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Investigation of Vaporization and Condensation Mechanisms in Electrothermal Vaporizers

by

Dianne M Hughes

**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
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Abstract

The mechanism of volatilization of tungsten from a graphite substrate has been investigated using electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). Vaporization temperatures in the range from 800 to 2700°C were studied where two distinct processes occur. Tungsten oxide is volatilized at temperatures as low as 850°C and tungsten carbide is vaporized at temperatures above 2500°C. Halide solution chemical modifiers were ineffective in preventing carbide formation.

NASS-3 (seawater) was studied for use as a physical carrier in ETV-ICP-MS. Its ability to increase the transport efficiency of analytes over wide ranging volatilities was investigated from a mechanistic viewpoint. Hydrolysis of MgCl_2 increases the transport efficiency of highly volatile elements, NaCl volatilization affects elements of intermediate volatility, and MgO vaporization affects elements of low volatility. A decrease in the ETV heating rate results in greater enhancements when the matrix element and the analyte covaporize.

The spatial and temporal non-uniformity of the condensation of vapours was investigated by the use of a charged coupled device for imaging of the interior of the graphite tube furnace. The non-uniform distributions of the condensed-phase particle clouds were attributed to the gas-flow patterns that developed in the graphite tube furnace during heating, and the steep temperatures gradients that developed along the longitudinal axis of the end-heated graphite tube of the Massmann-type graphite furnace.

The spectral interference with $^{31}\text{P}^+$ by the $^{14}\text{N}^{16}\text{O}^1\text{H}^+$ polyatomic ion was essentially eliminated using electrothermal vaporization sample introduction for ICP mass spectrometry (ETV-ICP-MS). The thermal vaporization characteristics of various phosphorus compounds were investigated. The interference from the presence of iron was investigated and was found to be most pronounced at high graphite tube heating rates. Nickel, La and Zr were used as chemical modifiers in order to stabilize P to higher vaporization temperatures through compound formation. Zirconium was found to be the best chemical modifier for removing the interference produced by the presence of an iron matrix and could be added in large amounts without itself causing P signal suppression. An absolute detection limit of 4 pg was obtained for P vaporized in the presence of 2 μg of zirconium.

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INTRODUCTION

The investigation of vaporization and condensation mechanisms in electrothermal vaporizers provides valuable information to facilitate their use at optimum levels and important knowledge so that freedom from interferences can be realized. Electrothermal vaporizers are used to vaporize analytes and produce a gaseous atomic population for graphite furnace atomic absorption spectrometry (GFAAS). L'vov pioneered the use of the graphite furnace and the first publication appeared in English in 1961 [1]. Over the years its use gained in popularity because of the extremely low detection limits attainable with this technique. A number of improvements in the instrumental design and methodologies have made the technique invaluable in the analysis of a wide range of elements in all types of samples. The electrothermal vaporizer is also becoming increasingly used for sample introduction for inductively coupled plasma mass spectrometry (ICP-MS). The use of ICP-MS rapidly has gained in popularity since its introduction because of its high speed, multi-element capability and low detection limits. The most common method of sample introduction in ICP-MS is solution nebulization, but this sample introduction technique does suffer some drawbacks that can be avoided by using an electrothermal vaporizer (ETV). Since vaporization of the analyte occurs in an electrothermal vaporizer the plasma no longer has to desolvate the sample and to vaporize it, this results in more energy being available for atomization, ionization and excitation [2]. The ETV as a sample introduction technique also offers the additional advantage of higher transport

efficiencies, lower detection limits, requires very little sample, can handle higher salt levels, suffers from greatly reduced isobaric interferences from solvent species and allows thermal pretreatment of the sample to remove unwanted matrix species [2]. Knowledge of vaporization, atomization and condensation mechanisms will enable these techniques to be used to their best advantage.

The mechanism of vaporization of tungsten was investigated in this thesis in order to determine the reason why it is indeterminable by GFAAS [3]. It was also considered to be an ideal element to study in order to investigate carbide formation and methods to reduce this occurrence. The optimum experimental conditions were also investigated to enable its routine determination by ETV-ICP-MS.

The use of NASS-3 (seawater CRM) was investigated in order to determine its mechanism of action and its ability to function as a multi-element physical carrier. The use of a physical carrier in ETV-ICP-MS is necessary to form a transportable aerosol and achieve good transport efficiency of the analyte [4]. Since analytes of interest have wide ranging volatilities it was expected that a "universal" physical carrier must be composed of a mixture of compounds so that concurrent vaporization of analyte and carrier takes place to facilitate the formation of a transportable aerosol. NASS-3 was investigated for this purpose because it was expected to possess the necessary attributes to fulfill this role. Numerous experimental parameters were investigated in order to elucidate how it functions and the factors that provide the highest transport efficiency.

A charge-coupled device (CCD) camera was used to image the interior of a graphite furnace to study the condensation of vapours produced from analytes, matrix species and chemical modifiers. During the vaporization of μg masses of analytes a non-homogeneous distribution of particles was found to occur over the cross-section of the graphite tube [5]. The study of the condensation of matrix vapours utilizing digital imaging was done in order to understand this phenomenon through its ability to provide both temporally and spatially resolved images during vaporization. Using the phenomenon of light-scattering by microparticles direct observation of the non-homogeneous distributions of microparticles was made with the CCD camera. The cause of the temporal and spatial non-uniformity of these condensed-phase particle clouds was investigated, as well as the dependence of their structures on experimental parameters. Experimental conditions that reduce their formation and the effect of these microparticles on accurate background correction were also studied. A thorough understanding of this phenomenon is necessary so that chemical modifiers can be used in GFAAS without background interference.

Finally, phosphorus was investigated to understand its mechanism of vaporization. While phosphorus is determinable by GFAAS it suffers from poor detection limits, mainly because of the necessity for using non-resonance lines [6]. Although a number of studies of phosphorus in GFAAS have been conducted the interpretation of their results are complicated by the fact that excited state species whose population is exponentially dependent on temperature are measured. In

addition, most phosphorus compounds are indeterminable without the presence of a chemical modifier to stabilize them thermally to higher temperatures [7]. The use of chemical modifiers in ETV-ICP-MS for the determination of phosphorus was also investigated for removal of the interference due to the presence of iron. The use of a chemical modifier to enable thermal pretreatment of the analyte in ETV-ICP-MS can produce non-spectroscopic interferences due to the presence of a large amount of material passing through the plasma and therefore their use and optimization requires an understanding of their function and vaporization properties [8]. The optimization of the chemical modifier mass and appreciation of their volatility are much more critical than in GFAAS where they are required in much larger quantities, but must be used without causing background absorption or light-scattering.

CHAPTER 1

MECHANISM OF VOLATILIZATION OF TUNGSTEN IN A GRAPHITE FURNACE INVESTIGATED BY ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

1.1 INTRODUCTION

Electrothermal vaporization (ETV) provides an alternative means of sample introduction for inductively coupled plasma mass spectrometry (ICP-MS). This technique has the advantage of use of small sample size and the possibility of removal of matrix interferences by thermal pretreatment of the sample prior to analyte vaporization. If these advantages are to be fully exploited, then a clearer understanding of sample volatilization processes and sample transport to the plasma is necessary. When graphite substrate electrothermal vaporizers are employed the extensive literature from graphite furnace atomic absorption spectrometry (GFAAS) provides some useful insight into sample vaporization mechanisms and optimum operating conditions for the ETV. However it should be emphasized that unlike GFAAS, where efficient formation of atomic species is paramount, in ETV-ICP-MS efficient vaporization of the sample and transport to the plasma is necessary [9]. The form of the analyte species, either molecular or atomic, is of less importance. Thus some of the problems associated with poor atomization efficiencies in GFAAS may not be directly applicable to ETV-ICP-MS.

