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**Mechanistic Studies on the Vaporization and Atomization of
Molecular and Atomic Species in an Electrothermal Vaporizer
using Spatial and Temporal Distributions**

by

Douglas M. Goltz

A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfilment of the
requirements for the degree of
Doctor of Philosophy in Science.

Department of Chemistry
Carleton University
Ottawa, Ontario
September 1995

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Chair, Department of Chemistry

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Thesis Supervisor

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ABSTRACT

Some of the matrix effects associated with the vaporization of selected elements ($^{59}\text{Co}^+$, $^{63}\text{Cu}^+$, $^{133}\text{Cs}^+$, $^{208}\text{Pb}^+$, $^{209}\text{Bi}^+$ and $^{238}\text{U}^+$) with electrothermal vaporization (ETV) inductively coupled plasma mass spectrometry (ICP-MS) were investigated. The temporal behaviour of water, HCl and HNO_3 showed that these species are retained in the ETV even after a pyrolysis temperature of 400°C . In most cases, higher concentrations of acid resulted in higher signals suggesting that the acids may act as a physical carrier and improve the vaporization and mass transport of many elements to the ICP-MS.

Mechanisms of vaporization and atomization of elements which form refractory oxides and carbides with a heated graphite surface were studied. Vaporization curves of $^{10}\text{B}^+$ using ETV-ICP-MS reveal the temporal distribution of molecular and atomic boron species. Experiments using the ETV-ICP-MS showed that for graphite furnace atomic absorption spectrometry (GFAAS), pre-atomization losses as molecular species at temperatures well below the appearance temperature for boron account for poor sensitivity of this elements by GFAAS. Vaporization and atomization of boron was also investigated using digital imaging techniques with a CCD camera. Using an interference filter and a molecular absorption band which is coincident with the BO band at 254 nm, high concentrations of molecular boron species were localized in the centre of the graphite tube at low temperatures (1800°C). At high temperatures (2600°C), the molecular boron species are probably reduced on the graphite tube wall and desorbed from the surface forming concentric rings of B (g) having different number densities.

Investigations of vaporization and atomization of uranium, yttrium and the Rare Earth Elements using ETV-ICP-MS and GFAAS were made. Investigations were also made on techniques to improve ETV-ICP-MS signal quality, sensitivity and to reduce memory effects associated with refractory carbide formation. The following methods for improving ETV-ICP-MS signal quality were established: (i) vaporizing the analyte from a tungsten surface; (ii) use of lower vaporization temperatures and (iii) use of 0.2% CHF₃ as a gas-phase matrix modifier in the internal argon carrier flow.

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Publications

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1. J.P. Byrne, D.C. Grégoire, D.M. Goltz and C.L. Chakrabarti, **VAPORIZATION AND ATOMIZATION OF BORON IN THE GRAPHITE FURNACE INVESTIGATED BY ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY**, *Spectrochimica Acta*, **49B**, 433-443 (1994).
2. D.M. Goltz, D.C. Grégoire, M.M. Lamoureux and C.L. Chakrabarti, **EFFECT OF ACIDS ON VAPORIZATION PROPERTIES IN ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY**, *Journal of Analytical Atomic Spectroscopy*, **9**, 919-926 (1994).
3. M.M. Lamoureux, C.L. Chakrabarti, D.M. Goltz and D.C. Grégoire, **MODIFICATION OF A COMMERCIAL ELECTROTHERMAL VAPORIZER FOR SAMPLE INTRODUCTION INTO AN INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER. PART. 1. CHARACTERIZATION**, *Analytical Chemistry*, **66**, 3208-3216 (1994).
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6. D.C. Grégoire, K. Ansdell, D.M. Goltz, C.L. Chakrabarti, **TRACE ANALYSIS OF SINGLE ZIRCONS FOR RARE EARTH ELEMENTS, U and Th BY ELECTROTHERMAL VAPORIZATION ICP-MS**, *Chemical Geology*, **124**, 91-99 (1993).
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8. D.M. Goltz, D.C. Grégoire, J.P. Byrne and C.L. Chakrabarti, **VAPORIZATION AND ATOMIZATION OF URANIUM IN A GRAPHITE TUBE ELECTROTHERMAL VAPORIZER. A MECHANISTIC STUDY USING ETV-ICP-MS AND GFAAS**, Accepted for Publication in Spectrochimica Acta, 1994.
9. D.M. Goltz, D.C. Grégoire, C.L. Chakrabarti, **THE MECHANISM OF VAPORIZATION OF YTTRIUM AND RARE EARTH ELEMENTS IN ETV-ICP-MS**, Accepted for publication in Spectrochimica Acta, 1995.
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Essentially three instrumental techniques were employed in this research to study the vaporization and atomization of a number of elements in a pyrolytically coated graphite tube electrothermal vaporizer (ETV). The techniques used were:

- 1) charge-coupled device (CCD) camera;
- 2) inductively-coupled plasma mass spectrometry (ICP-MS);
- 3) atomic absorption spectroscopy (AAS).

A brief description of the basic principles of these techniques, which are relevant to the discussions in this thesis, will be given on the following pages.

Charge-Coupled Device (CCD) Camera

The charge-coupled device (CCD) is a type of charge transfer device belonging to a group of detectors known as solid-state multichannel detectors [1]. The CCD is made of p-doped silicon (e.g. silicon doped with electr. deficient atoms or electron acceptors) which collect photogenerated electrons. In p-doped silicon, the majority current carriers are the electrons and the minority carriers are holes [2]. When the electrode is positively charged with respect to silicon, the region is energetically favourable to the migration of electrons as shown in Figure 1. Before being promoted into the semiconductor band, photogenerated electrons are created by the absorption of a photon. The photogenerated electrons can then be transferred to the semiconductor region by applying a positive charge to the semiconductor. By making regions of the semiconductor more positive, charge can be stored in specific regions or potential wells (Fig.1). In this way the potential wells collect available electronic charge until the

Figure 1. Schematic diagram of the migration of charge in charge transfer devices (e.g. CCDs). Negative sign indicates migration of an electron and positive sign indicates migration of a hole.

potential well is filled. The potential wells are photosites more commonly known as picture elements or pixels. When a CCD is struck by light, the resulting electronic charge is collected in a two dimensional imaging area called a parallel register, with each pixel acting as individual detectors, shown in Figure 2. The parallel register is an array of detectors which provides a two dimensional view of the spatial distributions of molecular and atomic species inside the ETV. The CCD camera used in this study is much like a video camera except that the film has been replaced by a computer chip, making the collection and manipulation of data relatively uncomplicated.

Application of an appropriate sequence of potentials causes the potential well to propagate in a given direction. Charge which has been collected on the parallel register is carried along with the potential well and is not lost or mixed with charge stored in other potential wells. Charge can then be transferred and readout on another one dimensional CCD called the serial register (Fig 2).

Graphite Furnace Atomic Absorption Spectroscopy and Electrothermal Vaporization

Introduction of analyte into the gas-phase by graphite furnace was first published by L'vov in 1959 [3] and 1961 [4]. Since then, a number of developments and improvements have been made to the furnace design and materials used, however, the basic principle of resistively heating the furnace to a high temperature has remained unchanged. Presently, the most commonly used graphite furnace design is the Massmann type, which resistively heats the centre of the graphite tube via electrical connections to the ends of the graphite tube.

Figure 2. Schematic diagram of the serial and parallel register of the CCD detector. Arrows indicate the direction of charge transfer from parallel to serial register to output node.

Since its introduction the use of graphite furnaces for graphite furnace atomic absorption spectrometry (GFAAS) has matured as a technique, capable of determining about 50 elements in the Periodic Table with high sensitivity. A number of books [5,6,7] and numerous review articles [8,9,10] have been published. There is an extensive amount of literature available on GFAAS and much of this information can be applied to electrothermal vaporization inductively-coupled plasma mass spectrometry (ETV-ICP-MS) studies. Hence, the relationship between GFAAS and ETV-ICP-MS has been accurately described as symbiotic [11].

Although pyrolytically coated graphite furnaces are used in both GFAAS and ETV-ICP-MS, there are some important differences in the gas-phase properties inside the graphite furnace. For example in GFAAS, gas-stop conditions are used to increase the vapour-phase temperature and convert the analyte of interest to ground state gaseous atoms. Gas-stop conditions also maximize atom residence time for increased sensitivity in GFAAS. For ETV-ICP-MS, gas flows of 1 L min^{-1} inside the ETV are used. In ETV-ICP-MS, the only requirement of the ETV is to completely vaporize the analyte of interest. Therefore, residence times inside the ETV are minimal with the use of a continuous flow of argon gas. A schematic diagram showing the flow of argon purge gas in the ETV of an ETV-ICP-MS is presented in Figure 3.

The choice of the term "vaporizer" for ETVs rather than "atomizer" has been suggested [12] and is deliberately used throughout this thesis since the ETV is not required to dissociate the sample to atomic components, rather, it is used to produce a vapour or dry aerosol suitable for transport to the ICP.

Figure 3. Schematic diagram of an ETV used in an ETV-ICP-MS, showing the flow of argon inside the graphite tube during the dry, pyrolysis and vaporization steps of the temperature programs.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The inductively coupled plasma (ICP) consists of a quartz torch surrounded at the top by a three-turn copper load coil. A radio frequency (rf) generator passes energy to the load coil usually at 27.1 or 40.08 MHz, which forms an oscillating magnetic field. The plasma gas (argon) is seeded with electrons from a tesla coil. The magnetic field causes the electrons to gain energy while travelling in circular paths which cause collisions with support gas atoms. These collisions, along with ohmic heating of the support gas, cause further excitation of the neutral argon atoms. This results in the generation of more electrons and ions in a cascade mechanism, until the plasma is formed and ultimately sustained by a continuous flow of argon [13].

The physical and chemical processes that a sample undergoes inside the plasma include: nebulization, desolvation, volatilization, atomization and ionization. Typical gas kinetic temperatures inside the ICP are approximately 5000-8000 K. Under normal flow rates (1 L min^{-1}), analytes inside the plasma have residence times of approximately 2 ms and thus are efficiently atomized. The efficiency of ionization can be estimated using the Saha equation [13]:

$$\frac{M^+}{M} = \frac{2}{n_e} \left(\frac{2 \pi m_e k T}{h^2} \right)^{3/2} \frac{Q^+}{Q} e^{\left(\frac{-I P}{k T} \right)} \quad (1)$$

where, n_e is the electron density (typically $10^{14} - 10^{15} \text{ cm}^{-3}$); m_e is the mass of the

electron (9.1×10^{-31} kg), k is Boltzmann's constant (1.38×10^{-38} J K⁻¹); T is absolute temperature (K); h is Planck's constant (6.625×10^{-34} J s⁻¹); Q^* and Q are partition functions for the ion and neutral species and IP is the first ionization potential (J or eV). For a normal running ICP ($T=7500$ K and $n_e = 5 \times 10^{14}$ cm⁻³), the formation of singly charged ions is very efficient. At least 54 elements are ionized with an efficiency of 90% or greater. Similarly, with the use of the Saha equation, multiply charged ions can also be estimated. Most elements have high enough second ionization energies (15 eV or greater) so that doubly charged ions should be negligible (10% max) for most elements except barium and possibly some Rare Earth Elements. Therefore, the ICP is an efficient ion source for producing singly charged ions making it an ideal method of ionization for mass spectrometric detection [13].

Positively biased ion lenses, located behind the sampler and skimmer cones collect focus and transmit ions to the mass spectrometer. A quadrupole mass spectrometer is used in the ICP-MS as a mass filter to select analytes of specific mass to charge ratios. By itself, the mass filter is not a detector. Rather, it is a path stability mass spectrometer and ions of certain mass to charge ratios are injected into a dynamic electromagnetic field. Only ions with the correct mass to charge ratio will have a stable path through the mass filter while ions with masses above or below this ratio will have an unstable trajectory and are filtered out by collision with the poles. The mass spectrometer consists of four parallel rods configured in two pairs opposite to each other, one pair in the vertical plane (x axis) and the other pair in the horizontal plane (y axis). Trajectories of ions take place in the z axis between the four rods into the

radio frequency field formed by the application of a DC voltage and an rf voltage applied to the four electrodes. The voltage on the positive electrodes is:

$$+ (U + V \cos \omega t) \quad (2)$$

and the voltage on the negative electrodes is:

$$- (U + V \cos \omega t) \quad (3)$$

where U is the DC voltage, V is the rf voltage, ω is the angular frequency of the applied field ($\omega=2\pi f$ where f is defined in Hertz) and t is time (s). Because the rf voltage (V) is larger than the DC voltage (U), the opposite poles change polarity at twice the rf frequency. Therefore, when the vertical poles are positive, the horizontal poles are negative and mass transmitted may be changed by varying the electrical potential. As the DC and rf voltages are varied (with a constant DC:rf ratio) different masses can be filtered and resolution (range of masses transmitted) can be varied by changing the DC:rf ratio.

The filtered ions of specific mass to charge ratio are detected by a channel electron multiplier (CEM) detector. The CEM is a curved hollow glass cone internally coated with a lead oxide semiconductor with a highly negative voltage at the entrance of the detector (for detecting positive ions) and ground at the base. As the ions strike the semiconductor surface, electrons are ejected from the surface in a cascade

Figure 4. Schematic diagram of ETV-ICP-MS.

mechanism similar to that of a photomultiplier tube. The gain is about 10^7 electron per ion and thus, the number of ions striking the detector surface can be converted to an electronic pulse. Figure 4 shows a schematic diagram of the ETV-ICP-MS used in this study.

Sample Introduction to Plasmas

The most common method for introducing analyte into a plasma is by solution nebulization (SN) and the sample solution containing the analyte of interest is introduced to the plasma as a wet aerosol. Although there are numerous advantages to using plasma spectrometry, one major drawback of this technique is the lack of an "ideal" sample introduction method [14]. Some of the problems include: low efficiency of sample introduction, high sample size requirement, matrix effects and oxide formation in the plasma. Consequently, alternative methods for sample introduction into plasmas have been developed including electrothermal vaporization (ETV). The ETV allows the analyte of interest to be vaporized and transported efficiently to the plasma as a dry aerosol.

Thermal Dispersion and Transport of Analyte

The process of generating and transporting an analyte as a dry aerosol or vapour-aerosol, has been described as "thermal dispersion" [15]. A number of monographs have described the fundamental properties of aerosol generation [16,17,18]. Kantor [15] has used these comprehensive works to describe thermal dispersion for ETVs.

Formation of an aerosol in an ETV generally arises by "physical condensation" which occurs when a vapour is cooled by transfer to a cooler region and/or mixing of the vapour with a turbulent stream of cold gas [15]. Condensation of vapour results in the formation of nuclei which can be present even in an unsaturated vapour as a result of collision among vapour species. When condensation nuclei are generated by the vapour itself, the process is known as homogeneous nucleation or self nucleation. Heterogeneous condensation occurs when condensation of vapour takes place on existing particles.

During the vaporization step condensation nuclei are clusters initially. With increasing concentration, they increase in size until a critical droplet diameter is reached. According to nucleation theory, the critical drop diameter can be calculated by:

$$d_p = \frac{4 \sigma V_m}{k T \ln S} \quad (4)$$

where σ is the surface tension of the liquid droplet (N m^{-1}), V_m is the molecular volume of the vapour species (m^3), k is Boltzmann's constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), T is temperature (K) and S is the saturation ratio. Clusters of analyte below the critical drop size tend to evaporate whereas droplets equal to or greater than the critical diameter are stable as long as $S > 1$ ($P_{\text{vap}} > P_{\text{sat}}$). The saturation ratio which defines the magnitude of

supersaturation (condensation of clusters forming nuclei) is given by:

$$S = \frac{P_{vap}}{p_e (T)} \quad (5)$$

where P_{vap} is the partial vapour pressure (atm.) and $P_e (T)$ is the equilibrium vapour pressure at the temperature of nucleation. Assuming ideal gas behaviour in the ETV:

$$P V = n R T \quad (6)$$

and by rearrangement of equation 6 and with the addition of a time component, partial pressures can be computed with an acceptable degree of accuracy from:

$$P_{vap} = \frac{n_s T_g R}{V_g t_v} \quad (7)$$

where, p_{vap} is the partial pressure (atm.), n_s is the amount of vapour from the evaporated sample (mole), T_g is the temperature of the carrier gas (K), and R is the gas constant ($0.082 \text{ atm. K}^{-1} \text{ mol}^{-1}$), V_g is the flow rate of the carrier gas without heating ($\text{m}^3 \text{ s}^{-1}$) and t_v is the mean evaporation time (s) of the major fraction of the sample.

Some deductions can be made about the properties of vaporization regarding vaporization inside an ETV. For example, a higher supersaturation ratio (S) is obtained for less volatile substances due to the lower $p_v(T)$. Increasing the supersaturation ratio (S) also results in an increase in the concentration of clusters and from equation (4), the critical drop size shifts to smaller particles. This shift to smaller particles results in a higher concentration of stable nuclei. Secondly, when low masses of analyte are vaporized, the concentration of clusters in the vapour state may be insufficient to promote nucleation and may not be transported efficiently (i.e condensation on transfer line) to the ICP. It can then be concluded that, when small masses of analyte are vaporized, co-evaporating a major component will likely increase the transport efficiency of analyte. Kantor also concluded that the condensation of analyte vapour on foreign particles is expected to be the most important process in electrothermal vaporization and a "carrier effect" will result [15]. Kantor's conclusions are supported in the literature [19,20]. For example, carrier effects are observed for volatile elements by increased linearity in calibration curves. Co-evaporating large amounts ($1\ \mu\text{g}$) of NaCl with pg quantities of Ag will give a linear increase in signal with concentration. When a physical carrier is not used, an increasingly concave calibration curve can be observed for Ag, depending on the matrix. Sparks et al. [21] used a micro laser particle counter for measuring the particle size distribution of analyte aerosol produced in an ETV. Interestingly, they showed that the addition of NaCl only increased the number of particles by 35% and did not alter the size distribution significantly. The results of this study may not reflect the true environment of a graphite furnace ETV since the

particle counter required a much higher volume of gas than is normally used in ETV-ICP-MS.

Electrothermal Vaporizers (ETVs)

Introduction of analyte into an ICP with a tantalum filament ETV was first reported by Nixon et al. [22]. The tantalum filament was placed in a quartz dome and a range of elements were vaporized at 1800°C. Platinum and tungsten filaments have also been used to vaporize 10 μ L samples of a number of elements [23]. Tikkanen and Niemczyk have used a tantalum boat for single elements [24] and multi-element analysis [25]. Park et al. [26,27,28] used a custom designed ETV based on the use of a metal filament in a conical glass envelope. Various operational parameters of the ETV were optimized, such as filament temperature and argon carrier flow. The analytical capability of this design was demonstrated by the successful determination of As, Cu, Mn, Pb, Rb, V, Zn and Ag in reference materials (NBS SRM 1571 and NBS SRM 1566). A tantalum tip ETV sample introduction device has been described by Evans et al. [29] for use with a microwave induced plasma (MIP). Detection limits using optical emission were reported for some volatile elements such as Ag, Cd, Pb and Br. More recently, a tungsten ETV for sample introduction into an ICP-MS was described by Tsukahara and Kubota [30], as well as by Shibata et al. [31,32,33]. Both groups completed extensive studies on the optimization of ETV parameters and plasma conditions. Hydrogen was also mixed with the argon carrier gas to prevent oxidation of the tungsten surface. Adding hydrogen also enhanced analyte signals as a result of increased ionization of the analyte in the plasma.

Use of a graphite rod ETV for sample introduction into an ICP-MS was first reported by Gray and Date [34]. They demonstrated the vaporization of lead and cadmium and laid the foundation for numerous studies in ETV-ICP-MS. A graphite rod was used by Kirkbright and co-workers [35,36,37] to study matrix, inter-element and sample transport effects for selenium and cadmium. They calculated sample transport efficiency of cadmium to be 60% in the presence of Se (VI). A graphite rod ETV was also used by Browner and co-workers [38,39]. They studied transport efficiency of a number of elements (Ag, Cd, Co, Cr, Cu, Mn, Ni, Zn) to the plasma. Using a U shaped tube and glass wool, the transport efficiency varied from 30 to 70%, depending on the element. A carbon cup ETV has been used by Ng and Caruso [40] for Zr, V, U and Cr with a NH_4Cl chemical modifier to convert the analytes to more volatile halides for more efficient volatilization and transport. Graphite, titanium and tungsten cups have also been used by Spencer and Winefordner [41] for the determination of Si in organic samples using atomic emission spectrometry. Using this set-up, they reported an absolute detection limit of 900 pg for Si. Park et al. [42,43] used a graphite platform from a previous design for the determination of Mo, W and Tl. This ETV was also used by Grégoire [44] for the determination of Pt, Pd Ru and Ir in geological materials such as silicates, iron formations and ores. Grégoire [45] also determined osmium isotope ratios using ETV-ICP-MS and the addition of tellurium increased the sensitivity by a factor of 18. Isotope ratios could be measured with a precision of 0.5% compared to 0.2% for solution nebulization.

A different approach to vaporization of analyte is the use of direct sample insertion devices (DSIs) most of which are constructed of graphite. The DSI device is placed in the plasma and a transfer line is not required. Haraguchi and co-workers used a carbon cup DSI device for the determination of alkaline earth elements in plant samples [46] as well as Cu and Fe in Pb and Zn metal [47]. Karanassios and Horlick published a series of papers on some spectral interferences [48], characteristics and properties of the DSI [49] device as well as vaporization of refractory carbide-forming elements [50] using a graphite cup DSI device. The form and shape of the graphite cup was studied by Zaray et al. for the application of the analysis of aluminum oxide [51]. Silver chloride has been added to the carbon cup DSI device as a thermochemical additive for the determination of refractory elements and was found to enhance volatilization. Aerosol deposition inside the DSI device has also been examined using thin-walled and thin-stemmed graphite cups [52]. Aerosol spraying improved detection limits by preventing the absorption of liquid into the graphite cup while the thinned walls of the DSI device allowed for more rapid and efficient heating. Relative merits of the ETV and DSI techniques were compared in a study by Hall et al. [53]. They showed that, while the DSI techniques has a higher transport efficiency, it is more susceptible to matrix effects (e.g. > 1% salt) than the ETV.

Some of the more successful ETV designs originate from modified commercial graphite furnace atomizers originally designed for AAS. Several research groups have modified Perkin-Elmer graphite furnaces for sample introduction into Plasmas. Aziz et al. [54] were probably the first to report the use of a modified graphite furnace ETV

for sample introduction into a plasma. They used an HGA-74B for the vaporization of micro amounts of biological samples into an ICP using AES for detection. Samples containing Cd, Mn, Pb and Zn were manually pipetted into the furnace. In a similar study [55], Aziz et al. used the same modified commercial instrument for introduction of analyte into a microwave induced plasma (MIP) (2.45 GHz). The ETV seems well suited to MIPs as they are a low power plasma (40-100 W) and more susceptible to loading by water than an ICP. Shen et al. [56] and Carey et al. [57] used a modified HGA-300 ETV system for the determination of Pb, Fe and As. Samples were deposited on a L'vov platform and the ETV was modified in such a way that a coolant argon flow was used to isolate the analyte vapour from the walls of the ETV which promoted efficient transport to the plasma. The HGA-300 was also modified by Marshall and Franks [58] for studying matrix and spectral interference using ICP-MS. Spectral interferences associated with the detection of vanadium in an HCl matrix and titanium in a sulphuric acid matrix were greatly reduced with the ETV-ICP-MS, compared to SN-ICP-MS. A Perkin-Elmer HGA-400 was used by Argentine et al. [59] for the determination of trace impurities in organometallic semi-conductor-grade reagents. Calibration methods for volatile impurities such as Si, Sn and Zn in trimethylaluminum were reported. Ren and Salin [60] evaluated and vaporized solid samples of oxides and carbides using a Perkin-Elmer HGA 2200 furnace and atomic emission spectrometry for detection [61,62]. Their ETV was connected to the plasma with only 15 cm of teflon tubing which is much shorter than most transfer lines (e.g.>60 cm). Grégoire and co-workers [63,64] modified a Perkin-Elmer HGA-76B graphite furnace using a teflon

transfer line (80 cm) and sampling the analyte vapour through the dosing hole. A large number of elements were analyzed and compared with a commercially available ETV. A Perkin-Elmer HGA-500 was modified by Matusiewicz et al. [65] using a novel configuration with custom graphite cuvettes. A number of properties such as length of transport tubing, temperature and argon carrier flow were studied.

Numerous studies have also been completed using commercial ETVs coupled to an ICP-MS including cadmium and zinc isotope ratios in sheep's blood and organ tissue [66] and heavy metals in Arctic snow [67]. Sturgeon and Grégoire [68] used pre-concentration and in situ collection of hydrides of As, Sb, Se, Bi and Sn with a Perkin-Elmer HGA-600MS interfaced to a Perkin-Elmer Sciex Elan 5000 ICP. A thin tungsten, tantalum and molybdenum strip coated with palladium was used as a platform inside an ETV for arsine trapping [69]. Trapping the analyte improved the linear dynamic range of arsenic by an order of magnitude over that reported for GFAAS. A commercial ETV manufactured by VG Elemental is the VG MicroTherm which also uses a graphite tube type of ETV. A 50 cm long PTFE transfer line, from the furnace directly to the plasma torch, is used for this ETV-ICP-MS. The VG instrument has been used to analyze high purity rhenium for a large number of elements [70]. Two studies were completed for the determination of chlorine. One study by Manninen [71] used a Fisons ETV MkIII electrothermal vaporizer for the determination of extractable organic chlorine from sediment by monitoring the m/z 35 using single ion monitoring mode. A separate study by Richner and Wunderli [72] was completed using the HGA-600MS to differentiate between organic and inorganic chlorine in waste oils. They

reported detection limits of between 0.5 and 10.0 μg per gram of oil depending on the oil.

Vaporization and Atomization Mechanisms

Historically, the vast majority of the mechanistic studies in graphite tube ETV pertain to atomization and GFAAS. Vaporization and atomization mechanisms have been extensively reviewed by Styris [73] and is recommended reading for anyone conducting research in this area.

Sturgeon and Chakrabarti [74] have proposed four potential routes by which atomic vapour is generated in a graphite furnace:

1) Reduction of the solid oxide on the graphite surface:

where $M = \text{Co, Cr, Cu, Fe, Mo, Ni, Pb, Sn and V}$.

2) Thermal decomposition of solid oxides:

where $M = \text{Al, Cd and Zn}$.

3) Dissociation of oxide molecules in the vapour phase:

where M = Cd, Mg, Mn and Zn.

4) Dissociation of halide molecules in the vapour phase:

where M = Cd, Fe and Zn; X = Cl.

A number of novel approaches have been used to elucidate the mechanisms of atomization in GFAAS including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), radioactive isotopes, Rutherford backscattering spectroscopy (RBS), gas chromatography (G.C.) atomic absorption, atomic emission and mass spectrometry [73].

