ETV-ICP-AES, is investigation of matrix effects and the ability of ETV to eliminate, or significantly reduce, these difficulties. The effects studied include both spectroscopic and nonspectroscopic types. These effects differ when using mass spectrometric detection due to the nature of the detector interface and lower background for the quadrapole mass filter when compared with atomic emission detection. The lower resolution of the quadrapole mass filter causes overlaps of different species with differing exact masses yet the same nominal mass. The plasma mass spectrometer interface system, consisting of two small (millimeter-sized) orifices, causes greater difficulties in analyzing samples containing high quantities of total dissolved solids or

TABLE 1
ETV-ICP-MS Detection Limits

Element	Detection limit (pg)	Ref.
Aluminum	0.05	17, 78, 91
Antimony	0.001–1.0	72, 78
Arsenic	0.005–1.5	71, 72, 78, 87, 91
Barium	N. R.[a]	78
Bismuth	0.1	68, 72, 73, 75, 78
Cadmium	0.3–0.5	72, 78, 89, 91
Calcium	1.4	91
Cerium	0.003	70
Cesium	0.1	72
Chromium	0.2	17, 78, 91
Cobalt	0.02	75–78
Copper	N. R.	17, 74, 75, 78, 89
Dysprosium	0.007	70
Erbium	0.005	70
Europium	0.006	70
Gadolinium	0.012	70
Gallium	0.05	72
Germanium	N. R.	78
Gold	0.002–0.5	72, 87
Holmium	0.001	70
Indium	0.001–0.1	68, 72, 75
Iridium	N. R.	85
Iron	0.2–10	71, 72, 74, 76, 78, 87, 89, 92
Lanthanum	0.002	70
Lead	0.002–0.5	68, 72, 75–78, 89–91
Lutetium	0.002	70
Manganese	N. R.	69, 74, 75, 78, 87
Mercury	0.03–0.5	72, 79
Molybdenum	150	87, 88, 92
Neodymium	0.008	70
Nickel	0.4	73–75, 78, 87, 89, 91
Osmium	N. R.	80
Palladium	N. R.	85, 87
Phosphorous	15	78
Platinum	N. R.	85
Plutonium	0.002 fg	81
Potassium	3	91
Praseodymium	0.002	70
Rhodium	N. R.	75, 78
Rubidium	0.5	72
Ruthenium	N. R.	85
Samarium	0.01	70
Selenium	11.4	91
Silicon	5.4	91
Silver	0.16	68, 91
Sodium	3	74
Strontium	0.1	72, 78
Tellurium	100	68, 83
Terbium	0.002	70
Thallium	90	68, 84, 86, 92
Thorium	0.5	72
Thulium	0.002	70
Titanium	N. R.	78
Tin	0.002–0.5	72, 78
Tungsten	300	88, 92
Uranium	0.001–0.05	72, 84
Vanadium	N. R.	78
Ytterbium	0.007	70
Zinc	0.4	78, 91

[a] N.R., not reported.

organic materials. Clogging the small orifices in the sampler and skimmer causes these problems.

1. Spectroscopic Matrix Effects

Spectroscopic matrix effects in ICP-MS primarily involve the formation of polyatomic species with the same nominal mass as the analyte of interest. This can lead to high readings and incorrect determinations. These types of interferences can be particularly troublesome when utilizing aqueous samples, such as those required for solution nebulization. An example of two of the possible interferences that are observed with solution nebulization is shown in Figure 9a. Many of these interferences result from the solution being introduced into the plasma; by removing the solution (the desolvation process), and forming a dry plasma, these interfering species are not observed (Figure 9b). Formation of a dry plasma is how an ETV device allows for the reduction of many isobaric interferences.

One of the elements most affected by isobaric interferences is iron. As indicated in Figure 6, the major isotope of iron has a nominal mass of 56, at which interference from $^{40}Ar^{16}O^+$ is predominant. The ability to reduce this effect by the separation

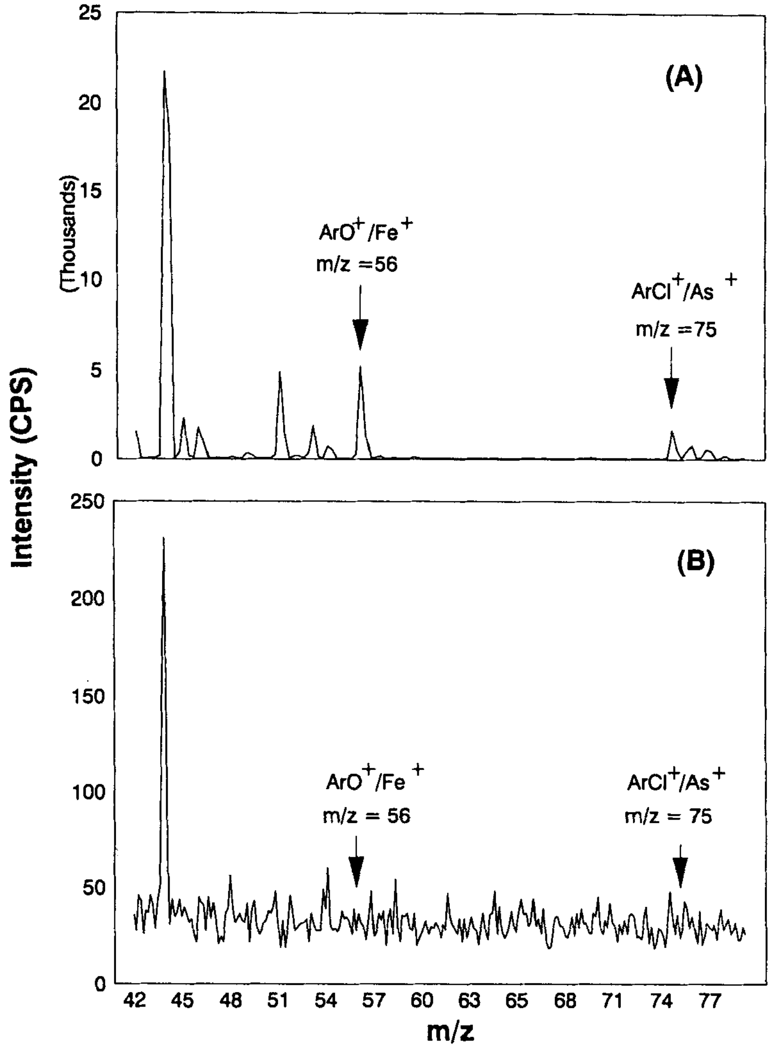

FIGURE 9. Comparison of signal obtained from: (A) wet plasma and (B) dry plasma. (Reproduced from Carey, J.M. et al. Spectrochim. Acta. 1991, *46B,* **1711**. With permission from Pergamon Press, Ltd.)

of oxygen-containing species in the matrix (such as water) has been investigated by Ida and co-workers,[17] Carey et al.,[71] Hulmston and Hutton,[72] Tsukahara and Kubota,[76] Marshall and Franks,[78] and Hall and co-workers.[87] Because the ArO^+ species is formed due to a combination of oxygen from solution components and the argon plasma gas, the interference is reduced in ETV by careful selection of drying and "ashing" temperatures to remove the oxygen-containing species in the solution prior to volatilization of the iron. Reducing this interference has allowed for detectability of iron to be improved by approximately one order of magnitude when compared with solution nebulization. It is interesting to note that it has been observed that the peak due to ArO, when drying is incomplete, is partially separated from the peak resulting from iron, indicating the ability to differentiate between certain species due to their peak position in time.[71] Each of these reports was successful in reducing the iron/ArO interference and indicates that the use of ETV for the analysis of samples containing iron in solution has definite advantages.

While the iron/ArO interference has been studied extensively, other interferences based on matrix constituents and other species, such as plasma gases, have been investigated. Carey et al.[71] have also investigated the interference of $^{40}Ar^{35}Cl$ on monoisotopic arsenic at $m/z = 75$. Matrix modifiers of nickel nitrate to complex with the arsenic and provide greater thermal stability, and ammonium hydroxide to combine with the chlorine and form the relatively volatile ammonium chloride compound were necessary. These additions may contaminate the sample and make the procedure tedious. Additionally, no data were presented on optimizing the amount of modifier required for given amounts of chlorine in the sample. The work by Carey et al.[71] was performed with nitric acid solutions, and an ArCl interference was observed. The opposite has been observed by Hall and co-workers,[87] who did not observe an interference with nitric acid solutions of arsenic.

Marshall and Franks[78] have investigated the reduction of an additional chlorine-related interference, namely, that of $^{35}Cl^{16}O^+$ on vanadium at $m/z = 51$. In this case, there was no matrix modification performed. It was found that when using an ashing step, solutions containing less that 5% hydrochloric acid gave no interference. However, at 5% or higher concentrations the interference was still present. No data were presented to indicate whether this might be eliminated with the use of a matrix modifier. A nonspectroscopic interference was the proposed cause, but no data were presented to substantiate this hypothesis.

Marshall and Franks[78] have also investigated the reduction of the isobaric interference from $^{14}N^{16}O^1H^+$ at $m/z = 31$ on phosphorous. This was accomplished in the same manner that the ArO interference was removed during the determination of iron. By removing the oxygen species in the sample, the background equivalent concentration is decreased, and the percent relative standard deviation is improved. The authors state that the detection limit should be improved by a factor of over 100. This was substantiated with a reported detection limit of 0.3 ng/ml for ETV-ICP-MS compared to 40 ng/ml for nebulization ICP-MS. Despite the obvious improvement in detectability, no results as to the determination of phosphorous in real sample were presented, and no mention of the sample matrix was presented.