Two of the major causes for reduced sensitivity in GFAAS are (i) loss of volatile molecular species from the furnace prior to atomization, and (ii) the formation of refractory oxides and carbides. The former is not a problem in ETV-ICP-MS because any molecular analyte species vaporized from the furnace are transported to the plasma, dissociated ionized and detected by the mass spectrometer. This point was illustrated by an ETV-ICP-MS investigation of the vaporization and atomization mechanisms for boron [10]. These results show that the optimum sensitivity for the determination of boron by ETV-ICP-MS is obtained at vaporization temperatures of around 1800°C. This temperature, which is well below the normal atomization temperature for boron in GFAAS, is high enough to vaporize boron as HBO_2 and BO molecules which are transported to the plasma, dissociated and readily detected by the mass spectrometer. However the problem of carbide formation and the extent to which experience of carbide formation in GFAAS is directly applicable to ETV-ICP-MS, has not been extensively studied. For example, tungsten, which is known to be particularly prone to carbide formation, is reported [3] as not determinable by GFAAS, yet it has been determined both by ETV-ICP-MS and by ICP-AES using sample introduction from a graphite ETV. Park and Hall [11] have measured tungsten in geological samples by ETV-ICP-MS, using a graphite strip vaporizer, and report detection limits of around 5 pg. Kirkbright and Snook [12] and Matousek [13] report detection limits for tungsten of around 0.06 ng for ICP-AES with sample introduction from a graphite electrothermal vaporizer. In the case of ICP-AES, detection limits for

tungsten are significantly improved ($\times 100$) when gaseous halide chemical modifiers such as Freon [12] and chlorine [13] are added to the ETV argon carrier gas. Similar sensitivity enhancements have also been reported [14] when 0.25 M NaF was used as a chemical modifier in the determination of Ca, Sr, Zr and Al by ICP-AES, using a graphite cup direct sample insertion device. These enhancements were attributed to the prevention of carbide formation by the NaF and the preferential volatilization of the analyte in the form of fluorides.

It is the purpose of this study to use ETV-ICP-MS to investigate the mechanism of vaporization of tungsten from a heated graphite substrate, and to assess the extent of the problem of carbide formation. The effectiveness of halide solution chemical modifiers in the prevention of carbide formation is also studied.

1.2 EXPERIMENTAL

1.2.1 Apparatus

A Perkin-Elmer Sciex Elan 5000 ICP mass spectrometer equipped with an HGA-600MS electrothermal vaporizer and a model AS-60 autosampler was used. Tube wall vaporization was used for all experiments using pyrolytically coated graphite tubes (Perkin-Elmer part No. 091504). A PTFE tube of 80 cm in length and 6 mm inner diameter was used to connect the HGA-600MS to the plasma torch. The experimental conditions for both the Elan 5000 and HGA-600MS are given in Table 1. Optimization of plasma and mass spectrometer conditions was accomplished using solution nebulization sample introduction. The operation of the HGA-600MS was completely

Table 1: Instrumental Operating Conditions**ICP mass spectrometer**

Rf power	1000 W
Coolant Ar flow rate	15.0 L min ⁻¹
Auxiliary Ar flow rate	900 mL min ⁻¹
Carrier Ar flow rate	750 mL min ⁻¹
Sampler	nickel
Skimmer	platinum

HGA-600MS electrothermal vaporizer

Sample volume	20 µL
Internal Ar flow rate (dry and pyrolysis steps)	300 mL min ⁻¹
Dry step (10 s ramp)	120°C for 40 s
Pyrolysis step	variable for 10 s
Vaporization step	variable for 6 s
Cleanup step	2750°C for 5 s

Data acquisition

Dwell time	10 ms
Scan mode	peak hopping
Points/spectral peak	1
Signal measurement	Area
Resolution	0.65 u at 10% maximum

computer controlled. 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 vapors through the dosing hole of the graphite tube. During the high temperature or vaporization step, a graphite probe was pneumatically activated to seal the dosing hole. Once the graphite tube was sealed, a valve located at one end of the HGA workhead directed the carrier argon gas flow originating from the far end of the graphite tube directly to the argon plasma at a flow rate of 750 mL min^{-1} .

1.2.2 Standards and Reagents

High purity argon gas (99.995%, Matheson Gas Products) was used. Solutions were prepared with ultra-pure water obtained from a Mill-Q 2 water purification system (Millipore Corp., Mississauga, ON). The nitric acid used was analytical grade (Ultrax). The W stock solution (10 ppm) was supplied by Spex Industries, Edison, NJ. For the determination of detection limits, a 5 ppb W solution was prepared from the stock solution and for all other experiments a 25 ppb W solution was used. The NaCl ($0.1 \mu\text{g } \mu\text{L}^{-1}$) chemical modifier was prepared by dissolving NaCl (99.9% pure, BDH Chemical, Analar grade) in ultrapure water.

1.3 RESULTS AND DISCUSSION

A preliminary experiment was conducted in order to determine the optimum flow rate for the ETV argon carrier gas and to ascertain if any molecular species, such as tungsten oxide or carbide, could be detected at various plasma sampling depths. In these experiments 250 pg of tungsten in a 0.01% HNO_3 solution were vaporized at a

temperature of 2700°C. Figure 1 shows that for ETV-ICP-MS the maximum sensitivity for tungsten is obtained with a nebulizer flow rate of 750 mL min⁻¹. This compares with an optimum flow rate of 1000 mL min⁻¹ for solution nebulization. At an r.f. power of 1000 W no significant amount of WO⁺ or WC⁺ was detected by the mass spectrometer. In all subsequent ETV-ICP-MS experiments the optimum flow rate of 750 mL min⁻¹ was used. The effect of the nebulizer flow rate on the analyte signals can be seen in figure 2 and on the stability of the argon dimer in figure 3. When a multielement analysis is being conducted it is necessary to pick the best conditions for the range of elements being studied. This would represent a compromise situation but would still enable good sensitivity. If only a single element is being examined, as in the present study, the plasma parameters can be set at their optimum settings to achieve the highest sensitivity.

1.3.1 Vaporization Mechanism for Tungsten

Fig. 4 shows the ETV-ICP-MS vaporization curve for tungsten, i.e. the variation of integrated signal intensity for ¹⁸⁴W⁺ as a function of vaporization temperature. In order to interpret the vaporization process for tungsten, this curve should be considered in conjunction with the series of ETV-ICP-MS signals shown in Fig. 5. The vaporization curve of Fig. 4 shows that tungsten begins to volatilize from the graphite surface at temperatures around 800°C. The amount of tungsten vaporized increases with increasing temperature up to 1000°C. Since the melting and boiling points of tungsten metal are extremely high (m.p. 3410°C, b.p. 5660°C) [15], atomic

Figure 1. Variation of ICP-MS signal intensity for $^{184}\text{W}^+$ as a function of nebulizer flow rate for (a) solution nebulization (SN); signal scale counts sec^{-1} and (b) electrothermal vaporization (ETV); signal scale integrated counts.

Figure 2. ETV-ICP-MS signal pulses for 250 pg of $^{184}\text{W}^+$ at various nebulizer flow rates.

Figure 3. ETV-ICP-MS signal pulses for $^{40}\text{Ar}^{40}\text{Ar}^+$ at various nebulizer flow rates.

Figure 4. ETV-ICP-MS vaporization curve for 250 pg of tungsten.

Figure 5. ETV-ICP-MS signals for 250 pg of tungsten at various vaporization temperatures, (a) 1000°C (b) 1300°C (c) 2300°C (d) 2700°C.

tungsten could not be volatilized at these low temperatures. However tungsten oxide, WO_3 , which would be expected to form when a tungstate solution is dried and heated [16], is much more volatile. It has a vapour pressure of 9.1 torr at 980°C [17] and is reported to sublime at around 1100°C [16]. Thus the single peak observed at a vaporization temperature of 1000°C (Fig. 5a) could be attributed to the volatilization of WO_3 .

As the vaporization temperature is raised above 1000°C the ETV-ICP-MS signal intensity, rather unexpectedly, begins to decrease and then levels off at around 20,000 counts when the vaporization temperature reaches 1400°C (Fig. 4). This decrease can be explained by the onset of tungsten carbide formation which is reported [17] to commence at about 850°C and be complete at 1410°C . As the temperature of the graphite surface rises above 1000°C any residual WO_3 which has not been vaporized will be converted to refractory WC which should not be then released until much higher vaporization temperatures. The amount of WO_3 converted to WC remains approximately constant for vaporization temperatures between 1400 and 2200°C . This is reflected by the flat portion of the vaporization curve in this temperature region and by the fact that the ETV-ICP-MS signal consists of a single peak throughout this temperature range. The peak shape at 1300°C , shown in Fig. 5b, is typical for this temperature range.