A number of studies of vaporization and atomization processes using mass spectrometry have been published. The advantage of using mass spectrometry is that a number of different masses can be monitored sequentially during a single vaporization/atomization step which allows both molecular and atomic species to be detected. The first mass spectrometric apparatus for monitoring molecular and atomic species was reported by Styris and Kaye [75]. They used a two stage pumping system and the atomization studies were carried out under vacuum. A quadrupole mass analyzer was used with an axial electron impact ionizer located at the entrance of the quadrupole. Further refinement of the mass spectrometric apparatus was carried out by

Styris [76] with the use of quadrupole mass spectrometers in tandem. The subsequent study was used for studying the atomization mechanism of barium chloride. One stage pumping and quadrupole mass spectrometry was used by Sturgeon et al. [77] and by Bass and Holcombe [78] for looking at the atomization mechanism for lead. The apparatus used by Sturgeon et al. required a pump down step before each sample was loaded and only a single mass was monitored during atomization. The apparatus by Bass and Holcombe had a dual chamber: one for the sample and one for the quadrupole mass spectrometer. Single masses were monitored sequentially, but nine masses could be monitored during a single atomization step. Ham and McAllister [79] constructed a one stage pumping system similar to Sturgeon et al. except that a separate pumping step was not required as the vacuum in the apparatus was not lost when the sample was loaded. This one stage pumping apparatus was used to examine atomization of cobalt.

When compared to conventional GFAAS, there are two significant differences to using quadrupole mass spectrometry in previous studies for investigating vaporization and atomization mechanisms in the graphite furnace. For example, one significant difference is that the sample size requirement is generally much higher in previous work, which may result in reactions causing the formation of gas-phase species. Hassel et al. [80] have used secondary ion mass spectrometry which allowed the vaporization and detection of small amounts of analyte which are typical for GFAAS. The second difference with previous studies of vaporization using mass spectrometry is that the vaporization of analyte takes place under low pressure which does not simulate the atmospheric pressure conditions used in GFAAS.

To overcome these two problems of vaporization under vacuum pressure, two approaches have been used by Styris [81] and Byrne and co-workers [82,83]. Styris developed an apparatus which samples the graphite furnace through the dosing hole at atmospheric pressure. The graphite furnace is positioned so that the gas phase species are sampled by a pair of cones similar to that used in an ICP-MS. The first tungsten cone (sample cone) samples the gas-phase of the graphite furnace and induces a free-jet expansion of the gases. The second nickel cone (skimmer cone) samples only molecular and atomic species with linear momenta parallel to the cone axis. Two vacuum pumps are used: one between the cones and one in the quadrupole mass spectrometer chamber.

The second approach by Byrne and co-workers [82,83] used a graphite furnace which was coupled to an ICP-MS by teflon tubing (80 cm). A purge gas carries the atomic and molecular species into the ICP, where atomization and ionization of the gas-phase species sampled from the ETV take place. This apparatus was used successfully to determine the mechanism of chloride interference on Mn and Mg in GFAAS. A second study was also completed to determine the mechanism of chemical modification by ascorbic acid on Mn in GFAAS (82). This successful approach by Byrne et al. [82,83] was extended in this thesis for examining the vaporization and atomization of a number of elements.

The initial success of coupling the graphite furnace to an ICP-MS for examining the chemistry inside this type of ETV was followed up in this thesis for studying the vaporization and atomization mechanisms of a number of elements in the Periodic table as outlined in the Objectives Section.

OBJECTIVES:

The primary objectives of this research are:

- 1) **To investigate some of the matrix effects associated with the ETV for sample introduction into an ICP-MS.** Matrix effects may enhance or decrease analyte signals. Analyte signal enhancements for most elements can arise from matrices which contain large amounts of salts (NaCl). Elements such as uranium and thorium, however, do not have signal enhancements in a chloride matrix.
- 2) **To study the vaporization and atomization of elements which are poorly determined by GFAAS.** Such studies can lead to the development of mechanisms of vaporization and atomization which can then be used to explain why some elements are poorly determined by GFAAS and why these same elements can be routinely determined by ETV-ICP-MS. Understanding the mechanisms of vaporization and atomization enables the analyst to optimize the heating programs for the ETV.
- 3) **To investigate novel approaches for increasing and improving analyte signals of some elements with ETV-ICP-MS.** Multiple peaks, memory effects and analyte signal tailing are some of the problems which plague some elements (e.g. carbide forming elements). Therefore, strategies for overcoming some of the problems will also be described.

CHAPTER 1 MATRIX EFFECTS AND PHYSICAL CARRIERS FOR ETV-ICP-MS

1.1 INTRODUCTION

The first experiments reported in this thesis are related to matrix effects as there were noticeable gaps in the literature when this research was started. Prior to any comprehensive mechanistic studies, these initial experiments provided a valuable starting point for understanding the properties of vaporization inside the ETV. Although studies on matrix effects associated with ETV-ICP-MS have been reported, few studies have investigated the chemical or physical behaviour of mineral acids in the ETV and their effects on ICP-MS analyte signal pulses. The effect of acids on $^{63}\text{Cu}^+$ signals from an ICP-MS using a rhenium strip electrothermal vaporizer was reported by Park and co-workers [27]. They showed that 1% HCl, HNO_3 , HF and H_2SO_4 suppressed $^{63}\text{Cu}^+$ signals compared to non-acidified copper solutions. For the acids studied, they observed peak broadening with 3% acid solutions, which was attributed to unexplained chemical effects. These authors also found that 3% HNO_3 or HF did not reduce the integrated signal, whereas 3% HCl or H_2SO_4 did. Some characteristics of a tungsten furnace were investigated by Tsukahara and Kubota [29], who showed that increased HCl concentrations resulted in an increase in the amount of tungsten vaporized.

Judicious selection of acids used in ICP-MS aids in avoiding many troublesome spectroscopic interferences. Nitric acid is frequently the acid of choice for solution nebulization ICP-MS determinations since the N^+ , O^+ and H^+ species or any polyatomic combination of these are already present in the plasma and originate from water, argon and atmospheric gases entrained into the argon plasma. The background spectra of

HNO_3 is relatively simple resulting in fewer spectroscopic interferences, compared with HCl , which can produce a number of chloride interferences such as the interference $^{35}\text{Cl}^{16}\text{O}^+$ on $^{51}\text{V}^+$. Sulphuric and phosphoric acid are generally avoided since a large number of S and P containing polyatomic species can occur [84].

The success of an ETV-ICP-MS determination is dependent on the complete vaporization of analyte from the graphite tube and the efficient transport of analyte to the argon plasma. The selection of acid, as well as the concentration used, may affect either analyte vaporization, transport or both. The retention of water or acid within the graphite ETV, even following extended high temperature (100-300°C) evaporation, is possible and may also impact on analyte ETV-ICP-MS signal pulses.

The objective of this research was to examine the effect of the vaporizer temperature program on the retention of water, HCl and HNO_3 . Varying the conditions of each step in the temperature program affects the amount of matrix retained on the graphite surface. The effects of acid concentrations on selected analyte signal pulses for a number of elements are reported for vaporization under compromise multi-element conditions using different concentrations of HCl , HNO_3 , H_2SO_4 and H_3PO_4 as diluents. For comparison, the mixed chemical modifier, NASS-3 (North Atlantic Standard Seawater), which is high in chloride, was also assessed. It may be hypothesized that increased amounts of acid will destroy the graphite surface of the ETV which could "load" the plasma resulting in signal suppression (as observed by Park et al.). On the contrary, it may also be hypothesized that increased amounts of acid enhance the ETV-ICP-MS signal intensities by acting as a physical carrier in much the same way as a halide salt.

1.2 EXPERIMENTAL

A Perkin-Elmer Sciex Elan model 5000 ICP-MS equipped with an HGA-600MS ETV was used. The ETV system was fitted with a Perkin-Elmer AS-60 autosampler. The experimental conditions for both the Elan 5000 and the HGA-600MS are given in Table 1. Standard pyrolytic graphite coated tubes were used for all experiments.

Solution nebulisation sample introduction was used to optimize the plasma and ion lens settings of the mass spectrometer. The ETV was interfaced to the plasma with an 80 cm length of teflon tubing (6mm i.d.). The flow of argon from the HGA-600MS power supply was regulated with a pneumatic valve and operation of the HGA-600MS was completely computer controlled. Under normal experimental conditions during the dry and pyrolysis steps of the temperature program, opposing argon gas flows (300 mL min.⁻¹) from the ends of the graphite tube removing water and other vapour phase decomposition products through the dosing hole. In this way, the matrix components are not introduced to the plasma. During the measurement of analyte signal pulses, typically the high temperature vaporization step, a graphite probe seals the dosing hole and the flow of argon is directed from the far end of the graphite tube directly to the plasma. For studying the temporal vaporization behaviour of HCl and HNO₃, however, the dosing hole was sealed during the entire temperature program in order to observe the amount of ³⁵Cl, ¹⁴N¹⁶O or ¹⁵N vaporized from the deposition of acid during each step in the temperature program. While this method allowed the observation of the temporal behaviour of these ions, a quantitative determination of acid retention after the drying or pyrolysis step using this method could be misinterpreted. This was due to the

Table 1. Instrumental operating conditions and data acquisition parameters of the Perkin-Elmer Sciex Elan 5000 ETV-ICP-MS for examining matrix effects.

Inductively Coupled Mass Spectrometer

RF power	1000 W
Coolant argon flow rate	15.0 L min. ⁻¹
Auxiliary argon flow rate	850 mL min. ⁻¹
Carrier argon flow rate	900 mL min. ⁻¹
Sampler/skimmer cones	platinum

Electrothermal Vaporiser: HGA-600MS

Sample volume	5 μ L
Internal argon flow rate	300 mL min. ⁻¹
Dry step	90-160°C (30 s)
Dry ramp	10 s
Pyrolysis Step	400-1400°C (10 s)
Pyrolysis Ramp	2 s
Vaporization Step	2400°C (10 s)

Data Acquisition

Resolution	High (0.7 amu at 10% peak Height)
Dwell time	20 ms
Scan mode	peak hop transient
Points/spectral peak	1
Signal measurement	integrated signal pulse

Analytes Examined

Acid Studies: ¹⁴N¹⁶O, ¹⁵N, ³⁵Cl

Carrier Studies: ⁵⁹Co, ⁶³Cu, ¹⁰⁷Ag, ¹³¹Cs,
²⁰⁷Pb, ²⁰⁹Bi and ²³⁸U

larger than expected signals for $^{35}\text{Cl}^+$, $^{15}\text{N}^{16}\text{O}^+$ and $^{15}\text{N}^+$, which arose due to the increased condensation of acid onto cooler surfaces, such as the transfer line, during the drying and pyrolysis steps when the dosing hole was sealed.

The temporal studies of HCl and HNO_3 were performed by monitoring the $^{35}\text{Cl}^+$, $^{14}\text{N}^{16}\text{O}^+$ and $^{15}\text{N}^+$ ions and the integrated ion counts were calculated with an "in-house" Turbo Pascal program using the trapezoidal rule of numerical integration. For studying the effect of acids on analytes signals, the integrated signal was reported using the Elan software provided. For all experiments, 5-20 μL of sample were pipetted onto the walls of the graphite furnace. For each experiment, a minimum of five runs were performed. All measurements were blank subtracted using water as a reagent blank for the acid studies, a dry tube for the water studies and NASS-3 seawater standard as the chemical modifier for experiments involving the use of a mixed carrier. The ICP-MS measurements were made at high resolution (0.7 amu at 10% peak height) because of the possible peak overlap of $^{36}\text{Ar}^+$ on the $^{35}\text{Cl}^+$ peak.

All solutions were prepared with ultra pure water obtained from a milli Q water purification system (Millipore Corporation, Mississauga, ON. Canada) The HCl, HNO_3 and H_2SO_4 solutions were Ultrex II ultrapure reagent grade (Baker Analyzed). Phosphoric acid (Baker Analyzed) was reagent grade. The ^{15}N -labelled HNO_3 was purchased from CIL (Cambridge Isotope Laboratories, Woburn, Massachusetts, USA). The ^{15}N -labelled nitric acid had a concentration of 40% (v/v) and the isotopic purity was 99% ^{15}N . Stock standard solutions were supplied by Spex (Spex Industries, Inc, Edison, NJ), and NASS-3 sea water was obtained from the Institute for Environmental

Chemistry of the National Research Council of Canada (Ottawa). For the mixed carrier work, NASS-3 sea water was purified by column chromatography to remove any trace elements [85]. A further reduction in trace contaminants was also achieved by diluting the purified NASS-3 sea water 500-fold with de-ionized water. The carrier gas for all of these experiments was high purity argon (99.9%).

1.3 RESULTS AND DISCUSSION

1.3.1 Vaporization Properties of Water

It is known that water absorbed on a graphite surface can react during the pyrolysis step to form hydrogen. Interestingly, it has been observed that water is actually difficult to remove from graphite, even at elevated temperatures [86]. Frech et al. [87] demonstrated and Welz reported [6] that, in an uncoated graphite tube, H_2O was actually retained in sufficient quantities, even after fifteen minutes at 1200°C . Frech et al. [88] also estimated the amount of residual H_2O in a graphite tube, following the drying step, to be $1\ \mu\text{mole}$ when $1\ \mu\text{L}$ of H_2O was deposited on a graphite tube and dried at 80°C . The ICP-MS background spectra has been documented for a dry argon plasma [89,90] and the intensity of $^{36}\text{ArH}^+$ signal has been shown to be indicative of the amount of water present. The temporal behaviour of the vaporization of water from the graphite furnace as monitored by $^{36}\text{ArH}^+$ is shown in Figure 5. Corrections for any spectral overlap from $^{37}\text{Cl}^+$ ion was accomplished by monitoring the $^{35}\text{Cl}^+$ ion and applying the appropriate correction. The HGA-600MS was equipped with a pneumatically controlled graphite probe which effectively sealed the dosing hole. The positive pressure of argon within the graphite furnace made it unlikely that significant

Figure 5. Temporal behaviour of water in the ETV monitored using the $^{36}\text{ArH}^+$ molecular ion. Drying temperature= 140°C (0-50 s), pyrolysis temperature= 400°C (50-60 s), vaporization temperature= 2400°C (60-70 s).

quantities of entrained air or water vapour entered the graphite tube through the dosing hole.

The temporal behaviour of $^{36}\text{ArH}^+$ in the ETV confirmed that the bulk of the water from a 10 μL sample is removed during the dry step of the temperature program. A pyrolysis step of 400°C was added, however, no significant signal for $^{36}\text{ArH}^+$ was observed until the high temperature vaporization step at 60-70 s. The temporal view of $^{36}\text{ArH}^+$ in Figure 5 provides only a qualitative view of water retained on the graphite surface of the ETV because some of the $^{36}\text{ArH}^+$ signal obtained during the vaporization step originated from water that had condensed on the graphite cones of the ETV as well as on the transfer line. It may also be postulated that the ArH^+ signal at 400°C is "free water", whereas the ArH^+ at 2400°C is "bound" and therefore, more difficult to remove from the graphite.

Retention of water in the ETV is of some importance in ETV-ICP-MS because of its role in the production of hydride and oxide species and was included as a pretext for studying the vaporization properties of acids. These hydride and oxide molecular ions can interfere with other analytes in a multi-element analytical scheme. For example, the production of $^{40}\text{Ar}^{16}\text{O}^+$ could interfere with the determination of trace $^{56}\text{Fe}^+$. The presence of water could also lead to the formation of refractory oxides for some analytes such as the Rare Earth Elements.

1.3.2 Vaporization Properties of Acids

Drying and pyrolysis steps in the temperature program of the ETV can result in the selective volatilization and removal of the bulk of sample matrix material from

the graphite furnace. During the drying step, most of the solvent matrix can be driven from the surface of the graphite furnace with the bulk of the remaining portion being removed at higher temperatures during the pyrolysis or vaporization steps. In the case of oxyacids, it is believed that these can be retained within the surface of the graphite itself, even at temperatures up to 1000°C [6]. Pyrolytically coated graphite tubes are less porous than uncoated graphite tubes. Therefore, they are less prone to solvent entrapment than uncoated tubes and the retention of acids is greatly reduced. By studying the temporal behaviour of these acids, a better understanding can be achieved of how they can affect analyte sensitivity in ICP-MS either by signal suppression (matrix effect or oxide formation) or by signal enhancement (improved analyte volatility and/or transport efficiency).

1.3.3 Hydrochloric Acid

i) Effect of Drying Step Temperature

To determine the importance of the temperature of the drying step on the removal of chloride from the graphite furnace, 10 μL of 1% (v/v) HCl was deposited on the walls of a pyrolytically coated graphite tube. The temporal behaviour of HCl during the heating cycle was monitored using the $^{35}\text{Cl}^+$ ion. Hydrochloric acid was chosen because it is a common sample diluent, it is a fairly volatile acid and thus, its behaviour is similar to other volatile acids, such as HF or possibly HNO_3 . The $^{35}\text{Cl}^+$ ion was monitored and the counts generated from this ion were proportional to the amount of HCl present. The drying step temperature for these experiments was varied from 90° to 160°C and the chloride remaining on the surface during the high temperature

vaporization step was monitored in each step. A pyrolysis step was not used as the intent of these experiments was to qualitatively assess the retention of chloride in the ETV after the drying step. The results of these experiments, shown in Figure 6, demonstrate the limits of the drying step in removing chloride from the furnace. Only a slight increase in the integrated $^{35}\text{Cl}^+$ ion count was obtained as the drying step temperature was increased from 90°C to 160°C, with the ion counts reaching a plateau after 120°C. Similarly, the number of counts measured during a subsequent vaporization step did not change significantly after 120°C. The fact that increasing the drying step beyond 140°C had no effect on the amount of $^{35}\text{Cl}^+$ removed from the ETV could also indicate that the acid was actually condensed on cooler regions of the ETV. Therefore, even with increased drying temperature or drying time, the retained acid was not removed from the ETV until the high temperature vaporization step.

To determine whether the $^{35}\text{Cl}^+$ signal originated from chloride condensed or adsorbed on the transfer line, rather than originating from chloride in the ETV, 10 μL of a 1% (v/v) HCl solution was dried in the graphite furnace in a manner similar to previous experiments. Prior to the high temperature vaporization step, the transfer line was disconnected and the ETV was cleaned by three separate 2400°C heating cycles for 10 seconds each. The transfer line was then re-connected and a 10 μL sample of H_2O was deposited on the walls of the ETV. The ETV was then subjected to a drying step and heated to 2400°C while the $^{35}\text{Cl}^+$ intensity was monitored in each step. In this manner, any chloride residing in the transfer line would be mobilized and detected by the ICP-MS. This experiment showed that approximately 65% of the retained $^{35}\text{Cl}^+$ was

Figure 6. Effect of drying temperature on the integrated signal of $^{35}\text{Cl}^+$ during the drying and vaporization steps using a 1% (v/v) HCl solution. Drying time=50 s, vaporization temperature=2400°C (10 s).

actually originating from the transfer line. Therefore, a 5 μ L sample of 1% (v/v) HCl, which yielded 18,000 counts during the vaporization step, of which approximately 12,000 counts would originate from the transfer line. This result is important to those using an ETV design [27] incorporating a waste vapour venting system located some distance downstream from the vaporizer surface. These devices allow for condensation of water and acids which can easily be volatilized with analyte to the argon plasma during the high temperature vaporization step.

ii) Effect of Pyrolysis Step Temperature

For these experiments, a drying step temperature of 140°C was used. This temperature was reached by constantly increasing the temperature of the ETV, or ramping, for 10 seconds until the desired temperature was reached. The drying step temperature was then held constant for 40 seconds. Following the drying step, the HCl retained in the graphite tube during the pyrolysis step was again monitored using the $^{35}\text{Cl}^+$ ion. Residual chloride remaining on the graphite was measured during the high temperature vaporization step. Three temperatures were chosen for these experiments, such that a constant heating rate was maintained under normal ramping conditions. The results of these experiments are summarized in Figure 7, which shows that a greater portion of chloride can be removed when a very high pyrolysis temperature is used. A significant portion of chloride, however, remained on the graphite, even after heating to 1400°C as shown by the number of $^{35}\text{Cl}^+$ ion counts remaining during vaporization. It should be noted that a pyrolysis temperature of 1400°C is excessively high and would result in significant analyte losses for many volatile elements, such as Cd, Zn,

Figure 7. Effect of pyrolysis temperature on the integrated signal of $^{35}\text{Cl}^+$ during the pyrolysis and vaporization steps. Sample solution 1% (v/v) HCl. Drying temperature=140°C (50 s), pyrolysis time= 12 s, vaporization temperature=2400°C (10 s).

Ag and Pb for which a pyrolysis temperature of 500°C should never be exceeded, unless a chemical modifier is used [20].

The effect of the temperature ramp was also investigated for its possible role in the evolution of chloride from the graphite surface. The temperature ramp time in the drying step was varied from 2-20 seconds and from 1-10 seconds for the pyrolysis step. These ramp times were chosen as they are typical of those used in GFAAS and ETV-ICP-MS. The temperature ramp of both the drying step and pyrolysis step had no significant effect on the amount of acid retained.

The temporal behaviour of the vaporization of HCl during an entire ETV temperature program (dry to clean-up) was monitored using the $^{35}\text{Cl}^+$ ion and is shown in Figure 8. The clean-up step in the temperature program is an additional high temperature heating step (2600°C or higher) at the end of the heating program. A 140°C drying step was used followed by a pyrolysis step of 1400°C. For this experiment, water was also monitored using the $^{36}\text{ArH}^+$ ion during the entire temperature program. Though not shown in Figure 8, very little $^{35}\text{Cl}^+$ from HCl was vaporized until most of the water was removed from the surface of the ETV, which was about 20 seconds into the heating step. Following the vaporization step at 2400°C, a cleanup step of 2650°C was included, during which a $^{35}\text{Cl}^+$ signal was still observed. The high temperature vaporization step and clean-up step have been magnified in Figure 8 (inset) to reveal some details of the analyte pulses in these steps. The $^{35}\text{Cl}^+$ pulse in the high temperature vaporization step is a sharp peak, lasting approximately 3-4 seconds. The more broadly shaped $^{35}\text{Cl}^+$ pulse in the clean-up step may be

Figure 8. Temporal behaviour for the vaporization of 1% (v/v) HCl in a pyrolytically coated graphite tube. Drying temperature=140°C (0-60 s), pyrolysis temperature=1400°C (60-82 s), vaporization temperature=2400°C (82-92 s), clean up temperature=2650°C (92-102 s).

indicative of chloride which is deeply intercalated in the graphite or $^{35}\text{Cl}^+$ which has condensed on the transfer line or contact cones. The integrated area of the $^{35}\text{Cl}^+$ pulse in the cleanup step was close to half the integrated area for $^{35}\text{Cl}^+$ volatilizing during the high temperature vaporization step. As pointed out in the Experimental section, this temporal picture of chloride in the ETV was obtained by sealing the dosing hole during the entire temperature program. During the drying and pyrolysis step, the flow of argon originates from one end of the ETV to the other instead of both ends and through the dosing hole giving the chloride a possible means of condensing on the transfer line. As a result, the $^{35}\text{Cl}^+$ peak during the high temperature vaporization step, in Figure 8, is larger than expected. This was probably caused by chloride condensed on the transfer line as well as chloride from the ETV. Under normal conditions, with the dosing hole open for the drying and pyrolysis steps, the $^{35}\text{Cl}^+$ signal in the high temperature vaporization step is much lower. Semi-quantitative analysis for $^{35}\text{Cl}^+$ retention, under normal conditions, from a 20 μL , 1% (v/v) HCl solution, following a 140°C drying temperature and a 400°C pyrolysis step, revealed that approximately 0.05% of the original quantity of acid as ^{35}Cl was retained under these conditions. This amount of $^{35}\text{Cl}^+$ retained corresponds to approximately 1.1×10^{-6} μmoles of ^{35}Cl or roughly 40,000 pg which is in large excess compared to the amount of analyte vaporized in the ETV, typically from 1-50 pg.

1.3.4 Nitric acid

To study the retention of HNO_3 on graphite, a suitable ion, either mono- or polyatomic, must be chosen that is solely derived from HNO_3 . Mass scans in the spectral

region of values from mass 14 to 60 were obtained for a 1% (v/v) HNO_3 solution and compared to the background spectrum obtained with deionized water. These experiments were similar to those reported in the literature for solution nebulization [91], except in this case the plasma was dry. Choosing a suitable ion was difficult because of the similarity between the mass spectra of the HNO_3 and the mass spectra of the blank, which was water. A number of ions were evaluated including: $^{14}\text{N}^{16}\text{O}^+$, $^{12}\text{C}^{14}\text{N}^+$, $^{40}\text{Ar}^{14}\text{N}^+$, $^{14}\text{N}^{16}\text{O}_2^+$ and $^{14}\text{N}^+$, but $^{14}\text{N}^{16}\text{O}^+$ was the only species which gave a satisfactory response for monitoring the vaporization of HNO_3 . Nitric acid is a major source of $^{14}\text{N}^{16}\text{O}^+$, however, another important source within the ETV is the formation of $^{14}\text{N}^{16}\text{O}^+$ resulting from the vaporization of water which reacts with $^{14}\text{N}^+$ in the plasma. Figure 9 shows the temporal behaviour of $^{14}\text{N}^{16}\text{O}^+$ from: (a) deionized water and (b) 1% HNO_3 . It is apparent that the temporal behaviour of $^{14}\text{N}^{16}\text{O}^+$ in each diluent can be differentiated. For these experiments, the sample was dried at 140°C and vaporized at 2400°C . A pyrolysis step was not used. It is clear, that even with a high drying temperature, a significant portion of $^{14}\text{N}^{16}\text{O}^+$ was retained until the high temperature vaporization step. A pyrolysis step temperature of 400°C was sufficient to remove any residual $^{14}\text{N}^{16}\text{O}^+$ from the graphite furnace. In practice, the $^{14}\text{N}^{16}\text{O}^+$ ion was not well suited for quantifying the amount of HNO_3 retained on the ETV, because the experiments were difficult to reproduce compared with HCl and were susceptible to high ion background sources such as residual water in the ETV or water condensed in the transfer line. For this reason, ^{15}N -labelled HNO_3 was substituted and $^{15}\text{N}^+$ was used as an alternative ion to $^{14}\text{N}^{16}\text{O}^+$, for monitoring the temporal behaviour of HNO_3 in the

ETV. Thus, a direct correlation could be made between the integrated signal of an ion from the acid and the amount of acid remaining in the furnace. At $m/z=15$, relatively low background counts were observed, which were in the order of approximately 2000 counts s^{-1} . As with previous experiments using HNO_3 , a 1% (v/v) solution was prepared and the temporal behaviour of the HNO_3 was monitored using the $^{15}N^+$ ion. As shown in Figure 10, the $^{15}N^+$ ion appeared to behave in a manner similar to the $^{35}Cl^+$ ion. During the drying step of the temperature program, the bulk of the $^{15}N^+$ was not removed until most of the water was evaporated from the graphite surface. The vaporization of water was observed by monitoring the intensity of the $^{36}ArH^+$ molecular ion during the heating program. Like the $^{35}Cl^+$ from HCl , most of the $^{15}N^+$ from $H^{15}NO_3$ was removed during the drying step, however, 10-15% of the original $^{15}N^+$ appeared to be retained until the high temperature vaporization step. The signal for $^{15}N^+$ during the vaporization step appeared to be unusually large, especially when compared to the $^{35}Cl^+$ signal from a 1% HCl solution. A pyrolysis step was added to remove the residual $^{15}N^+$ from the ETV. Neither a 400°C nor a 900°C pyrolysis step had any effect on reducing the intensity of the $^{15}N^+$ signal during the high temperature vaporization step, indicating that the $^{15}N^+$ was not originating within the graphite tube.