The work of Marshall and Franks[78] also presented an investigation on the interferences due to S–O combinations on titanium in sulfuric acid solutions. The interfering species are $^{32}S^{14}N^+$ at $m/z = 46$, $^{32}S^{14}N^1H^+$ at $m/z = 47$, $^{32}S^{16}O^+$ at $m/z = 48$, $^{32}S^{17}O^+$ or $^{32}S^{16}O^1H^+$ at $m/z = 49$, and $^{32}S^{18}O^+$ or $^{32}S^{17}O^1H^+$ at $m/z = 50$. While small improvements were observed in the background signal when utilizing ETV for sample introduction when compared with solution nebulization, the reduction was not sufficient to justify using the more expensive and complex ETV system. Further, investigation into the use of ETV for these sample types is warranted, however, because no investigation into the use of matrix modifiers or optimization of drying and ashing parameters was performed.

Hall and co-workers[87] have investigated a number of isobaric interferences and the effect of ETV on them. Besides the previously mentioned iron/ArO pair, they have investigated the interferences of $^{44}Ca^{16}O^+$ and $^{44}Ca^{16}O^1H^+$ on Ni^+ at $m/z = 60$ and 61. The determination of nickel in a river water sample using an isotope dilution method was performed, and no correction was found to be necessary for interferences. Despite the favorable results presented, there was no discussion of optimization and little discussion was provided about reducing isobaric interferences.

The sample matrix and plasma gases are not the only sources of isobaric interferences in ICP-MS. While the ETV has been demonstrated to reduce the presence of interfering species, it can also add to the difficulties because of components of the ETV furnace. Park and Hall[86] have shown that the choice of filament in a furnace can be crucial for the measurement of certain elements. In particular, they discuss the interference from $^{186}W^{16}O^{1}H^{+}$ and $^{187}Re^{16}O^{+}$ on $^{203}Tl^{+}$. Therefore, they chose to use a graphite filament for the determination of thallium. It may be possible that using a graphite furnace, or filament, may cause difficulties in the determination of chromium, whose major isotope is isobaric with $^{40}Ar^{12}C^{+}$ at $m/z = 52$. There may be other possible problems with furnace material. Many investigators have observed problems with impurities in the furnace or filament material causing an increased background (e.g., see Reference 77).

The choice of furnace material is not the only consideration when designing an ETV experiment for ICP-MS detection. The use of common matrix modifiers can also cause interferences with the detection of certain elements. One example of this is the partial overlap of the silver peak at $m/z = 107$ by the palladium peak at $m/z = 106$.[87] Despite the possible problems here, silver is generally vaporized completely before the palladium volatilization, and the resolution of the quadrapole should be sufficient to resolve the peaks in terms of their mass to charge ratio. However, there may be problems encountered with other common matrix modifiers (such as nickel nitrate) due to the formation of polyatomic species or spectral overlap of elemental peaks. Clearly, this type of possible interference could be a deterrent when it is necessary to perform matrix modification prior to analysis. The possible problems and solutions need to be studied in greater detail to allow full utilization of the capabilities of ETV.

Another possible matrix-related spectral interference is overlap or skewing of peaks by other elements present in the sample rather than from matrix modifiers or polyatomic species. This has been observed in a few cases, such as the interference[86] from ^{206}Pb on ^{205}Tl and the interferences from ^{204}Hg on ^{204}Pb.[90] Interferences such as Pb/Tl arise in quadrapole mass spectrometry because the peaks obtained are asymmetric and skewed toward the low mass end. In the presence of a high concentration of matrix element with a mass one m/z value higher than the mass of interest, a spectral interference occurs.[86] This is a type of interference that cannot be removed by the use of ETV sample introduction. In fact, when performing multimass acquisitions in a peak hopping mode, the transient nature of the ETV signal may cause further interference due to a slight shift in the peak position; therefore, the sampling mass position is slightly off maximum. This type, and the Hg/Pb type of interference, can be detected with the careful measurement of isotope ratios and blank matching.

A final phenomenon that has been observed with ICP-MS analysis is the formation of metal oxides and other elemental oxides such as the previously mentioned argon species. This is an undesirable event, because it degrades detection limits for that particular element because some of the analyte is not detected at the typical mass. Formation of oxides and doubly charged species has been investigated extensively with solution nebulization and has also been well characterized with ETV sample introduction. These effects have been studied for a variety of elements, in particular an extensive study has appeared that focuses on the oxide formation of rare-earth elements.[70]

The formation of polyatomic and doubly charged species can also cause spectroscopic interferences when they have the same nominal mass-to-charge ratio as an element of interest. An example of this type of interference is the overlap of LaO and Gd at $m/z = 155$. This is greatly reduced when utilizing ETV-ICP-MS compared with solution nebulization ICP-MS. Through the use of a hydrogen gas flow added to the argon carrier gas flow, the oxide formation can be reduced. This was demonstrated with the study of the LaO/La ratio at a variety of temperatures and hydrogen gas flow rates.[70] This reduction in oxide formation is caused by an oxidation suppression due to the presence of hydrogen. The metal oxide/metal ratios for each of the elements studied, although lesser in amount, show the same trends with respect to dissociation energies as those observed with nebulization ICP-MS.

2. Nonspectroscopic Matrix Interferences

Nonspectroscopic interferences are common difficulties in both ICP-MS and ICP-AES. These types of interferences generally involve the suppression or enhancement of signals due to the presence of high matrix component concentrations, such as salts or organics. These nonspectroscopic matrix interferences are particularly important when analyzing "real world" samples that often have complex matrices. Extensive study has been done on the extent of these types of interferences with ETV. Varying results have been produced with a wide variety of samples.

Park and coworkers[91] performed an extensive study of the nonspectroscopic matrix effects in an ETV-ICP-MS configuration. In their work, a special ETV device was constructed with two identical filaments. Through this construction they intended to study the effect of plasma loading separately from the other matrix effects associated with the ETV-ICP-MS system. The elements investigated were arsenic, cadmium, and copper in matrices consisting of sodium, chromium, nickel, calcium, and selenium. Their work indicated that the physical and chemical plasma loading aspects of the matrix effects were the major contributors to the signal changes with high matrix element concentrations. However, it was observed that vaporization interferences are also present, caused by incomplete vaporization of the analyte due to matrix presence. Despite extensive data presented on the ionization suppression effect of the matrix in the plasma, no work was presented indicating that the use of ETV allows for reduction of these interferences through "selective volatilization" of the matrix from the analyte.

Hall and coworkers[87,88] have discussed the ability to reduce matrix-induced interferences for samples containing high salt content. They point out that, depending upon the volatility of the analyte of interest, it may be possible to reduce the interference either by removing the matrix concomitants prior to the volatilization of the analyte of interest[88] or by volatilizing the analyte and leaving the matrix in the furnace.[87] They successfully demonstrated the first of these two methods for the determination of molybdenum in a sodium matrix. This was easily accomplished because the two elements have widely different volatilities, with molybdenum being relatively nonvolatile. The second method was discussed; however, no data were presented illustrating applicability of this technique. It was also noted that the standard addition method is available for use with ETV-ICP-MS as well as solution nebulization.[87] While this may be effective, it does require dilution of the sample and additional sample pretreatment. Additionally, no advantage over conventional solution nebulization, other than the reduction of nebulizer clogging, is provided, especially when ETV instrument cost, complexity, and reliability are taken into consideration.

An additional source of nonspectroscopic effects is the use of matrix modifiers such as nickel nitrate. These materials are generally added to the sample in relatively high concentrations and may therefore cause changes in the signal obtained from an analyte. Addition of nickel nitrate to a sample for the determination of platinum has been investigated utilizing ETV-ICP-MS.[85] In this work it was found that the nickel indeed had a matrix effect when investigated utilizing nebulization sample introduction. A concentration of approximately 500 ppm Ni caused a 50% suppression in the analyte signal. However, with electrothermal vaporization the signal was found to be enhanced by factors of 10% with 500 ppm. This is attributed to an increase in the rate of analyte vaporization and/or a decrease in the loss of analyte vapor (thus increasing the vaporization and transport efficiencies). The enhancement observed is most likely due to the latter of the two. This is the entire point of utilizing a matrix modifier and is, therefore, not surprising. Possible mechanisms put forth by the authors included vapor-phase and surface interactions. This indicates that nonspectroscopic matrix interferences are not always undesirable;

in fact, when correctly manipulated, they can be of great importance to the analysis.

Although the use of organic matrices has not found extensive study with ETV-ICP-MS, it is likely to become an important topic as the need for maintaining the form of the element becomes more important. Extraction methods, liquid chromatographic techniques, and organometallic compounds often require organic solvents. Other samples, such as petroleum, are organic in nature and require the system to be able to accept organics. The different fractions collected during an extraction or a liquid chromatographic separation could be analyzed to determine the amount of a particular element in a species soluble or eluted in that fraction. The difficulty encountered with organic species is plasma instability due to the quenching of the plasma energy from the necessity of breaking down organic materials resulting from the solvent. A second problem often encountered is clogging of the ICP-MS interface sampling cone due to carbon deposition. ETV sample introduction should be ideal for the determination of samples in organic matrices, due to its ability to decompose and selectively remove the organic material prior to the volatilization of the analytes of interest.

Sample types that are of interest for elemental analysis, due to the presence of catalysts used in the cracking process, are petroleum products. These samples present difficulties for solution nebulization into the ICP-MS due to the organic nature of the matrix. There has been a recent report on the quantification of mercury in petroleum by ETV-ICP-MS.[79] In this study useful information was obtained for mercury in a matrix consisting of C_{18} molecular weight species or less; however, better results are obtained in samples containing an average molecular weight of C_{12} or less. A loss of signal was observed with the ETV-ICP-MS system as the length of the carbon chain was increased. This was attributed to the increased plasma loading and a more diffuse sample profile in the plasma. These results are surprising because one would expect less difficulties from these types of problems utilizing an ETV sample introduction device. However, these results are better understood when one realizes that no ashing or drying stages were used in this work. There was no explanation given for this omission, but it would seem that the idea of selective volatilization (separation of the matrix from the analyte) would be appropriate here. The lack of ETV program optimization suggests that the use of ETV for sample introduction in this work is unnecessary.