At a temperature around 2300°C the vaporization curve of Fig. 4 begins to rise as more tungsten is released from the graphite surface. This coincides with the

appearance of a small shoulder on the trailing edge of the ETV-ICP-MS signal at 2300°C (Fig. 5c). As the temperature is further increased to 2700°C the vaporization curve rises steeply and a large second peak between 2 and 8 s now appears in the ETV-ICP-MS signal pulse (Fig. 5d). This second peak can be explained by the volatilization of WC at temperatures above 2500°C. According to Sykes [18], WC melts to form a eutectic with W_2C at 2525°C and then decomposes at 2600°C to form a tungsten rich liquid and solid carbon. Thus when tungsten is vaporized from a graphite substrate there are two distinct vaporization processes. At low temperatures WO_3 is volatilized to give a single peak in ETV-ICP-MS; at temperatures above about 2500°C this signal becomes double peaked as WC is released at the higher temperature. Associated with this second and much larger carbide peak is the problem of memory effect. Figure 5d shows a typical blank signal from a refiring at a temperature of 2700°C. For this blank firing there is no memory effect associated with the early WO_3 peak between 1 and 2 s, but the memory effect from the larger carbide peak, between 2 and 8 s, amounts to about one third of the signal for 250 pg of tungsten. Double peaks and memory effects pose practical problems for the analysis of tungsten by ETV-ICP-MS. Possible strategies to overcome these problems include: (i) prevention of formation of carbide by the use of chemical modifiers, and (ii) use of lower vaporization temperatures which release only WO_3 giving a single but smaller peak without memory effects. These two strategies are explored in the remainder of this chapter.

1.3.2 Effect of Halide Solution Chemical Modifiers

Use of halide solutions as chemical modifiers have been reported to enhance the sensitivity of refractory elements in ICP-AES. Karanassios et al [14] found that the detection limits for a number of elements including Ca, Sr and Zr were improved when 0.25 M NaF was added to a graphite cup direct sample insertion device for ICP-AES. These enhancements were attributed to the prevention of carbide formation and the preferential volatilization of these elements as halides. Similar results were reported by Ng and Caruso [19] for Zr, V and Cr using 7% NH_4Cl solution as a chemical modifier. However Park and Hall [11] found that for ETV-ICP-MS NH_4Cl solution gave no significant enhancement for tungsten and that memory effects still persisted with high temperature vaporization.

In order to evaluate the efficiency of halide solution chemical modifiers in preventing the formation of tungsten carbide, 250 pg of tungsten was vaporized in the presence of two different chemical modifiers, NaCl and NaF. The amount of chemical modifier used was 0.2 μg and a high vaporization temperature (2700°C) was chosen. At this temperature the formation and release of carbide should be evidenced by the appearance in the ETV-ICP-MS signal of the second peak between 2 and 8 s. The ETV-ICP-MS signals of Fig. 6 show that neither NaCl nor NaF are effective in preventing the formation of tungsten carbide. The large carbide peak persists in the presence of these chemical modifiers and is in fact slightly enhanced, as is the earlier peak between 1 and 2 s. This enhancement can probably be attributed to the "carrier

Figure 6. Effect of halide modifiers on the ETV-ICP-MS signal for tungsten at a vaporization temperature of 2700°C (a) — 250 pg W (b) - - 250 pg W + 0.2 μ g NaCl (c) ··· 250 pg W + 0.2 μ g NaF.

effect" reported [4, 20] for a number of elements in ETV-ICP-MS where the addition of halide chemical modifiers improves the transport efficiency of the analyte between the ETV and the plasma.

The effect of one of these chemical modifiers, NaCl, was investigated for a range of lower vaporization temperatures. Figure 7 shows that for vaporization temperatures between 1300 and 2300°C NaCl chemical modifier gives only very marginal enhancements for the ETV-ICP-MS signal for tungsten. The maximum enhancement (about a factor of 2) occurs at a vaporization temperature of 1100°C. This enhancement factor is comparable with that reported [4] for a number of elements when similar amounts of NaCl modifier were used. Again these enhancements are typical of those for carrier effects in ETV-ICP-MS and cannot be attributed to suppression of carbide formation.

A question that then arises is why the large sensitivity enhancements observed for halide solution chemical modifiers with ICP-AES, using sample introduction from heated graphite surfaces, does not occur with ETV-ICP-MS. A possible explanation is that the enhancement effect is dependent on the mass of analyte used. Ng and Caruso [19] have found that when uranium was vaporized from a heated graphite cup and determined by ICP-AES, the enhancement produced by 7% m/v NH_4Cl solution was dependent on the mass of uranium analyte used. The NH_4Cl modifier gave about a ten-fold enhancement of emission intensity when a 5 μL sample of 10 p.p.m. uranium was used. However when the uranium concentration was reduced to 100 p.p.b. there was

Figure 7. Effect of NaCl modifier on the integrated signal for tungsten at various vaporization temperatures.

no significant enhancement. In our ETV-ICP-MS experiments, where no significant enhancement by chloride modifier is observed, the tungsten concentration is even lower (25 ppb). The same argument might apply to the results of Karanassios et al [14] where 0.25 M NaF solution is reported to produce large enhancements for ICP-AES analysis when a graphite cup direct sample insertion device is employed. With this direct insertion device the amount of analyte used was 250 ng, a thousand-fold greater amount than the 250 pg of tungsten used in our ETV-ICP-MS experiments. For whatever reason, it seems that experience with halide solution chemical modifiers in ETV-ICP-AES may not be directly applicable to ETV-ICP-MS, where the amount of analyte vaporized from the graphite surface is far smaller. However it is possible that the use of gaseous halide chemical modifiers, such as Freon [12] or chlorine [13], which have been applied successfully in ETV-ICP-AES, may be more effective. This point is yet to be investigated in detail.

1.3.3 Optimum Vaporization Conditions for Tungsten

Fig. 5d illustrates the two problems likely to be encountered if high vaporization temperatures are used for the ETV-ICP-MS analysis of tungsten, i.e. occurrence of double peaks and a large memory effect. Both of these problems can be avoided if lower vaporization temperatures are used. At these lower temperatures, only tungsten oxide is volatilized giving rise to a single peak, which returns to background after about 3 s. The second carbide peak and its concomitant memory effect does not occur at this temperature (see Fig. 5a, 5b). However this strategy will result in a lower

sensitivity for tungsten since the integrated signal count for tungsten at lower temperatures is less than at 2700°C (Fig. 4). An important consideration though is the ratio of the tungsten signal to background blank at various vaporization temperatures. Fig. 8 plots the signal to background ratio for 250 pg of tungsten as a function of vaporization temperature in the range 1000 to 2700°C. The same function is plotted for 250 pg of tungsten in the presence of 0.2 µg of NaCl modifier. These results show that much higher signal to background ratios are obtained at lower vaporization temperatures. In the absence of a chemical modifier this ratio has a maximum value of about 90 at a vaporization temperature of 1000°C. At 2700°C there is a considerable carbide memory effect and the signal to background ratio is reduced to around 3.1. In the presence of NaCl modifier the maximum in the tungsten signal to background ratio still occurs at a low vaporization temperature (1100°C), but it should be noted that the addition of this chemical modifier has an adverse effect on the signal to background ratio at all vaporization temperatures.

Since the signal to background ratios for tungsten show considerable variation with temperature, the limit of detection should also show some variation with vaporization temperature. Table 2 gives the limit of detection for tungsten at three different vaporization temperatures. These results show that better limits of detection are obtained at low vaporization temperatures when only WO_3 is volatilized. The limit of detection at 2700°C is about a factor of six higher. At this high temperature, tungsten carbide is also volatilized (see Fig. 5d) giving rise to two peaks and much

Figure 8. Signal to background ratio for tungsten as a function of vaporization temperatures for (a) 250 pg, no modifier and (b) 250 pg W + 0.2 µg NaCl modifier.

Table 2. Effect of vaporization temperature on limit of detection

Temperature (°C)	Absolute LOD*/pg
1000	0.68
1100	0.51
2700	3.0

* 3 x standard deviation of blank (n = 5), 10 µL sample

higher blank values from the carbide memory effect. As a result of these higher, and less reproducible blank values, the limit of detection is degraded at higher vaporization temperatures. Hence for optimum limits of detection, low vaporization temperatures should be used; however this may not always be a practical option for samples which contain a high concentration of matrix and which require thermal pretreatment for matrix removal. For example, in the ETV-ICP-MS analysis of tungsten in geological materials Park and Hall [11] used a 1700°C ashing step in order to remove the high concentration of sodium matrix introduced in the sample digestion procedure. This was followed by a high temperature vaporization step at 3000°C. This procedure resulted in limits of detection of about 5 pg, i.e. about one order of magnitude higher than we have obtained using lower vaporization temperatures.