In the experimental section and explained for the temporal behaviour of chloride from HCl , the temporal behaviour of $^{15}N^+$ was studied with the dosing hole sealed during the entire temperature program. As with the $^{35}Cl^+$ from HCl , when the dosing hole was sealed and the argon flow was directed from one end of the ETV to the other, the HNO_3 vapours had an opportunity to condense on the transfer line or possibly on

Figure 9. Temporal behaviour of $^{14}\text{N}^{16}\text{O}^+$ vaporization in a pyrolytically coated graphite tube from (a) deionized water and (b) 1% HNO_3 . The dry step temperature = 120°C (0-50 s), vaporization temperature= 2400°C (50-60 s).

Figure 10. Temporal behaviour for the vaporization of 1% (v/v) HNO_3 in a pyrolytically coated graphite tube using a ^{15}N -labelled H^{15}NO_3 solution. Drying temperature= 120°C (0-40 s), pyrolysis temperature= 400°C (40-50 s), vaporization temperature= 2400°C (50-60 s).

the graphite contact cones of the furnace housing, resulting in a larger than expected $^{15}\text{N}^+$ signal. When the dosing hole was left open during the drying and pyrolysis steps (140°C and 400°C respectively), as would be the normal procedure with the ETV, the flow of argon originates from the ends of the ETV and exits via the dosing hole removing any vaporized HNO_3 from the ETV. Under these conditions, almost all (>99.97%) of the HNO_3 could be removed from the ETV during the drying step of the temperature program. Experiments were performed both on old tubes (>200 firings) as well as new tubes and it was found that tube age was not a significant factor in the retention of HNO_3 in the ETV.

1.3.5 Effect of Acid on Analyte Signal Pulses

For these experiments, the analytes were vaporized at 2400°C following a 140°C drying step. A pyrolysis step was not used because the objective of these experiments was to use experimental conditions which are similar to those reported in the literature and to explore the actual need, if any, of this heating step. For example, under compromise conditions, relatively low pyrolysis temperatures such as 200°C have been used to prevent pre-vaporization losses of volatile elements such as Ag or Pb during these heating steps [5]. The implications of using any acid as diluent for ETV-ICP-MS determinations can be important, particularly for multi-elemental analysis where compromise conditions are required. The effects of 0.05% (v/v) and 1.0% (v/v) HNO_3 , HCl , H_2SO_4 and H_3PO_4 was determined for seven elements: $^{59}\text{Co}^+$, $^{63}\text{Cu}^+$, $^{107}\text{Ag}^+$, $^{133}\text{Cs}^+$, $^{208}\text{Pb}^+$, $^{209}\text{Bi}^+$ and $^{238}\text{U}^+$. These elements were chosen both to cover a large atomic mass range of the Periodic Table as well as a range of analyte volatilities.

The results of these experiments are summarized in Table 2. For all elements vaporized in the presence of HNO_3 , a 1% (v/v) HNO_3 matrix gave higher integrated signals than the 0.05% HNO_3 matrix. For some elements such as $^{107}\text{Ag}^+$ or $^{208}\text{Pb}^+$, the effects were fairly pronounced, with close to two-fold increases in the integrated signal with increased acid concentration. Initially, it would appear as though higher concentrations of HNO_3 would simply mobilize more analyte from the graphite surface, however, this is not likely the primary cause for the higher analyte signals in higher concentrations of acid. It is possible that a carrier effect with higher acid concentrations is occurring, whereby HNO_3 is acting as the physical carrier. Another possibility is the increased destruction of the graphite surface in the ETV with higher acid concentrations which could result in the formation and liberation of soot particles during the high temperature vaporization step. These fine carbon particles could then act as physical carriers themselves or possibly as sources of nucleation for the analyte.

For HCl, increasing the acid concentration in the sample matrix from 0.05% (v/v) to 1.0% (v/v), did not have a significant effect on any of the elements. The integrated signal remained unchanged, within experimental error, with increased HCl concentration. The integrated signal for most of the elements was quite similar in either 1% (v/v) HNO_3 or 1% (v/v) HCl except for $^{238}\text{U}^+$, which was noticeably lower in the HCl matrix. The HCl matrix could act in two ways which are beneficial to analysis by ETV-ICP-MS. Firstly, the HCl could act as a physical carrier and thereby improve the mass transport of the analyte to the plasma. Alternatively, HCl could react with the analytes forming halides, which are more volatile than their corresponding oxide,

**Table 2. Effect of acid concentration on integrated analyte signal (50 pg).
Integrated Signal (Counts)**

	$^{59}\text{Co}^+$	$^{63}\text{Cu}^+$	$^{107}\text{Ag}^+$	$^{133}\text{Cs}^+$	$^{208}\text{Pb}^+$	$^{209}\text{Bi}^+$	$^{238}\text{U}^+$
0.05% HNO_3	16300	7140	12500	164000	123000	174000	136000
RSD % (n=5)	2.5	6.4	3.8	4.5	7.6	8.5	7.7
1.0% HNO_3	19700	11400	22300	196000	197000	263000	225000
RSD % (n=5)	5.6	8.1	9.9	3.6	7.7	5.6	5.4
0.05% HCl	19800	10500	20100	187000	250000	213000	106000
RSD % (n=5)	1.1	3.6	1.00	0.9	0.70	6.1	6.3
1.0% HCl	19600	10200	19900	187000	248000	200000	99600
RSD % (n=5)	4.8	4.7	3.1	3.6	6.3	4.3	12.0
0.05% H_2SO_4	25200	15700	13500	123000	129000	136000	116000
RSD % (n=5)	6.5	6.5	6.3	5.1	5.7	4.2	5.3
1.0% H_2SO_4	34900	21500	18100	269000	239000	368000	217000
RSD % (n=5)	5.1	5.6	5.0	8.8	7.0	7.4	8.4
0.05% H_3PO_4	45000	-	23300	189000	-	207000	335000
RSD % (n=5)	9.7	-	9.9	12.6	-	5.6	10.1
1.0% H_3PO_4	27100	-	13200	372000	-	193000	239000
RSD % (n=5)	10.6	-	2.5	9.4	-	4.0	6.4

making this a potentially useful acid for many analytes.

When H_2SO_4 was used, the integrated signal for most of the elements studied increased significantly with a 1% acid solution compared with 1% HNO_3 or 1% HCl . The effects of increasing the acid concentration of H_2SO_4 were also significant, indicating the potential for severe matrix effects. As with HNO_3 , when the H_2SO_4 concentration was increased from 0.05% (v/v) to 1.0% (v/v), the integrated signal also increased. This was especially true for elements such as $^{133}\text{Cs}^+$ and $^{209}\text{Bi}^+$.

Phosphoric acid gave data which was unlike that for the other three acids because as the acid concentration was increased, the integrated signal did not increase for all the elements. Rather, $^{59}\text{Co}^+$ and $^{107}\text{Ag}^+$ both decreased with increased H_3PO_4 concentration, $^{209}\text{Bi}^+$ remained unchanged and $^{133}\text{Cs}^+$ increased significantly. In comparison with the other acid matrices, the integrated signals for most analytes were greater in H_3PO_4 than either HNO_3 or HCl and similar to the integrated signals obtained in the H_2SO_4 matrix. Both H_2SO_4 and H_3PO_4 have very high boiling points ($>200^\circ\text{C}$) and will remain in the graphite tube, especially when a pyrolysis step is not used. Although H_2SO_4 and H_3PO_4 are not commonly used in trace analysis in GFAAS, they were included in this study for their potential as matrix interferences in ETV-ICP-MS. Certain field samples, especially biological samples, contain both S and P which in acid media, produce H_2SO_4 and H_3PO_4 during the drying and pyrolysis steps. It is possible that the matrix effects observed with these acids were due entirely to the presence of acids in the graphite tube and not to other processes such as those occurring in the plasma. The interaction between these acids and analytes in the ETV is complex and

Table 3. Effect of pyrolysis temperatures on integrated analyte signal pulses (50 pg).

	Integrated Signal (Counts)						
	$^{50}\text{Co}^+$	$^{63}\text{Cu}^+$	$^{107}\text{Ag}^+$	$^{133}\text{Cs}^+$	$^{208}\text{Pb}^+$	$^{209}\text{Bi}^+$	$^{238}\text{U}^+$
1% HNO_3							
none	18500	14800	24200	268000	236000	163000	172000
RSD % (n=5)	12.1	8.5	11.1	6.1	5.1	4.3	4.8
400°C	16700	13700	12600	263000	183000	110000	207000
RSD % (n=5)	3.9	2.6	9.1	2.7	8.1	6.5	2.5
900°C	16100	14700	5500	268000	176000	81800	217000
RSD % (n=5)	3.4	5.3	4.08	5.86	7.04	3.33	3.26
1% HCl							
none	25500	13500	20300	158000	182000	171000	120000
RSD % (n=5)	5.2	8.9	4.5	5.0	8.7	8.4	12.2
400°C	24200	14000	19300	156000	125000	135000	87800
RSD % (n=5)	4.2	5.7	3.6	5.8	8.9	9.9	12.5
900°C	26100	15000	15800	127000	44900	25800	82300
RSD % (n=5)	2.0	4.1	1.9	4.7	22.9	2.9	6.3

thus, would require further study. A pyrolysis step was used to study its effect on 1% (v/v) HNO_3 and HCl , since these acids are the most common diluents used in ETV-ICP-MS. When a pyrolysis step was used, a different analytical response was obtained. Two pyrolysis temperatures were used, 400°C and 900°C , using 1% (v/v) acid solutions as the matrix. The lower pyrolysis temperature at 400°C was chosen because it is well below the standard pyrolysis conditions for volatile elements such as $^{107}\text{Ag}^+$ [20]. Therefore, any effect seen would not be associated with pyrolysis step losses at 400°C . The higher pyrolysis temperature, of 900°C , was chosen since it is in the temperature range for a number of less volatile elements such as Cu or Co . Initially, it was postulated that a high temperature pyrolysis step would remove more acid from the surface of the ETV and result in a lower integrated analyte signal as was illustrated in Table 2. The results of these experiments are summarized in Table 3. Maximum integrated signal intensities were achieved when a pyrolysis step was not used with 1% (v/v) HNO_3 in the matrix. In a 1% (v/v) HNO_3 matrix, increased pyrolysis temperatures had a detrimental effect on the volatile elements such as $^{107}\text{Ag}^+$, $^{208}\text{Pb}^+$ and $^{209}\text{Bi}^+$. For the other elements there was no change in signal intensity, within experimental error, with the use of a pyrolysis step except for $^{238}\text{U}^+$, which showed only a slight increase in integrated signal intensity with a pyrolysis step. While the signal intensity was decreased using a pyrolysis step, the reproducibility of integrated signals was greatly improved with the use of a pyrolysis step as indicated by the improved relative standard deviation (RSD). This is probably indicative of the chemistry occurring in the pyrolysis step during which a single species is formed in the ETV. Converting all of the analyte

to a single species would result in the uniform volatilization of the analyte compared with the volatilization of a range of analyte species, producing more reproducible integrated signals.

The use of an increased pyrolysis temperature in a 1% HCl matrix was also not beneficial for increasing the signal intensity of any of the elements. In general, the integrated signals obtained without a pyrolysis step were generally higher than when a pyrolysis step was used for a 1% HCl matrix. The integrated signal decreased for most elements in 1% HCl with the higher pyrolysis temperature of 900°C and in the case of elements which form volatile halides such as $^{107}\text{Ag}^+$ or $^{208}\text{Pb}^+$, the effects of using a pyrolysis step was striking. For many of the elements, the increased pyrolysis temperature resulted in a significant improvement in the reproducibility, as indicated by the decrease in the RSD of the integrated signal. The only exception was $^{208}\text{Pb}^+$ in 1% (v/v) HNO_3 or HCl, however, the RSD of the integrated signal decreased for all elements when a pyrolysis step was used. These results are consistent with the experiments completed on the acid concentrations (Table 2). Clearly, when a higher concentration of acid was used, signal intensity increased. Therefore, a pyrolysis step which removes any traces of acid from the ETV, should also result in lower integrated signals. The results indicate that when a pyrolysis step was used, the beneficial carrier effects of retained HCl are also removed, and hence the lower signal. As with HNO_3 , a pyrolysis step did improve the reproducibility of the analyte signal intensity as indicated by the decrease in the RSD, however, unlike the 1% (v/v) HNO_3 solution, the effects were not nearly as significant with 1% (v/v) HCl. This result was expected since

the 1% (v/v) HCl is acting more as a physical carrier and less as a chemical modifier. As well, earlier acid retention experiments indicated that chloride from an HCl solution was retained on the surface of the ETV with pyrolysis temperatures up to 1400°C.

In summary, this work has shown that the use of a pyrolysis step is beneficial for a HNO₃ matrix even though the integrated signal intensity is decreased. A pyrolysis step is not always desired, however, if the sample matrix contains a high chloride matrix, the benefit of increased reproducibility is not great enough to overcome the drawback of decreased integrated signal intensity for most elements under compromise conditions.

1.3.6 Effect of a Mixed Modifier/Physical Carrier

The addition of a physical carrier was evaluated for its role in reducing the matrix effects associated with different acid concentrations. The physical carrier increases the integrated signal in ETV-ICP-MS by improving mass transport of the analyte of interest [19,20]. The physical carrier chosen for this work was NASS-3 sea water. Purified NASS-3 (see Experimental section) sea water acts as a mixed modifier in the ETV, since seawater is essentially a mixture of major ions which include: Na⁺, K⁺, Mg⁺², Ca⁺², Sr⁺², Cl⁻ and Br⁻. Use of NASS-3 sea water is advantageous because it is readily available, a high purity modifier and free of trace elements typical of other modifiers such as Pd [92]. The results of the experiments with NASS-3 used as a physical carrier are summarized in Table 4. As before, the analytes were vaporized immediately after the drying step and a pyrolysis step was not used. The integrated signals for all of the elements in the presence of NASS-3 were significantly enhanced

indicating an improvement in the mass transport of the analytes to the plasma. The use of NASS-3 also reduced the effects of increased acid concentration for all of the acid matrices. The change in integrated signal, when acid concentration was increased, was not nearly as significant with NASS-3 used as a physical carrier. This was observed for all of the acids, though less so for H_3PO_4 . The reproducibility of the integrated signals was also improved as shown by the decrease in the relative standard deviation (RSD) when NASS-3 sea water was used as a chemical modifier/physical carrier.

The use of NASS-3 as a chemical modifier in effect introduces into the sample matrix μg quantities of chloride. This excess chloride (compared to pg of analyte) may serve to convert most of the analytes to their chloride form and interferes with or prevents the formation of analyte oxides, which are more refractory. These oxides tend to vaporize or be reduced at much higher temperatures compared to the vaporization of chlorides and for some elements such as the rare earth elements, oxides are vaporized in the graphite tube at a time when little carrier is present to ensure efficient transport to the argon plasma.

Table 4. Effect of acid concentration on analyte signal (50 pg) and NASS-3 as a physical carrier.

Integrated Signal (Counts)							
	⁵⁹ Co ⁺	⁶³ Cu ⁺	¹⁰⁷ Ag ⁺	¹³³ Cs ⁺	²⁰⁸ Pb ⁺	²⁰⁹ Bi ⁺	²³⁸ U ⁺
0.05% HNO ₃	30400	10100	29400	126000	220000	373000	53400
RSD % (n=5)	9.4	8.1	3.3	8.1	5.4	2.4	6.3
1.0% HNO ₃	28500	11200	27800	115000	225000	366000	49000
RSD % (n=5)	7.9	3.3	4.1	3.3	7.3	2.8	5.4
0.05% HCl	23100	9300	24800	150000	257000	224000	30700
RSD % (n=5)	2.3	10.4	5.5	7.9	4.7	4.2	8.3
1.0% HCl	21600	9410	19400	144000	257000	182000	48000
RSD % (n=5)	2.9	5.6	1.3	5.4	6.9	5.1	8.4
0.05% H ₂ SO ₄	40400	29300	37900	322000	284000	300000	58500
RSD % (n=5)	3.42	4.1	7.8	3.5	6.0	3.1	5.3
1.0% H ₂ SO ₄	42500	30100	27200	394000	381000	481000	115000
RSD % (n=5)	5.34	4.3	7.0	3.7	1.6	6.7	6.8
0.05% H ₃ PO ₄	46600	-	31000	182000	-	209000	469000
RSD % (n=5)	9.1	-	4.6	5.9	-	17.8	9.5
1.0% H ₃ PO ₄	27600	-	13600	419000	-	390000	188000
RSD % (n=5)	5.6	-	2.0	4.4	-	5.0	13.6

1.4 SUMMARY AND CONCLUSIONS

This work has shown that the use of aqueous external standards for calibration could lead to significant analytical error depending on the sample matrix. The use of a chemical modifier/physical carrier in both standard and sample solutions was shown to be beneficial to the successful application of ETV-ICP-MS to the quantitative analysis of complex materials. Of the acids studied, HCl was least influential in altering analyte sensitivity, especially in the presence of NASS-3 chemical modifier/physical carrier. Residual chloride remaining after the drying and pyrolysis steps served as an effective physical carrier for transporting analyte from the ETV to the argon plasma, while at the same time, prevented the formation of more refractory analyte oxides.

The relatively lower sensitivity of analytes, except for $^{238}\text{U}^+$, in the presence of high concentrations of HNO_3 compared to HCl can be explained in part by the chemical nature of these acids. In the case of HNO_3 , the analytes formed oxides that were reduced to metal atoms during the high-temperature vaporization step making them less volatile compared with their corresponding halides. The behaviour of the less volatile H_3PO_4 and H_2SO_4 acids and their effects on analyte signal pulses is complex and could involve both chemical and physical effects. Sample matrices containing large amounts of these acids will probably require detailed study for each analyte determined and may require alternate calibration schemes such as the method of standard additions or isotope dilution.

**CHAPTER 2. VAPORIZATION AND ATOMIZATION OF BORON.
PART I. INVESTIGATED BY ELECTROTHERMAL
VAPORIZATION INDUCTIVELY-COUPLED PLASMA
MASS SPECTROMETRY**

2.1 INTRODUCTION

The first mechanistic studies reported in this thesis were carried out on the vaporization and atomization of boron. The sensitivity for determination of boron by graphite furnace atomic absorption spectrometry (GFAAS) is poor when compared to other elements such as Ag. Characteristic masses, defined as the amount of analyte required to obtain an atomic absorbance value of 0.0044, have been reported to be as high as 24 ng for boron when a chemical modifier is not used [93]. The use of modifiers, such as barium and calcium hydroxides [94], nickel [93,96] and magnesium nitrates [95,96], calcium chloride [97] or titanium with ascorbic acid [98], give improved detection limits. Memory effects and shortened graphite tube lifetimes may result in carbide formation and can cause problems with boron determinations. These can be minimised either by pre-treating the tubes with zirconium solution [93] or by insitu coating of the tubes with pyrolytic graphite [99]. By using appropriate modifiers and tube pre-treatment, detection limits are improved and reported values range from 20 to 70 $\mu\text{g L}^{-1}$. These values, however, are still around two orders of magnitude higher in comparison with many elements determined routinely by GFAAS.

One explanation for the low sensitivity for boron implicates the formation of non-volatile refractory carbides; on the other hand, Slavin [5] has proposed that pre-atomization loss of volatile B_2O_3 could be responsible, though no direct evidence for this has been reported. Thermodynamic equilibrium calculations by Frech [100] predict

that a number of volatile boron molecular species should be formed in the graphite furnace at temperatures well below the appearance temperature of boron atoms. These include $B_2O_3(l)$, $HBO_2(g)$, $B_2O_2(g)$ and $BO(g)$ as well as involatile $B_4C(s)$. According to Frech's calculations, these species should form in various temperature ranges below 2300°C . They are listed above in the order of increasing temperature of formation, i.e. the first gaseous species listed, HBO_2 , forms between 900 and 1600°C . Solid boron carboide is not predicted to form until about 2000°C , just prior to the appearance of boron atoms. If this is the case, then boron should begin to vaporize and be lost from the furnace as gaseous molecular species at temperatures above 900°C , which is well before the onset of atomization.

The objective of this study was to investigate the extent of pre-atomization loss in the graphite furnace using electrothermal vaporization inductively-coupled plasma mass spectrometry (ETV-ICP-MS). It may be hypothesized that pre-atomization loss of molecular species, which cannot be detected by GFAAS, should be observed using ETV-ICP-MS where any molecular species removed from the furnace, either during the pyrolysis step or in the temperature ramp to atomization, will be dissociated by the plasma and detected as atomic ions by the mass spectrometer. This method has been used to investigate the pre-atomization loss of manganese analyte in the presence of a magnesium chloride matrix [82]. The technique has the added advantage of being able to detect some molecular ions, particularly diatomic molecules with high bond dissociation energies. For example, the BO molecule has a bond dissociation energy of 806 kJ mol^{-1} [101]. The identification of such species, as well as the temporal and

thermal regions in which they are formed, should provide important information about the vaporization and atomization processes for boron which is relevant to both GFAAS and ETV-ICP-MS techniques.

2.2 EXPERIMENTAL

2.2.1 Instrumentation

A Perkin-Elmer Model 5000 atomic absorption spectrophotometer equipped with a Zeeman Background Corrector and a Heated Graphite Atomizer (HGA) model 500, was used. Test solutions of 10 μL were injected onto the walls of the graphite tube using a Perkin-Elmer AS-40 auto sampler. For all experiments, standard pyrolytic graphite coated tubes (Perkin Elmer Part No. B0091504) were used and a Perkin-Elmer hollow-cathode lamp (Intensitron) was used for the boron atomization curve. Peak height absorbance and peak area were recorded directly from the spectrophotometer and the absorbance profiles were recorded with an IBM computer using the software program, TGP (Tech Graph Pad for scientists and engineers). The experimental operating conditions for the graphite furnace atomic absorption experiments are summarized in Table 5.

For the ETV-ICP-MS experiments, a Perkin-Elmer Sciex Elan 5000 ICP mass spectrometer equipped with an HGA-600MS ETV was used. A model AS-60 autosampler was used to deposit sample onto the walls of standard pyrolytic graphite coated tubes. The plasma and mass spectrometer were optimized using solution nebulization sample introduction. The HGA-600MS was connected to the plasma with a teflon tube which was 80 cm in length and 6 mm (i.d.).

Table 5 Experimental and operating conditions of the Perkin-Elmer Zeeman 5000 graphite furnace used for atomization of boron.

Sample volume	10 μL
Dry Step	10 s ramp 120°C for 40 s
Internal gas flow	300 mL min ⁻¹
Pyrolysis step	2 s ramp 900°C for 10 s
Internal gas flow	300 mL min ⁻¹
Atomization step	0 s ramp various temperatures for 7 s
Internal gas flow	0 mL min ⁻¹

During the dry and pyrolysis steps of the temperature program, opposing flows of argon gas (300 mL min^{-1}), originating from both ends of the graphite tube, removed water and other matrix vapours through the dosing hole. During the "read" step, typically during the high-temperature vaporization step, the dosing hole was sealed pneumatically with a graphite probe. A valve located at one end of the HGA workhead directed the carrier argon flow from one end of the graphite tube to the argon plasma at a flow rate of 900 mL min^{-1} . The number of analyte ions monitored was limited to four because of the transient nature of the signal pulses. The peak-hopping mode of data acquisition was used with a 10 ms dwell time for each ion monitored. The experimental operating conditions of the Elan 5000 and the HGA-600MS are summarized in Table 6.

2.2.2 Standards and Reagents

Argon gas of high purity (99.995% pure, Matheson Gas Products, Canada) was used. Ultra-pure water (Millipore-QTM) and analytical grade nitric acid (Ultrex, Baker) were used throughout. For the GFAAS experiments, a 500 ppm boron solution was prepared by dissolving 0.287 g of boric acid (Baker Analyzed) in 100 mL of water. The stock nickel modifier solution of 5000 ppm was prepared by dissolving 0.500 g of nickel (SPEX 99.995% pure) in 10 mL of 1:1 HNO_3 and diluting it with ultra-pure water to 100 mL. A 4% NaF solution was used to clean the graphite tube between firings [93]. For the GFAAS experiments, the $10 \mu\text{L}$ sample contained 25 ng of boron with $2.5 \mu\text{g}$ nickel modifier.

Table 6. Instrumental operating conditions and data acquisition parameters for the ETV-ICP-MS for the vaporization of boron.

ICP MASS Spectrometer

RF power	1000 W
Coolant argon flow rate	15.0 L min ⁻¹
Auxiliary argon flow rate	900 mL min ⁻¹
Carrier argon flow rate	900 mL min ⁻¹

HGA-600MS Electrothermal Vaporizer

Sample volume	10 μ L
Dry step	10 s ramp 120°C for 40 s
Pyrolysis step (no modifier)	2 s ramp 400°C for 10 s
Pyrolysis step (Ni modifier)	2 s ramp 900°C for 10 s
Vaporization Step	0 ramp (2000°C s ⁻¹) various temperatures for 6 s

Data Acquisition

Dwell Time	10 ms
Scan mode	peak-hopping
Points/spectral peak	1
Ions monitored/measurement cycle	4
Signal measurement	Integrated area
MS resolution	0.7 dalton at 10% peak height
Ions monitored	¹⁰ B, ¹⁰ B ¹⁶ O, ⁶¹ Ni, ²⁶ Mg, ⁴⁴ Ca

For the ETV-ICP-MS experiments, a 250 ppb boron solution was prepared from the stock solution. A nickel modifier was mixed with this boron solution to give a final concentration of 50 ppm nickel. For these experiments, the 10 μ L sample contained 2.5 ng of boron and 0.5 μ g of nickel modifier.

2.3 RESULTS AND DISCUSSION

2.3.1 Atomization and Vaporization Curves for Boron

Thermal pretreatment (pyrolysis) - atomization curves provide useful information about atomization processes and optimum conditions for atom formation in GFAAS. For a given thermal pre-treatment temperature, the atomization curve shows the variation of atomic absorbance with atomization temperature. Figure 11 gives the GFAAS atomization curve for 25 ng of boron using water atomization and nickel nitrate (500 ppm) as a chemical modifier [93]. A pyrolysis temperature of 900°C was used. Peak height absorbance rather than peak area is plotted because of the problem of peak tailing, particularly at lower atomization temperatures. This atomization curve shows that boron atoms are not formed in the furnace at temperatures below about 2200°C.