An additional report on the investigation of samples containing a high organic content matrix has been reported by Hall and coworkers.[87] This report details the determination of gold in isobutyl methyl ketone extractions from standard reference materials. In this work, no interference was found from the organic nature of the sample matrix, and no modification of the plasma, oxygen addition to the nebulizer gas flow, was found to be necessary. As would be expected, the authors reported that the organic vapors generated during the drying and ashing stages are vented to waste and the analyte is then vaporized and sent to the plasma. These results would be expected for petroleum samples when the careful optimization of the furnace parameters is performed and any steps necessary for matrix modification are performed.

B. Isotope Ratio Measurements

One of the advantages of using ICP-MS for elemental analysis over emission and absorption techniques is the ability to measure isotope ratios. This has proven difficult for ETV sample introduction due to the transient nature of the signal produced and the sequential nature of the quadrapole. This necessitates a trade-off between the number of masses that can be monitored, sensitivity, and peak resolution when compared with truly simultaneous data acquisition methods, such as the use of a polychromator for multielement emission measurements, and steady-state methods of sample introduction, such as pneumatic nebulization. The trade-off can be minimized with sufficiently fast data acquisition methods and rapid scanning of the quadrapole or use of peak-hopping techniques. The measurement of isotope ratios is important to make it possible for the use of isotope dilution methods. Several workers have studied the determination of lead isotope ratios by ETV-ICP-MS.[77,90,91] Other reports have demonstrated the ability to measure isotope ratios of iron,[71,92] osmium,[80] thallium,[86,92] molybdenum,[92] tungsten,[92] and uranium.[72] Several different reports have demonstrated the feasibility of performing isotope dilution measurements (e.g., see Reference 92).

Shen et al.[77] obtained isotope ratios by performing multiple firings of the ETV furnace and monitoring each of the lead masses separately. The difficulty in this determination is that the peak width was only approximately 1.3 s, which required a dwell time on the order of 10 ms or less; however, the settling dead time of the quadrapole MS was also approximately 10 ms, which caused difficulties. Values for the isotopic ratios were 52.38, 21.11, and 25.11 for the lead isotopes at *m/z* values of 208, 207, and 206, respectively. The large difference between the *m/z* = 206 experimentally determined value and the natural isotope abundance was attributed to the manual setting of the quadrapole. While this work clearly demonstrates the ability to determine isotope ratios, the method of data acquisition is undesirable because it requires multiple runs for a measurement that makes it ineffective for isotope dilution determinations.

Work by Date and Cheung[90] on the determining lead isotope ratios by ETV-ICP-MS was performed by rapidly scanning the quadrapole between the masses of 100 and 201. The range was chosen to allow for the determination of some trace elements in the samples utilized, as well as isotope ratios. Utilizing this setup the following ratios were obtained for a NIST 981 standard reference material: 16.62, 15.33, 35.39 for ratios of *m/z* 206/204, 207/204, and 208/204, respectively. These values gave errors between 1 and 4%. The advantage of this technique compared with that of Shen et al.[77] is that the information is obtained in a single run for a given sample. A problem is that this technique does not provide intensity vs. time information. This may be of interest because the peak shape and vaporization rate affect the sensitivity, and, therefore, detectability of the technique. The most advantageous situation would be the ability to resolve the peak not only by mass, but also by time.

The previously mentioned data acquisition method has been utilized by Park and co-workers.[91] In this case the quadrapole is operated in a peak hopping mode, and in a single "scan" each mass is sampled once. Therefore, in one scan, when monitoring four masses, there are four measurements. When the data acquisition is complete, a time vs. intensity profile results that consists of every fourth point at each mass monitored. By this technique the isotope percentages obtained analyzing NIST 981 reference material were 1.56, 23.87, 22.52, and 52.03% for mass-to-charge ratios of 204, 206, 207, and 208. These values gave absolute errors of 0.13, 0.26, 0.44, and 0.31%, respectively, for *m/z* 204, 206, 207, and 208. This mode of data acquisition is the most desirable of the three methods. While this method requires some specialized data acquisition software, and a great deal of computer power, the benefits of the method seem well worth the cost. This mode would also appear to be beneficial for multielement determinations. The disadvantage associated with this type of data acquisition is the possibility that the mass calibration may be slightly off, causing data collection at an incorrect mass.

Iron isotope measurements were also performed utilizing a commercially available time resolved data acquisition method. In this case, the masses monitored were 54, 56, and 57.[71] Mass 58 was not monitored due to possible interferences from erosion of the nickel sampler and skimmer cones. The purpose of the isotope measurements in this case was to determine the extent, if any, of an ArO^+ interference on the major isotope of iron. A display of the responses obtained at each mass is shown in Figure 10. The values obtained were 6.37, 91.13, and 2.17% for *m/z* values of 54, 56, and 57, respectively. These values yield errors of 7.97, 0.43, and 3.56%. The large error for *m/z* 54 was attributed to an interference from ArN^+. This work indicates another advantage of utilizing isotope ratios, the ability to determine the presence of an interferant at a given mass-to-charge ratio value.

The isotope ratios of osmium have also been determined by ETV-ICP-MS.[80] In this work, the data acquisition was performed in a manner similar to that described by Park and co-workers[91] for the measurement of lead isotope ratios. The transient nature of the signal and limited speed of data acquisition allowed for the measurement of only four isotopes of osmium and caused a greater error in the measurements when compared with

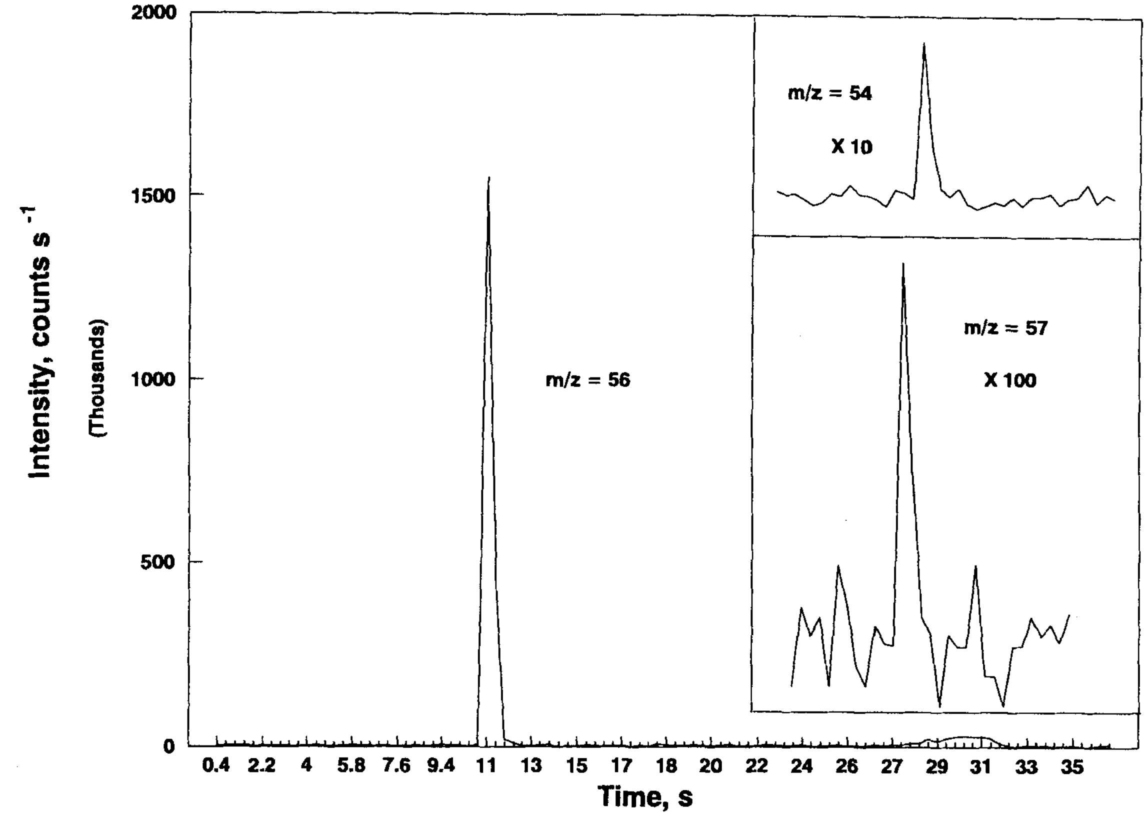

FIGURE 10. Isotope ratio signals at indicated *m/z* for Fe. (Reproduced from Carey, J.M. et al. Spectrochim. Acta. 1991, *46B,* **1711.** With permission from Pergamon Press, Ltd.)

solution nebulization and OsO_4 vapor generation. The technique has been applied to a number of reference materials with acceptable results. The advantage of ETV when compared with the other techniques was its sensitivity, sample consumption, and analysis time. Despite the relatively high error in measurement, the precision was adequate for most applications. Thallium, molybdenum, tungsten, and uranium isotope ratio determinations have also been reported; however, additional information on the reliability of the values acquired was not presented. In addition, no detailed description of the method of data acquisition was provided.

C. Multielement Determinations

With the previously mentioned advances in data acquisition capabilities of the ICP-MS instrument, it has become possible to obtain multielement information for a single sample firing in the ETV. A pair of reports has appeared describing the feasibility of such a technique and indicating the possible figures of merit that could be obtained with such a system.[72,78] Difficulties of this technique are greater than for determination of isotope ratios. The primary reason for this being that the mass range necessary that needs to be sampled during the 1- to 5-s analyte peak is much larger. This should result in a loss of sensitivity for any multielement detection scheme for a transient signal, such as with ETV, when compared with a steady-state signal such as solution nebulization. These problems result from the sequential scanning nature of the quadrapole mass spectrometer.