Inclusion of a thermal pretreatment step will also result in premature loss of analyte during ashing. This point is illustrated in Fig. 9. In this experiment 250 pg of tungsten was vaporized at 2700°C following a 10 s ashing step at 1500°C. Figure 9 clearly shows two peaks for tungsten. The first peak, between 4 and 7 s, occurs during the ashing step whilst the second peak, after 15 s, occurs during the 2700°C vaporization stage. These two peaks correspond to those shown in Fig. 5d at a vaporization temperature of 2700°C. The first can be attributed to loss of volatile WO_3 during the ashing stage, whilst the second peak originates from tungsten carbide volatilized during the high temperature vaporization process. This loss of analyte

Figure 9. Temporal behaviour of $^{184}\text{W}^+$ during ashing at 1500°C (<16 s) and vaporization at 2700°C (>16 s).

during ashing will occur if a thermal pretreatment step, at any temperature above 1000°C, is included in the analytical procedure.

1.4 SUMMARY AND CONCLUSIONS

When tungsten is volatilized from a graphite substrate, two distinct vaporization processes occur resulting in two separate peaks in ETV-ICP-MS. At temperatures below 1100°C, WO_3 begins to volatilize, giving rise to the earlier peak. The intensity of this peak decreases at vaporization temperatures above 1100°C as carbide formation occurs. The tungsten carbide formed is then vaporized at temperatures above 2500°C, giving rise to a second and more intense peak in ETV-ICP-MS. Associated with this carbide peak are the problems of memory effects and consequent high blank values. Despite these problems tungsten can be determined effectively by ETV-ICP-MS, using a graphite electrothermal vaporizer, if the vaporization conditions are chosen carefully. The optimum signal to background ratio, optimum limits of detection and minimum memory effects are obtained if low vaporization temperatures can be employed. Under these conditions the higher temperature carbide peak does not appear and the memory effects and high blank values resulting from carbide release can be avoided.

This study also has implications important to the determination of W by GFAAS. Our results show that WC is in fact volatilized at 2700°C yet Slavin [3] reports that W is not determinable by GFAAS. This suggests that any WC which is vaporized is not subsequently dissociated to form W atoms. The high WC bond strength and high

vapour pressure of $C_{(g)}$, at this temperature, could combine to force the $WC_{(g)} \rightleftharpoons W_{(g)} + C_{(g)}$ equilibrium toward the left, thus effectively preventing the dissociation of $WC_{(g)}$ to produce $W_{(g)}$.

CHAPTER 2

SEAWATER AS A MULTI-COMPONENT PHYSICAL CARRIER FOR ETV-ICP-MS

2.1 INTRODUCTION

Pneumatic nebulization, the most popular form of sample introduction, suffers from poor transport efficiency (~1-2%), whereas that for ETV is much higher (up to 80%). Analyte loss during transport in electrothermal vaporization is reported to increase as the sample mass decreases, resulting in less efficient nucleation, condensation and formation of a transportable aerosol [21]. Transport efficiency has been studied by a number of workers using ETV-ICP-AES [22-28]. Transport efficiency at low sample masses, especially with volatile elements, is an important phenomenon which must be understood so that response in ETV-ICP-AES and ETV-ICP-MS can be optimized. Transport loss results in decreased sensitivity and non-linearity of calibration curves at analyte masses close to the limit of detection. The problem is especially severe when using mass spectrometry since the detection limits for ETV-ICP-MS are in the femtogram to picogram range for most elements where transport losses are very serious.

Recently, the use of physical carriers in ETV-ICP-MS has been investigated in order to improve transport efficiency [4, 20, 29]. Formation of an aerosol can enhance

efficiency by decreasing analyte deposition within the vaporization chamber and transport tubing [25]. Free atoms, being highly reactive, are more prone to deposition loss than analyte that travels in a molecular or aggregated form [25]. Formation of an aerosol occurs by condensation of the vapour on clusters which serve as nucleation sites and are present, even if the vapour is unsaturated, due to collisions among vapour species [21]. Supersaturation for a small mass (pg) of a volatile substance is difficult to achieve and therefore volatile substances are expected to suffer more transport loss [21]. Aerosol formation, even for a small mass of a volatile analyte, can be achieved by co-evaporating a larger mass of concomitant element or compound to provide condensation nuclei onto which the analyte can condense [21] and thus be efficiently transported. Grégoire [29] reported a large enhancement in response when using Te as a chemical modifier for the determination of Os. It has also been reported [20] that a Mg/Pd mixed chemical modifier can increase the mass transport efficiency of volatile elements. Ediger and Beres [4] demonstrated the effects of Pd, Mg and Na as chemical modifiers for ETV-ICP-MS detection of a number of elements and concluded that such agents were necessary for quantitative analysis.

This chapter reports on the use of NASS-3 sea-water and its major components (NaCl and MgCl_2) as physical carriers in ETV-ICP-MS applied to the determination of 10 elements (Ag, Bi, Cd, Co, Cs, Ga, In, Pb, Rb and Tl). In order to elucidate the mechanism of action, a number of experimental parameters were studied,

including the heating rate, the graphite tube vaporization temperature, chemical modifier mass, acid content and chemical modifier species. These parameters all impact on the vaporization of analyte and concomitant [21] with the result that changes in transport efficiency can occur due to an alteration in aerosol formation.

2.2 EXPERIMENTAL

2.2.1 Apparatus

A Perkin-Elmer Sciex ELAN 5000 ICP mass spectrometer equipped with an HGA-600MS electrothermal vaporizer and a model AS-60 autosampler were used. Tube wall vaporization was used for all experiments in conjunction with pyrolytically coated graphite tubes (P-E Part No. 091504). An 80 cm x 6 mm ID PTFE tube was used to connect the HGA-600MS to the plasma torch. The experimental conditions for both the Elan 5000 and HGA-600MS are summarized in Table 3. Optimization of plasma and mass spectrometer conditions was accomplished using solution nebulization sample introduction. Some of the data were collected using the "OmniRange" facility of the ELAN 5000 (Figs. 10, 21, 39) in order to bring all analyte signals on scale. This feature selectively reduces the sensitivity for a given m/z by changing the applied voltage on one of the ion lenses of the mass spectrometer system.

2.2.2 Standards and Reagents

High purity argon gas (99.995%, Matheson Gas Products, Canada) was used. Solutions were prepared with ultra-pure water obtained from a Milli-Q water

Table 3: Instrumental operating conditions**ICP mass spectrometer**

Rf power	1000 W
Coolant argon flow rate	15.0 l/min
Auxiliary argon flow rate	900 mL/min
Carrier argon flow rate	900 mL/min
Sampler	nickel
Skimmer	platinum

HGA-600MS electrothermal vaporizer

Sample volume	20 µL
Internal argon flow rate	300 mL/min
Dry stage (10 s ramp)	120°C for 40 s
Pyrolysis stage (2 s ramp)	variable for 10 s
Vaporization stage (variable ramp)	variable for 6 s
Cooldown stage (1 s ramp)	20 °C for 10 s
Cleanup stage (0 s ramp)	2750 °C for 5 s
Cooldown stage (1 s ramp)	20 °C for 10s