Similar curves can also be obtained from ETV-ICP-MS experiments, though at the time of this study, none had been reported. These should more correctly be called "vaporization curves" rather than atomization curves, since the atomic ions detected by the mass spectrometer could be formed from molecular species vaporized from the graphite furnace and subsequently dissociated in the plasma. Figure 12 shows such a vaporization curve for boron. Because of the higher sensitivity for boron with ETV-ICP-MS, no modifier was used in this experiment and the amount of boron (2.5 ng)

Figure 11 Graphite furnace atomic absorption spectrometry atomization curve for 25 ng of boron with 2.5 μg of nickel modifier.

was ten times less than in GFAAS experiments. The less abundant ^{10}B isotope (19.9% natural abundance) was monitored to avoid potential isobaric interference from the wing of the strong $^{12}\text{C}^+$ signal produced as a background feature by the ETV [92]. The sample was pyrolysed at 400°C for 10 seconds prior to vaporization at each temperature and after vaporization, a high temperature clean up step of 2650°C was included. The GFAAS atomization curve from Figure 11 is overlaid in Figure 12 for comparison. Since the design and heating characteristics of the HGA-500 furnace used for the GFAAS experiments and HGA-600MS furnace used for the ETV-ICP-MS are essentially the same, this comparison is legitimate. Peak areas given for the ETV signals at each vaporization temperature are the average of three measurements and have had suitable blank readings, typically around 500 counts, subtracted.

The most striking feature of Figure 12 is the marked difference in the appearance temperature for boron in the GFAAS and ETV-ICP-MS experiments. In GFAAS, where only boron atoms are detected, boron is not observed below 2200°C . In the ETV-ICP-MS experiments, the boron signal appears at a vaporization temperature of about 800°C . Since atomic boron is not detected by GFAAS below 2200°C , the boron observed by ETV-ICP-MS at vaporization temperatures between 800 and 2200°C clearly originates from boron molecular species. These would be vaporized and lost from the graphite furnace at some stage prior to atomization, either in the pyrolysis step or the atomization ramp normally employed in GFAAS. This pre-atomization loss, commencing at temperatures as low as 800°C , accounts for the low sensitivity for boron analysis in GFAAS.

Figure 12 Electrothermal vaporization ICP-MS spectrometry vaporization curve for 2.5 ng of boron (no modifier) and GFAAS atomization curve for 25 ng boron with modifier. The temperature regions in which molecular species are predicted to form are shown above the figure.

These experimental results are in agreement with the thermodynamic calculations of Frech [100], which show that gaseous HBO_2 and BO should be formed in the temperature range of 900 to 2100°C. The temperature regions in which these species are predicted to form is shown schematically, in Figure 12, for comparison. This suggests that the molecular precursor for boron vaporized at temperatures between 800 and 1600°C should be HBO_2 . This agrees with results of Meschi et al. [102], who used Knudsen effusion and mass spectrometry techniques to investigate the vapour phase species in the boron oxide/water system at temperatures between 1060 and 1450 K. They reported the major vapour species in this region as HBO_2 . At temperatures above 1600°C, Frech predicts the formation of $\text{BO}(\text{g})$, with solid B_4C beginning to form above 1800°C. In the absence of a chemical modifier, no significant amounts of $^{10}\text{B}^{16}\text{O}^+$ or $^{10}\text{B}^{12}\text{C}^+$ could be detected in the ETV-ICP-MS experiments. Although an ICP-MS signal was observed at mass 26, when this was corrected for spectral interference from $^{26}\text{Mg}^+$ and blank subtracted, no significant residual could be assigned to $^{10}\text{B}^{16}\text{O}^+$.

An interesting feature of the vaporization curve in Figure 12 is the decrease in peak area for $^{10}\text{B}^+$ at higher vaporization temperatures. The peak area decreases from a maximum of approximately 16,000 counts at 1800°C to approximately 6000 counts at 2600°C. This provides indirect evidence for the presence of either BO or BC at higher vaporization temperatures. Since BO has a very high bond dissociation energy (806 kJ mol^{-1}) and a high ionization potential (13.5 eV) [101], it might well survive the plasma unionized and undetected. Thus, as more BO forms at higher temperatures, there would be a reduction in the amount of atomic boron and a concomitant reduction in

signal for $^{10}\text{B}^+$. This again correlates with Frech's calculations [100] which predict the formation of both BO and B_4C at temperatures above 1800°C . The observation also has implications for boron analysis by ETV-ICP-MS since, unlike GFAAS, the optimum boron sensitivity is not obtained at the maximum vaporization temperature, but rather at temperatures around 1800°C .

2.3.2. The Effect of a Nickel Chemical Modifier

The effect of the nickel chemical modifier used in the GFAAS experiments, described earlier, was also investigated using ETV-ICP-MS. Nickel nitrate was chosen in preference to the more commonly used magnesium or calcium modifiers [94,95,97] because of anticipated isobaric interferences. Magnesium was excluded because of the isobaric interference of $^{26}\text{Mg}^+$ with $^{10}\text{B}^{16}\text{O}^+$. Calcium was rejected because of the possibility of doubly charged $^{44}\text{Ca}^{+2}$ ions obscuring the signal for $^{10}\text{B}^{12}\text{C}^+$ at mass 22. In addition, the thermal decomposition mechanism for nickel nitrate modifier in the graphite furnace has been investigated [103] using vacuum mass spectrometry and x-ray photoelectron spectroscopy. These results show that nickel nitrate decomposes at about 350°C , leaving adsorbed nickel oxide on the graphite surface. The oxide begins to reduce to nickel at about 900°C , with the simultaneous evolution of both CO and CO_2 observed by mass spectrometry at this temperature. Elemental nickel then desorbs from the surface between 1400 and 2300°C , with the maximum mass spectral peak intensity at approximately 1700°C . This process is described by the following equations,

Figure 13 shows the ETV-ICP-MS vaporization curve for 2.5 ng of boron in the presence of 0.5 μg of nickel modifier. The sample was pyrolyzed at 900°C for 10 seconds prior to vaporization at each temperature. A 2650°C "clean-up" step was also incorporated after each firing. The GFAAS atomization curve is again superimposed. Comparison of these two curves clearly shows that even in the presence of the chemical modifier, the ETV-ICP-MS signal for the $^{10}\text{B}^+$ appears at a much lower temperature than does the atomic absorption signal for boron in GFAAS. In the presence of the nickel modifier, the maximum in the $^{10}\text{B}^+$ signal occurs at a vaporization temperature of 1650°C compared with 1800°C in the absence of the modifier (Fig.12). Thus, the nickel modifier is ineffective in preventing the bulk of pre-atomization loss from the graphite furnace since the maximum amount of boron is vaporized at approximately 1650°C, which is well below the appearance temperature (2200°C) for boron atoms in GFAAS.

The effect of the nickel modifier on boron vaporization is better understood if the vaporization curve of Figure 13 is considered in conjunction with the series of ETV-ICP-MS peaks, at various vaporization temperatures, presented in Figure 14. At a vaporization temperature of 1150°C (Fig.14a), boron is already vaporized from the furnace despite the presence of the modifier. As the vaporization temperature is increased to 1300°C (Fig.14b), more boron appears in the same temporal region (0.5-

Figure 13 ETV-ICP-MS vaporization curve for 2.5 ng of boron with 0.5 μg of nickel modifier: (-●-) $^{10}\text{B}^+$; (-■-) $^{10}\text{B}^{16}\text{O}^+$; (-○-) GFAAS atomization curve for boron.

Figure 14 ETV-ICP-MS signal pulses for boron with nickel modifier at various vaporization temperatures. The ⁶¹Ni⁺ signal (---) is shown at 1500°C and 1650°C.

1.8 s) as the 1150°C peak. The $^{10}\text{B}^+$ peak, however, now shows a small tailing beyond 2.0 seconds. Figure 14c shows the $^{10}\text{B}^+$ signal at 1500°C, with the $^{61}\text{Ni}^+$ signal superimposed. Because of the relatively large amount of nickel present and its high sensitivity in ETV-ICP-MS, the ^{61}Ni signal was attenuated using the Omni-Range facility of the ICP-MS. According to the mass spectral studies of Drossler and Holcombe [103], nickel should be vaporized as elemental nickel at this temperature. The tailing of the $^{10}\text{B}^+$ peak is now much more evident at 1500°C and coincides with the development of the $^{61}\text{Ni}^+$ signal. Both peaks continue to tail throughout the 6 second "read" period. This suggests that, (i) the boron species, vaporized after 2.0 seconds, is co-volatilized with nickel metal and (ii) the vaporization of both boron and nickel is incomplete at this temperature, since the tails of both peaks have not returned to baseline after 6 seconds. This becomes clearer in Figure 14d (1650°C), where the tail at 1500°C now develops into a distinct and larger second peak.

Before discussing this double peak at 1650°C, it is important to dismiss the argument that it could arise from ion suppression effects caused by the presence of nickel in the plasma. This point has been addressed by Grégoire and Sturgeon [92] who showed that large ratios ($10^6:1$) of palladium modifier (10 μg) to tin analyte (10 pg) caused apparent "double" peaks for tin when the centre of the tin analyte signal was suppressed by the presence of a large excess of palladium in the plasma. This was accompanied by a simultaneous suppression of the argon dimer signal. This effect was not observed when the amount of palladium modifier was reduced to 0.5 μg . In our experiments, only 0.5 μg of nickel modifier was used, no perturbation of the argon

dimer was observed and the ratio of modifier to analyte used (200:1) was orders of magnitude lower than that used by Grégoire and Sturgeon. The ratio is also well below the values reported [104] to cause signal suppression in solution nebulization ICP-MS. Finally, the double peak observed at 1650°C does not occur when the vaporization temperature is increased to 1800°C (Fig.14e). At this temperature, the amount of nickel vaporized and transported to the plasma is equal to or greater than the amount vaporized at 1650°C, however, no peak doubling is observed at 1800°C. Thus, the double peaks should be interpreted in terms of changes to the graphite furnace chemistry rather than plasma effects.

The temperature region in which these double peaks occur (around 1650°C) coincides with the temperature at which the $^{61}\text{Ni}^+$ signal maximizes and also the temperature at which the maximum amount of boron is vaporized from the graphite furnace (Fig.14). Of the two peaks observed at this temperature, the earlier and smaller peak (0.5-1.8s) precedes the $^{61}\text{Ni}^+$ peak, while the larger peak, after 2 seconds, follows the release of nickel metal from the modifier. This suggests that there are two release mechanisms for boron at 1650°C. The earlier peak (about 20% of the total peak area) consists of boron that is not stabilized by the modifier. The larger peak originates from boron co-volatilized with the nickel modifier. This is confirmed by the increased peak width observed at 1650°C, in the presence of the modifier (Fig.14d). Here the peak tails beyond 5 seconds paralleling the tailing of the $^{61}\text{Ni}^+$ signal, which returns to background at the same time as the $^{10}\text{B}^+$. This can be compared with the much narrower peak obtained at 1600°C when no modifier is present (Fig.15). The precise chemical form

Figure 15 ETV-ICP-MS signal pulse for 2.5 ng of boron without a nickel modifier. The vaporization temperature used was 1600°C.

of the boron vaporized in each peak cannot be determined from these experiments, nor can the form in which the boron is bound within the nickel modifier be deduced. It is obvious, however, that the boron must be released in some molecular form, possibly as an oxide at this low temperature since no atomic boron appears in GFAAS below 2200°C. As the vaporization temperature is increased to 1800°C and 2600°C (Fig.14e,f), the two peaks now appear to coalesce into a single peak, although the earlier peak observed at 1650°C may have become the small shoulder on the leading edge of the peak at 1800°C. The single peak is now much narrower than the early peak at 1650°C. This is not surprising since the nickel modifier is vaporized more rapidly over a shorter time span as the temperature is ramped through 1650°C on its way to the higher vaporization temperatures.

The nickel modifier produces a marked enhancement effect for boron in ETV-ICP-MS. If the two vaporization curves for boron (Figs.12,13) are compared, the peak areas for $^{10}\text{B}^+$ are higher at all vaporization temperatures when the nickel modifier is present. Enhancement factors as high as ten are observed at vaporization temperatures of 1600 to 1800°C. This effect is unlikely to be caused by any specific chemical changes within the graphite furnace, but is more likely to arise from enhanced transport efficiency between the ETV and the plasma. A range of chemical modifiers [20] including $\text{Ni}(\text{NO}_3)_2$ [44] have been reported to enhance the analyte sensitivity in ETV-ICP-MS by reducing transport losses.

2.3.3 Boron Oxide Formation

In the presence of the nickel nitrate modifier, an increased signal was obtained in ETV-ICP-MS at mass 26. When this was corrected for isobaric interference from $^{26}\text{Mg}^+$ and blank subtracted, a relatively small residual peak area of up to 5000 counts remained. This is attributed to $^{10}\text{B}^{16}\text{O}^+$, which must be formed in the graphite furnace rather than by recombination in the plasma or interface region. If boron were to recombine with oxygen in the plasma, then boron oxide would be expected to be seen in the absence of the modifier, but when no modifier was present, no appreciable boron oxide was detected above background. The amount of $^{10}\text{B}^{16}\text{O}^+$ measured at each vaporization temperature is shown in Figure 13. Note that the peak area counts are scaled by a factor of 10.

The question that then arises is why should a small amount of $^{10}\text{B}^{16}\text{O}^+$ be observed in the presence of the nickel modifier, when none is formed in its absence. This can be explained by considering the nickel nitrate decomposition mechanism discussed earlier. As the nickel oxide begins to reduce at the graphite surface by reaction (12), at temperatures above 900°C, both CO and CO₂ are released into the graphite furnace. These gases can then react at higher temperatures with boron containing species to form boron oxide. Frech [100] has reported that the addition of as little as 0.3% CO to the argon purge gas is sufficient to almost completely suppress the boron atomic absorption signal in GFAAS. This suppression was explained using thermodynamic calculations, which show that the CO would convert boron to its oxide. This reaction would also explain the appearance of $^{10}\text{B}^{16}\text{O}$ in the presence of the nickel

modifier, which also produces an excess level of CO in the graphite furnace. No explanation can be provided for the decrease in the amount of boron oxide measured between 1500 and 1650°C, other than to comment that the minimum in the $^{10}\text{B}^{16}\text{O}^+$ signal corresponds with the maximum in the $^{10}\text{B}^+$ signal at 1650°C.

2.3.4 The Extent of Boron Pre-atomization Loss in GFAAS

In order to estimate the extent of pre-atomization loss occurring during a normal GFAAS determination of boron, the following experiment was conducted. After a 10 second pyrolysis step, the ETV was ramped at maximum power heating (0 second ramp) to 2000°C, held for the minimum possible time (1 second with the HGA-600MS furnace) and then cooled to room temperature in 2 seconds. After a 10 second hold at 20°C, the ETV was then re-heated to 2600°C. Any boron remaining after the initial vaporization ramp should then be detected in the re-firing. A temperature of 2000°C was chosen for the first vaporization ramp because this is just below the appearance temperature for boron in GFAAS and species removed from the furnace below this temperature would be those not detected in GFAAS. This experiment was conducted both with and without the nickel modifier and the results are shown in Figure 16.

When no modifier is present (Fig.16a), the larger peak at around 1 second corresponds to the pre-atomization loss in the initial temperature ramp. Any boron released in the firing at 2600°C should then appear at around 15 seconds. The expanded scale on the inset shows that it is difficult to detect any boron above background on re-firing. This means that in the absence of any modifier virtually all of the boron is removed from the furnace at temperatures below its atomization temperature. With the

2

PM-1 3½"x4" PHOTOGRAPHIC MICROCOPY TARGET
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Figure 16. ETV-ICP-MS signal pulses for 2.5 ng of boron during vaporization to 2000°C (<3 s), cool down at 20°C (3-15 s) and re-vaporization at 2600°C (>15 s): (a) without modifier; (b) with modifier.

addition of the nickel modifier (Fig.16b), the majority of the boron is still lost in the vaporization ramp, but a small percentage remains and is released in the firing at 2600°C, as evidenced by the small peak after 15 seconds in the inset. The mechanism by which the nickel modifier retains this relatively small amount of boron is unclear. It has been shown [103], however, using XPS and depth profiling of the graphite surface with Ar⁺ sputtering, that nickel is intercalated with graphite to depths of 50 μm after the high temperature atomization step. It is possible that boron is retained in some form bound with the intercalated metal.

2.4 SUMMARY AND CONCLUSIONS

The poor sensitivity for the determination of boron in GFAAS can be explained by extensive pre-atomization loss of molecular species from the graphite furnace at temperatures well below the appearance temperature of boron atoms. The onset of this loss is at around 800°C, far below the temperature at which boron carbide would be expected to form. Thus, carbide formation is not the major cause for the reduced sensitivity; in fact it may well be that the very small fraction of total boron observed at atomization in GFAAS originates from retained boron carbide. These results show that the addition of a chemical modifier such as nickel nitrate is largely ineffective in preventing pre-atomization loss. In the presence of the modifier, there is an improvement in the amount of boron retained during atomization, but the majority (>95%) is still lost prior to atomization. In addition, the amount of BO formed during vaporization is enhanced by the presence of the nickel modifier. If a major improvement in the sensitivity for boron determination by GFAAS is to be achieved,

then a more effective chemical modifier is required. Such a modifier should (i) retain the boron analyte to a higher vaporization temperature and (ii) promote the release of boron analyte as atoms, rather than in the form of oxide, during vaporization.

With regard to ETV-ICP-MS, our results show that the optimum vaporization temperature for the determination of boron is around 1800°C. Above this temperature, the boron peak areas decrease possibly because of the formation of molecular species, either BO or BC, which remain undissociated or unionized in the plasma. The addition of a nickel chemical modifier results in sensitivity enhancements of up to a factor of 10 for the determination of boron by ETV-ICP-MS. This enhancement is higher than that reported for a number of elements [20] and suggests that boron may be particularly prone to transport loss in ETV-ICP-MS at temperatures above 2000°C.

CHAPTER 3. VAPORIZATION AND ATOMIZATION OF BORON. PART II. INVESTIGATED BY DIGITAL IMAGING WITH A CHARGE COUPLED DEVICE (CCD) CAMERA

3.1 INTRODUCTION:

The spatial and temporal distributions of atomic and molecular species in graphite tube electrothermal vaporizers (ETVs) have been reported by a number of researchers [105-114]. Understanding the spatial and temporal evolution of the gas composition inside the graphite tube is crucial for delineating the mechanisms of analyte atomization in graphite furnace atomic absorption spectrometry (GFAAS) and of analyte desorption in electrothermal vaporization inductively-coupled plasma mass spectrometry (ETV-ICP-MS). Such understanding could lead to improvements in the use of heated graphite tubes as sample introduction devices for ETV-ICP-MS.

A number of experimental techniques have been described for determining the spatial and temporal distribution of analytes during atomization for GFAAS. Using a spatial isolation wheel (SIW), Holcombe and co-workers [105,106,107] obtained spatial and temporal absorbances over the vertical diameter of the furnace. The SIW technique clearly revealed the extremely non-uniform distributions of many atomic species inside the graphite tube. Spatial mapping of sodium atoms using a laser-based silicon vidicon imaging system was described by Huie and Curan [108-109]. Their studies also confirmed the non-uniform distribution of free atoms as well as pointed to a strong interaction of sodium atoms with the graphite surface. Frech and co-workers [110] used a simpler, more direct, approach for determining such spatial distributions of atomic and molecular species. For their work, two circular apertures placed at the centre of the

optical axis at both ends of and close to the atomizer permitted spatially resolved absorbance measurements to be made across the tube diameter, as the graphite tube was transversed up and down relative to the incident light beam.

The study of spatial and temporal distributions of atoms and molecules in a graphite tube atomizer was significantly advanced by Gilmudtinov et al.[111,112,113] using the technique of shadow spectral filming (SSF). Their SSF technique employed a cine camera as a detector while the interior of the graphite furnace was backlighted with an appropriate light source, such as a hollow cathode lamp. Chakrabarti and co-workers [114] improved the SSF technique by replacing the film and cine camera with a charge-coupled device (CCD) camera system. The CCD was connected to a personal computer, making data acquisition convenient. The digital images of the interior of the graphite tube are readily available for data manipulation, enabling the development of refined computer models [115]. For this work, CCD imaging of the graphite tube atomizer was used to investigate the spatial and temporal distribution of molecular and atomic boron species during the high-temperature atomization step. Boron is one of a number of elements exhibiting poor sensitivity in GFAAS. It can be routinely analyzed, however, with ETV-ICP-MS at the nanogram level. The data obtained from the CCD camera can be combined with data from ETV-ICP-MS and GFAAS techniques to identify gaseous species. Experiments presented in the previous chapter showed that $^{10}\text{B}^+$ could be detected at 800°C using ETV-ICP-MS, which is well below the appearance temperature for atomization (2200°C) in GFAAS. It was concluded that most of the boron was vaporized in molecular form prior to the appearance of boron

atoms in GFAAS. This conclusion is in agreement with the thermodynamic equilibrium calculations of Frech et al. [100].

The objective of this research was to obtain spatial and temporal distributions of molecular boron species and atomic boron species during the high temperature vaporization/atomization step. Spatial measurements of molecular and atomic species can provide chemical information regarding the mechanism of vaporization and atomization of boron. The information gained from the CCD images can then be used to evaluate the extent of pre-atomization loss of boron as oxide in GFAAS. Previous work with the ETV-ICP-MS demonstrated that higher $^{10}\text{B}^+$ signals could be obtained at 1800°C, compared to those generated at 2600°C. Imaging experiments with the CCD camera provided useful information with which to explain this phenomenon.

3.2 EXPERIMENTAL

A Perkin-Elmer HGA-500 graphite furnace together with its power supply was used for all experiments. The temperature programs for the vaporization and atomization of molecular and atomic species are summarized in Table 7. Perkin-Elmer pyrolytic coated graphite tubes (part No. B0091504) were used in all experiments. Temperature measurements of the graphite tube were made by focusing an Ircon 1100 Series (Ircon, Inc. Niles, IL) automatic optical pyrometer onto the surface of the interior tube wall and collecting the output on a Nicolet Series 4094 oscilloscope (Nicolet Corp.).

Strong molecular absorption bands for BO exist at 254.4 and 255.1 nm [116]. The 253.7 nm resonance line of mercury is coincident with this molecular boron

Table 7. Temperature program for determining the spatial distribution of molecular and atomic boron species during vaporization and atomization in a graphite tube ETV.

Step	Temperature (°C)	Time (s)	Internal Purge Gas Flow (mL min ⁻¹)
Dry	130	Ramp=10 Hold=30	300
Pyrolysis	400	Ramp=2 Hold=10	300
Vaporization (molecular)	2000	Ramp=0 Hold=6	0-20
Atomization	2600	Ramp=0 Hold=6	0
Clean-up	2700	Ramp=0 Hold=5	300

absorption band. Therefore, a mercury electrodeless discharge lamp (Perkin-Elmer) was used to illuminate the graphite tube interior for imaging the distributions of molecular species inside the tube. Other molecular species, which absorb light between 250 and 260 nm (such as CN), were ruled out as their molecular absorption bands are not intense [116] and no molecular absorption was observed during blank firings. Carbon monoxide molecular absorption bands, which are intense at these wavelengths, are also ruled out as no molecular absorption was observed during blank firings. Boron nitride (BN) is also ruled out as there are no molecular absorption bands at these wavelengths [116]. A boron hollow cathode lamp (Perkin-Elmer) was used for imaging the spatial distribution of boron atoms at 249.7 nm. A plano-convex lens (focal length 150 mm) collimated the emitted radiation from the primary light source and a bi-convex lens (focal length 125 mm) focused the light from the interior of the graphite tube onto the CCD. Narrow bandpass interference filters (Andover Corporation) were used to isolate the molecular bands and atomic lines. For both the molecular boron species and atomic boron, a 254 ± 5 nm interference filter was used. The molecular boron species could easily be differentiated from atomic boron by large differences in their appearance temperatures. This was confirmed by imaging both molecular and atomic boron at different temperatures. Because μg quantities of boron were used, experiments were performed to check for light scattering inside the graphite tube. For these experiments, a Perkin-Elmer 603 atomic absorption spectrophotometer was used with an HGA-500 graphite furnace, together with its power supply. A Perkin-Elmer deuterium arc background corrector was also used in some of these experiments. The current in the

continuum source (deuterium lamp) was maintained constant and the gain on the photomultiplier tube was adjusted to normalize the measured light intensity over the range of wavelengths studied. Because boron oxide (BO) has a large number of absorption bands in both the visible and the ultraviolet regions of the spectrum [116], several hollow cathode lamps were used to isolate specific spectral lines. The hollow cathode lamps used were: Hg at 253.7 nm; Pt at 265.9 nm; Cr at 357.9 nm and Y at 407.7 nm. The ETV-ICP-MS was used to check for contamination of any of these elements in the boric acid solution and subsequently, none was found. For all of the light scattering experiments, a spectral band width of 0.14 nm was used.

The CCD detector was a Photometrics Series 200 CCD camera consisting of a CH250/A camera and a Thomson Th7883 CCD chip. Detection in the ultraviolet region is made possible by a Metachrome II coating on the working surface of the chip. The CCD chip was used in the frame transfer mode, whereby only half of the CCD chip is illuminated. The collected images were subsequently transferred to the other half of the chip to be read out and digitized. A variable frequency chopper was used to avoid image blurring during data transfer. An iris diaphragm was placed between the lens and the filter to reduce the amount of background radiation striking the CCD chip. Flexible bellows were used to house the filters as well as to keep stray light from interfering with the image. Figure 17 shows a schematic diagram of the apparatus used to image boron molecular and atomic species.

To obtain absorbance values with the CCD camera, three images were collected. The first image (Signal) was obtained with the hollow cathode lamp and graphite

furnace power supply turned on. The second image (Background) was obtained with the power supply turned off and the hollow cathode lamp turned on. The third image (Reference) is obtained with the hollow cathode lamp turned off and the graphite furnace power supply turned on. Absorbance can then be calculated by:

$$A = -\log \left(\frac{\text{Signal} - \text{Background}}{\text{Reference}} \right) \quad (15)$$

A $500 \mu\text{g mL}^{-1}$ standard stock solution of boron was prepared by dissolving boric acid (Baker Analyzed) in ultra pure water, obtained from a Milli Q water purification system ($18.3 \text{ M}\Omega\text{cm}$ resistivity; Millipore Corp.) and high purity argon gas (Liquid Carbonic Inc.) was used throughout. Typically, $5 \mu\text{g}$ of boron (deposited as the boric acid) was used for imaging the atomic and molecular boron species with the CCD camera.

3.3 RESULTS AND DISCUSSION

A 5 ms exposure time was used, which in conjunction with the data transfer time (approx. 44 ms), permitted images to be collected at a rate of 20 Hz. In all images (Figs.20(a)-23(a)), the dark regions inside the graphite tube represent areas of highest absorption of light and therefore, highest concentrations of either atoms or molecules of boron.

Figure 17. Schematic diagram of the CCD imaging apparatus.