One report has detailed the multielement detection capabilities of ETV-ICP-MS for 21 elements utilizing a commercially available time-resolved data acquisition software package.[78] The background equivalent concentrations for the ETV-ICP-MS system were lower or comparable to solution nebulization values utilizing the same data acquisition parameters. It was found that the precision for most of these multielement measurements was adequate and typically less than 10%, with the exceptions of zinc, titanium, cadmium, lead, and arsenic. The values of cadmium and zinc in particular were poor and on the order of 20% R.S.D. No explanation for this was presented; however, the peaks displayed indicated that few points per peak were taken. This finding suggests that the described precisions may be misleading. If newer versions of software allow the operator to extract more points per peak to obtain a "true" profile of the peak, these precisions might be obtained more consistently. Despite the comprehensive study presented in this report; none of the usual figures of merit, other than precision, were presented. No detection limits are reported utilizing the multiple mass monitoring system; however, the authors do speculate on these limits. The linearity of the technique is not presented, and judging by the poor precision obtained for several of the elements, this may be a concern. Finally, no application of this mode of data acquisition was presented with complex matrices where it may be necessary to "selectively volatilize" certain matrix materials prior to the analyte vaporization.

Another discussion of multielement detection of ETV by quadrapole ICP-MS has been presented by Hulmston and Hutton.[72] In this work, they described the detection of 14 elements in a single firing of the ETV device. The described system utilizes a multichannel analyzer (MCA) for data acquisition. The MCA allowed for the full mass spectral information to be captured from a transient signal, even one with a signal of 1 to 2 s duration, and essentially acts as a buffer between the ICP-MS and the data collection system, eliminating dead time due to data transfer. While this approach seems promising, the work reported only provides a mass spectrum and the peak profile is lost. For example, loss of the peak profile can be a major disadvantage when analyzing iron in an aqueous solution, because it does not provide for observing different species that may volatilize at different times. Removal of matrix interferences early in the ETV program may not be recognized without access to the time-intensity profile for that particular mass. Despite this limitation, the configuration demonstrates excellent sensitivity, providing detection limits in the subpicogram range. When compared with detection limits obtained with single ion monitoring data acquisition, approximately two orders of magnitude of detectability is lost. However, for a sample not having parts per trillion or lower concentrations and a large number of elements to be determined, this method seems advantageous. The combination of the MCA and the time-resolved acquisition software capabilities described by Marshall and Franks[78] would provide the capability for good detectability as well as time-intensity profiles for each of the masses.

D. ETV-ICP-MS Sample Types

One of the primary advantages of ETV sample introduction is the ability to analyze a wide variety of samples. This has been borne out in the literature presented for ICP-MS. Table 2 shows a list of "real world" samples that have been analyzed utilizing ICP-MS with ETV sample introduction and any sample pretreatment steps performed. As the table indicates, a majority of the samples that have been analyzed by ETV-ICP-MS have been placed in solution form prior to analysis. This pretreatment step, while necessary for solution nebulization sample introduction, may not be necessary for these samples. One of the benefits of ETV, which has yet to be investigated for ICP-MS detection, is the ability to analyze solids directly. While none of the reports detailed here describe such work, other direct analysis applications have been described.

Primarily, these investigations have involved biological samples, such as blood, plasma, and urine, that are not amenable to direct analysis by solution nebulization ICP-MS. These types of samples are well suited to analysis by ETV-ICP-MS because they are often volume limited, and ETV allows for the use of small volumes of sample. Samples of a biological nature often contain extremely small quantities of the element of interest and the detection capabilities of ICP-MS are often required. The ability to analyze these samples directly lowers the detection limits, because no dilution from sample pretreatment is required. Other samples have been investigated directly by ETV-ICP-MS, primarily marine and river waters. However, an important area of future work in ETV-ICP-MS research is the investigation of the

TABLE 2
ETV-ICP-MS Sample Types

Sample Type	Pretreatment step(s)	Ref.
Andesite	Digestion, fusion, and leaching procedures	86, 88
Basalt	Digestion, fusion, and leaching procedures	86, 88
Carbonaceous, siliceous shale	Digestion, fusion, and leaching procedures	86
Carbonaceous chert	Digestion, fusion, and leaching procedures	86
Cody shale	Digestion, fusion, and leaching procedures	86, 88
Composite outcrop materials	Digestion, fusion, and leaching procedures	86
Copper millhead	Digestion, fusion, and leaching procedures	86
Fly ash	Slurry formation	27
Gabbro	Digestion, fusion, and leaching procedures	86
Iridosmine	Fusion procedures	80
Jasperoid	Digestion, fusion, and leaching procedures	86
Marine sediment	Digestion, fusion, and leaching procedures	86, 88
Mica schist	Digestion, fusion, and leaching procedures	86, 88
Orchard leaves	Acid digestion	91
Oyster tissue	Acid digestion	91
Petroleum products	None	79
Petroleum shale	Digestion, fusion, and leaching procedures	86
Photoresists for very large integrated circuits	Dissolved in ethoxyethyl acetate	74
Plasma and urine	None	83
Pure iron	Acid digestion	17
Quartz latite	Digestion, fusion, and leaching procedures	86, 88
Rhyolite	Digestion, fusion, and leaching procedures	86, 88
River sediment	Digestion, fusion, and leaching procedures	86
River water	None	87
Rock powders	Nickel sulfide fire assay technique	85
Rutheniridosmine	Fusion procedures	80
Seawater	None	75, 92
Semiconductor materials	Acid digestion	84
Silicate rock	Acid digestion	90
Soil	Digestion, fusion, and leaching procedures	86, 88
Steel	Acid digestion	73
Stream sediment	Digestion, fusion, and leaching procedures	86, 88
Syenite	Digestion, fusion, and leaching procedures	86, 88
Urine	None	81
Whole blood	None	91

direct analysis of solid samples. Without these capabilities, much of the usefulness of ETV as a sample introduction technique will not be realized.

IV. ETV-ICP-AES

Electrothermal vaporization as a sample introduction technique for inductively coupled plasma atomic emission spectrometry has been studied extensively. There have been a number of excellent reviews that have appeared recently on electrothermal vaporization with ICP-AES detection.[128–131] Because these reviews are extensive regarding the use of ETV-ICP-AES, it is not necessary, nor practical, to cover all of the reports that have appeared on the technique. This discussion therefore concentrates on the situations where ETV sample introduction is most beneficial to ICP-AES and provides examples for each of these particular advantages. An extensive list of references for ICP-AES is included for completeness sake. Table 3 indicates the elements that have been analyzed utilizing ICP-AES and a range of

TABLE 3
ETV-ICP-AES Detection Limits

Element	Detection limit (ng)	Ref.
Aluminum	0.5 pg–0.04	26, 29, 39, 43, 45–47, 52, 60, 62–64
Antimony	0.1–0.3	1, 20, 43, 67
Arsenic	0.06–2	1, 14, 17, 20, 25, 39, 43, 45, 57, 61, 63, 66, 67
Barium	0.3 pg–0.5 pg	1, 17, 45
Beryllium	0.001–0.002	1, 17, 22, 31, 37, 43, 47, 67
Bismuth	0.2	1, 17, 43
Boron	0.004–3	1, 2, 5, 10, 13, 45, 56
Cadmium	0.001–0.6	1, 5, 8, 11, 17–20, 24, 25, 30, 32, 33, 36, 37, 40, 43, 45, 46, 57, 61–63, 65–67
Calcium	0.015	43, 45, 47
Carbon	N.R.[a]	30
Cerium	N.R.	4, 15
Cesium	N.R.	17
Chromium	0.009–1.03	2, 5, 8, 11, 14, 16, 26, 32, 38, 46–49, 53, 55, 58, 61, 62, 64–66
Cobalt	0.012–0.45	11, 14, 19, 32, 33, 37, 63–65
Copper	0.0015–0.5	9, 11, 18, 19, 26, 30, 32, 33, 37, 43, 45–49, 61–65
Dysprosium	N.R.	4, 15
Erbium	0.034	4, 15, 28
Europium	0.012	4, 15, 28
Gadolinium	N.R.	4, 15
Gallium	0.01	17, 43, 67
Germanium	0.01–0.06	45, 56, 63
Gold	0.01–0.02	29, 57, 60, 63, 67
Hafnium	N.R.	2
Holmium	N.R.	4, 15
Indium	0.02	17, 64, 67
Iron	0.01–0.1	9, 11, 14, 17, 19, 24, 37, 39, 43, 45, 47, 63–65
Lanthanum	N.R.	4, 15