Data acquisition

Dwell time	10 ms
Scan mode	peak hop transient
Points/spectral peak	1
Signal measurement	Integrated area
MS resolution	high (0.6 u at 10% peak height)

purification system (Millipore Corp., Mississauga, ON). Nitric acid and hydrochloric acid were analytical grade (Ultrex), except for experiments performed with ^{15}N labelled nitric acid. The stock solution containing Ag, Bi, Cd, Co, Cs, Ga, In, Pb, Rb, Tl and Zn (10 ppm) was a multi-element ICP-MS standard (Spex Industries, Edison, NJ). A 5 ppb solution was prepared by serial dilution of the stock solution except for studies where the amount of analyte vaporized was greater than 20 pg (such as in the construction of calibration curves where a 10 ppb standard was used). The mixed carrier was NASS-3 seawater, a CRM from the National Research Council of Canada (Ottawa). The NASS-3 was purified by passage through a column of immobilized 8-hydroxyquinoline to remove trace elements and then diluted 500-fold with de-ionized water. The resulting solution contained $\approx 0.07 \mu\text{g}/\mu\text{L}$ of dissolved solids. If only chloride salts of the principle cations formed their concentrations would be $0.055 \mu\text{g}/\mu\text{L}$ NaCl, $0.011 \mu\text{g}/\mu\text{L}$ MgCl_2 , $0.0022 \mu\text{g}/\mu\text{L}$ CaCl_2 , $0.0015 \mu\text{g}/\mu\text{L}$ KCl in addition to other minor species. The above salt concentrations are higher than the true values since there is insufficient chloride in seawater for the formation of all the principle seawater cations (Na, Mg, Ca and K). The evaporation of seawater to dryness would probably result in the formation of a complex mixture of carbonates, sulphates and chlorides. Seawater contains ≈ 0.55 moles/kg chloride and therefore NaCl and MgCl_2 were investigated separately since they are two of the major species in seawater. Sodium chloride ($0.07 \mu\text{g}/\mu\text{L}$) carrier was prepared by dissolving NaCl

(99.9% pure, BDH Chemical, Analar grade) in de-ionized water. A MgCl_2 (0.07 $\mu\text{g}/\mu\text{L}$) carrier was prepared by dissolving high purity Mg metal (Spex, Industries, Inc Edison, N.J.) in minimum amount of hot HCl (Ultrex) and diluting with de-ionized water. The ^{15}N -labelled nitric acid was obtained from CIL (Cambridge Isotope Laboratories, USA). The labelled acid has a concentration of 40% (v/v) with an isotopic purity of 99% ^{15}N .

For all experiments, a 20 μL volume of sample was pipetted onto the inner wall of the graphite furnace. The total volume was maintained at a constant 20 μL for differing carrier masses by the automatic addition of diluent water by the autosampler.

2.3 RESULTS AND DISCUSSION

2.3.1 Temporal Characteristics of Physical Carriers and Analytes

A physical carrier used in ETV-ICP-MS can increase the transport efficiency of the analyte from the graphite tube to the argon plasma by providing a co-evaporating major component. To work efficiently, such a carrier must be physically present in the graphite tube at the time the analyte is vaporized. NASS-3 was selected for detailed study because it had been earlier demonstrated to be a potentially ideal mixed chemical modifier for ETV-ICP-MS use [8, 30]. The seawater CRM is readily available, inexpensive and, even prior to cleanup, contains extremely low concentrations of trace elements. Additionally, the variety of salts present in seawater provide for a near continuum release of material from the surface of the graphite tube over the duration of

the heating cycle. This affords improved transport efficiency for an extended range of elements possessing widely differing volatilities.

Figure 10A shows ETV-ICP-MS signal pulses for the major components of NASS-3, illustrating the sequential volatilization of the component salts. Figure 10B shows ETV-ICP-MS signal pulses for several analytes of widely differing volatility. This figure clearly illustrates why a single element physical carrier is only useful for a small number of analytes which possess vaporization characteristics similar to that of the carrier. The signal pulses shown in Figure 10 were obtained using maximum power heating (2000 °C/s). Even at this heating rate, a single component carrier may not be released at the appropriate time to help generate a transportable aerosol. Use of a multi-component physical carrier should prove advantageous when multi-element determinations of analytes of different volatilities are sought.

2.3.2 Effect of NASS-3, NaCl and MgCl₂ as Physical Carriers

In order to better understand the manner in which NASS-3 acts as a physical carrier, its effects on ETV-ICP-MS signal pulses from 20 pg of several analytes were studied. As well, the effects of major components of NASS-3 were individually investigated. Sodium chloride and magnesium chloride were selected since these salts comprise the majority (> 80 %) of NASS-3 dissolved solids by weight. The next most abundant species is CaCl₂ which comprises less than 3 % of the dissolved solids. The amount of carrier added was varied between 0 and 1.05 µg. The formation of coarse

Figure 10. ETV-ICP-MS signal pulses for A: 0.35 μg NASS-3 a) $^{35}\text{Cl}^+$ b) $^{23}\text{Na}^+$ c) $^{24}\text{Mg}^+$ d) $^{44}\text{Ca}^+$ and B: for 20 pg of analyte a) $^{114}\text{Cd}^+$ b) $^{69}\text{Ga}^+$ c) $^{59}\text{Co}^+$. Vaporization temperature of 2400 $^{\circ}\text{C}$ with a 0s ramp.

particles by coalescence and sintering, which could lead to settling loss, should not be a problem since the carriers were added in amounts much smaller than required to produce coarse particles. Coarse particles are reported to form only when 50-100 μg amounts of salt are vaporized [21]. Analyte solutions were acidified to 1% with either HCl or HNO_3 . The carrier compound, its mass and the accompanying acid were studied to observe their effects on the signals from 20 pg of analyte present in a multi-element standard solution. A 300 $^{\circ}\text{C}$ pyrolysis temperature was chosen so that volatile elements would not be lost before the high temperature vaporization step. A vaporization temperature of 2400 $^{\circ}\text{C}$ was selected as a compromise setting for all elements studied. Ediger and Beres [4] reported that a vaporization temperature of 2400 $^{\circ}\text{C}$ was near optimal for many elements. Solutions were acidified to a constant 1% acid as the integrated response for analyte signal pulses has been reported to be sensitive to the acid concentration [31]. Increase in the acid concentration from 0.05 % to 1.0 % results in enhancements as large as a factor of two for 50 pg of analyte in nitric and sulfuric acid. An increase in hydrochloric acid concentration has little effect on analyte signal pulse intensity. The acid itself may function in some manner to increase the transport efficiency.

The results of these studies are summarized in Table 4, with examples of the enhancement patterns illustrated in Figures 11-20. The best enhancements observed were for the most volatile elements (Cd, Rb, Cs and Tl shown in Figs. 11-14

Table 4: Effect of acid and carrier on enhancement factors for integrated areas
(ion counts) from 20 pg of analyte vaporized at 2400 °C using 0s ramp

Analyte 20 pg (m/z)	1% acid	NASS-3 µg			NaCl µg			MgCl ₂ µg		
		0.07	0.35	1.05	0.07	0.35	1.05	0.07	0.35	1.05
¹¹⁴ Cd	HNO ₃	2.9	3.2	2.5	2.2	1.9	1.8	1.8	4.5	6.1
	HCl	1.2	4.2	8.5	1.0	0.4	0.2	3.5	8.5	11.5
²⁰⁵ Tl	HNO ₃	1.8	1.6	1.5	2.0	1.7	1.6	0.8	2.1	2.4
	HCl	0.8	0.7	0.8	0.9	1.0	1.0	0.9	1.8	2.6
²⁰⁸ Pb	HNO ₃	1.8	1.5	1.3	1.8	1.7	1.6	1.6	1.9	2.2
	HCl	1.0	0.9	0.9	1.0	0.8	0.7	1.7	1.2	1.1
¹³³ Cs	HNO ₃	1.3	1.2	1.2	1.1	1.2	1.2	1.0	1.1	1.3
	HCl	2.6	2.2	2.1	2.5	2.2	2.2	1.6	2.5	2.8
⁸⁵ Rb	HNO ₃	1.3	1.1	0.9	1.2	1.1	1.0	1.0	1.0	1.2
	HCl	1.3	0.9	0.8	1.2	0.9	0.9	1.1	1.6	1.8
²⁰⁹ Bi	HNO ₃	1.8	1.1	1.0	2.1	1.4	1.3	0.9	1.1	1.6
	HCl	1.2	1.1	0.9	1.3	1.0	1.0	1.0	0.9	1.1
¹⁰⁷ Ag	HNO ₃	1.5	0.7	0.5	1.4	0.6	0.5	1.0	1.1	1.5
	HCl	1.3	0.7	0.5	1.2	0.7	0.5	1.0	1.2	1.8
¹¹⁵ In	HNO ₃	1.7	1.3	0.9	1.7	1.5	1.2	1.3	1.2	0.9
	HCl	0.8	0.9	1.0	0.9	0.8	1.0	1.0	1.0	1.0
⁶⁹ Ga	HNO ₃	1.2	0.8	0.7	1.3	1.0	0.8	0.8	0.7	0.7
	HCl	1.2	1.0	0.9	1.3	1.0	0.8	0.9	0.7	0.7
⁵⁹ Co	HNO ₃	1.4	1.2	1.0	1.3	1.2	1.1	1.2	1.1	1.1
	HCl	1.4	1.2	1.0	1.1	0.9	0.8	1.2	1.1	1.1

Figure 11. Effects of carriers and acids on integrated areas for 20 pg of Cd : a) NASS-3 with 1% HNO_3 b) NASS-3 with 1% HCl c) NaCl with 1% HNO_3 d) NaCl with 1% HCl e) MgCl_2 with 1% HNO_3 f) MgCl_2 with 1% HCl . Vaporization temperature of 2400 °C with a 0s ramp.