3.3.1 Light Scattering of the Primary Source

Light scattering of the primary source of radiation was tested using the HGA-500 power supply and the same graphite furnace as that used for the CCD imaging experiments. The absorption signals were recorded using a Nicolet Series 4094 oscilloscope (Nicolet Corp.). Atomization of boron at 2600°C produced no light scattering at 249.7 nm. At a temperature of 1800°C, suitable for imaging boron-containing molecules, Frech and L'vov [117,118,119] have reported that μg quantities of analyte will scatter light. Evidence for the occurrence of light scattering in these experiments at 1800°C was obtained by recording non-specific absorbance signals at a number of wavelengths, specifically, the wavelength region where BO molecular absorption bands were absent. The non-specific absorbance signals were recorded and their wavelength dependence is shown in Figure 18. For Rayleigh scattering, the intensity of scattered light should vary inversely as the fourth power of the wavelength. Frech et al. [119] have demonstrated that this relationship is applicable to the rising part of the absorbance signal, when μg amounts of analyte are used. Figure 18 shows that the absorbance signal below 254 nm was independent of the wavelength, whereas above 254 nm, the results show some correlation with Rayleigh scattering. For particles which are larger than the wavelength of the incident radiation, Mie scattering will also arise. Mie scattering predicts that the intensity of scattered light varies inversely as a power of wavelength, depending on the particle size. The non-specific absorbance seen in Figures 18,19 may be due in part to Rayleigh and Mie scattering, but this does not account for all of the signal, particularly at the lower wavelengths. Therefore, some of

Figure 18 Absorption signals at various wavelengths using $5\ \mu\text{g}$ of boron at 1800°C under gas-stop conditions. (A) 254 nm ; (B) 231 nm ; (C) 213 nm ; (D) 360 nm.

the absorbance must be a result of absorption of light by molecular boron species.

For at least semi-quantitative delineation of the individual contributions of the light scattering component and the molecular absorbance component of the measured signals, the signals were recorded at a non-specific wavelength of 360 nm, with and without the dosing hole of the graphite furnace sealed and compared with absorbance signals obtained for the BO at 254 nm. Frech et al. [117] reported that when the ingress of air through the dosing hole was eliminated by sealing it, light scattering disappeared completely. In agreement with their findings, the non-specific absorbance signal at 360 nm (due to light scattering) was reduced almost to zero when the dosing hole was sealed, as shown in Figure 19. When similar experiments were conducted at 254 nm, however, sealing the dosing hole did not greatly reduce the absorbance signal, indicating that, in this case, a major portion of the attenuation of light could be attributed to factors other than light scattering. This suggests that with the dosing hole open, the images obtained with the CCD camera contain a light scattering component and a molecular absorption; whereas when the dosing hole is sealed, the images correspond to the absorption by molecular bands of boron oxide species only. Because the absorbance at 254 nm was reduced by approximately 50% when the dosing hole was sealed, the molecular absorption images obtained with the CCD camera probably contain approximately a 50% light scattering component of the absorbance observed with the dosing hole open.

Figure 19. Effect of (i) open and (ii) sealed dosing hole at: (a) a wavelength specific to BO absorption (254 nm) and (b) a non-specific absorption (360 nm), for vaporization of 5 ng boron at 1800°C.

3.3.2 Vaporization of Molecular Boron Species

Imaging of molecular boron species was performed using 10 μL of a boric acid solution (corresponding to 5 μg of boron) deposited on the wall of the graphite furnace. This amount of boron was more than that required for detection by GFAAS and was significantly more than that required for detection by ETV-ICP-MS, however, it was the minimum amount for reliably imaging molecular boron species using the CCD with a 5 ms exposure time. The images in Figures 20-23 clearly reveal highly non-uniform distributions of these boron species in the graphite furnace during the high temperature vaporization step. Figure 20 ((a) and (b)) presents a temporal sequence of images due to absorption by molecular boron species and a light scattering component. The absorbance contour maps (Fig 20(b)) correspond to the images in Figure 20(a) that have the same Roman numeral. Because the molecular band component and the light scattering component of the absorbance signal are both due to boron species, (the former vapour-phase boron species and latter particulate boron species) and these two components cannot be experimentally differentiated with our facilities, the resulting signal will be simply called 'molecular absorbance'.

Early in the heating cycle (Figs.20(a) ii and iii), molecular boron species are evolved predominantly from the top of the graphite tube. In Figure 20((a) i), the molecular boron species first appear at 350 ms into the high temperature step, corresponding to an estimated appearance temperature of $1670 \pm 30^\circ\text{C}$. Between 400 ms and 500 ms, the molecular boron species gradually fill most of the graphite tube volume, as the temperature increases (from 1700°C to $1810^\circ\text{C} \pm 30^\circ\text{C}$). From Figure

Figure 20a. Vaporization of molecular boron species at 2000°C under gas-stop conditions using 5 μ g B with the dosing hole open. Sequence of images obtained using the CCD (i) 350ms; (ii) 400 ms; (iii) 450 ms; (iv) 500 ms; (v) 550 ms; (vi) 600 ms; (vii) 650 ms; (viii) 700 ms.

Figure 20b. Absorbance contour maps corresponding to Fig. 20a using $5 \mu\text{g}$ boron, with the dosing hole open.

20 ((a) ii to v), a radial decrease in the concentrations of molecular boron species toward the tube walls is observed, which becomes especially evident at the bottom of the graphite tube. The contour maps (Fig.20(b) ii and iii) reveal, quantitatively, a non-uniform distribution of molecular boron species inside the graphite tube early in the vaporization step. With increasing temperature of the graphite tube, this non-uniformity is intensified. Subsequent distributions are influenced by such factors as: increased partial pressure of molecular boron species caused by increasing temperature and convective flows of gas convoluted with light scattering in the vicinity of the dosing hole (Fig.20(b) iv and vii). The appearance of molecular boron species at the centre of the tube, away from the graphite walls, suggests that a gas-phase process is occurring. The region at the bottom of the graphite tube has the lowest concentration of molecular boron species, probably because it has lower levels of O_2 and is more reducing than the region at the top of the graphite tube.

Formation of a number of volatile boron oxide species in the graphite tube at temperatures below 2000°C , including HBO_2 (g), B_2O_2 (g) and BO (g), have been reported. The maximum concentrations of molecular boron species are formed at temperatures of 1800 - 2000°C [100]. According to Frech et al. [100], the formation of HBO_2 (g) occurs in the temperature range 800 - 1600°C , B_2O_2 between 1800 - 2200°C and BO (g) between 1400 - 2200°C . It should be noted that although the above species are thermodynamically predicted, the graphite furnace is not in thermodynamic equilibrium, but as an approximation, it is not reasonable to conclude that the absorbance signals measured in this study are due to boron oxide species and include both the light

scattering and the molecular absorbance components.

The significantly lower concentrations of molecular boron species near the tube walls may be due to heterogeneous reactions which occur at the heated graphite surface, transforming the boron oxide species to elemental boron and boron carbide, $B_4C(s)$. The predicted appearance temperature of boron at 2300°C , reported by Frech et al. [100], correlates well with the appearance temperature of boron obtained using the CCD camera and confirms that atomic boron is not formed below 2300°C . Additionally, the formation of $B_4C(s)$, which can occur at temperatures as low as $1800\text{--}2400^\circ\text{C}$, may account for the significantly lower concentration of gaseous molecular boron species near the tube walls.

The observed appearance of molecular boron species at the top of the graphite tube is unusual. Gilmudinov et al. [111,112,113], by contrast, observed the evolution of molecular aluminum oxide from the bottom of the graphite tube. A possible explanation is that a volatile molecular boron oxide, such as B_2O_3 or boron suboxides are vaporized and redistributing, via the gas phase, over the walls of the graphite tube.

Experiments were conducted to examine the effect of an internal purge gas flow in the graphite tube. Frech et al. [117] have shown that the scattering intensity of particles was highest near the dosing hole. Argon flows up to 20 mL min^{-1} were successfully used. It has been reported [117] that a mini-flow (10 mL min^{-1}) in the graphite furnace eliminates the light scattering component entirely. Higher argon purge gas flows (50 mL min^{-1}) were attempted but, with the use of the maximum heating program of the Perkin-Elmer graphite furnace, no boron molecular species were

observed. This is to be expected since images are obtained at a rate of 20 Hz and only seven frames of useful absorbance data can be collected during vaporization under stop-flow conditions. This number of frames requires about 0.35 s to collect. As the internal volume of the graphite tube is 0.8 mL, a flow rate of 20 mL min⁻¹ would sweep the internal volume once every 0.33 s. Therefore, flow rates higher than 20 mL min⁻¹ significantly reduce the number of useful images collected during the vaporization. Figures 21 ((a) and (b)) show the distribution of molecular boron species obtained under gas-flow conditions (10 mL min⁻¹). The absorbance contour maps (Fig.21(b)) correspond to the images in Figure 21(a) that have the same Roman numeral. For these experiments, 5 μ g of boron from the boric acid solution was deposited on the walls of the graphite tube. As with the images obtained under gas-stop conditions, the radial distribution of molecular boron species during the vaporization is non-uniform and the concentration decreases toward the bottom of the tube (Fig.21(a) i-vii). Again, the highest concentrations of molecular boron species are found at the top of the graphite tube. As expected, the absorbance contour maps show less radial uniformity in the distribution of molecular boron species from the walls of the graphite tube (Fig.21(b) ii and iii) under gas-flow conditions compared to gas-stop conditions. It is clear that, under gas-flow conditions, there is now a decrease in the concentrations of molecular boron species at the centre of the graphite tube. Assuming a laminar flow of the purge gas, the gas velocity should be highest at the graphite tube centre, decreasing to zero at the wall surface, resulting in dilution of the analyte species at the centre of the graphite tube. As well, there should be a decrease in the flux of O₂ diffusing into the

Figure 21a. Vaporization of molecular boron species at 2000°C under gas-flow conditions (10 mL min^{-1}) using $5 \mu\text{g}$ of B (as boric acid). Sequence of images obtained using the CCD: (i) 350 ms; (ii) 400 ms; (iii) 450 ms; (iv) 500 ms; (v) 550 ms; (vi) 600 ms; (vii) 650 ms; (viii) 700 ms.

Figure 21b. Absorbance contour maps corresponding to Fig. 21a using 5 μg boron under gas-flow conditions.

graphite tube against the outward flow of the exiting internal purge gas, resulting in a decrease in the oxidizing atmosphere at the centre of the graphite tube, just below the dosing hole. The relatively high concentration of molecular boron species (probably oxides) close to the dosing hole suggests that they are still being formed under these conditions. It is of interest to note that, although a flow of argon is exiting the dosing hole, the highest concentration of molecular boron species is still located at the top-central position of the graphite tube, but not directly under the dosing hole.

To determine the influence of the dosing hole in the evolution of molecular boron species, a third set of experiments was undertaken in which the dosing hole was sealed with a graphite plug. Figure 22 ((a) and (b)) shows the images for vaporization of 5 μg boron, (taken as the boric acid) from the wall of the graphite tube with the dosing hole sealed. The absorbance contour maps (Fig.22(b)) correspond to the images in Figure 22(a) that have the same Roman numeral. The small shadow in the upper left corner of the images is the tip of the graphite plug protruding through the dosing hole. As shown in Figure 19, sealing the dosing hole reduces the light scattering at 360 nm inside the graphite tube almost completely, making the molecular boron species the predominant contributor to the observed absorbance. This has a noticeable effect on the resultant images, particularly at the centre of the graphite tube, compared to those obtained with an open dosing hole. When the dosing hole is open, the distribution of the boron molecular species during the vaporization process is non-uniform and their concentrations gradually decrease toward the bottom of the graphite tube (Fig.22(a) i-viii)). The absorbance contour maps (Fig.22(b) ii-vii) clearly show the highest

Figure 22a. Vaporization of molecular boron species at 2000°C under gas-stop conditions using 5 μg B with the dosing hole sealed. Sequence of images obtained using the CCD: (i) 350 ms; (ii) 400 ms; (iii) 450 ms; (iv) 500 ms; (v) 550 ms; (vi) 600; (vii) 650 ms; (viii) 700 ms.

(ii)

(ii)

(iii)

(vii)

Figure 22b. Absorbance contour maps corresponding to Fig. 22a, using 5 μg of boron with the dosing hole sealed.

concentrations at the top of the graphite tube. The radial distributions of the desorbed molecular boron species appear to be less uniform, compared with those obtained with the dosing hole open. When the dosing hole is sealed, high concentrations of molecular boron species are still observed in the graphite furnace. The prominent maximum, in the tube centre, however, is now absent, suggesting that sealing the dosing hole, prior to the vaporization step, reduces the light scattering component of the signal, possibly by preventing the ingress of cooler air into the graphite furnace. As the graphite plug is cooler than the tube wall, condensation of boron oxide on the plug may occur. The condensed boron oxide may then be reduced and released as boron suboxides. There is no experimental evidence to prove this process is occurring because the highest concentrations of molecular boron oxide appear to originate in the centre of the graphite furnace and away from the plug.

In all experiments, molecular boron species initially appeared at the top of the graphite tube and were not found to originate from the initial deposition site under any conditions. This became more evident following experiments using a lower heating rate which revealed the appearance of molecular boron species in the upper centre of the graphite tube. At low temperatures, volatile boron oxide(s) (probably $B_2O_3(g)$ [120,121] and possibly $HBO_2(g)$ and $B_2O_2(g)$, which do not absorb or scatter light at 254 nm) are probably formed. Atomic boron is not produced at these temperatures, as evidenced by GFAAS measurements. No atomic boron could be seen using either a photomultiplier tube or the CCD camera as a detector at these initial, low temperatures. Once vaporized from their initial site of deposition, the boron-containing oxide(s) may

be thermally dissociated in the gas phase, or possibly reduced, upon collision with the furnace wall, forming sub-oxides, which have higher boiling points. When the atmosphere inside the graphite tube becomes saturated with the partial pressures of the molecular boron species, they may condense into fine particles, thereby adding a light scattering component to the absorbance signal obtained with the CCD camera.

The concentration of molecular boron species is highest in the middle of the furnace and decreases toward the bottom of the furnace. This may be due to the fact that, with this experimental set-up, there is no significant axial flow of gas in the centre of the tube under gas-stop conditions. Using images for aluminum, obtained from the CCD camera study done by Chakrabarti et al. [114], L'vov [122] interpreted the aluminum cloud structure in the graphite furnace as the formation of condensed-phase particles at the furnace ends rather than at the furnace centre. Unlike the aluminum species, the images of the boron species appear at the beginning of the vaporization step and it is impossible to say with any certainty whether the vapour cloud forms at the cooler ends of the furnace and/or in the centre of the furnace.

3.3.3 ATOMIZATION OF BORON

Figures 23 ((a) and (b)) show the spatial distribution of boron atoms in the graphite furnace at 2600°C. The absorbance contour maps (Fig.23(b) correspond to the images in Fig.23(a) that have the same Roman numeral. For these experiments, 5 μg of boron (as boric acid) was deposited on the bottom wall of the graphite furnace. Atomization was carried out under gas-stop conditions using the maximum power heating mode. Atomization temperatures as high as 2700°C were studied but, as there

Figure 23a. Wall atomization of $5\ \mu\text{g}$ boron at 2600°C under gas-stop conditions with the dosing hole open. Sequence of images obtained using the CCD: (i) 350 ms; (ii) 400 ms; (iii) 450 ms; (iv) 2500 ms; (v) 2550 ms; (vi) 2600 ms; (vii) 2650 ms; (viii) 2700 ms.

(ii)

(iii)

(iv)

(vi)

Figure 23b. Absorbance contour maps corresponding to Fig. 23a for the atomization of 5 μg boron.

was no improvement in the CCD images at such high temperatures, a temperature of 2600°C was subsequently used throughout. No atomic boron was detected with the CCD camera below 2400°C and no molecular boron species were observed above 2200°C. Unlike the molecular boron species, atomic boron concentrations were highest along the graphite furnace walls and lowest at the tube centre, notably at the beginning and the end of the high temperature atomization event. The spatial distribution of boron atoms at the beginning (Fig.23(a) ii and iii) and at the end of atomization (Fig.23(a) vii and viii) show the least uniformity. Unlike the distribution of molecular boron species during vaporization, a near-uniform distribution of boron atoms can be observed at the time of the occurrence of the maximum atom population (Fig.23(a) v and vi). The absorbance contour maps of boron atomization reveal that early in the atomization step (Fig.23(b) ii) and late in the atomization step (Fig.23(b) vi), the absorbance signal near the tube walls was about two-fold higher than that at the centre of the graphite furnace. A question arises as to whether the atomic boron signal contains a component of absorption by molecular boron species. Experiments were conducted at 283 nm where a strong BO absorption band occurs without a boron atomic absorption line. Images of molecular boron species were obtained with no evidence of atomic boron at 1800°C. When images were collected at 2600°C, neither atomic nor molecular species were detected. Based on these experiments, it was concluded that the atomic boron signal contains no contribution from molecular boron oxide absorption.

A transient absorbance signal for boron was recorded by GFAAS using 25 ng of boron and is shown in Figure 24. The absorbance signal rises sharply to its

maximum, then falls off gradually and does not return to the baseline. This observation is in agreement with that of Wiltshire et al. [123] who suggest that once formed, boron atoms undergo a series of "condensation-vaporization steps" resulting in a persistent plateau in the atomic absorption signal. This tailing may be indicative of slow atomization of refractory boron carbide (B_4C (s)) at high temperatures.

Transient signals for $^{10}B^+$ were also detected using ETV-ICP-MS at the two temperatures used in this study. Figure 25 shows the transient $^{10}B^+$ signal at 1800°C and at 2600°C, under the experimental conditions used for CCD imaging of both the molecular boron species and the atomic boron. In chapter 2 it was suggested that there was a 95% loss of boron, as molecular species, prior to atomization in GFAAS. The ETV-ICP-MS results combined with the CCD images confirm the observed atomization loss of boron as molecular species in GFAAS. The extent of pre-atomization loss of boron is evident with the ETV-ICP-MS system (Fig.25) as molecular boron species can be observed with the CCD camera at 1800°C. At this temperature, no atomic signal for boron is detected in GFAAS using either a photomultiplier tube or a CCD camera; hence, the ETV-ICP-MS signal arises from vaporization of molecular boron species. At higher temperatures (2600°C), the ETV-ICP-MS signal pulse is smaller than that at 1800°C. Since the ETV-ICP-MS signal is comprised of $^{10}B^+$ originating from molecular boron species as well as from atomic boron, the CCD makes it possible to determine qualitatively how much of the $^{10}B^+$ signal originated from the vaporized boron molecular species in the graphite tube at 2600°C. At temperatures greater than 2200°C, molecular boron species were not observed with the CCD; hence it is reasonable to

Figure 24. Transient absorbance signal of 25 ng boron using GFAAS at 2600°C.

Figure 25. Transient signal of 2.5 ng $^{10}\text{B}^+$ using ETV-ICP-MS at two temperatures:
(a) 1800°C and (b) 2600°C.

conclude that relatively more of the $^{10}\text{B}^+$ signal pulse is due to atomic boron and possibly boron carbide, originating in the graphite tube at 2600°C rather than at 2200°C. The decreased signal observed with ETV-ICP-MS at 2600°C (relative to that at 1800°C) may be explained by the difference in transport efficiencies of different species vaporized in the graphite tube. In general, gaseous atoms are more reactive than their corresponding oxides, therefore, at the lower vaporization temperature, the volatilized species, being predominantly molecular boron species, are less prone to interaction with the ETV or the transfer line. Since boron oxide species are more volatile than atomic boron, they are also less likely to condense on the cooler surfaces of the ETV or the transfer line. Vaporizing boron as the oxide at 1800°C increases the vaporization and the transport efficiency of boron to the ICP-MS compared to vaporizing boron as atomic species at 2600°C. The absence of molecular boron species at 2600°C confirmed with the CCD technique shows that the decrease in $^{10}\text{B}^+$ ETV-ICP-MS signal at 2600°C is not due to boron species remaining undissociated and unionized in the plasma; rather, it is likely caused by the vaporization of boron atoms (at 2600°C) which are less efficiently transported to the plasma.

The CCD images and the ETV-ICP-MS results are consistent with the following reactions occurring during the vaporization and atomization of boron in the graphite furnace.

Vaporization of Boron Oxide in the Gas Phase: (<1800°)

At low temperatures, $\text{B}_2\text{O}_3(\text{s})$ is vaporized, possibly forming sub-oxides [120,121] as follows:

The vaporization of boron oxide (at temperatures < 1800°C) is supported by the evidence obtained from the ETV-ICP-MS results in the previous chapter where $^{10}\text{B}^+$ was produced by sampling the vapours evolving from the graphite furnace at temperatures as low as 800°C. Similar results have been reported for boron using a tungsten boat and measured by ICP-AES [124]. The absence of absorption by molecular species near the initial site of deposition indicates that volatilization of boron occurs predominantly as boron oxide species which do not absorb light at 254 nm.

Thermal Dissociation of Boron Oxide in the Gas Phase: (1800-2000°C)

Figures 20 ((a) and (b)) show that the highest absorption/scattering appear at the centre, near the top of the graphite furnace. Since the highest concentrations of molecular boron species are not detected at the tube wall, direct desorption of $\text{BO}(\text{g})$ is not likely. The absence of detectable molecular boron species at the graphite wall suggests that either complete reduction of boron oxide occurs or desorption occurs predominantly as non-absorbing higher oxides (at 254 nm). The latter is not likely, as no atomic boron is produced in coincidence with the detection of atomic boron. As the furnace temperature increases, thermal dissociation of boron oxide [120,121] occurs as a homogeneous reaction shown below.

The persistence of $\text{BO}(\text{g})$ at the centre of the graphite furnace is consistent with the above scheme of reactions since the bond strength of BO (806 kJ mol⁻¹) is relatively

high [125].

When the dosing hole is open, temperature and concentration gradients of O_2 exist inside the graphite furnace [115,117]. When the dosing hole is sealed (Fig.22 ((a) and (b))), the light scattering component is significantly reduced or eliminated and therefore, the majority of the absorption signal is a result of molecular absorption. It should be noted, however, that sealing the dosing hole leads to a large, rapid increase in the pressure inside the graphite tube, which may alter the distribution of vaporized molecular boron species; hence, a rigorous comparison of these distributions with those obtained for boron oxide under normal experimental conditions (i.e., with an open dosing hole) is not justified.

Reduction of Boron Oxide at the Graphite Tube Wall Surface: ($>2300^\circ C$)

When the atomization temperature is reached ($2300^\circ C$), only a small amount of boron ($<5\%$) is retained in the graphite furnace, probably as boron oxide, elemental boron or boron carbide. Reduction and redistribution of boron oxide is likely the single most important event to occur prior to atomization. Desorption of atomic boron from the graphite tube walls only occurs at higher temperatures ($>2200^\circ C$), resulting in the observed radial symmetric cloud of $B(g)$ desorbing from the tube walls (Fig.23(b) ii). The absence of molecular boron species near the tube wall under all conditions rules out a homogeneous atomization mechanism of $BO(g)$ in the gas phase. Since the BO and the $B^\circ(g)$ signals obtained with the CCD camera do not overlap temporally, they probably do not share a common precursor. Therefore, the AAS signal for boron is not likely due to direct dissociation of any boron oxide species in the gas-phase. Possible

sources of boron atoms in the graphite furnace include homogeneous and/or heterogeneous atomization of boron oxide from the graphite surface and heterogeneous atomization of $B_4C(s)$ from the graphite surface. It is likely that much of the atomic boron signal is a result of desorption of B from the decomposition of $B_4C(s)$. The following reaction occurs at higher temperatures ($>2300^\circ C$) only:

The formation of refractory $B_4C(s)$ accounts for the tailing in the GFAAS signal for B; additionally, the slow release kinetics of B from $B_4C(s)$ accounts for the low analytical sensitivity.

3.4 SUMMARY AND CONCLUSIONS

Some researchers [126,127,128] have suggested that the primary reason for the poor sensitivity for boron by GFAAS is the formation of boron carbide. From this study, it is clear that this element is vaporized as molecular boron species (probably oxide) prior to atomization. It is this pre-atomization loss of boron, as the oxide, that is the main cause for the poor analytical sensitivity. Vaporization of molecular boron species at low temperatures in the graphite furnace is supported by the evidence provided by the ETV-ICP-MS results in Chapter 2.

By using the CCD camera as a detector, it was possible to image molecular boron species over a range of temperatures up to about 1800 to $2000^\circ C$, but not higher. This strongly suggests that the decreased $^{10}B^+$ signals with ETV-ICP-MS at temperatures above $2600^\circ C$ are probably a result of the lower transport efficiency of the atomic boron species, compared to molecular boron species.

4.1 INTRODUCTION

Electrothermal atomizers have been used for the determination of Rare Earth Elements by atomic absorption spectrometry (AAS) [129,130,131] for thirty years, however, the formation of thermally stable oxides, monoxides and refractory carbides results in memory effects and decreased sensitivity for these elements. Metal vaporization surfaces such as tungsten or tantalum have been successful to some extent in overcoming these problems [132,133,134] and limits of detection have been improved by 2 orders of magnitude.

More recently, inductively coupled plasma mass spectrometry (ICP-MS) has been employed for determining trace levels of REEs. Several papers have been published using solution nebulization (SN) ICP-MS for the determination of REEs [135,136,137]. Solution nebulization as a means of sample introduction loads the argon plasma with water, which results in relatively high levels of analyte or matrix component oxides while requiring sample volumes of 1 to 10 mL for a single analysis. Electrothermal vaporization introduces analyte into a dry plasma, substantially reducing oxide formation, while requiring only μL volumes of sample solution. Other advantages include the removal of matrix components via a pyrolysis heating step and/or the use of chemical modifiers.

To date, few studies have been published on the use of ETV-ICP-MS for the determination of REEs. Shibata et al. [31,33] studied the use of a tungsten furnace for

the vaporization of REEs into an ICP-MS. Various plasma and ETV conditions were examined and optimized for Y and the REEs. Grégoire et al. [140] applied ETV-ICP-MS to the determination of some REEs in single zircons. A mixed component carrier (NASS-3 open ocean sea water) was used in this study to improve transport of the analyte from the ETV to the argon plasma. Peak height, rather than integrated signal, was used [12], because of signal tailing and memory effects at high vaporization temperatures.

The objectives of this study are to investigate the vaporization and atomization of Y and the REEs with the use of GFAAS and ETV-ICP-MS. By investigating the temporal distributions, it may be possible to propose a general mechanism of vaporization and atomization for most of these elements. As with boron, it may be hypothesized that the low sensitivity of these elements by GFAAS determination is due to molecular oxide or carbide formation in the ETV. The use of metal and graphite vaporization surfaces are compared and the application of Freons as a chemical modifier is assessed. Optimum instrument and signal measurement conditions for Y and the REEs as well as analytical figures of merit are reported for these elements.

4.2 EXPERIMENTAL

A Perkin-Elmer Sciex Elan 5000 ICP mass spectrometer equipped with an HGA 600MS electrothermal vaporizer was used. The electrothermal vaporization system was equipped with a model AS-60 autosampler. Pyrolytic graphite coated tubes were used throughout. The instrumental conditions and operating for both the Elan 5000 and the HGA-600MS are given in Table 8.

Table 8. Instrumental operating conditions and data acquisition parameters for the vaporization of Y and Rare Earth Elements.

ICP MASS SPECTROMETER

RF Power	900-1200 W
Coolant argon flow	15.0 L min ⁻¹
Auxiliary argon flow	900 mL min ⁻¹
Carrier argon flow	800-1200 mL min ⁻¹
Sampler/Skimmer	nickel

HGA-600MS Electrothermal Vaporizer*

Sample volume	10 μ L
Drying stage	120°C for 30 s 10 s ramp
Pyrolysis stage	400°C for 10 s 2 s ramp
Vaporization Stage	2000-2700°C for 6 s max. power ramp

Data Acquisition

Dwell time	10 ms
Scan mode	peak-hopping
Points/peak	1
Resolution	High (0.7 dalton at 10% peak height)
Signal measurement	Area Counts

* identical furnace conditions were used for the GFAAS experiments.