TABLE 3 (continued)
ETV-ICP-AES Detection Limits

Element	Detection limit (ng)	Ref.
Lead	0.004–6.5	1, 5, 11, 12, 17–20, 23, 25, 27, 30, 32, 33, 35–39, 42–45, 47, 51, 53, 55, 56, 59, 61, 63–65, 67
Lithium	0.0015–0.02	29, 43, 45, 46, 57, 60, 63, 67
Lutetium	0.054	4, 15, 28
Magnesium	0.1 pg–0.005	9, 14, 17, 22, 36, 43, 45, 47, 51, 63, 65
Manganese	0.3 pg–0.160	1, 8, 11, 14, 17, 19, 22, 30, 32, 33, 37–39, 43, 45–47, 49, 53, 55, 61–65, 67
Mercury	0.004–0.2	1, 17, 41, 43, 63, 67
Molybdenum	0.007–0.5	2, 5, 7, 14, 26, 61
Neodymium	N.R.	4, 15
Nickel	0.027–4.85	11, 14, 17, 32, 33, 37, 48, 53, 55, 61, 63–65
Osmium	N.R.	29
Palladium	N.R.	29
Phosphorous	0.1–2	1, 26, 43, 56, 67
Platinum	0.025–0.05	29, 40, 60
Potassium	1.2–3	45, 46, 63
Praseodymium	N.R.	4, 15
Rhenium	0.1	43, 67
Rubidium	2.8	17, 63
Ruthenium	0.095	29
Samarium	N.R.	4, 15
Scandium	0.017	4, 15, 28
Selenium	0.45–3	1, 17, 45, 61, 66
Silicon	0.1–2.5	9, 45, 52
Silver	0.001–0.15	1, 17, 43, 49, 63, 64, 67
Sodium	0.4	45, 47
Strontium	0.005	17, 45, 47
Sulphur	N.R.	9
Tellerium	0.05–4.3	1, 43, 63, 65, 67
Terbium	N.R.	4, 15
Thallium	0.3	1, 17
Thulium	N.R.	4, 15
Tin	0.02–2	1, 14, 47, 56, 57, 63
Titanium	0.0057–6.4	2, 5, 14, 61
Tungsten	0.16–1.2	2, 5
Uranium	0.003–0.03	58
Vanadium	0.0059–2	2, 5, 14, 17, 45, 58, 61
Ytterbium	0.018	4, 28
Yttrium	0.025	4, 28
Zinc	0.6 pg–0.8	6, 17–20, 25, 30, 32, 33, 36, 37, 43, 45, 46, 51, 56, 57, 59, 61, 63–65, 67
Zirconium	0.004–0.4	2, 5, 14, 58

[a] N. R., not reported.

detection limits reported. In constructing this table there has been no attempt to normalize the detection limits with respect to the sample matrix or the calculation method (3 σ vs. 2 σ).

A. Matrix Effects

As with ICP-MS, the ICP-AES technique is influenced by the presence of high concentrations of easily ionized elements and other matrix components. One of the advantages of ETV sample introduction is the ability to eliminate or significantly reduce these interferences. Generally, this is accomplished through selective volatilization of the undesirable matrix constituents prior to the vaporization of the analyte of interest. This procedure requires optimization of the temperature profile for the electrothermal vaporizer, and may require the use of a matrix modifier to increase the volatility of the matrix elements and/or decrease the volatility of the analyte. The process of removing interferences from the matrix constituents has also been investigated utilizing hardware modifications, through the incorporation of a refractor plate.

A thorough investigation of adding various inorganic salts of a trace element of interest has been performed.[37] In this report, not only were a variety of different matrix elements investigated, but a number of different analyte elements were also investigated. When investigating matrix interferences, this is particularly important because different elements are affected in different ways by the matrix constituents. From the results obtained, the interferences varied greatly from analyte to analyte and between different matrices.

In general, it was found[37] that when easily ionized elements (such as the alkali or alkaline earth elements) were present in large concentrations in the matrix the signal from the analyte was enhanced. It was determined that the increased signal did not result from spectral interferences or other background changes. The authors attributed the signal enhancement to a combination of vaporization interferences, changes in transport efficiencies, and changes in plasma characteristics. However, no investigation was made into determining which of these effects was the greatest contributor to the signal enhancement. Because the background did not change significantly during the vaporization, background correction was not necessary, but it is desirable. Attempts were also made to reduce or eliminate the interferences through selective volatilization and temperature programming.

Optimization of the viewing height and forward power were the only attempts made at reducing the interferences from the matrix constituents.[37] This result is not surprising, as these parameters may help to reduce some of the interference effects since the matrix is still being introduced into the plasma simultaneously with the analyte and some changes in the plasma conditions would be expected. A better method of reducing interferences is to optimize the heating rate of the furnace and then perform matrix modifications to allow for volatilization of the analyte prior to vaporization. In this manner, the analyte and matrix constituents could be separated and, therefore, the changes in plasma conditions and vaporization conditions at the time of analysis would not be altered by the matrix.

The primary advantage of the time gating system described by Tikkanen and Niemczyk[39] is the ability to monitor and integrate the data at a particular wavelength only during the period at which the analyte signal would be expected to appear. The system studied, which involved a spectral interference, was the arsenic line at 193.696 nm and the interference from the aluminum ion-electron recombination continuum (between approximately 193 and 210 nm). By integrating the signal during the appearance of the arsenic peak, the signal-to-noise ratio is increased and the contribution to the signal from the aluminum continuum is removed because arsenic and aluminum differ in volatility. This example illustrates a drawback to this system. While the method of increasing the signal-to-noise ratio is beneficial, the reduction of the spectral interferences still requires that they be separated in time. This means optimizing the temperature profile to achieve separation of the interferant from the analyte. The primary advantage of this system for separating these species in time is that it allows simultaneous monitoring of several wavelengths, providing the optimum separation of elements with differing emission profiles.

The utility of this instrument in attempting to reduce the effect of easily ionized elements at the analyze emission intensity also was investigated. Optimization of the temperature program to effectively "distill" off the matrix components prior to vaporizing the analyte is facilitated by the ability to monitor the wavelength at which the interferant emits radiation simultaneously with the wavelength characteristic of the analyte. Use of this technique was illustrated for a number of analytes and matrix interferences with varying success. Despite the ability to optimize the distillation, the success of the method still depends upon the matrix element and the analyte having differing volatilities.

While this system provides more efficient optimization of the conditions for drying and ashing the sample, the complicated data collection scheme is not necessary to perform such a procedure. By monitoring the wavelength of a blank solution containing only the matrix and comparing it to the time-vs.-signal profile of the analyte, the temperature program can be effectively optimized. This single channel optimization method offers the advantage of being instrumentally simpler, but this advantage may be offset by some of the pluses of the time gated system. If the matrix element alters the vaporization profile of the analyte, then monitoring the easily ionized element (EIE) profile simultaneously with the analyte profile is necessary to obtain a true representation of the separation, and is less time consuming. If it is de-sired to perform analyses on samples containing large amounts of a known matrix element, this detector system may be useful for optimizing the analysis.

A refractor plate has been incorporated in an ICP-AES system to perform background correction on analyses utilizing ETV sample introduction.[12] This is particularly important when dealing with samples that have spectral interferences. The refractor plate is positioned in the monochromator behind the entrance slit. By modulating this plate at suitable frequencies (1 to 40 Hz), it is possible to correct for background shifts caused by interfering elements in the sample. When the refractor plate is modulated, the detector is exposed to two different wavelengths allowing correction for the contribution to the signal at the analyte wavelength from a nearby wavelength.

This background correction technique[12] eliminates the need for attempting to matrix match the standards to the sample. The authors illustrated the utility of their system by investigating the determination of lead in an aluminum matrix at a wavelength of 220.353 nm. Aluminum interferes with this determination due to the presence of aluminum emission lines at 220.462 nm and 220.467 nm. By modulating the signal between these two wavelengths, the contribution to the emission profile at the lead line from the aluminum matrix can be subtracted through the data collection system. Through the use of a drying program, it is possible to separate these analytes in terms of their volatility. However, this "simple" modification to the monochromator removes the necessity for complete separation of the interferant from the analyte of interest.

Disadvantages of this type of interference correction[12] are the necessity for increased computer power in the data collection system and the need for precise control of the refractor plate modulation. An additional difficulty with the method is the inability to apply it in a situation where the interfering peak directly coincides with the analyte peak. Overall, because the inclusion of the refractor plate was not found to degrade the utility of themonochromator (no losses in resolution, stability, or sensitivity were observed) this correction seems to be useful for transient signal sample introduction methods, such as ETV, providing there is sufficient computational power. Despite the apparent utility of the system, the optimization of the temperature program to separate the matrix and element of interest would still be a more cost-effective method where such a technique is plausible.

An additional type of matrix has been investigated utilizing ETV. Traditionally, inductively coupled plasmas have had difficulties in handling organic solutions. The problems commonly associated with the introduction of organic solvents into the ICP include increased plasma instability, a reduction of sensitivity due to quenching of the plasma, and increased plasma flicker. The use of ETV allows for the analysis of samples containing high concentrations of organic species and those prepared in organic solvents by removing the organic vapor from the sample prior to introducing the analyte into the plasma. An investigation into the ability of ETV-ICP-AES to analyze samples in organic solvents has been reported[59] and has indicated that this type of analysis is certainly feasible. Investigating samples that are organic in nature is of importance because many biological and environmental samples contain a high concentration of organic materials.

The material presented in this report[59] indicates the feasibility of determining trace metal concentration in both motor oil and gasoline samples. An analysis of these samples was accomplished without venting the solvent vapor. These results were attributed to the fact that only microliter amounts of the organic solvent were introduced into the plasma. When analyzing for tetramethyllead and tetraethyllead in gasoline, the use of an iodine matrix modifier was necessary to avoid analyte losses during the sample drying steps. A difficulty with the analysis of samples prepared in organic solvents is the necessity of matching the solvent in the standards used for calibration to those contained in the sample. The results presented indicated that the solvent had an effect on the intensity of the signal obtained for a given analyte. This phenomenon may be due to vaporization suppression in the furnace, or it may be a plasma effect from residual solvent left in the furnace after the drying stages and/or from solvent introduced into the plasma during the drying stages. The authors attribute these findings to the organic solvent soaking into the carbon cup. However, there is no mechanism proposed for the interference, either plasma phenomena or vaporization suppression.

Overall, this report indicates that it is feasible to analyze 100% organic solvent samples for trace metals directly using ETV-ICP-AES. It does point out that these analyses may not be as straightforward as one might assume. Care must be taken to avoid vaporization changes with solvent type and to attempt to match the solvent type to the standards. A possible improvement in the design of these experiments is the inclusion of a drying vent to remove the solvent vapor during the drying stages. Another possible area of investigation is the use of different furnace materials that might not absorb the organic solvents to the degree that the pyrolitically coated graphite did in this work.