Figure 12. Effects of carriers and acids on integrated areas for 20 pg of Rb :
 a) NASS-3 with 1% HNO_3 , b) NASS-3 with 1% HCl c) NaCl with 1% HNO_3 , d) NaCl with 1% HCl e) MgCl_2 with 1% HNO_3 , f) MgCl_2 with 1% HCl. Vaporization temperature of 2400 °C with a 0s ramp.

Figure 13. Effects of carriers and acids on integrated areas for 20 pg of Cs :
 a) NASS-3 with 1% HNO_3 , b) NASS-3 with 1% HCl c) NaCl with 1% HNO_3 , d) NaCl with 1% HCl e) MgCl_2 with 1% HNO_3 , f) MgCl_2 with 1% HCl . Vaporization temperature of 2400 °C with a 0s ramp.

Figure 14. Effects of carriers and acids on integrated areas for 20 pg of Tl :
 a) NASS-3 with 1% HNO_3 , b) NASS-3 with 1% HCl c) NaCl with 1% HNO_3 , d) NaCl with 1% HCl e) MgCl_2 with 1% HNO_3 , f) MgCl_2 with 1% HCl . Vaporization temperature of 2400 °C with a 0s ramp.

Figure 15. Effects of carriers and acids on integrated areas for 20 pg of Pb :
 a) NASS-3 with 1% HNO₃, b) NASS-3 with 1% HCl c) NaCl with 1% HNO₃, d) NaCl with 1% HCl e) MgCl₂ with 1% HNO₃, f) MgCl₂ with 1% HCl. Vaporization temperature of 2400 °C with a 0s ramp.

Figure 16. Effects of carriers and acids on integrated areas for 20 μg of Ag :
a) NASS-3 with 1% HNO_3 , b) NASS-3 with 1% HCl c) NaCl with 1% HNO_3 , d) NaCl with 1% HCl e) MgCl_2 with 1% HNO_3 , f) MgCl_2 with 1% HCl . Vaporization temperature of 2400 $^\circ\text{C}$ with a 0s ramp.

Figure 17. Effects of carriers and acids on integrated areas for 20 pg of In :
 a) NASS-3 with 1% HNO_3 , b) NASS-3 with 1% HCl c) NaCl with 1% HNO_3 , d) NaCl with 1% HCl e) MgCl_2 with 1% HNO_3 , f) MgCl_2 with 1% HCl. Vaporization temperature of 2400 °C with a 0s ramp.

Figure 18. Effects of carriers and acids on integrated areas for 20 pg of Ga :
 a) NASS-3 with 1% HNO_3 , b) NASS-3 with 1% HCl c) NaCl with 1% HNO_3 , d) NaCl with 1% HCl e) MgCl_2 with 1% HNO_3 , f) MgCl_2 with 1% HCl. Vaporization temperature of 2400 °C with a 0s ramp.

Figure 19. Effects of carriers and acids on integrated areas for 20 pg of Bi :
 a) NASS-3 with 1% HNO_3 , b) NASS-3 with 1% HCl c) NaCl with 1% HNO_3 , d) NaCl with 1% HCl e) MgCl_2 with 1% HNO_3 , f) MgCl_2 with 1% HCl . Vaporization temperature of 2400 °C with a 0s ramp.

Figure 20. Effects of carriers and acids on integrated areas for 20 pg of Co :
 a) NASS-3 with 1% HNO₃, b) NASS-3 with 1% HCl c) NaCl with 1% HNO₃, d) NaCl with 1% HCl e) MgCl₂ with 1% HNO₃, f) MgCl₂ with 1% HCl. Vaporization temperature of 2400 °C with a 0s ramp.

respectively) and these were greatest when MgCl_2 was used as the carrier. The enhancement capability of MgCl_2 decreases as the volatility of the analyte decreases. Peak-areas for these elements were augmented most when the largest mass of carrier ($1.05 \mu\text{g MgCl}_2$) was added and the analyte was present in a 1% HCl matrix. Enhancement factors obtained with $1.05 \mu\text{g MgCl}_2$ in 1% HCl for Cd, Tl, Cs and Rb were 11.6, 2.6, 2.8, and 1.8, respectively. The enhancement factor of 11.6 for Cd was the largest obtained in this study. This is not surprising since Millard et al. [22] reported a transport efficiency of only 9% for 1 ng of Cd in ETV-ICP-AES. The effect of different carriers and acids on the response from Cd can be seen in Figure 11. Magnesium chloride and NASS-3 in HCl were very effective carriers but NaCl was very poor, probably because it is volatilized too late to facilitate aerosol formation for the analyte. For the volatile elements the general trend observed was that MgCl_2 produced the greatest enhancements and NaCl the least. Magnesium chloride, when added in the largest amount investigated ($1.05 \mu\text{g}$), did not cause any signal suppressions. Larger additions of NASS-3 or NaCl often resulted in decreased enhancements and even suppressions in response for most elements. Elements of intermediate volatility (Pb, Ag, In, Ga and Bi shown in Fig. 15-19 respectively) showed good enhancement factors with $0.07 \mu\text{g NaCl}$ in 1% HNO_3 , viz., 1.8, 1.4, 1.7, 1.3 and 2.1, respectively. Figure 17 shows the effects of carriers and acids on signals from 20 pg of In. It can be seen that NaCl or NASS-3 in HNO_3 produced significant

enhancements. It is also evident that $MgCl_2$ in HCl is a very poor carrier for In. Figure 20 shows the results of chemical modifier additions for Co. The best carrier for this relatively involatile element was NASS-3, although the enhancements observed were not as large as those for the more volatile elements. The significant enhancements obtained for very volatile elements in the presence of a large amount of $MgCl_2$ in an HCl matrix are probably the result of a combination of factors. The hydrolysis of $MgCl_2$ in the graphite tube has been well-documented [32-34]. During heating, loss of Cl in the form of HCl gas occurs with formation of MgO:

Using ETV-ICP-MS, Byrne et al. [34] studied the interference of chloride ($MgCl_2$) on the determination of Mn. At pyrolysis temperatures above 700 °C, manganese is lost during the hydrolytic decomposition of the $MgCl_2$ matrix as it is removed from the furnace by the evolving HCl gas. The mass of interferent added was 100-200 µg of $MgCl_2$, much greater than the maximum amount added as a carrier in the present study. Kántor et al. [32] found that the degree of hydrolysis of $MgCl_2$ was dependent on the amount present. When 1 µg or less of Mg ($MgCl_{2(aq)}$) was studied, the signal due to $MgCl_{2(g)}$ was not detected, suggesting complete hydrolysis. At a mass of 20 µg Mg ($MgCl_{2(aq)}$), an additional signal pulse was observed and attributed to the vaporization of $MgCl_{2(g)}$. These data were obtained using a very slow heating rate of 10-16 °C s⁻¹. A study by Chaudry et al. [33] also suggested that the mass of $MgCl_2$ influenced the

extent of hydrolysis, with the smaller masses hydrolysing to a greater degree. Chaudry et al. [33] studied the effects of pyrolysis temperature on the loss of Cl and Mg from MgCl_2 placed on a heated graphite platform. The residue remaining after charring (50, 108, or 200 μg) MgCl_2 was dissolved in 100 mm^3 of 1M nitric acid, made up to a final volume of 10 cm^3 with distilled water and then analyzed for Cl, using ion chromatography, and Mg using flame atomic absorption spectrometry. For temperatures up to 700-800 $^\circ\text{C}$ a steady decrease in the amount of Cl remaining on the platform was noted but there was no corresponding loss of Mg. The remaining Cl was lost between 700-800 and 1000 $^\circ\text{C}$ and it was in this temperature range that a significant loss of Mg was detected. The un-hydrolysed MgCl_2 was vaporized in the temperature range 700-1000 $^\circ\text{C}$ with the remaining Mg probably present as MgO .