The optimization of plasma and mass spectrometer parameters was initially accomplished using solution nebulization (SN). Final optimization of the plasma conditions for ETV work required only minor adjustments ($\pm 50 \text{ mL min}^{-1}$) to the argon carrier gas flow. The HGA-600MS was interfaced to the argon plasma using an 80 cm length of 6 mm (i.d.) teflon tube. The operation of the HGA-600MS was completely computer controlled. During the dry and pyrolysis stages of the temperature program, opposing flows of argon gas (300 mL min^{-1}) originating from both ends of the graphite tube removed water and other vapours through the dosing hole of the graphite tube. During the high temperature vaporization step, a graphite probe was pneumatically activated which sealed the dosing hole. Once the graphite tube was sealed, a valve located at one end of the HGA workhead directed the carrier argon flow originating from the far end of the graphite tube to the argon plasma.

For GFAAS experiments, a Perkin-Elmer Model 5000 atomic absorption spectrophotometer equipped with a Zeeman background corrector and an HGA-500 graphite furnace was used. An AS-40 autosampler deposited analyte solution on the walls of standard pyrolytic graphite-coated graphite tubes. Westinghouse and Varian Techtron hollow cathode lamps were used. Peak height absorbance and peak area were recorded using a personal computer and a commercial software package. For both GFAAS and ETV-ICP-MS experiments, the temperature selected on the power supply was accepted as true without further calibration. The quantity of analyte used for GFAAS and ETV-ICP-MS experiments is summarized in Table 9.

Table 9. Analyte masses and appearance temperatures for Y and the Rare Earth Elements.

Element	Atomic Mass,(m/z)	Analyte Mass, ng	Analyte Mass, pg	Appearance Temperature °C	Appearance Temperature °C
		GFAAS	ETV-ICP-MS	GFAAS	ETV-ICP-MS
Y	89	10	50	2200	2200
La	139	500	50	2200	2200
Ce	140	-	50	-	2250
Pr	141	250	50	2250	2200
Nd	144	100	50	2300	2300
Sm	150	50	50	2050	2050
Eu	152	0.10	50	1800	1800
Gd	157	500	50	2300	2300
Tb	159	250	50	2200	2200
Dy	163	1.0	50	2300	2200
Ho	165	2.5	50	2100	2100
Er	167	25	50	2150	2150
Tm	169	1.0	50	2000	2000
Yb	173	25	50	1800	1600
Lu	175	250	50	2300	2200

Single element standards (Spex Industries, N.J., USA) were used for constructing atomization and vaporization curves. A multi-element standard (Spex Industries, N.J., USA) was used for determination of limits of detection. Analytical grade acids (Ultrex, Baker) and ultra-pure water (Millipore Corp., Mississauga, ON) were used throughout.

4.3 RESULTS AND DISCUSSION

Minimizing spectral interferences is crucial for multi-element analysis using ETV-ICP-MS because typically, the maximum number of analyte isotopes determined is limited to 6 or 7. Correcting for an isobaric interference requires monitoring an additional isotope, thereby reducing the number of analytes that can be determined during a multi-element run [138].

The REE isotopes used for this work were those not affected by isobaric interferences from isotopes of other elements. This selection criteria for analyte isotopes meant that a less abundant isotope than reported in the literature [135] was used for the determination of Nd, Eu, Tb and Yb . Spectral interferences from oxide species are common using solution nebulization and the formation of light REE oxides in the plasma often interferes with the determination of the heavier REEs (Table 10). This is especially important because light REEs are generally many times more abundant in nature than heavier REEs. Therefore, a study of the effect of plasma conditions on minimizing oxide interferences is an important consideration. Table 11 summarizes a number of the important chemical and physical properties of Y and all of the REEs, which are relevant to discussions contained in this chapter.

Table 10. Rare Earth oxide polyatomic interferences

Element	Atomic Mass (<i>m/z</i>)	% Abundance	Polyatomic Ion Interference*
Y	89	100	-
La	139	99.9	-
Ce	140	88.5	-
Pr	141	100	-
Nd	146	17.2	-
Sm	147	15.0	-
Eu	153	52.2	-
Gd	157	15.7	¹⁴¹ PrO (100%)
Tb	159	100	¹⁴³ NdO (12.2%)
Dy	163	24.9	¹⁴⁷ SmO (15.0%)
Ho	165	100	¹⁴⁹ SmO (13.8%)
Er	166	23.0	¹⁵⁰ NdO (5.6%); ¹⁵⁰ SmO (7.4%)
Tm	169	100	¹⁵³ EuO (52.2%)
Yb	172	21.9	¹⁵⁶ GdO (20.5%)
Lu	175	97.4	¹⁵⁹ TbO (100%)

* note: bracketed numbers indicate the abundance of rare earth isotopes.

Table 11. Physical properties of Y and the Rare Earth Elements

Isotope	Boiling Point, °C (Element)	Boiling Point, °C (M ₂ O ₃)	Boiling Point, °C (MF ₃)	Boiling Point, °C (MCl ₃)	*Bond Strength (kJ mol ⁻¹) (M-O, M ₂ O ₃)	*Bond Strength (kJ mol ⁻¹) (M-C, MC, MC ₂)	*Heat of Vaporization (kJ mol ⁻¹)
⁸⁹ Y	3338	-	2610	1507	714	418	424
¹³⁹ La	3464	3620	2334	2700	791	506	431
¹⁴⁰ Ce	3443	3730	2300	1925	791	456	423
¹⁴¹ Pr	3520	3760	2136	1905	743	-	357
¹⁴⁴ Nd	3074	3760	2258	1600	704	-	328
¹⁵⁰ Sm	1794	3780	2670	-	569	423	206
¹⁵² Eu	1527	3790	2657	-	463	326	175
¹⁵⁷ Gd	3273	3900	2402	1577	714	-	399
¹⁵⁹ Tb	3230	-	2521	1547	704	-	391
¹⁶³ Dy	2567	3900	2568	1627	711	-	293
¹⁶⁵ Ho	2700	3900	2230	1507	618	-	303
¹⁶⁷ Er	2868	3920	2507	1497	611	-	318
¹⁶⁹ Tm	1950	3945	2269	1487	560	-	233
¹⁷³ Yb	1196	4070	2402	-	418	322	153
¹⁷⁵ Lu	3402	3980	2284	1477	695	-	428

*Bond strengths were calculated from Reference [101].

4.3.1 Effects of the Plasma and ETV Parameters on Oxide Formation

For Y and the REEs, only La and Ce formed significant oxide levels with changing plasma conditions ($\text{LnO:Ln} > 0.01$, where Ln = lanthanide). Praseodymium and Nd formed low levels of oxide ($\text{LnO:Ln} = 0.01$) and the remaining REEs formed negligible quantities ($\text{LnO:Ln} \ll 0.01$). The relationship between Ln-O bond strength (Table 11) and the ratio of metal oxide to metal for some REE elements determined by ETV-ICP-MS is shown in Figure 26. This figure qualitatively illustrates why oxide formation is negligible for most of the REEs using ETV sample introduction. For example, La-O and Ce-O both have the highest bond strengths [101, 127] (791 kJ mol^{-1}), whereas Pr (743 kJ mol^{-1}) and Nd (704 kJ mol^{-1}) have lower levels of oxide formation and Gd (714 kJ mol^{-1}), Dy (711 kJ mol^{-1}) and Tm (560 kJ mol^{-1}) have negligible levels of oxide formation. Though not shown in Figure 26, oxide levels for Ce were about two-fold higher than for La.

The effects of the various plasma and ETV conditions on the formation of oxide is shown in Figure 27 (a,c,e and f) for Ce. Other REEs such as La, Nd and Pr behaved similarly to Ce, however, since the highest levels of oxide were observed with Ce, only the results using this element will be shown. For comparison, the effects of plasma conditions with solution nebulization are also shown in Figure 27 (b and d) for Ce.

The single most important parameter for oxide formation with the ETV was the argon carrier flow to the plasma. For these experiments, an RF power of 1000 W was used. Figure 27 (a) shows the effect of varying the argon carrier flow from 800 mL min^{-1} to 1200 mL min^{-1} with the ETV. Increasing the argon flow generally increased

Figure 26. Relationship between metal-oxide bond strength and the metal - oxide:metal ratio for selected rare earth elements using ETV-ICP-MS.

the ratio of CeO to Ce, especially at flow rates above 1050 mL min⁻¹. The five-fold increase in the CeO:Ce ratio (from 1050 to 1200 mL min⁻¹) is due in part to a 2-fold increase in CeO as well as a 2.5-fold decrease in the ¹⁴⁰Ce⁺ signal. The maximum Ce signal was achieved with an argon carrier flow of 900-950 mL min⁻¹ with the ETV. With solution nebulization, shown in Figure 27(b), the maximum signal intensity occurred at approximately the same carrier flow, however, the signal intensity increased and decreased more with changing argon carrier flow. Using solution nebulization, the CeO:Ce ratios were much higher and increased to much higher values with flow rates above 950 mL min, when compared to those obtained with the ETV.

The effects of plasma power on the formation of oxide is shown in Figure 27(c). For these experiments, an argon carrier flow of 1050 mL min⁻¹ was chosen in order to obtain a measurable level of oxide at all plasma power settings. Generally, increasing the plasma power decreases appreciably the level of oxide formation while increasing the ¹⁴⁰Ce⁺ signal. Using the ETV, an increase in RF power from 900 to 1000 W resulted in a six fold decrease in the CeO: Ce ratio. This was due in part to a two-fold increase in the ¹⁴⁰Ce⁺ signal as well as a three-fold decrease in CeO. Setting the RF power of the plasma at 1000 W or higher is suitable for rare earth determinations using the ETV. Unlike experiments with the argon carrier flow, similar trends were observed with solution nebulization which are shown in Figure 27(d).

Varying the vaporization temperature did have a small effect on the formation of CeO in the ETV. The results of these experiments are shown in Figure 27(e). For these experiments, a slightly higher flow rate of 1050 mL min⁻¹ was used with a

slightly lower plasma power, of 950 W, to determine the oxide level at all vaporization temperatures. Higher vaporization temperatures resulted in lower CeO:Ce ratios, however, most of the decrease in the oxide ratio can be attributed to the increase in the $^{140}\text{Ce}^+$ signal at higher vaporization temperatures. Temperatures of 2600°C, or higher, should be used to minimize the formation of oxide with maximum signal intensity for all of the REEs.

Varying the argon flow inside the ETV had an even smaller effect, both on the $^{140}\text{Ce}^+$ signal and the Ce oxide signal. The results of these experiments are shown in Figure 27(f). For these experiments an RF power of 950 W was used. As well, the argon carrier flow to the plasma was appropriately modified, such that the total argon flow to the plasma was constant for each argon flow setting inside the ETV. Increasing the flow of argon inside the ETV resulted in only a small increase in the $^{140}\text{Ce}^+$ signal, with a correspondingly small increase in the CeO:Ce ratio. Flow rates of 1000 mL min^{-1} , or higher, in the ETV do not result in significant increases in oxide formation and are recommended for the determination of REEs.

In summary, the most important parameter associated with the formation of oxides using ETV-ICP-MS is the argon carrier flow. The remaining experimental conditions such as plasma power, vaporization temperature, or the internal argon flow of the ETV had only a negligible effect on oxide formation. The optimum argon carrier flow rate using ETV is slightly lower (50 mL min^{-1}) than for SN. Using SN, the CeO:Ce ratios were at least ten-fold greater than for ETV.

Figure 27a. Relationship between CeO:Ce ratio (—●—) and the argon carrier flow using ETV-ICP-MS. The corresponding integrated signal intensity of ¹⁴⁰Ce⁺ (—■—) is also shown.

Figure 27b. Relationship between CeO:Ce ratio (—●—) and the argon carrier flow using SN-ICP-MS. The corresponding integrated signal intensity of $^{140}\text{Ce}^+$ (—■—) is also shown.

Figure 27c. Relationship between CeO:Ce ratio (—●—) and the argon plasma power flow using ETV-ICP-MS. The corresponding integrated signal intensity of $^{140}\text{Ce}^+$ (—■—) is also shown.

Figure 27d. Relationship between CeO:Ce ratio (—●—) and the argon plasma power using SN-ICP-MS. The corresponding integrated signal intensity of $^{140}\text{Ce}^+$ (—■—) is also shown.

Figure 27e. Relationship between CeO:Ce ratio (—●—) and the vaporization temperature using ETV-ICP-MS. The corresponding integrated signal intensity of $^{140}\text{Ce}^+$ (—■—) is also shown.

Figure 27f. Relationship between CeO:Ce ratio (—●—) and the internal argon flow of the graphite tube ETV. The corresponding integrated signal intensity of ¹⁴⁰Ce⁺ (—■—) is also shown.

4.3.2 Vaporization of Y and the Rare Earth Elements

For this study, Y and the REEs were arbitrarily divided into two groups. The first group comprises: Pr, Nd, Sm, Ho, Er, Eu, Dy, Th and Yb, which are elements whose ETV-ICP-MS signals were sharp and did not tail appreciably. The second group of elements all have tailing ETV-ICP-MS signals at all vaporization temperatures and includes Y, Gd, Tb, Lu, La and Ce. Since it is known that REEs form carbides [139], this tailing may be attributed to the volatilization of carbides at high temperatures. The REEs are further subdivided into smaller groups or discussed singly in accordance with physical characteristics such as boiling points (Table 11) and similarities in their atomization (GFAAS) and vaporization (ETV-ICP-MS) curves. For the sake of simplicity and brevity, only specific atomization/vaporization curves are shown, since some REEs and their individual ETV-ICP-MS signals are representative of other REEs.

Using GFAAS, only atomic species are detected and hence, an atomization curve will show the change in concentration of only atomic species with changing temperature. Similarly, using ETV-ICP-MS, both atomic and molecular species are detected thus, vaporization curves show the change in concentration of molecular and atomic species reaching the argon plasma with changing temperature. The appearance temperature, as used in this paper, refers to the temperature on the atomization or vaporization curve for a particular element at which a signal becomes measurable above background noise.

For all Group I elements, no multiple peaks, shoulders or appreciable signal tailing was observed at any temperature or graphite tube heating rate. This suggests that either

a single species, or possibly multiple species with similar thermal properties, are vaporized. With the exception of Ce, no multiple peaks were observed for Group II elements, however, significant signal tailing at high temperatures was noted.

Group I: Non-Tailing Analyte Signals

a) Pr, Nd, Ho, and Er

Except for Pr, each of the above REEs have boiling points below those REEs which had ETV-ICP-MS signals that tailed. Since the atomization and vaporization curves for Pr, Nd, Ho and Er were similar in appearance, only the curves for Pr are presented in Figure 28(a) as representative of the entire group. The atomization curves for Pr, Nd, Ho and Er increased gradually with increasing temperature over the temperature range studied. Like most REEs, the atomization curves for these elements did not reach a maximum at 2700°C, which is in agreement with the results of Haines [140]. The vaporization curve for Pr at temperatures below 2500°C is more easily viewed on an expanded scale, shown in Figure 28(a-inset).

At temperatures above 2550°C, the slope of the vaporization curves for Pr, Nd, Ho and Er increased dramatically to a temperature of 2750°C. The slope of the vaporization curve is greater than the slope of the atomization curve suggesting that molecular species vaporize at temperatures above 2500°C, resulting in greater sensitivity for the ETV-ICP-MS measurement. As with the atomization curve, no maximum was reached with the vaporization curve indicating that higher temperatures (>2750°C) are required to vaporize all of the Pr, Nd, Ho and Er from the graphite surface. With the use of ETV-ICP-MS, the appearance temperatures for all four

Figure 28.

(a) Vaporization (—●—) and atomization curves (—■—) for Pr in 0.2% HNO_3 , with expanded view (inset); (b) ETV-ICP-MS signals for $^{141}\text{Pr}^+$ vaporized at (i) 2750 $^{\circ}\text{C}$; (ii) 2700 $^{\circ}\text{C}$; (iii) 2650 $^{\circ}\text{C}$; (iv) 2600 $^{\circ}\text{C}$.

elements were equal (within error) to the appearance temperature determined by GFAAS, which may indicate that a similar species is detected.

Figure 28(b) shows the ETV-ICP-MS signals for Pr vaporized at various temperatures. The absence of peak tailing may indicate that carbides are not easily vaporized, however, memory effects were observed, which may indicate that Pr, Nd, Ho and Er form carbides on the graphite surface. Carbides of Pr including Pr_2C_3 and PrC_2 are known to exist [141]. The carbide, PrC_2 forms a eutectic with graphite at 2254°C and melts congruently at 3230°C , whereas the carbide Pr_2C_3 forms a eutectic with graphite at 800°C and melts congruently at only 1545°C [141].

Praseodymium has been determined in biological tissues with a limit of detection of 5 ng reported by Horsky et al [142]. Grobowski et al.[129] showed that Nd GFAAS signals obtained using an uncoated graphite tube did not tail, but exhibited memory effects. L'vov [143] used a tantalum lined graphite tube for the determination of Nd and reported no memory effects.

b) Sm, Dy and Tm

The atomization and vaporization curves for Sm are shown in Figure 29a and are representative of those for Dy and Tm. The atomization and vaporization curves for Sm, Dy and Tm exhibited a gradually increasing slope with increasing temperature over the entire temperature range studied. Both the atomization and vaporization curves for Sm, Dy and Tm did not reach a maximum at temperatures up to 2700°C , which is in agreement with GFAAS studies [140]. The slope of the vaporization and atomization curves (Fig.29a) were similar at all temperatures. Figure 29a (inset) shows an expanded

Figure 29.

(a) Vaporization (—●—) and atomization (—■—) curves for Sm in 0.2% HNO_3 with expanded view (inset); (b) ETV-ICP-MS signals for $^{150}\text{Sm}^{+}$ vaporized at (i) 2750 $^{\circ}\text{C}$; (ii) 2700 $^{\circ}\text{C}$; (iii) 2600 $^{\circ}\text{C}$; (iv) 2500 $^{\circ}\text{C}$.

view of these curves for Sm between 2100°C to 2500°C. As will be seen below, this feature is uncommon among other REEs.

Figure 29(b) shows individual ETV-ICP-MS signals for Sm obtained over a range of temperatures. These signals did not tail at any temperature and no significant peak broadening was observed at temperatures as low as 2500°C.

Although serious peak tailing was not observed, memory effects were, suggesting that Sm carbide or other refractory compounds may be formed. As with all REEs, Sm is known to form carbides. The thermodynamic properties of SmC_2 and sub-stoichiometric disamarium tricarbide have been reported [144].

A number of GFAAS studies have also been carried out on these elements. Daidoji and Tamura [145] estimated an appearance temperature of 2200°C for Dy. This is in agreement with the appearance temperature obtained in this study, using either GFAAS or ETV-ICP-MS. Appearance temperatures obtained by ETV-ICP-MS and GFAAS were also in good agreement for Dy and Tm.

Atomic absorption signals for Dy showed no tailing when a pyrocoated graphite tube was used [129]. Thulium has been efficiently vaporized from a tantalum platform [132,143,146]. In these papers, the vaporization of Tm was studied in the presence of other REEs and it was concluded that using a Ta vaporization surface eliminated absorbance signal tailing. Acids such as HCl and HNO_3 in the sample matrix suppressed Sm [129,144] and Dy [144] absorbance signals. None of these matrix effects were observed for ETV-ICP-MS when up to 2% acid (v/v) (HCl , HNO_3 , H_2SO_4) was used as the sample matrix. The presence of various concomitant elements at low

concentrations have also been shown to give both signal enhancement and suppressive effects on Dy absorbance signals [147]. This was not observed for ETV-ICP-MS when a 400°C pyrolysis step was used prior to the high-temperature vaporization step.

c) Eu and Yb

Europium and Yb are the most volatile of the REEs with boiling points below 2000°C (Table 11). Atomization and vaporization curves for Eu and Yb were similar and therefore, only the curves for Eu are shown in Figure 30a. A number of GFAAS studies on Eu vaporized alone [148,149] or with other REEs [129,134,150,151,152] have been published. Haines [140] showed the atomization curve for Eu as reaching a maximum at about 2600°C, which is comparable to the atomization curves for Eu and Yb obtained in this study. As was observed for Sm, Dy and Tm, the atomization curve followed the vaporization curve over the entire temperature range. At temperatures approaching 2700°C, both the atomization curve and the vaporization curve reach a maximum.

The GFAAS appearance temperature for Eu obtained during this study was 1800 $\pm$ 100°C. This is in agreement with Wie et al. [153], who reported an appearance temperature of 1870°C for Eu, vaporized from a graphite surface, while Yizai and Di-Jun [154] reported an appearance temperature of 1750°C with a pyrolytic graphite coated tube. With ETV-ICP-MS, an appearance temperature of 1600°C was obtained for Yb, which is about 200°C lower than the appearance of Yb atoms (GFAAS). This suggests that a volatile molecular Yb species, possibly the oxide, is vaporized prior to atomization, which begins at a temperature of 1800°C. Individual ETV-ICP-MS signals

Figure 30. (a) Vaporization (—●—) and atomization (—■—) curves for Eu in 0.2% HNO₃ with expanded view (inset); (b) ETV-ICP-MS Signals for ¹⁵²Eu⁺ vaporized at (I) 2750°C; (II) 2600°C; (III) 2400°C; (IV) 2200°C.

for Eu obtained over a range of temperatures are shown in Figure 30a (inset). Lower temperatures did not result in a broadening of the peaks for either Eu or Yb, however, analytically useful signals were obtained at temperatures above 2200°C only.

Group II: Tailing Analyte Signals

a) Y, Gd, Tb, Lu

The vaporization and atomization curves for Y were typical for this group of elements and are shown in Figure 31(a). The increase in the Y absorbance with temperature was nearly linear from 2300°C to 2600°C and did not reach a maximum. Between the appearance temperature and about 2500°C, the slope of the vaporization curve is similar to the slope of the atomization curve (Fig. 31a, inset). Above 2600°C, however, the slope of the ETV-ICP-MS curve rises dramatically and is much greater than the slope of the atomization curve. This suggests that while both molecular and atomic species are being vaporized, more Y is vaporized from the graphite surface as a molecular species than as atoms, especially at temperatures above 2500°C.

The appearance temperature for Y was $2200 \pm 100^\circ\text{C}$, which is slightly higher than that reported by Wahab et al. [155]. Using ETV-ICP-MS, the appearance temperature of Y was $2200 \pm 100^\circ\text{C}$, which is the same as that obtained using GFAAS. Appearance temperatures using either GFAAS or ETV-ICP-MS were also the same for Gd, Tb and Lu (Table 11).

Prell and Styris studied the mechanism of atomization of Y using mass spectrometry [156]. Their findings demonstrated the formation of various molecular species in the graphite tube and showed that Y atomization resulted from the

Figure 31.

(a) Vaporization (—●—) and atomization (—■—) curves for Y in 0.2% HNO₃ with expanded view (inset); (b) ETV-ICP-MS signals for ⁸⁹Y⁺ vaporized at (i) 2750°C; (ii) 2700°C; (iii) 2600°C; (iv) 2500°C.

dissociation of YO which was chemisorbed on the graphite surface or from Y which was directly reduced on the graphite surface. They reported an appearance temperature of 2107°C for YO, 2177°C for Y(OH)₃ and 2487°C for YC. The appearance temperature of YC₂ reported by Prell and Styris [156] correlates with the temperatures at which the slope of the vaporization curve (2500°C) increases dramatically, suggesting that it is the carbide that is vaporized at temperatures above 2500°C. In the study by Prell and Styris [156], all of the Y molecular species were present in quantities at least 50-fold lower than were atoms. This was not observed using ETV-ICP-MS as the slope of the vaporization curve was higher than the slope of the atomization curve. The high concentration of molecular species in the vapour state may be caused by the short residence time of analyte vapour inside the ETV during the high temperature vaporization step, during which an internal argon flow rate of 1 L min⁻¹ is continually removing analyte as it is vaporized. These conditions favour the volatilization of REE oxides and/or the rapid oxidation of metal with trace amounts of oxygen and water vapour contained in the argon stream.

Figure 31(b) shows the ETV-ICP-MS signals for Y obtained at temperatures between 2400°C and 2750°C. At all temperatures, there is significant tailing of the ETV-ICP-MS signals. Peak broadening and tailing of the Y ETV-ICP-MS signal may be indicative of the formation of a refractory oxide or carbide, which is more slowly vaporized from the graphite surface. Of all the REEs studied using ETV-ICP-MS, signal tailing was most severe for Gd and may be due to the formation of Gd carbide. Both sesquicarbide and dicarbide species of Gd have been documented [139].

b) La

Figure 32(a) shows the atomization and vaporization curves for La. Both atomization or vaporization curves had not reached a maximum at 2750°C. Unlike other REEs in Group II, the atomization curve for La closely resembles that of the vaporization curve at high temperatures. The slopes of the atomization and vaporization curves were nearly the same between 2200°C and 2550°C (Fig.29a, inset). At temperatures above 2600°C, the slopes of these curves increased dramatically. The similarity in the slopes of the two curves suggests that at all temperatures, dissociation of a molecular species may be occurring, resulting in the formation of atomic La on the surface of the graphite tube. Figure 32(b) shows the ETV-ICP-MS signals for La vaporized at various temperatures.

Both the GFAAS and ETV-ICP-MS appearance temperatures for La was $2200 \pm 100^\circ\text{C}$, which is significantly higher than an appearance temperature of 1900°C reported by Miao-Kang and Yin-Yu [157], who atomized La in a graphite tube lined with tungsten foil. These authors also noted that the absorbance signal for La reached a maximum at about 2500°C, which was not observed in this study.

c) Ce

Figure 33(a) shows the vaporization curve for Ce. An atomization curve could not be obtained because of the poor sensitivity of GFAAS for Ce. Using argon as the purge gas, Ce is only 5% atomized in a graphite furnace at 2700°C [158]. The poor sensitivity for Ce in GFAAS can partially be attributed to the weak intensity of the hollow cathode emission line at 567 nm. Cerium has been determined with good

Figure 32.

(a) Vaporization (—●—) and atomization (—■—) curves for La in 0.2% HNO_3 with expanded view (inset); (b) ETV-ICP-MS signals for $^{139}\text{La}^{+}$ vaporized at (i) 2750 $^{\circ}\text{C}$; (ii) 2700 $^{\circ}\text{C}$; (iii) 2650 $^{\circ}\text{C}$; (iv) 2600 $^{\circ}\text{C}$.

sensitivity using a graphite furnace lined with tungsten foil [132]. Since Ce is so insensitive by GFAAS, the ETV-ICP-MS signal for $^{140}\text{Ce}^+$ likely arises from the vaporization of Ce in molecular form, probably an oxide. Using ETV-ICP-MS, the appearance temperature for Ce was 2250°C.