B. Multielement Detection

As with the ICP-MS technique, the detection of transient signals in a multielement mode with ICP-AES presents difficulties. However, unlike ICP-MS, the ICP-AES technique offers simultaneous detection scheme alternatives. These schemes involve the use of a polychrometer that typically incorporates several photomultiplier tubes positioned such that several wavelengths are detected simultaneously. With the correct data collection routine, this should allow for the simultaneous acquisition of time-vs.-intensity profiles for a number of elements. This has obvious implications when compared with the multielement detection schemes with the ICP-MS that must be obtained in a sequential mode. First, this should provide for less loss in sensitivity and, resolution, and second, the number of elements that can be detected simultaneously is only limited by the number of photomultiplier tubes in the instrument and the data collection capabilities.

Two reports have appeared that utilize such a system for multielement determinations using ETV sample introduction.[30,47] One of the systems described utilizes 31 channels, of which any 10 can be monitored simultaneously.[47] This particular system is a commercially available instrument that has had some minor modifications performed on it. The other system is an eight-channel instrument that is of a homemade design.[30] In both cases, it is necessary to obtain an adequate sampling rate, reasonable speed, and the maximum efficiency for the maximum number of channels. The signal must be sampled frequently enough to acquire enough points per peak to define the signal-vs.-time profile, but the number of points must not overload the data acquisition capabilities. Care must also be taken so the duty cycle is sufficient.

With careful optimization of these parameters, the sensitivity and other figures of merit obtained for each of the elements should not be degraded relative to a single-element measurement. A possible disadvantage, in addition to instrument cost, is the necessity of realigning the photomultiplier tubes in order to make measurements at elements not in the current elemental program. The two instruments[30,47] have been used to analyze complex "real world" samples in the solid form and liquid form. These analyses illustrate another advantage of multielement determinations with ETV sample introduction, namely, the ability to determine each analyte of interest in a sample during one furnace firing. When analyzing samples that are volume limited (typical of the types of samples that find utility with ETV sample introduction) this reduces the amount of sample required for an analysis.

C. Coupling of ETV-ICP-AES to Additional Techniques

Although ETV as a sample introduction technique for ICP-AES is generally used as a standalone technique, it has been combined with other methods to acquire additional information. Two examples of these procedures are coupling high-performance liquid chromatography (HPLC)[44] and coupling a mercury film electrode (MFE) for preconcentration of the analyte[32] to the ETV device for sample introduction into the ICP. These coupled techniques can provide speciation information, or enhance analyses in ways not possible by ETV-ICP-AES alone.

There is a current trend in environmental and other trace metal analyses to obtain speciation information rather than just total element concentrations in a given sample. However, ETV sample introduction alone provides, at best, a crude means of speciation through volatility programming. By coupling ETV to a chromatography technique such as HPLC, additional speciation information is obtained. One report of such a system has been given by Nisamaneepong et al.[44] In this report, the ETV-HPLC interface is similar to that utilized with GFAAS. Using the HPLC-ETV-ICP-AES instrument they were able to speciate a pair of lead compounds (tetraphenyllead and hexaphenyldilead) with detection limits that were nearly four orders of magnitude better than those obtained using HPLC-ICP-AES (nebulization sample introduction). These detection limits were also approximately one order of magnitude better than those observed with HPLC-UV methods. The detection is performed by collecting fractions at a given interval and analyzing them by ETV-ICP-AES.

This method[44] is not ideal, because it requires collecting fractions and analyzing them off-line. Chromatographically, this method provides no information about the quality of the separation. Due to the inability to acquire points more frequently than every 50 s, this system also requires that the chromatographer obtain greater than baseline resolution so that true speciation is obtained. The method eliminates the possibility of analyzing complex mixtures and requires increased analysis times, because the optimal time is that required to just give baseline resolution. Despite the many drawbacks of the described method, it is a step in the right direction if ETV sample introduction is to remain a viable alternative method of sample introduction. Future work needs to focus on developing an on-line method of detection that takes advantage of the ability of ETV to introduce organic samples (such as typical HPLC mobile phases) into the ICP with minimal ICP perturbation.

Another technique involving ETV sample introduction is the use of a MFE for preconcentration of metals and matrix separation prior to vaporization by ETV and detection by ICP-AES.[32] In the procedure described, the separation of the matrix and analyte, the preconcentration of the desired elements is achieved through controlled potential electrolysis onto mercury-plated, glassy-carbon electrodes. This causes a preconcentration of the analytes into a small volume of mercury and the potential is fixed so the matrix is not concentrated in the mercury film. The carbon electrode is then inserted into an ETV furnace where the mercury film is selectively volatilized and the trace metals are evaporated and determined in a simultaneous manner by ICP-AES.

This method[32] provides the advantage of matrix removal prior to sample introduction to the furnace. By eliminating the need for the ETV system to remove the matrix constituents, the electrochemical system helps further reduce the possibility of matrix-related interferences. Although ETV-ICP-AES has been shown to be an extremely sensitive method for trace metal analyses, there are cases that require greater sensitivity. By preconcentrating the elements onto the electrode it allows for a greater sample volume to be analyzed. Therefore, greater quantities of analyte are present to be detected by the ETV-ICP-AES detection. Disadvantages of such a system include the necessity of using a mercury electrode that may have metal contaminants and may cause matrix effects due to the large amounts introduced into the plasma during the drying stages. Another difficulty is that, although the sample matrix has been removed, optimization is still required to selectively evaporate the mercury film. Finally, this technique eliminates the advantage of sampling small volumes, because a sample volume of about 5 ml is required for electrodeposition. From a user standpoint the use of mercury is not desirable due to its relatively high human toxicity.

The coupling of additional techniques to ETV-ICP-AES may have definite advantages for meeting specific needs. However, the likelihood that any of these methods would ever find use in routine analyses seems slim. Perhaps if an on-line method for chromatographic detection with these methods could be developed, they might have some benefit. Another possibility is to trap gaseous samples in the furnace and then vaporize them into the plasma. This has potential for gas chromatography, hydride generation methods, and possibly supercritical fluid chromatography. Until these methods are perfected, ETV sample introduction is likely to remain applicable to total elemental concentrations.

D. ETV-ICP-AES Sample Types

Table 4 illustrates the types of samples analyzed by ETV-ICP-AES and the pretreatment steps taken, if any. Unlike the reported analyses with ETV-ICP-MS, there have been a number of reports of the direct analysis of solid samples as well as "real world" liquid samples. A majority of the samples analyzed are of a biological or environmental nature. Primarily, the samples analyzed have been standard reference materials and the recoveries, amount detected, have been consistent with those certified for each sample. As with most solid analysis techniques in atomic spectrometry, there is a great deal of work remaining before ETV-ICP-AES becomes a routine method for the analysis of solid samples.

V. ETV-MIP SPECTROMETRY

Of the two main plasma types discussed in this review, the one that stands to gain the most from utilizing ETV sample introduction is the microwave-induced plasma (MIP). The MIP has been shown to be extremely well suited for gaseous sample introduction methods and is commercially available as a detector for gas chromatography. However, due to the small size and less robust nature of the plasma its solution-handling capabilities are limited. Because the method produces a vapor from the sample, ETV offers an alternative means of introducing liquid (and solid) samples into the plasma. While microwave plasmas have been shown to be excellent sources for both atomic emission and mass spectrometric detection, there has only been one report on MS detection of ETV-MIP.[93] A list of the elements that have been investigated using ETV-MIP is shown in Table 5. As with the other lists of elements, there has been no attempt to normalize the detection limits with respect to the sample matrix or the calculation method (2 σ vs. 3 σ). Additionally, the detection limits reported with ETV-MIP-MS as reported in Table 5 are the lower limits of the reported values indicated in the footnotes.

A. Analysis of Nonmetallic Elements

The MIP offers the advantage, over ICP, of allowing the analysis of nonmetals such as the halogens. This behavior is primarily due to the capability of the helium MIP to produce high energy electronically excited states and ions of nonmetals. Due to this tendency, the He-MIP facilitates monitoring nonmetal ions (MS) and atom or ion electronic transitions between high energy excited states (AES). Because the ability to analyze these elements is one of the greatest advantages of MIPs, it is not surprising that considerable effort has gone into studying the feasibility of vaporizing these elements in an ETV and introducing them into a MIP.[93,95,101,102,104,105,109]

Evans et al.[93] found that the power required by the MIP was greater for iodine than for either metallic element, lead or silver. Despite this increased power requirement, possibly due in part

TABLE 4
ETV-ICP-AES Sample Types

Sample type	Pretreatment step(s)	Ref.
Alumina	None	2
Animal tissue	None	54
Bovine liver	PTFE slurry formation	7
Bovine liver	Acid digestion	32, 65
Cadmium mercury telluride	Treatment with hot aqua regia	64
Ceramic powders	Mixture with a thermochemical additive	24
Coal	None	51
Coal fly ash	None	51
Cotton cellulose	Hydrogen peroxide pressure decomposition	45
Dried wood	Hydrogen peroxide pressure decomposition	45
Drinking water	None	41
Fly Ash	Slurry formation	27
Garlic	PTFE slurry formation	7
Gasoline	None	59
Hemodialysis solution	None	52
Iron	Acid digestion	17
Lanthanum sesquioxide	DDTC/CCl_4 extraction	11
Milk powder	PTFE slurry formation	7
Motor oil	Dilution in xylene	59
Nickel-based alloys	None	36
Norway maple	Pressed into a pellet	6
Ocean water	None	57
Orchard leaves	Acid digestion	65
Orchard leaves	None	51
Phosphorus trichloride	None	9
Pine needles	None	51
Plant tissue	None	54
Pollen	PTFE slurry formation	7
Rice flour	PTFE slurry formation	7
River sediment	None	20
Seawater	Impregnation in a poly(dithiocarbamate) resin	30
Serum	None	16, 29, 34, 52
Serum	Acid digestion	60
Silica	Acid digestion followed by extraction to toluene	10
Silicon	Acid digestion followed by extraction to toluene	10
Spinach	PTFE slurry formation	7
Suspended particulate matter	None	38
Tomato leaves	PTFE slurry formation	13
Tomato leaves	None	51
Urine	Acid digestion	32, 60
Urine	None	29, 34, 35, 48, 52, 61
Urine	Impregnation in a poly(dithiocarbamate) resin	30, 61