Since larger enhancements in analyte signals were observed for volatile elements in an HCl matrix when MgCl_2 was used as the carrier, it is probable that the hydrolysis of MgCl_2 is involved in the overall mechanism. Analyte signal pulses were not delayed until Mg vaporized suggesting a mechanism different from that reported for GFAAS [35].

Slavin et al. [35] studied the effects of $\text{Mg}(\text{NO}_3)_2$ as a matrix modifier in GFAAS and found that it permitted higher charring temperatures and delayed atomization (analyte release). The delay in signal generation was surmised to be the result of the analyte being embedded in a matrix of MgO [35]. In this study, the mass of Mg added as a chemical modifier is much less ($\approx 1/50$) than is commonly used in

GFAAS [35, 36] and it is probable that the trapping of the analyte in a magnesium oxide matrix does not occur to any significant extent when the carrier is present at masses of 1.05 μg or less. The increased enhancements of ETV-ICP-MS peak-areas obtained when using MgCl_2 are believed to be due to the hydrolysis of MgCl_2 supplying $\text{HCl}_{(g)}$ early in the vaporization step (much earlier than the vaporization of MgO). The hydrolysis of MgCl_2 will not be complete after a 30s pyrolysis step at 300°C [33] and will undergo further hydrolysis during the vaporization step. Volatile elements are vaporized concurrently with the release of $\text{HCl}_{(g)}$ and prior to the vaporization of the Mg . Release of $\text{HCl}_{(g)}$ was observed by monitoring the $^{35}\text{Cl}^-$ ion. The generation of $\text{HCl}_{(g)}$ prior to vaporization of Mg is shown in figure 21 A and B, where it can be seen that the presence of HNO_3 greatly reduces the amount of HCl produced. Volatilization of chloride began very early in the vaporization step with an appearance time of $<0.2\text{s}$, preceding the release of all of the analyte elements studied. The appearance time is defined as the time after the beginning of the vaporization step when the analyte signal appears above the background. Release of $\text{HCl}_{(g)}$ together with volatile elements can promote the formation of molecular chloride analyte species. In studies of the transport efficiency of Cd in ETV-ICP-AES [25, 26] it was found that Cd was transported to the plasma more efficiently when the analyte was present as molecules rather than atoms. The ratio of chloride to analyte would be $\sim 5000:1$ for

Figure 21. ETV-ICP-MS signal pulses for $0.35 \mu\text{g MgCl}_2$ in a) 1% HCl and b) 1% HNO_3 . $^{35}\text{Cl}^+$ — — — and $^{24}\text{Mg}^+$ —. Pyrolysis at 300°C for 30s, cooldown to 20°C and vaporization at 2400°C with maximum power heating (2000°C/s).

1.05 μg of MgCl_2 assuming 10% hydrolysis during the vaporization step. This excess could promote analyte chloride formation. The use of tube wall vaporization and high internal gas flow may provide enough cooling to permit analyte halides to survive even if their dissociation energies are quite low. Vaporization from the tube wall during a high flow (900 mL min^{-1}) would help suppress the dissociation of any analyte chlorides that are formed, as the gas temperature would be much cooler than when a platform and gas-stop (0 mL min^{-1}) conditions are used [37] wherein dissociation of weak halides would be expected to be almost complete [38]. Welz et al [37] found that the tube wall and gas temperature at the centre of the tube under miniflow (50 mL min^{-1}) conditions were virtually identical to those for gas-stop (0 mL min^{-1}) conditions. At a position 0.5 mm from the end of the tube the influence of a forced gas flow on gas phase temperature becomes substantial. The maximum and steady-state temperatures for miniflow (50 mL min^{-1}) were observed to be 200-500 K lower than under gas-stop conditions. For this study, a very high gas flow rate was used (300 mL min^{-1}) wherein the difference between tube wall and gas temperature could be substantial, especially close to the ends of the tube. Supplying HCl to the gas phase through the use of a hydrolysing salt would promote the formation of molecular analytes to a greater extent than simply depositing the analyte in the tube in a HCl acid matrix with no additional salts present. The reason for this is that some analyte elements themselves undergo hydrolytic decomposition in a manner similar to MgCl_2 . Kántor et al [39] observed

that even when an aqueous solution of cadmium chloride is applied to a graphite surface, the vapour does not necessarily consist of cadmium chloride as it can undergo hydrolysis with the formation of $\text{CdO}_{(s)}$. Vaporization of the analyte chloride form does not necessarily arise from the chloride salt. As well the graphite itself does not retain a large fraction of HCl through to the vaporization step when it is used as a dilute acid. It has been reported [31] that when 20 μL of 1% HCl is deposited in a pyrolytic graphite tube only $\sim 0.05\%$ of the original solution is retained by the graphite after heating for 10 s at 140 $^{\circ}\text{C}$ and 30 s at 400 $^{\circ}\text{C}$. The HCl that was retained was released very quickly during the vaporization step. More HCl gas could be released during the vaporization step by hydrolysis of a salt such as MgCl_2 than could be supplied by retained HCl being released from the hot graphite.

Gaseous analyte halides are also known to form in the presence of salts such as NaCl [38]. Many salts which can promote the formation of analyte halides can have a negative effect on the plasma due to their low ionization energies and can cause a suppression of analyte signals [40]. The addition of concomitant elements can also result in other non-spectroscopic interferences which can suppress analyte signals [41-43], the severity of which increases as the concomitant elements mass and degree of ionization increases [41, 42]. This suppression is most severe for analytes of low mass-to-charge ratio (m/z) and low degree of ionization. When 20 pg of analyte is present with 1 μg of carrier the salt will be present in a 50,000-fold excess. At such high

absolute quantity of salt and ratio of carrier-to-analyte, it would be expected that even matrix elements of low m/z , such as Na and Mg, will cause interference effects. Cadmium would be very susceptible since it has a relatively low mass ($m/z=114$) and a high ionization energy (8.993 eV) [44]. Zinc should display characteristics similar to those of Cd and be affected more severely because of its lower mass ($m/z=66$) and higher ionization energy (9.394 eV). An added problem with these analytes is that they are very volatile and will enter the plasma at the moment when it has been destabilized by the initial hot plug of expanding gases exiting the furnace.

It appears from this study that HCl released during hydrolysis reactions improves the transport efficiency of volatile elements. It is also probably that analyte chloride formation plays a role. Increased transport efficiency in the presence of HCl, however, cannot be due solely to promotion of aerosol formation since HCl is extremely volatile and will not provide condensation nuclei onto which the analyte may aggregate. The transport of the analyte along with HCl gas may in some manner decrease deposition loss. It can be seen from Table 4 that a difficult to ionize element such as Cd can actually suffer severe signal suppression when a chemical modifier such as NaCl is used. Easy to ionize analytes such as Cs appear to suffer the least signal suppression from physical carriers [41]. An additional trend in Table 4 is that only a very small amount of carrier (0.07 μg) is required if the chemical modifier contains sodium.

Low volatility analytes such as Ga and Co are not significantly enhanced by the use of MgCl_2 as a carrier. Only suppressions were observed for Ga with MgCl_2 whereas some enhancement was seen for Co in the presence of a small amount of MgCl_2 . For Ga, release of HCl occurs too early and vaporization of MgO occurs too late to aid in the formation of an aerosol. In the case of Co, co-vaporization with MgO occurs. For elements that are vaporized near coincident with NaCl, such as Bi, In, Ag and Pb, good enhancements (~ 1.5 -2) were observed when a small amount of NaCl or NASS-3 was used. For these elements the enhancements were larger when HNO_3 was the diluent acid. This is probably because of the fact that when HNO_3 is added, most of the chloride is removed and the sodium no longer vaporizes as NaCl but as the oxide species (as discussed below). When HNO_3 was used with NaCl, the sodium appearance time was earlier and the maximum of the Na signal pulse occurred later when compared to the volatilization of NaCl in HCl. This improved overlap with some analytes, including Pb, Bi, and In. Magnesium chloride is a poorer carrier in HNO_3 because the hydrolysis reaction is greatly suppressed and less HCl is released.