The most common valence state for the REEs is +3, however, Ce differs from most REEs since it is also found in the +4 state. In nature, cerium oxides exist as CeO_2 or Ce_2O_3 . Figure 33 (b) shows ETV-ICP-MS signals for Ce obtained at various vaporization temperatures. These signals show some tailing, however, the effect of tailing is less severe than for other REEs such as Gd. At all temperatures, however, a small signal appears in advance of the larger second peak, indicating that two different species are vaporized. Figure 33 (c) shows, on an expanded scale, the ETV-ICP-MS signal for $^{140}\text{Ce}^+$ obtained at 2600°C. Clearly, the first peak is a more volatile molecular cerium species that is separated temporally from the second, less volatile molecular species.

A number of experiments were carried out to investigate some of the characteristics of Ce vaporization in the graphite tube. Higher vaporization temperatures (>2700°C) and rate of heating of the graphite tube increase the intensity of the Ce signal significantly. Unfortunately, heating the ETV to temperatures above 2700°C damages the graphite surface and shortens tube life-time. At vaporization temperatures below 2650°C, tube condition and pyrolysis temperatures have a noticeable effect on the quality of ETV-ICP-MS signals for Ce. For example, an older graphite tube (>200 firings) or a graphite tube with a damaged pyrolytic coating was found to exhibit more

Figure 33.

(a) Vaporization (—●—) curve for Ce in 0.2% HNO₃; (b) ETV-ICP-MS signals for ¹⁴⁰Ce⁺ vaporized at (i) 2750°C; (ii) 2700°C; (iii) 2650°C; (iv) 2600°C; (c) ETV-ICP-MS signal for Ce vaporized at 2600°C shown in expanded scale.

Figure 34.

Vaporization of 100 pg Ce in 0.2% HNO₃ at 2700°C, at three pyrolysis temperatures: (---); No pyrolysis; (.....) 900°C and (—) 1400°C.

severe double peaks for $^{140}\text{Ce}^+$ signals, with the first peak increasing in size. Figure 34 shows the effect of pyrolysis temperature on the ETV-ICP-MS signal for Ce. As the pyrolysis temperature is increased, the magnitude of the first $^{140}\text{Ce}^+$ peak is reduced and at temperatures of 1400°C , the first peak is nearly gone. Thus, in practice, higher pyrolysis temperatures should be used to promote surface reduction of the more volatile species (CeO_2) to the less volatile species (CeO).

4.3.4 Mechanism of Vaporization of Y and REEs

For the REEs, except for Yb and Eu which are relatively volatile, the slope of the vaporization curves were similar to the slope of the atomization curve between the appearance temperature and about 2500°C . The similarity in the slopes of the atomization/vaporization curves and appearance temperatures suggests that vaporization of a single species, rather than multiple species is operative in both ETV-ICP-MS and GFAAS. This may also indicate that analyte detected using either technique shares a common precursor.

Partial thermal decomposition studies have been reported for some REE compounds, including those of Nd [159], Gd [160], Ho [160] and Er [160]. These studies have demonstrated that at temperatures below 500°C , REE nitrates, $\text{Ln}(\text{NO}_3)_3$ decompose to $\text{LnO}(\text{NO}_3)$, which can decompose further at higher temperatures to the monoxide. The thermal decomposition of $\text{Ce}(\text{NO}_3)_3$ has been described by Strydom and Van Vuuren [161], who demonstrated that anhydrous cerium nitrate begins to decompose at temperatures between 230°C to 360°C forming CeO_2 , unlike other REE nitrates. This confirmed earlier work by Wentlandt who used thermobalance studies to show that

CeO_2 formed without going through an intermediate nitrate [162]. Clearly, in a reducing environment (hot graphite surface) and at high temperatures ($>2000^\circ\text{C}$) further decomposition of Ln_2O_3 or LnO_2 to LnO is likely. At higher temperatures, the vaporization of REE sesquioxide can be described by the general equation:

Based on Knudson effusion studies, Ames et al. [163] and White et al. [164] found that x varied only slightly over the entire temperature range of the vaporization experiments. Thus, the vaporization mechanisms for Y and the REEs can be described as a 2-stage process where the first step involves the vaporization of the oxide [165]:

Since the appearance temperatures for Y and the REEs using GFAAS is identical to those obtained by ETV-ICP-MS, atomic species are likely produced via step 2 from the dissociation of the monoxide, especially for GFAAS [163]:

This vaporization mechanism can be used for all of the REEs, except possibly Yb. Effusion and mass spectrometric studies of the vaporization of Yb_2O_3 have shown that

only Yb^+ and O^+ were detected [163]. These studies indicate that Yb sesquioxide is unusual in that it vaporizes predominantly by dissociation to the elements. This can be explained using the relative bond strengths (Table 11) of the REE monoxides, since YbO has the weakest bond strength of all the REE monoxides.

At temperatures above 2500°C , the slope of the vaporization curve (ETV-ICP-MS) increases dramatically to a much higher value than the slope of the atomization curve (GFAAS). Therefore, at temperatures above 2500°C , the predominant Y or REE species vaporized inside the graphite tube is likely molecular. There are a number of mechanisms that can be used to explain this increase in slope of the vaporization curve. One mechanism may involve the formation of monoxide from the metal and the sesquioxide, following the general reaction scheme:

Synthesis of some REE monoxides by this reaction have been reported for several REEs including Eu, Yb, Nd and Sm, by mixing the sesquioxide with the pure metal [166]. This mechanism is likely not realistic for ETV-ICP-MS, which operates at one atmosphere, since a pressure of 50 K barr and temperatures of 1000°C were required to drive reaction 24.

Traces of water vapour may result in the formation of hydroxy radicals at about 2480°C causing the formation of Ln(OH)_3 [156], but further reduction would result in the formation of LnO.

A second vaporization mechanism at temperatures above 2500°C involves the formation of carbides, which are well known for all of the REEs [139]. Further reduction of LnO(l) by graphite could result in the formation of both the element and carbides, which would not begin to vaporize until temperatures above 2500°C are reached:

where $x=1,2$

Using high temperature Knudson effusion mass spectrometry, numerous La carbides have been identified including La_2C_2 , La_2C_3 , La_2C_4 , La_2C_5 , La_2C_6 and La_2C_8 [167]. Intercalation of some of the REEs in the graphite matrix is not likely for all REEs, except for Eu and Yb because REE carbides are so readily formed [168].

Sesquicarbides (Ln_2C_3) for all of the REEs have been synthesized from an arc melt or by mixing the elements with graphite powder [139]. Traces of water vapour hydrolyse the sesquicarbide to $\text{Ln}_2\text{C}_2\text{O}_2$ and ultimately to the oxide [169,170]. It may be, however, that insufficient water vapour is present within the ETV at temperatures above 2500°C to hydrolyse these carbides [171].

Experimental evidence from this work which support carbide formation include the strong memory effects observed with most of the REEs and severe tailing of the ETV-ICP-MS signal for Y, La, Ce, Gd, Tb and Lu. From this data alone, it is not

possible to conclude whether the tailing observed with Y, Ce, La, Lu, Gd, and Tb is due to the slow volatilization of refractory rare earth oxides (LnO) or carbide (LnC , LnC_2). Experiments described below on the vaporization of the REEs on a tungsten surface give additional support to the view that carbide formation results in significant analyte loss in the graphite ETV.

4.3.4 Optimization of Y and REE Analyte Signals

A number of approaches were investigated to improve ETV-ICP-MS signal characteristics. One strategy involved the vaporization of REEs from a tungsten surface. Experiments were conducted to determine if the tailing observed with the ETV-ICP-MS could be eliminated using a tungsten metal insert inside the graphite tube. The results of these experiments are summarized in Figure 35. For these experiments, Ce was chosen because both memory effects and severe tailing of the ETV-ICP-MS signal were observed. As well, at lower vaporization temperatures (2600°C), the transient $^{140}\text{Ce}^+$ signal had two peaks. Figure 35(a) shows the vaporization of 100 pg Ce on a graphite surface at 2600°C . Figure 35(b) shows the vaporization of 100 pg Ce on a tungsten surface at 2300°C . For comparison, Ce was also vaporized at 2300°C from a graphite surface, shown in Figure 35(c). Clearly, vaporization from a metal surface eliminated any of the tailing associated with Ce suggesting that carbide formation may be playing a role. This approach was successfully used for overcoming the signal suppression of U due to carbide formation and intercalation in the presence of a chloride matrix [172]. Vaporization of REEs from a tungsten surface did prevent the tailing observed from a graphite surface. It should be noted, however, that vaporization from a tungsten surface

Figure 35. Vaporization of 100 pg Ce in 0.2% HNO₃: (a) (—) graphite surface, 2600°C; (b) (---) tungsten surface, 2300°C and (c) (.....) graphite surface, 2300°C.

had to be carried out within a narrow temperature range (2100-2300°C) because the temperature had to be high enough to obtain a useful analytical signal, while at the same time not destroy the tungsten surface. A reducing gas, such as hydrogen, is useful in preventing the oxidation of the tungsten surface at temperatures above 2300°C. It is worth noting, however, that noticeable $^{140}\text{Ce}^+$ signal enhancement was observed using a tungsten vaporization surface at 2300°C when compared to signals obtained using a graphite surface at 2650°C, suggesting that volatilized tungsten or tungsten oxide served as a physical carrier.

Another means of improving analyte signal involves lowering vaporization temperatures which has been shown to increase the integrated peak area for boron, improve the signal to background ratios for tungsten [173] and prevent the volatilization of uranium as the carbide species [20]. The use of lower vaporization temperatures for the determination of the REEs by ETV-ICP-MS was not advantageous because it did not reduce the tailing observed with Y and La, Ce, Gd, Tb and Lu. Vaporization temperatures below 2400°C, in effect, broadened the signals significantly for all but the more volatile REEs such as Yb and Eu. Although the use of lower vaporization temperature may reduce the peak tailing associated with carbide formation, the oxides themselves are not volatile enough (as was the case for U) for this strategy to be practical.

The vaporization of REEs in the presence of a suitable physical carrier is a third approach that can be used to improve Y and REE ETV-ICP-MS signals. A mixed modifier (NASS-3) was used by Grégoire et al. [138] for the determination of some

REEs in single zircons. Freon added to the argon carrier gas has also been suggested as a gas phase physical carrier/chemical modifier [20]. Using Freon in the argon carrier gas promotes the formation of volatile halide species (cf. Table 11) which are more readily transported to the ICP than atomic REEs, while at the same time preventing the formation of carbides on the graphite surface [174]. For these experiments, three REEs, whose ETV-ICP-MS signals tailed noticeably (Gd, Tb, Lu), were selected to study the effect of Freon on analyte signal characteristics. The effects of adding 0.3% of Freon-23 (CHF_3) to the argon carrier gas during the vaporization of 100 pg of Lu, Tb and Gd on a graphite surface at 2650°C is shown in Figure 36. Clearly, the use of CHF_3 enhanced all of the ETV-ICP-MS signals and eliminated the tailing associated with carbide formation. Interestingly, Lu actually vaporized at a lower temperature when CHF_3 was used, suggesting that a more volatile halide species may have been formed. The greatest signal enhancement was observed for Gd which exhibited both severe signal tailing and high blanks between firings.

4.3.5 Analytical Figures of Merit

Table 12 summarizes the analytical figures of merit for the determination of Y and REEs by ETV-ICP-MS. A vaporization temperature of 2750°C was used for all REEs and signal is reported in integrated peak area counts. Freon (0.3%) was added to the argon carrier gas.

For all elements, the relative standard deviation for a series of separate measurements was below 10% and below 5% for the majority of REEs. A graphite tube that had been previously used for the determination of REEs was used to simulate

Figure 36. ETV-ICP-MS signals of 100 pg (a) $^{175}\text{Lu}^+$: (—) Ar carrier gas; (---) Ar + 0.3% CHF_3 ; (b) $^{159}\text{Tb}^+$: (—) Ar carrier gas; (---) Ar + 0.3% CHF_3 and (c) $^{157}\text{Gd}^+$: (—) Ar carrier gas; (---) Ar + 0.3% CHF_3 .

Table 12. Analytical figures of merit for Y and the Rare Earth elements.

<u>BLANKS</u>	⁸⁹Y	¹³⁹La	¹⁴⁰Ce	¹⁴¹Pr	¹⁴⁶Nd
Intensity	730	7823	1541	305	191
3σ (n=6)	68.6	93.0	462	103	63.1

STANDARDS

Mass/pg	100	100	100	100	100
Net Intensity	130,176	228,820	234,426	506,682	109,621
RSD% (n=5)	12.1	10.3	10.4	6.37	5.87
LOD/pg*	.053	.041	.197	.020	.057

<u>BLANKS</u>	¹⁴⁷Sm	¹⁵³Eu	¹⁵⁷Gd	¹⁵⁹Tb	¹⁶³Dy
Intensity	152	50.0	144	406	128
3σ (n=6)	28.2	78.8	118	59.2	136

STANDARDS

Mass/pg	100	100	100	100	100
Net Intensity	84,651	275,143	49,840	466,990	187,660
RSD% (n=5)	4.80	2.40	6.92	6.53	6.74
LOD/pg*	.035	.029	.091	.038	.072

<u>BLANKS</u>	¹⁶⁵Ho	¹⁶⁶Er	¹⁶⁹Tm	¹⁷²Yb	¹⁷⁵Lu
Intensity	166	155	76.6	126	308
3σ (n=6)	89.1	84.0	12.2	65.8	160

STANDARDS

Mass/pg	100	100	100	100	100
Net Intensity	828,488	278,085	738,304	140,620	765,855
RSD% (n=5)	3.19	2.84	0.74	2.00	2.54
LOD/pg*	.011	.030	.002	.046	.021

* Based on 10 μ L sample volume

actual analytical conditions. Blank values for some elements are high showing the ability of Freon to mobilize analyte from the graphite matrix. Repeated "blank" firings did reduce background signal substantially indicating that limits of detection well below these quoted in Table 12 can be achieved. Aside from background signals which degrade limits of detection, differences in the absolute limits of detection among the REEs are controlled by the relative abundance of the specific isotope monitored by the ICP-MS. For example, the limits of detection for monoisotopic or nearly monoisotopic elements such as Pr, Tb, Ho, Tm and Lu are much better than those for Gd (15.7% abundance) and Sm (15.0%).

4.4 SUMMARY AND CONCLUSIONS

The proposed mechanism of vaporization of Y and the REEs accounts for the high sensitivity of ETV-ICP-MS for the determination of these elements when compared to GFAAS. Limits of detection from three to six orders of magnitude better than GFAAS were obtained by ETV-ICP-MS. The data presented here suggests that Y and REE ETV-ICP-MS signals are produced as a result of the vaporisation of primarily oxide at low temperatures and, at higher temperatures, oxides and/or carbides. This mechanism is consistent with the physical and thermodynamic properties of Y and the REES and explains the analytical performance of both GFAAS and ETV-ICP-MS for the determination of these elements.

Vaporizing some of the REEs from a tungsten surface may prevent peak tailing associated with carbide formation. Freon has been shown to be an effective chemical modifier allowing for the vaporization of Y and REEs at the high temperatures required to give high sensitivity determinations of Y and the REEs by ETV-ICP-MS.

CHAPTER 5.

VAPORIZATION AND ATOMIZATION OF URANIUM IN A GRAPHITE TUBE ELECTROTHERMAL VAPORIZER: A MECHANISTIC STUDY USING ETV-ICP-MS AND GFAAS

5.1 INTRODUCTION

Uranium is the heaviest naturally occurring element. It is widely distributed in the earth's crust and has an average concentration of about $0.4 \mu\text{g g}^{-1}$. Although U has been determined by graphite furnace atomic absorption spectroscopy (GFAAS), the detection limits are poor [175,176]. Norval [176] has reported a detection limit of $0.6 \mu\text{g g}^{-1}$, using pyrolytically coated graphite tubes and an atomization temperature of 2750°C . Other techniques such as inductively coupled plasma emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS), using solution nebulization, are suitable for the determination of uranium with detection limits of $40 \mu\text{g L}^{-1}$ and $0.01 \mu\text{g L}^{-1}$ respectively. The use of an electrothermal vaporizer (ETV), as a sample introduction technique for ICP-MS, has been shown to be effective for the determination of trace metals [92].

A number of studies have been published on the determination of $^{238}\text{U}^{+}$ using an ETV for sample introduction into an argon plasma. Kirkbright and Li-Xing [177] volatilized uranium from a graphite rod direct sample insertion (DSI) device coupled to ICP-AES, using 0.1% Freon-23 (CHF_3) in the argon carrier gas. A calibration curve for uranium was constructed and was linear over a concentration range of four orders of magnitude. Ng and Caruso [40] volatilized uranium into an ICP using a carbon cup and a 7% NH_4Cl solution as a chemical modifier to convert the uranium to a more

volatile halide, however, they reported uranium has "reasonable detectability" without the modifier. Using a DSI device, Karanossios and Horlick [48] were able to reduce the suppressive matrix effect of uranium on zinc signals by differential thermal volatilization. They reported that uranium, lanthanides and actinides are thermally stabilized by non-volatile carbide formation and therefore, can be selectively vaporized at a higher temperature than Zn. The feasibility of using ETV-ICP-MS for the determination of femtogram levels of uranium and plutonium in urine was demonstrated by Hall et al. [178]. These authors showed that ETV-ICP-MS is capable of measuring low levels of uranium in biological samples such as urine, which are high in dissolved salts. Hulmston and Hutton [174], showed that the volatilization of 30 pg of uranium produced an erratic and poorly defined analytical signal pulse. These results were attributed to uranium forming "vapour phase carbides" at temperatures above 2500°C. The formation of these carbides resulted in severe memory effects and decreased analyte transport efficiency. Using 0.1% Freon-23 in the carrier gas, however, these workers showed that a sharp and well defined uranium signal pulse was obtained and the memory effects greatly reduced. Ediger demonstrated some interesting contrasts between GFAAS and ETV-ICP-MS using uranium as a test element [179]. Using a pyrolytically coated graphite tube and a high heating rate during vaporization, he showed that uranium produced a transient signal similar to manganese, with little peak broadening associated with carbide formation. In a NaCl matrix, however, he reported peak broadening which was attributed to carbide formation resulting in less efficient vaporization and reduced sensitivity. Similarly, Ediger and Beres [20] studied the

effects of several chemical modifiers on a large number of elements, including uranium, using ETV-ICP-MS. They reported suppression of uranium signals in the presence of NaCl, MgCl₂ and Pd. Using Freon-23, added to the argon carrier gas, the uranium signal was enhanced by a factor of 2 or 3 which they suggest is due to the formation of volatile fluorides. More recently, Grégoire et al. [138] applied ETV-ICP-MS to the trace analysis of uranium, thorium and Rare Earth Elements in single zircons. Limits of detection of 80 ppb for uranium in a single zircon weighing 10 µg and an absolute limit of detection of 16 femtograms were reported. Sea water (NASS-3) was used as a chemical modifier and although most elements experienced enhanced sensitivity, both uranium and thorium were suppressed in the presence of chloride salts.

In this study, the vaporization and atomization of uranium in a graphite tube ETV was studied in a manner similar to studies presented in previous chapters in this thesis for boron and the REEs. By combining information gained from both GFAAS and ETV-ICP-MS, mechanisms of vaporization and atomization can be elucidated [11]. Transient signals obtained by GFAAS provide information on the temporal behaviour of atomic species only, while those obtained by ETV-ICP-MS, arise from both atomic and molecular analyte species. The objective of this study was to apply ETV-ICP-MS and GFAAS to investigate the mechanism of vaporization of uranium from a pyrolytically coated graphite tube, to assess the role of uranium carbide formation and investigate the cause of the uranium signal suppression (ETV-ICP-MS) in the presence of chloride.

5.2 EXPERIMENTAL

A Perkin-Elmer Sciex Elan 5000 ICP-MS equipped with an HGA-600MS ETV and an AS-60 autosampler was used. The ETV was interfaced to the ICP-MS with a teflon tube, 80 cm in length and 6 mm (i.d.). The experimental conditions for the ETV-ICP-MS measurements are summarised in Table 13. Plasma conditions and ion lenses were optimized using solution nebulization prior to the ETV experiments and needed no further adjustment when switching to the ETV sample introduction mode with the exception of small changes ($\pm 50 \text{ mL min}^{-1}$) to the argon carrier gas flow. The major uranium isotope at m/z 238 with a natural abundance of 99.28% was monitored for all ETV-ICP-MS experiments. Operation of the HGA-600MS was computer controlled, such that during the drying and pyrolysis steps, opposing flows of argon gas (300 mL min^{-1}) originating from both ends of the graphite tube, removed water and matrix vapours through the dosing hole prior to the high temperature vaporization step. During the high-temperature vaporization step, the dosing hole was sealed by a pneumatically-controlled graphite plug, at which time a switching valve directed the argon carrier flow from one end of the graphite furnace to the plasma. Data was collected in the "peak hopping" mode to monitor plasma effects. For example, the argon dimer $^{80}\text{Ar}_2^+$, is useful for observing "plasma loading", which is coincident with severe signal suppression at $m/z=80$. Other potential species monitored, though not observed, were $^{235}\text{U}^{16}\text{O}^+$ and $^{238}\text{U}^{12}\text{C}^+$. For all ETV-ICP-MS experiments, 10 ng mL^{-1} solutions were prepared from a $10 \mu\text{g mL}^{-1}$ stock solution supplied by Spex Industries, Edison, NJ.

Table 13. Instrumental operating conditions and data acquisition parameters for the ETV-ICP-MS for the vaporization of uranium.

ICP MASS Spectrometer

RF power	1000 W
Coolant argon flow rate	15.0 L min ⁻¹
Auxiliary argon flow rate	900 mL min ⁻¹
Carrier argon flow rate	1000 mL min ⁻¹

HGA-600MS Electrothermal Vaporizer

Sample Volume	10 μ L
Dry Step	10 s ramp 140°C for 30 s
Pyrolysis Step(no modifier)	2 s ramp 400°C for 10 s
Vaporization Step	0 ramp (2000°C s ⁻¹) 1100-2750°C for 6 s

Data Acquisition

Dwell Time	20 ms
Scan Mode	peak-hopping
Points/Spectral Peak	1
Ion monitored/measurement cycle	4
Signal Measurement	Area Counts
MS Resolution	0.7 dalton at 10% peak height
Ions monitored	$^{238}\text{U}^+$, $^{238}\text{U}^{16}\text{O}^+$, $^{238}\text{U}^{12}\text{C}^+$, $^{35}\text{Cl}^+$

For GFAAS experiments, a Perkin-Elmer Model 5000 atomic absorption spectrophotometer equipped with a Zeeman background Corrector and an HGA-500 graphite furnace was used. An AS-40 auto sampler was also used to deposit analyte on the walls of a standard pyrolytic graphite tube. A $100\ \mu\text{g mL}^{-1}$ solution of uranium was prepared by dissolving uranium oxide (Spex Industries, Edison, NJ) in 0.2% HNO_3 . Analytical grade acids (Ultrex, Baker) and ultra-pure water (Millipore Corp, Mississauga, ON) were used throughout.

5.3 RESULTS AND DISCUSSION

5.3.1 Vaporization and Atomization of Uranium.

In Figure 37 the atomization curve for uranium, obtained by GFAAS, shows the variation in atomic absorbance signal with atomization temperature. Also shown in Figure 37 is the vaporization curve for U obtained by ETV-ICP-MS, which gives the variation in the integrated ion counts for $^{238}\text{U}^+$ (atomic and/or molecular) with vaporization temperature. For the GFAAS experiments, $1\ \mu\text{g}$ of uranium in 0.2% HNO_3 was atomized and for the ETV-ICP-MS experiments, $100\ \text{pg}$ of uranium in 0.2% HNO_3 was used. The transient atomic absorbance signals for uranium were broad and tailed significantly at all atomization temperatures, suggesting that the signals were affected by the formation, vaporization and subsequent atomization of a less volatile compound, probably, uranium carbide. For this reason, peak height measurement was chosen, rather than peak area, for the AAS data collection. The GFAAS data provided information on the temporal distribution of the atomic U species inside the ETV. The appearance temperature for uranium atoms was about $2400 \pm 100^\circ\text{C}$. Below 2400°C , there was no

Figure 37. GFAAS atomization curve (-■-) of 1 μg uranium in 0.2% HNO_3 . ETV-ICP-MS vaporization curve (-○-) for 100 pg of uranium in 0.2% HNO_3 . Samples were atomized from the walls of a pyrolytically coated graphite tube.

detectable atomic absorbance signal indicating that uranium atoms are not formed below this temperature. Unlike that observed for more volatile elements (Eu, Yb), the atomization curve for uranium did not plateau at higher atomization temperatures, indicating that uranium was not completely vaporized even at temperatures as high as 2750°C. Temperatures above 2750°C were not used since, at these temperatures, graphite tube life is severely reduced.

The ETV-ICP-MS vaporization curve (Fig.37) gives an appearance temperature for uranium of approximately $1100^{\circ}\text{C} \pm 50^{\circ}\text{C}$, which is considerably lower than the appearance temperature of atomic uranium (2400°C) suggesting that the $^{238}\text{U}^{+}$ signals, recorded between 1100 and 2300°C, are due to volatile molecular uranium species and not uranium atoms. This is not surprising considering the high melting (1132°C) and boiling (3818°C) points of uranium metal [127]. The appearance of molecular uranium species, below 2300°C, would at least partially account for the poor sensitivity of uranium by GFAAS. In GFAAS, pre-atomization loss of uranium as molecular species would occur during the pyrolysis step at temperatures above 1100°C or during the atomization step at temperatures, below 2400°C. In Figure 37, the $^{238}\text{U}^{+}$ signal rises rapidly, above 1100°C, to approximately 10,000 counts at 1300°C. A number of volatile uranium oxide species such as U_3O_8 , U_3O_5 and U_2O_4 are known to exist, however, in the absence of excessive amounts of oxygen, these oxides would thermally decompose to form UO_3 , UO_2 and UO , with UO_3 further decomposing to U_3O_8 and finally to UO_2 , at temperatures above 925°C [180].

In the temperature range between 1300 and 2400°C (Fig.37), the amount of uranium vaporized from the ETV increases gradually, reflecting the increasing vapour pressure of UO_2 over this temperature range [180]. Uranium dioxide is relatively volatile with a vapour pressure of 0.9 torr at 2363°C. Uranium monoxide, UO , is much less volatile and is formed very slowly at temperatures above 2000°C in mixtures of UO_2 and uranium [181]. Of all the uranium oxides, uranium dioxide, UO_2 , is the only one to sublime in the temperature range between 1100°C and 2400°C. Hence, the primary uranium oxide species formed in the ETV within this temperature range is UO_2 with a lesser amount of UO being formed at temperatures above 2000°C. Reduction of uranium dioxide to uranium metal with carbon is not significant below 2000°C [182], thus it is unlikely that significant amounts of uranium metal exist on the graphite surface until higher temperatures are attained. The reduction of UO_2 to metallic uranium or uranium carbide by CO is also not favoured since carbon monoxide is only capable of reducing higher oxide species such as U_3O_8 or UO_3 to UO_2 [183]. This interpretation is supported by examining the series of $^{238}\text{U}^+$ ETV-ICP-MS signals shown in Figure 38. The ETV-ICP-MS signals for uranium at 1400°C (Fig.38a) and 2400°C (Fig.38b) appear as single peaks, starting at approximately 0.8 seconds into the high temperature vaporization step. The peak shapes shown at these temperatures are typical for ETV-ICP-MS, with a gradual increase in peak height with increasing temperature. Despite the fact that uranium melts at 1132°C and that as a liquid, it readily dissolves carbon, the solubility of carbon in uranium is negligible below 2000°C [181]. Thus, between 1300°C and 2000°C, uranium carbide is probably not formed, whereas, between 2000°C

Figure 38. ETV-ICP-MS signals for 100 pg of uranium in 0.2% HNO₃ at various vaporization temperatures: (a) 1400°C; (b) 2400°C; (c) 2600°C; (d) 2700°C.

and 2400°C, uranium carbide could be formed. Uranium carbide, however, would not be vaporized until higher vaporization temperatures [181], hence the single $^{238}\text{U}^+$ peak observed for uranium at lower temperatures.