TABLE 4 (continued)
ETV-ICP-AES Sample Types

Sample type	Pretreatment step(s)	Ref.
Wheat flour	PTFE slurry formation	7
White birch	Pressed into a pellet	6
Whole blood	Dilution with nitric acid, Triton X, and distilled water	23
Xi Shui Bai	PTFE slurry formation	13

TABLE 5
ETV-MIP Detection Limits

Element	Detection limit (ng)	Ref.
Arsenic	0.12–300	94, 97, 98, 107
Bromine	1.5 pg[a]–8	93, 95, 101, 109
Cadmium	0.09 pg[a]–12.5	93, 95, 96, 106, 108
Calcium	3.85	108
Carbon	700–10000	105, 107
Chlorine	0.12–8	95, 104, 108
Chromium	1.5–4.2	105, 108
Cobalt	N.R.[a]	105
Copper	0.03–0.9	95, 103, 105, 106, 108
Hydrogen	400–20000	107
Iodine	0.2–2.4	93, 102, 104
Iron	0.5–11	103, 106, 108
Lead	0.75 pg[a]–2.5	93, 96, 100, 103, 106, 108
Magnesium	0.1–0.12	108
Manganese	0.35–2.85	103, 105, 108
Mercury	6–100	97, 107
Nickel	0.11–3.8	100, 108
Nitrogen	5000–240000	107
Oxygen	800–4000	107
Phosphorous	0.66–5	96, 106
Selenium	0.2	94
Silver	0.03 pg[a]–0.078	93, 105
Sodium	N.R.	105
Sulphur	12–13	104
Tellurium	4.5	108
Zinc	0.4–0.5	103, 106, 108

[a] Lower limit is for MS detection.
[b] N.R., not reported.

to the higher ionization energy of iodine, the AES detection limits were two orders of magnitude greater when compared with the metallic elements. While the loss in detectability was partially attributed to a high background at the 516.118-nm line monitored, the authors stated that this background is not as great at 258.280 nm. Although the background is lower at this wavelength, the signal obtained from the analyte is significantly lower. With MS detection the same trend was observed for bromine in that a higher forward power was required when compared with metallic compounds. The detection limits observed for bromine were only slightly poorer than those obtained for lead and approximately one order of magnitude poorer than those obtained for silver and cadmium. This indicated the magnitude of the blank contamination for the iodine measurements and substantiates the authors' claims that the detection limits in this case was blank limited. No data were presented to indicate any investigation into the furnace operating conditions, such as vaporization temperature, and no investigation of real samples was attempted.

The study by Wu and Carnahan[95] discusses the difficulties in vaporizing halogens in an ETV system because of their high volatility. Because of the low vaporization temperature of the halogens, it is often necessary to perform matrix modification to avoid losses during the drying and ashing stages of the furnace program. Lead nitrate was added to samples containing chlorine and bromine ammonium salts. The chlorine and bromine in an excess of lead nitrate form lead chloride or lead bromide that have high boiling points. Optimization of the amount of lead nitrate necessary for analysis of Cl and Br was performed and the results indicated that 0.1% of lead nitrate was necessary to effectively "trap" the analyte prior to volatilization. Amounts of modifier greater than this exhibited no enhancement effects (nonspectroscopic matrix interference), but did cause shifts in the baselines at the wavelengths being monitored. It is interesting to note that with the use of the lead modifier the furnace required a higher voltage for atomization of the halogens than for cadmium and copper. This suggests that the matrix modification was successful in complexing the chlorine and bromine prior to their volatilization. Despite the success in modifying the matrix in a manner that allows for more certain volatilization of the halogens, no complex matrix study was described.

An interesting related application, which involves the determination of iodine in hydrochloric acid, has been investigated by Barnett and Kirkbright.[102] In this work the iodine calibration was obtained by vaporizing aqueous samples into the MIP and the iodine content in hydrochloric acid was determined by the method of standard additions. The authors discuss and compare the ETV technique to GC for determination of iodine. However, because the primary reason for using GC is to obtain a separation of different species in the sample, and ETV is a total element concentration technique, this is somewhat analogous to comparing apples and oranges.

B. Interferences

While the MIP is subject to greater matrix effects due to the smaller, less robust nature of the plasma, these effects have not been investigated in detail. There has, however, been an interesting study of the effect of introducing easily ionized elements (EIEs) into an MIP system with a graphite furnace vaporizer.[103] In this report, the authors discuss possible mechanisms of the EIE interferences for both an enhancement effect and a signal depression phenomenon. Because coupling ETV-MIP to MS has only been detailed in one report, there is only limited information available as to spectroscopic and nonspectroscopic interferences with MIP-MS and ETV sample introduction.

In the report by Matousek et al.,[103] the effect of a number of chloride salts, and one nitrate salt, on the determination of copper by ETV-MIP-AES was investigated. From these studies, they found that at low EIE concentrations there was a signal enhancement for copper and above an approximately 10 m*M* concentration of the salt, the enhancement reaches a plateau. The amount of enhancement was related to the ionization potential of the EIE and the counterion (anion) had some effect on the response. These phenomena were explained by a radiative transfer mechanism. While enhancements were observed for copper determinations, there was a signal depression for lead measurements. The enhancement of the emission signal was attributed to reduced power dissipation in the plasma caused by a decoupling of the plasma from the microwave power source.

After establishing the possible causes of the interferences, the authors studied the ability of the ETV to separately volatilize the EIE and the analyte.[103] In this experiment, the analyte was placed in one vaporization boat, while the EIEs were placed in a separate boat. The authors performed this procedure to separate vaporization interferences due to the EIEs from actual plasma effects. From these studies, they determined that vaporization effects play an important role in the interferences observed from EIEs. There was a marked difference between the amount of interference for the measurements with the sample and matrix in the same boat and from those where the sample is vaporized in a separate boat from the EIE.

While the work presented in this report is interesting and provides a thorough investigation of the effect of easily ionized elements on the emission profile of copper in MIP-AES with ETV sample introduction, it does not suggest ways for ETV to reduce these problems.[103] Optimization of the sample heating profile would have been a worthwhile investigation to determine if ETV could reduce the effects through selective volatilization. Investigating the vaporization interference contribution from the ETV did provide indications that separation of the matrix from the analyte prior to volatilization is a worthwhile procedure because the vaporization of the analyte can be severely affected by these elements as well as the plasma conditions.

An investigation of the interferences from matrix constituents on the volatilization of halogens, and interferences on their detection would be beneficial because the ability to analyze these types of elements is a primary advantage of the He-MIP. In addition, although the MIP does not have as great a problem from isobaric interferences, due to the lower mass of helium the polyatomic species all appear at much lower mass-to-charge ratios, it would be interesting to evaluate the ability of ETV to improve the detectability of certain elements by MIP-MS. A study to reduce molecular band interferences in AES detection would also contribute to understanding the viability of ETV as a sample introduction method for MIP spectrometry.

C. ETV-MIP Sample Types

A variety of sample types have been investigated using ETV as a sample introduction technique for MIP spectrometry. A majority of the "real world" samples that have been analyzed by ETV-MIP are solid in nature, and many have been analyzed without sample pretreatment. Of course, this is an advantage of ETV sample introduction because, like the ICP, the traditional MIP sample introduction methods are not amenable to solid samples and require some form of sample pretreatment. As is indicated in Table 6, the analysis of solid (primarily biological) samples has been well demonstrated for a variety of sample types with ETV-MIP spectrometric methods.

Unlike the ICP, the MIP also has difficulties analyzing liquid samples. These difficulties arise from the less robust nature of the MIP and its inability to efficiently desolvate, vaporize, atomize, excite, and/or ionize an analyte. Because of this, most sample introduction methods, such as hydride generation, GC, etc., require that the analyte be converted to a gaseous form. ETV, in comparison to many other methods of dry aerosol generation, allows for the analysis of a much broader range of analytes in solution form. In this manner, the ETV can also be thought of as an alternative method of solution sample introduction, and not only as a method for the direct analysis of solids.

An interesting application of ETV-MIP-AES to the analysis of liquid samples involves coupling two of the dry aerosol generation methods commonly employed in plasma sample introduction. Matusiewicz and co-workers[98] have performed *in situ* hydride generation in a graphite furnace for the analysis of arsenic in aqueous samples. This technique further enhanced the ability of the sample introduction method to remove interfering species prior to introduction of the analyte into the plasma. The generation of the hydride occurs only with those elements capable of volatile hydride formation, the hydride is then trapped on a palladium surface in the graphite furnace and released through volatilization. This method would seem applicable to other methods of analysis for arsenic such as ion-exchange liquid chromatography.

VI. ETV WITH ADDITIONAL PLASMA SOURCES

While the majority of studies with analytical plasma spectrometry have involved either an ICP or a MIP, other plasma sources have been investigated. These sources include the direct current plasma (DCP) and capacitively coupled plasma (CCP). The DCP involves the ETV furnace in a manner very similar to that found in the ICP and

TABLE 6
ETV-MIP Sample Types

Sample Type	Pretreatment step(s)	Ref.
Animal bone	Acid digestion	100
Bovine liver	None	107
Bovine liver	Acid digestion	96, 108
Brewers yeast	None	107
Citex BC-26	None	109
Coastal seawater	*In-situ* hydride generation	98
Milk	None	105
Orchard leaves	None	107
Orchard leaves	Acid digestion	96, 108
Oyster tissue	None	107
Pine needles	None	107
Rice flour	None	107
Spinach	None	107
Sulfur	Acid digestion followed by hydride generation	94
Tomato leaves	None	107
Tomato leaves	Acid digestion	96
Tuna fish tissue	None	107
Wheat flour	None	107

MIP methods described previously, but the CCP involves forming the plasma in the furnace. This second method is often referred to as furnace atomization plasma emission spectrometry (FAPES). Each of these methods have only been reported as sources for AES; however, the use of MS detection may be a possibility in the future. Because neither of these methods is well established, there is not a wealth of information available on them, but a brief list of the detection limits obtained in the manuscripts covered here is given in Table 7. There has been no attempt in constructing this table to normalize the reported detection limits with respect to plasma type, sample matrix, or calculation method (3 σ vs. 2 σ).

A. Direct Current Plasmas

Direct current plasmas (DCP) are also known as plasma jets and are currently available commercially. A DCP is formed by a flow of partially ionized gas that is forced out of a small orifice. This forms a plasma due to the formation of a d.c. discharge produced by two or more electrodes. The DCP has the advantages of good stability, low power requirements, and, unlike the ICP and MIP, the ability to handle organic and high solid content samples. Disadvantages include different optimum viewing positions for different elements, increased matrix interferences (changes in the plasma conditions), cost, and complexity.

From these characteristics, it is clear that ETV should provide some advantages for sample introduction into a DCP, primarily in reducing the effect of the matrix interferences. As discussed with the ICP and MIP, the use of ETV allows the user to remove matrix constituents prior to or after vaporizing, depending on the volatility, the analyte of interest. The reduction of these effects has been studied in some detail in a recent report.[110] This work investigated the effect of introducing EIEs into a sample and using ETV for sample introduction to the DCP. The plasma utilized was a magnetron rotating d.c. arc plasma, and the study found that the presence of an EIE does not significantly alter the sample/plasma interaction. However, a significantly higher intensity was found for lines of the analyte in the presence of potassium or lithium. This was attributed to an increased electron density in the plasma. Species that are not easily ionized were not found to have a significant effect of the figures of merit obtained by the technique, while EIE concomitants severely degraded the detection limits. This same system has also been investigated for the

TABLE 7
ETV-Other Plasmas Detection Limits

Element	Plasma type	Detection limit (pg)	Ref.
Aluminum	DCP	600	112
Arsenic	CCP	1.3–200	113
Beryllium	DCP	N.R.[a]	2
Beryllium	CCP	5–16	114
Bismuth	CCP	25–55	114
Boron	DCP	N.R.	2
Cadmium	DCP	300–1650	110
Cadmium	CCP	2-9	114, 115, 117
Calcium	DCP	N.R.	2
Chromium	DCP	N.R.	2, 110
Copper	DCP	600	111, 112
Copper	CCP	0.86–14	113, 114
Gallium	DCP	N.R.	2
Iron	DCP	960–16500	2, 110, 111
Iron	CCP	0.4–281	113, 114
Lead	CCP	21–310	114, 115
Magnesium	DCP	30–210	2, 110, 111
Manganese	DCP	600	111, 112
Manganese	CCP	52	117
Nickel	DCP	N.R.	111
Nickel	CCP	8.6–405	113, 114
Phosphorous	CCP	94–152	114
Potassium	DCP	N.R.	2
Silicon	DCP	N.R.	2
Silver	CCP	0.3–4.8	113, 114, 116
Sodium	DCP	N.R.	2
Strontium	DCP	N.R.	110
Titanium	DCP	N.R.	2
Zinc	DCP	N.R.	110, 111

[a] N.R. not reported.

direct analysis of powdered solid samples.[111] These sample types are shown in Table 8. The accuracy of the technique, utilizing the standard additions method, was found to be satisfactory, giving percent errors between 1 and 20% relative to the certified values of the reference materials analyzed.

Another report details the construction of a graphite furnace for sample introduction into either a DCP or an ICP.[2] This furnace design makes use of the fact that a halogenating atmosphere promotes more rapid vaporization of the sample. The data presented indicate the feasibility of determining solid samples (see Table 8) directly, thus taking full advantage of the ability of the furnace to vaporize samples with minimal pretreatment. An integrated system is described where the DCP is formed immediately after the exit from the furnace, thus maximizing the transport efficiency of the analyte. The furnace was found to adequately remove vaporization interferences arising from sodium chloride; however, as with the study by Slinkman and Sacks,[110] a strong enhancement of the emission intensity was observed with the presence of the salt matrix. This was attributed to the same effect as described previously.

B. Capacitively Coupled Plasmas

A capacitively coupled plasma (CCP) involves the formation of a plasma in a contained vessel, such as a graphite furnace. The furnace has a central tungsten electrode that is connected to an rf generator. This electrode-generator connection

TABLE 8
ETV-Other Plasmas Sample Types

Sample Type	Plasma Type	Pretreatment step(s)	Ref.
Alumina	DCP	None	2
Bovine lLiver	DCP	None	111
Citrus leaves	DCP	None	111
Coastal marine sediment	CCP	Acid digestion	115
Dogfish muscle	CCP	Acid digestion	115
Lobster hepatopancreas	CCP	Acid digestion	115
Oyster tissue	DCP	None	111
Pine needles	DCP	None	111
Rice flour	DCP	None	111
Tomato leaves	DCP	None	111

is performed through an antenna tuner that allows the impedance of the plasma and generator to be matched, thus producing a stable plasma. The plasma typically operates at a forward power of 50 to 70 W and the previously described arrangement theoretically provides for no reflected power. The advantage of using a plasma generated directly in the furnace is that all the material vaporized in the furnace reaches the plasma. This efficient transport allows for improved sample throughput because the sample has a longer residence time and an increased linear dynamic range. ETV when coupled to a CCP in this manner, acts essentially in the same manner as GFAAS, except that the technique is based on optical emission and the furnace is only required for volatilization of the analyte rather than atomization. When the CCP is formed in an ETV furnace, the technique is commonly called furnace atomization plasma emission spectrometry or FAPES. Such a system has been investigated recently for the determination of a number of elements and sample types (see Tables 7 and 8).

The primary aim of the majority of the reports on CCP sources utilizing a graphite furnace as a plasma vessel have dealt with the characteristics of the plasma itself.[113,117] However, reports have appeared recently that report the analytical capabilities of the system and the characteristics of the furnace.[114-116] A FAPES system has been found to provide absolute detection limits for a number of elements in the picogram range.[114,116] The precision of the technique was found to be comparable to those found with the more traditional plasmas (2 to 12% R.S.D.). Sensitivities were found to be comparable to those found with ICP-AES pneumatic nebulization;[114] however, no comparisons were presented with ETV-ICP-AES. Matrix effects from sodium-containing species have also been investigated on a limited scale.[116] At low sodium concentrations, the signal obtained from silver was enhanced. This finding was attributed to a suppression of the Ag ionization equilibrium. At higher concentrations of sodium, the silver signal was suppressed, caused by either a decrease in the free Ag atom population or a change in the plasma excitation characteristics. The feasibility of directly analyzing solid samples has not been investigated in these reports; however, a number of standard reference materials have been analyzed after acid digestion.[115] While this by no means utilizes the full capability of the system, it does indicate the applicability of the system to samples with complex matrices. The results indicated that the system was reasonably accurate and provided values near those certified for several standard reference materials.

VII. CONCLUSIONS AND FUTURE DIRECTIONS

Electrothermal vaporization has been shown to be a viable alternative to traditional pneumatic nebulization for sample introduction in plasma source spectrometry. The usefulness of ETV sample introduction stems from its ability to produce a gaseous sample for introduction into the plasma. A gaseous sample eliminates several of the difficulties encountered when utilizing pneumatic nebulization, including poor transport efficiency; solution and matrix related interferences; clogging of the nebulizer, sampler, and skimmer orifices; poorer detectability due to insufficient plasma energy for complete excitation/ionization. The first difficulty is only overcome with proper design of the ETV device. If care is not taken to prevent condensation of the hot atomic vapor on the transfer line, transport efficiency may not be significantly improved. Removal of solution and matrix-related interferences and removal of clogging difficulties may be the greatest advantage of ETV sample introduction. However, these advantages can only be achieved through the careful optimization of the temperature program for the ETV device and, if necessary, the selection of a suitable matrix modifier. Increasing the detectability is an advantage of ETV because the plasma is not required to desolvate, vaporize, and completely atomize the analyte. Despite this, the low sample volumes and transient nature of the signal produced can present difficulties with detection. Many of these difficulties are being overcome through the advance of data collection technology and improvement of instrument sensitivity.

Despite the rosy prospects of ETV as a sample introduction technique, it is likely to remain a complementary method to pneumatic nebulization. There are many reasons for this, but perhaps the most constraining is the much greater cost and complexity of an ETV system when compared with a pneumatic nebulizer. Additionally, the unreliability of the system is a major obstacle to the routine use of ETV sample introduction in plasma spectrometry. The most likely uses in the future of ETV lie in the areas of the direct analysis of solids and the investigation of alternative plasma sources such as CCPs. If the system design can be improved to provide a more reliable instrument and the complexity can be reduced, the main use of ETV sample introduction may be with plasma source mass spectrometry, as the optical technique provides no real advantage to the GFAAS technique. Additionally, the possibility of coupling ETV to various chromatographic techniques, to obtain speciation information in addition to total elemental information, is intriguing. Overall, the technique of ETV sample introduction offers some definite advantages over traditional methods of sample introduction. These advantages are sufficient to warrant the use of the ETV method for complex samples for which matrix effects may cause severe interferences.

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