At temperatures above 2500°C, the integrated signal for $^{238}\text{U}^+$ increases significantly as more uranium is vaporized from the ETV surface. Above 2400°C, both UO_2 and UO may be vaporized, however, only single peaks were observed until 2600°C (Fig.38c) when a shoulder appeared on the trailing edge of the $^{238}\text{U}^+$ peak. A further increase in temperature to 2700°C resulted in a dramatic increase in integrated signal for uranium. The increase is primarily due to the large second peak of the ETV-ICP-MS signal (Fig.38d) between two and five seconds into the high temperature vaporization step. This second peak results from the vaporization of a second species of uranium, probably the carbide. At temperatures above 2000°C, complete mutual solubility of UC and UC_2 has been reported [181]. Both UC and UC_2 are thermally stable with melting points of 2560°C and 2400°C, respectively. Uranium carbide (UC_2) has a boiling point of 4378°C. Under normal vaporization conditions, with maximum power heating, uranium is vaporized as a single peak below 2600°C. At higher temperatures, however, the ETV-ICP-MS signal for $^{238}\text{U}^+$ becomes "doubled peaked".

Significant memory effects were observed following the vaporization of uranium at all temperatures, but especially for lower vaporization temperatures. The extent of this memory effect is reflected by the signal to background (S/B) ratios. Table 14 summarizes the effect of vaporization temperatures on the S/B ratios for 100 pg of uranium vaporized in three different matrices. The uranium signal was measured using

100 pg of uranium and the background signal was obtained by the signal obtained from an appropriate sample blank, containing 0.2% HNO₃, fired prior to the 100 pg sample. For 0.2% HNO₃ and 0.2% HCl solution, the maximum S/B ratios was obtained at a vaporization temperature of 1400°C.

Clearly, lower vaporization temperatures result in higher signal to background ratios for all matrices. Although the ETV-ICP-MS signals for ²³⁸U⁺ were severely suppressed in the presence of NaCl, a similar trend was observed with a maximum S/B ratio obtained at 1600°C. These lower vaporization temperatures correspond to the region where uranium is released as UO₂. Although the ²³⁸U⁺ signal intensity is increased significantly at 2700°C, the formation of uranium carbide is also increased and hence, the background signal is much greater.

For all three matrices, a dramatic reduction in S/B ratio occurs above 2600°C, with the ratio reduced to 3.5 in the NaCl matrix, to 2 in 0.2% HCl and to 2.6 in a 0.2% HNO₃ matrix. This reduction in S/B ratio and increase in memory effect occurs, coincidentally, at a temperature where the second peak (Fig. 38d) attributed to the release of UC₂ is well developed. Hence, for the determination of uranium by ETV-ICP-MS, the optimum vaporization temperature should be below 2500°C, where only single ²³⁸U⁺ peaks are observed and the S/B ratio is not degraded significantly by memory effects from the release of carbide species.

5.3.2 Uranium Signal Suppression by Chloride.

The suppression of ²³⁸U⁺ ETV-ICP-MS signals by NaCl has been reported by a number of researchers [20,179]. Because most environmental and biological

Table 14. Effect of vaporization temperature on the signal to background (S/B) ratio for the vaporization of 100 pg uranium from different matrices.

Vaporization Temperature, °C	Signal to Background (S/B) Ratio		
	0.2% HNO ₃	0.2% HCl	0.5 µg NaCl
1000	21.6	25.1	17.6
1100	41.4	44.5	12.1
1200	51.1	59.2	15.5
1300	58.1	63.6	18.4
1400	64.5	74.0	19.9
1600	32.3	58.8	29.8
1800	34.0	40.8	28.5
2000	26.5	40.0	21.5
2300	22.1	40.2	28.0
2600	10.8	25.9	13.3
2700	2.6	2.0	3.5

samples contain some NaCl, the sensitivity of uranium determination in these matrices would be adversely affected. Thus, understanding the nature and control of $^{238}\text{U}^+$ signal suppression by chloride salts is of interest.

Figure 39 shows the vaporization curve for 100 pg uranium in 0.2% HCl and with 0.5 μg of NaCl as well as in 0.2% HNO_3 . The vaporization curve for uranium in both chloride matrices is qualitatively similar to the vaporization curve for uranium obtained in 0.2% HNO_3 . The only significant difference is the magnitude of the $^{238}\text{U}^+$ signal suppression in the presence of 0.2% HCl and in 0.5 μg of NaCl. The vaporization curve (Fig.39) increases gradually between 1600°C and 2500°C in the presence of a halide matrix, as does the vaporization curve obtained for uranium in the presence of 0.2% HNO_3 . A small rise at 1300°C was observed in the NaCl matrix, however, this may be due to the condensation of uranium oxide on the transfer line.

Figure 40 shows a series of ETV-ICP-MS signal pulses for the vaporization of uranium in a 0.5 μg NaCl matrix. The similarity in the peak shapes, the appearance temperature (1100°C) and the appearance time (0.8 s), obtained for the three vaporization curves, suggests that the species vaporized in the two chloride matrices are the same as that vaporized in 0.2% HNO_3 , i.e. UO_2 at lower temperatures and uranium carbide at temperatures above 2400°C. Although the formation of uranium halides such as UCl_3 and UCl_4 in the pyrolysis step is possible, all of the uranium chlorides have melting points and boiling points well below 1000°C. Therefore, the vaporization of uranium as uranium chloride complexes is extremely unlikely as no $^{238}\text{U}^+$ is detected at temperatures below 1100°C. Trace of water vapour may also form uranyl chloride,

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Figure 39. Vaporization curve for 100 pg of $^{238}\text{U}^+$ in various matrices: (a) 0.2% HNO_3 ; (b) 0.2% HCl ; (c) $0.5\ \mu\text{g}$ NaCl . Samples were vaporized from the walls of a pyrolytically coated graphite tube.

Figure 40. ETV-ICP-MS signals for 100 pg of uranium in 0.5 μ g NaCl at various vaporization temperatures: (a) 1400°C; (b) 2400°C; (c) 2600°C; and (d) 2700°C.

UO₂Cl₂. Uranyl chloride is only stable up to temperatures of 450°C, at which point it decomposes, giving uranium dioxide and chlorine:

This suggests that for temperatures between 1100°C (Fig.40a) and 2400°C (Fig.40b), uranium is not vaporized as the chloride (UCl₄), or as uranyl chloride.

Figure 39 also shows that the integrated signal for uranium rises sharply at temperatures above 2600°C, in both halide matrices, in much the same manner as the ²³⁸U⁺ signal in 0.2% HNO₃. This sharp increase in the integrated ²³⁸U⁺ signal corresponds to an increase in a second peak of the ²³⁸U⁺ ETV-ICP-MS signal. One noticeable difference between the ETV-ICP-MS signals in 0.2%HNO₃ matrix (Fig.38) and the NaCl matrix (Fig.40) is the change in relative intensities of the first and second peaks at 2600° and 2700°C. In the presence of NaCl, at 2600°C (Fig.40c), the intensity of the earlier peak attributed to the vaporization of UO₂ is suppressed, relative to the intensity of the later peak, which arises from the vaporization of uranium carbide signal. This suggests that the addition of NaCl promotes the conversion of some UO₂ to carbide and that the suppression of the ²³⁸U⁺ signal by NaCl could be caused by the formation of additional carbide.

In order to test this hypothesis, 100 pg of uranium was vaporized at 2700°C, followed by 10 firings of the ETV at 2650°C, using a sample blank as 0.2% HNO₃. Ideally, an increase in the amount of uranium retained in the ETV as the carbide with a NaCl matrix would be reflected by an increase in the sum of the integrated signal of

the ten re-firings with the ETV. The results of these experiments, summarized in Figure 41, show that the number of ETV re-firings required to remove the carbide at 2650°C was similar in all three matrices. In each case, the number of re-firings required for the $^{238}\text{U}^+$ signal to return to baseline was six or seven. This may suggest that the amount of carbide formed is similar in all three matrices, however, these data revealed that, as a percentage of the total signal, the sum of ten re-firings of the ETV for vaporization in a 0.2% HNO_3 and 0.2% HCl was about $52\% \pm 5\%$, whereas for uranium vaporized in a matrix of $0.5\mu\text{g}$ NaCl , the sum of ten re-firings of the ETV was slightly higher at $64\% \pm 5\%$. This would indicate that slightly more uranium is retained on the ETV, possibly as the carbide in the NaCl matrix, however, the large amount of uncertainty in this type of experiment makes the result somewhat inconclusive. Whereas slightly more uranium is retained (12%) in the NaCl matrix, this does not account for $^{238}\text{U}^+$ signal suppression of 50% or more. As well, the formation of uranium carbide in the ETV at temperatures above 2000°C may explain the $^{238}\text{U}^+$ signal suppression, it does not explain the $^{238}\text{U}^+$ signal suppression at lower temperatures (below 2000°C) in a NaCl matrix where uranium carbide is not expected to form.

A close examination of the ETV-ICP-MS $^{238}\text{U}^+$ signals in each matrix, however, suggest a mechanism for chloride suppression of the $^{238}\text{U}^+$ signal. Figure 42 shows the ETV-ICP-MS signal for 100 pg of uranium in 0.2% HNO_3 (Fig.42a), 0.2% HCl (Fig.42b) and $0.5\mu\text{g}$ of NaCl (Fig.42c) vaporized at 2700°C. At this temperature, the $^{238}\text{U}^+$ signal is suppressed by both chloride matrices, but more so with NaCl . This is not surprising since more chloride is retained on the graphite surface with the less volatile

Figure 41. Integrated signal intensity of ETV blank refiring after vaporizing 100 pg uranium at 2600°C in various matrices: 0.2% HNO₃; 0.2% HCl; and 0.5µg NaCl.

NaCl than with HCl, at higher temperatures. Figure 43 illustrates the simultaneous vaporization of chloride from NaCl clearly overlapping the first peak, UO_2 at 2700°C (Fig.43a) and at 2500°C (Fig.43b). Chemically, the thermal decomposition of uranium oxide is similar in either the nitrate or chloride matrices, therefore, the nature of the $^{238}\text{U}^+$ signal suppression by NaCl at lower temperatures (below 2000°C) is likely due to a physical effect such as intercalation of uranium species by graphite. At higher temperatures (above 2000°C), the $^{238}\text{U}^+$ signal suppression may be a result of uranium carbide formation. Chlorides are known to form intercalation compounds with graphite and the formation of sodium intercalation compounds has also been reported [30,184]. Sodium chloride may cleave graphite along its basal plane. The resulting larger interlayer distance between the parallel planes of carbon atoms could allow intercalation once this cleavage has occurred.

In order to determine the roles of NaCl and graphite in the suppression of the $^{238}\text{U}^+$ signal, the graphite surface was replaced by a tungsten surface. For these experiments, a strip of tungsten foil (< 0.1 mm thick) was inserted manually into the graphite tube, preventing sample solution from interacting with the graphite. Spreading of the sample solution was more severe with a metal surface than with graphite. A small volume ($5\ \mu\text{L}$) of solution was deposited to prevent possible spreading of the sample from the graphite strip onto the graphite. By using a tungsten surface, chemical reactions between NaCl and uranium could still occur and the effects of the graphite surface are eliminated. Vaporization temperatures above 2200°C were not used to avoid plasma loading by tungsten [185]. Figure 44 shows the ETV-ICP-MS signal for 100 pg

Figure 42.

Comparison of ETV-ICP-MS signals for 100 pg of uranium at 2700 °C in three matrices: (a) 0.2% HNO₃; (b) 0.2% HCl; (c) 0.5 μg NaCl. Note the progressive suppression of the UO₂ peak with increased amounts of chloride.

Figure 43. Vaporization of 100 pg uranium at two temperatures: (a) 2700 °C; (b) 2500 °C; showing the coincident vaporization of chloride from sodium chloride with the suppressed UO₂ peak.

of $^{238}\text{U}^+$ in 0.2% HNO_3 (Fig.44a) and 1.0 μg of NaCl (Fig.44b) from a graphite surface and a tungsten surface. Using the same tube and temperature program, ETV-ICP-MS $^{238}\text{U}^+$ signals for 100 pg of uranium in 0.2% HNO_3 (Fig.44c) and 1.0 μg NaCl (Fig.44d) from a tungsten surface at 2200°C are shown. Vaporizing uranium from a tungsten surface in a NaCl matrix did not suppress the ETV-ICP-MS signal. These results demonstrate that chemical reactions alone between NaCl and uranium oxide do not result in the $^{238}\text{U}^+$ signal suppression and that the graphite surface also plays an important role in the $^{238}\text{U}^+$ signal suppression by NaCl. Because of the high temperatures required for uranium carbide formation, NaCl probably enhances the intercalation of uranium in the graphite at lower temperatures (below 2000°C). At higher temperatures (above 2000°C), this increased intercalation results in increased uranium carbide formation. Since the amount of uranium vaporized as a carbide does not appear to increase significantly with NaCl, when compared to a matrix containing 0.2% HNO_3 , its role in promoting the formation of uranium carbide is probably minimal. It is likely that temperature plays a more important role in uranium carbide formation in the graphite tube. Intercalation seems the most logical explanation for this phenomenon.

5.3.3 Analytical Figures of Merit

Table 15 summarizes analytical figures of merit obtained for the determination of uranium vaporized from graphite and tungsten surfaces in 0.2% HNO_3 matrix and in the presence of 0.5 μg NaCl. Integrated ion counts obtained for the vaporization of uranium from a tungsten surface are about 4.5-fold greater than those obtained for

Figure 44. Vaporization of 50 pg uranium at 2200 °C on graphite from: (a) graphite surface in 0.2% HNO₃; (b) graphite in 0.05 μg NaCl; (c) tungsten surface in 0.2% HNO₃; (d) tungsten surface in 0.5 μg NaCl.

vaporization from a graphite surface. This improvement in sensitivity (integrated ion counts) is largely due to the effect of the tungsten liner in reducing uranium losses due to intercalation of uranium into the graphite and uranium carbide formation. Vaporized tungsten also acts as an effective carrier for uranium. The addition of NaCl does not affect the integrated $^{238}\text{U}^+$ signal when vaporization takes place on a tungsten surface, with and without NaCl. The data in Table 15 also show that a tungsten vaporization surface improves the relative standard deviation for the measurement of integrated ion signals.

Limits of detection obtained for uranium under various experimental conditions show that although vaporization from a tungsten surface improves sensitivity, a high $^{238}\text{U}^+$ background originating from contamination in the tungsten itself serves to degrade detection limits. Clearly, if a uranium-free source of tungsten or some other refractory metal such as Ta or Re were found, then limits of detection could be improved by at least an order of magnitude over those obtained using a graphite vaporization surface. The use of a tungsten vaporization surface eliminates uranium carbide formation, signal tailing and a continuously increasing (with each firing) uranium background characteristic of vaporization from a graphite surface. A vaporization temperature of up to 2200°C can be used without significantly degrading the tungsten foil surface or loading the plasma with excess tungsten vapour.

5.3.4 Chemical Modification

Attempts to control $^{238}\text{U}^+$ signal suppression in the presence of NaCl by varying vaporization conditions met with little success. Careful studies of the effect of pyrolysis

Table 15. Analytical figures of merit for the determination of uranium by ETV-ICP-MS.

	Graphite Surface		Tungsten Surface	
Matrix	0.2% HNO ₃	0.5 μ g NaCl	0.2% HNO ₃	0.5 μ gNaCl
Net Intensity (RSD, %)	60,409(7.1)	26,079(8.5)	263,885(9.0)	268,860(4.7)
Blank (FSD, %)	93(13)	40(23)	1320(9.0)	7164(2.7)
Absolute LOD (fg)	29	51	69	109
Relative LOD* (pg g ⁻¹)	0.29	0.50	0.69	1.1

*Based on a 50 μ L sample volume; LOD = limit of detection based on the mass or concentration of uranium giving integrated counts equivalent to 3 x Standard Deviation (SD) of the background signal; 50 pg uranium, n=7. Vaporization temperatures: Graphite: 2650 °C; Tungsten: 1800 °C.

temperatures and cycle duration times on the removal of the NaCl matrix prior to the vaporization of uranium resulted in a reduction of analyte signal suppression by only 10%. Pyrolysis temperatures over 900°C resulted in lower $^{238}\text{U}^+$ signals because of the volatilization of uranium oxide. Therefore, because of the high volatility of uranium oxide and the high "sticking probability" of NaCl to graphite, varying the conditions of the pyrolysis step alone have a minimal effect on recovering the uranium signal.

Chemical modifiers which preferentially remove chlorides from NaCl have been extensively studied for use in GFAAS. For example, Ediger [186] used ammonium nitrate to remove the interference of NaCl forming the more volatile NH_4Cl and NaNO_3 . The use of NaNO_3 also allowed the investigation of the effects of Na and Cl on uranium. When NH_4NO_3 was used with the vaporization of uranium in the presence of NaCl, this modifier was only partially successful in reducing the $^{238}\text{U}^+$ signal suppression by about 10%. Higher concentrations of up to 1% HNO_3 had a smaller effect on reducing the effects of $^{238}\text{U}^+$ signal suppression by NaCl and did not recover the suppressed uranium signal significantly. Clearly, the chemical modifiers investigated in this study were ineffective in preventing the $^{238}\text{U}^+$ signal suppression caused by NaCl.

Chemical modifiers can improve the sensitivity of an analyte and reduce matrix effects by converting the analyte of interest to a more volatile species. For example, conversion of the more thermally stable oxide to a volatile halide which is more easily vaporized and transported to the plasma. For the determination of uranium by ETV-ICP-MS, Freon-23 (CHF_3) has been used to improve sensitivity [174]. The suggested mechanism responsible for signal enhancement with Freons is by the formation of

volatile uranium fluoride, in the gas phase, which is more easily vaporized and transported to the plasma than metallic uranium [174].

Two types of fluorine compounds were investigated for use as chemical modifiers: 0.2% HF and 0.3% CHF_3 (Freon-23) added to the argon carrier gas. Each was examined to evaluate their usefulness in reducing memory effects by preventing the formation of uranium carbides. For these experiments, 100 pg of uranium was vaporized from the walls of the graphite tube ETV using a pyrolysis temperature of 400°C and vaporization temperatures between 2000°C and 2700°C . Uranium signals using a 0.2% HF modifier were identical in peak shape and size to those obtained in a 0.2% HNO_3 matrix and thus, did not prevent the formation of uranium carbide or the double peaks observed at 2700°C .

Figure 45 shows $^{238}\text{U}^+$ signals for 100 pg uranium vaporized alone (Fig.45a) and in the presence of $0.5\ \mu\text{g}$ NaCl (Fig. 45b) using pure argon (solid lines) and argon containing 0.3% CHF_3 (broken lines) as a carrier gas. Figure 45(a) shows that when CHF_3 is added to the argon carrier gas, the $^{238}\text{U}^+$ signal is significantly enhanced with the integrated $^{238}\text{U}^+$ signal increasing from a value of 78,720 counts to 131,000 counts. When NaCl is added to the solution containing uranium, the $^{238}\text{U}^+$ signal is clearly suppressed (Fig.45b - solid line). When 0.3% CHF_3 is added to the argon carrier gas flow (Fig.45 b - broken line), the $^{238}\text{U}^+$ signal is almost totally recovered giving an integrated signal of 113,400 counts, or 87% of the signal obtained when uranium is vaporized alone (without NaCl). In both cases, the presence of CHF_3 in the argon carrier gas results in a single-peak $^{238}\text{U}^+$ signal with no tailing or memory effect. These

Figure 45. Vaporization of 50 pg uranium with (.....) and without (—) 0.3% CHF₃ in the argon carrier flow in two different matrices: (a) 0.2% HNO₃ and (b) 0.5 μg NaCl.

results show that CHF_3 is an effective chemical modifier, capable of preventing, to a large extent, the formation of uranium carbide and the intercalation of uranium in graphite in the presence of NaCl. It is reasonable to conclude that the use of CHF_3 could improve limits of detection given in table 15 by a factor of 2 or more.

5.4 SUMMARY AND CONCLUSIONS

The results from the ETV-ICP-MS demonstrate that uranium vaporizes primarily as molecular species. Although the ETV-ICP-MS provides only indirect evidence, the ETV-ICP-MS signals for $^{238}\text{U}^+$ indicate that more than one species is vaporized in the ETV, probably oxide species at lower temperatures and uranium carbide at higher temperatures. The existence of molecular species during the high temperature vaporization/atomization step explains the poor sensitivity of uranium using GFASS, by the pre-atomization loss of uranium as the oxide. Further studies on metal vaporization surfaces (W, Mo or Re), may provide useful alternatives to the graphite surface. It is unlikely, however, that such surfaces will gain as widespread use as the standard pyrolytic graphite tube, except possibly for elements which form carbides.

CONCLUSIONS AND FUTURE RESEARCH

Vaporization studies for a number of elements showed that matrix effects are observed with a number of commonly used mineral acids. The formation of molecular species, such as oxides or halides, is not a serious problem with electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). Vaporization of analyte as molecular species is actually favourable for ETV-ICP-MS since the transport efficiency of these species is higher than their elemental form. Clearly, one must exercise caution with "real world" samples and employ a pyrolysis step with a calibration scheme such as the method of standard additions. For ETV-ICP-MS determinations, matrices which are high in salts may not be a problem for most elements since most of the matrix can be removed prior to vaporization using a pyrolysis step. Furthermore, the matrix itself may act as a physical carrier which can assist in the mass transport of analyte to the ICP.

The ETV-ICP-MS has provided the much-needed tool to study the mechanisms for loss of analyte elements as refractory species (e.g. oxides and carbides) in graphite furnace atomic absorption spectrometry (GFAAS). The similarity in GFAAS and ETV-ICP-MS make these techniques complementary for studying the vaporization and atomization properties of almost any element in the Periodic Table. One exception in this study was cerium, however, the ETV-ICP-MS did provide useful information regarding the vaporization of this element.

It was speculated in the literature for boron that carbide formation was responsible for the poor sensitivity with GFAAS. The results from this study show that boron is lost as a molecular species which is vaporized at relatively low temperatures.

Studies of the spatial distribution of molecular and atomic boron species, with digital imaging using a CCD camera provided complementary information regarding the vaporization and atomization of this element. The results obtained with the CCD camera also show that the reduced ETV-ICP-MS signals for $^{10}\text{B}^+$ at temperatures above 1800°C are likely due to decreased levels of boron oxide and increased levels of elemental boron, the latter being less efficiently transported to the ICP-MS.

Investigations on the mechanism of vaporization and atomization of Rare Earth Elements in this study were hampered by the lack of fundamental data for these elements. The similarity of the appearance temperatures using either GFAAS or ETV-ICP-MS suggest the same species was detected by both techniques. For most REEs, comparison of the slopes of vaporization and atomization curves suggest that molecular species, probably carbides, were vaporized and detected by ETV-ICP-MS at temperatures above 2500°C .

Studies on the vaporization and atomization of uranium revealed that a molecular species was volatilized at low temperatures, suggesting that an oxide was formed. At high temperatures (2700°C), the ETV-ICP-MS signal for $^{238}\text{U}^+$ had two peaks, indicating the vaporization of a second uranium species. This strongly suggests that at high temperatures, uranium forms carbides.

The investigation of mechanisms of vaporization and atomization can lead to improved methods with the ETV-ICP-MS. Research of this nature can lead to a better way of using this technique. For example, one should not use vaporization step temperatures which are higher than that required for the vaporization of the analyte, possibly in its molecular form. This has been clearly demonstrated for boron and

uranium. For boron, maximum $^{10}\text{B}^+$ signals are obtained at 1800°C and higher temperatures result in a decrease in the analyte signal. This decrease is probably caused by the decreased transport efficiency of the elemental form of the analyte compared to that of the oxide. For uranium, single peaks are obtained at temperatures of 2600°C or lower. Higher temperatures which cause high background signals and low reproducibility of the peak area should be avoided. Unlike boron and uranium, the highest possible temperatures must be used for many of the Rare Earth Elements as most have very low volatilities.

On its own, the ETV-ICP-MS approach does not provide a direct method for determining atomization mechanisms or identifying surface and gas-phase species. If ETV-ICP-MS is used in conjunction with other complimentary techniques, such as atomic absorption spectrometry (AAS) will provide useful information regarding the chemistry inside the graphite furnace.

As an extension of the investigations of this thesis, future studies which can be made are: (i) the vaporization of analyte from a metal-surface ETV and (ii) the study of mechanisms of chemical modification for ETV-ICP-MS.

In this thesis, tungsten was the only alternative surface to graphite for the vaporization of uranium and a few REEs. A comprehensive study of the vaporization of elements from other metal surfaces should be productive. Some of the metal surfaces worth studying include tungsten, rhenium, tantalum and molybdenum. The benefit of using metal-surface ETVs is that the volatilization of the metal from the metal-surface ETV, at high temperatures, can act as a physical carrier. This would be especially beneficial to elements such as silver or cadmium which vaporize in their elemental form

and thus, are prone to transport losses. Metal surfaces such as tungsten, rhenium, tantalum or molybdenum may be useful for elements which suffer from severe memory effects associated with carbide formation of the graphite ETV. Preliminary studies should be carried out to investigate the vaporization properties using a metal surface ETV. Some of the problems which may arise include "loading" of the plasma with metal vapour from the ETV, which could suppress analyte signals. Also, high purity- metals contain significant traces of impurity which may make them unsuitable for ultratrace analysis of some elements.

A second area of research may involve the study of physical carriers and chemical modifiers. A detailed study of Freon as gas-phase chemical modifiers is desirable since it is unclear exactly how this type of chemical modifier works in the gas phase. For example, Freon appears to lower the appearance temperature of many vaporized elements, but for some elements there is no effect, suggesting that some elements may not form halide molecules with Freon in the gas phase. Perhaps most elements form molecular halides but, for some elements, their bond strength is too low and these molecules dissociate, either on the graphite surface or in the gas phase.

It is likely that with Freon a combination of carrier effects, from increased soot particles which act as nucleation sites, and the formation of halide molecules is responsible for the enhanced signals when this physical carrier/chemical modifier is used. Some experiments which should be conducted to investigate the mechanism of this modifier should include: an investigation of the effects of heating rates and vaporization curves both with and without Freon in the argon carrier gas flow. If a high enough heating rate is used, then it is possible that Freon is not beneficial for some elements.

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