In general, it can be seen from the data in Table 4, that the best carrier for an extremely volatile element is MgCl_2 in HCl. Enhancement factors with carriers were greatest for the most volatile elements, as expected, since they are least likely to form an aerosol. Additionally, for elements of intermediate volatility, NaCl or NASS-3 is the best chemical modifier because NaCl co-volatilizes along with these elements. When a

small amount of NASS-3 (0.07 μg) was used as a carrier, analyte signals (peak-area) could be enhanced 1.2 to 8.5 fold. The greatest enhancements observed with NASS-3 occurred for the most volatile elements.

2.3.3 Effect of Vaporization Temperature on Analyte Signals Using NASS-3

The effect of NASS-3 as a physical carrier was investigated at different vaporization temperatures to determine the importance of this parameter. Cadmium, Pb, Ag and Co were studied. A pyrolysis temperature of 300 °C and vaporization temperatures of 2600, 2200, 1800, and 1400 °C were used. At lower temperatures, the peak-areas with and without carriers were larger. The increases were most pronounced for Cd, as shown in Fig. 22. Millard et al. [22] reported similar results for Cd when using ICP-AES detection. Almost no increase in signal intensity was seen with Co when lowering the vaporization temperature and only modest increases were observed for Ag and Pb. The increased signals at lower vaporization temperatures for volatile elements could be due to incomplete atomization producing molecules (rather than atoms) that are more easily transported to the plasma in the presence of a carrier. An additional factor may be that expansion of gas in the furnace during rapid heating causes a shock-pulse which perturbs the plasma. If the furnace is heated to lower final temperatures, gas expansion is reduced as are any perturbations to the plasma. A lower vaporization temperature may thus allow very volatile elements to enter the plasma and be sampled under optimum conditions. A second consequence of reducing

Figure 22. Effect of vaporization temperature at a 0s ramp on integrated areas for 20 pg of ^{114}Cd with the addition of varying amounts of NASS-3 as a modifier. Vaporization temperature: A) 2600 °C B) 2200 °C C) 1800 °C D) 1400 °C.

the vaporization temperature may be earlier formation of micro-particles as a consequence of more extensive nucleation in a cooler environment.

2.3.4 Effect of NASS-3 on Analytical Calibration Curves

Calibration curves using peak-area and peak-height data were plotted without carrier and in the presence of 0.07 and 0.70 μg of NASS-3. Addition of a chemical modifier linearizes calibration curves as well as improves sensitivity [4, 20, 21]. For this study, a pyrolysis temperature of 300 $^{\circ}\text{C}$ (30 s hold) and a vaporization temperature of 2400 $^{\circ}\text{C}$ (10s hold) were used. Figure 23 shows calibration curves for Ag. The addition of NASS-3 clearly linearizes the curves. Figure 23 shows that even if more than the optimum amount of carrier is used and enhancement factors are reduced, the linearity of the calibration curve is not adversely affected. This decreased sensitivity is the result of the salt having a deleterious effect on the plasma and sampling efficiency but not on the transport efficiency of the analyte. Calibration curves, constructed for five elements (Ag, Co, Zn, Cd and Pb), revealed that the curvature was most severe for the very volatile Cd and Zn. In all cases, when NASS-3 was added, linear plots resulted for both peak-areas and peak-heights, even with the addition of 0.70 μg of salt.

2.3.5 Effect of Heating Rate

The effect of the heating rate during the vaporization step was studied with and without NASS-3. The pyrolysis temperature was 300 $^{\circ}\text{C}$ (30s hold) and the

Figure 23. Effects of NASS-3 on ETV-ICP-MS calibration curves. A) Integrated areas: a) $\circ$ 0 μg NASS-3 b) Δ 0.07 μg NASS-3 c) $\square$ 0.70 μg NASS-3. B) Maximum peak-heights: a) $\circ$ 0 μg NASS-3 b) Δ 0.07 μg NASS-3 c) $\square$ 0.70 μg NASS-3.

vaporization temperature was set at 2400 °C (10s hold). The vaporization ramp was varied between 0 and 10 s initially, giving a range of 2000 °C/s to 210 °C/s. There was no significant change between a heating rate of 300°C/s or 210°C/s therefore a heating rate of 300°C/s was the slowest investigated further. Using a 0.1% HNO₃ matrix, 20 pg masses of Rb, Ag, Cs, In, Bi, Tl, Ga, Cd, Pb and Zn were investigated. When the analyte was vaporized without carrier a lower heating rate always resulted in decreased peak-areas. The slower the heating rate, the greater the loss. This most probably arises as a consequence of the decreased partial pressure of the analyte with slow heating, making it more difficult for supersaturation to be attained with consequent condensation and formation of an aerosol.

The opposite trend, was generally observed when the analytes were vaporized in the presence of 0.35 µg of NASS-3. With the exception of Tl, Cd and Zn, a lower heating rate resulted in increased peak-areas for all other analytes. A reduced heating rate caused the NASS-3 component peaks to spread out more in time with the result that the matrix elements in NASS-3 had poor overlap with Tl, Cd and Zn and did not provide the necessary condensation nuclei for efficient aerosol transport. Good temporal overlap was obtained with the other analytes. The effect of the heating rate on the peak-areas can be seen in Fig. 24 where 20 pg of In was vaporized with and without NASS-3. The signal profiles for 20 pg of In are presented in panel B of Figure 25 which shows response when NASS-3 is present. Again, the peaks are shifted later in

Figure 24. Effect of heating rate on integrated signal pulses for 20 pg of ^{115}In a) -○- 0 μg NASS-3 b) -□- 0.35 μg NASS-3. Vaporization temperature 2400 °C.

Figure 25.

Effect of vaporization heating rate on ETV-ICP-MS signal pulses for 20 pg of In. A) 0 μg NASS-3 a) 2000 $^{\circ}\text{C/s}$ b) 1050 $^{\circ}\text{C/s}$ c) 420 $^{\circ}\text{C/s}$ d) 210 $^{\circ}\text{C/s}$, B) 0.35 μg NASS-3 a) 2000 $^{\circ}\text{C/s}$ b) 1050 $^{\circ}\text{C/s}$ c) 420 $^{\circ}\text{C/s}$ d) 210 $^{\circ}\text{C/s}$. Vaporization temperature 2400 $^{\circ}\text{C}$.

time and are broader with NASS-3. Peak-heights are not appreciably decreased with NASS-3 resulting in increased peak-areas. Table 5 shows the effect on the integrated areas (in comparison to maximum power heating (2000°C/s)) of changing the heating rate. The peak-areas generally increased by 30 to 50 % when the vaporization heating rate was decreased from 2000 °C/s to 300 °C/s. The larger increases were seen for the more volatile elements such as Cs and Rb with more modest increases for the less volatile elements such as Ga and Co. Analyte signal pulses are shown in figures 25-37 at different heating rates with and without the addition of 0.35 µg of NASS-3. As the heating rate was further decreased, double peaks appeared for some elements which could be indicative of mixed vaporization mechanisms or of condensation and re-vaporization from cooler tube ends or cones. Double peaking could usually be controlled by a change of acid, as is evident from the data in Fig. 38. ETV-ICP-MS signal pulses for ⁸⁵Rb with and without NASS-3 are presented in either 0.1% HNO₃ (panel A), or 0.1% HCl (panel B). With a heating rate of 300 °C/s, Rb forms double peaks with NASS-3 in the presence of HNO₃ but in an HCl matrix the signal has a more well defined single peak. The need for selection of an appropriate acid can be avoided by using a sufficiently high heating rate where double-peaking is not observed for any of the analytes and enhancements remain significant. The increased signals observed with NASS-3 with low heating rates may be related to the release of the analyte later in the vaporization cycle and the decrease in the expansion shock wave

Table 5. Effects of the heating rate on enhancements compared to maximum power heating (2000°C/s). Analyte (20 pg) in the presence of 0.35 µg of NASS-3 and 0.1% HNO₃

Analyte 20 pg (m/z)	Change in integrated area (% increase or decrease) in the presence of NASS-3 compared to maximum heating			
	Heating rate (°C/s)			
	1050	700	420	340
¹¹⁴ Cd	+2	+8	-14	-14
²⁰⁵ Tl	-28	-38	-44	-56
²⁰⁸ Pb	+25	+30	+25	+31
¹³³ Cs	+39	+40	+46	+46
⁸⁵ Rb	+35	+37	+46	+48
²⁰⁹ Bi	+30	+27	+28	+24
¹⁰⁷ Ag	+20	+26	+35	+34
¹¹⁵ In	+31	+40	+44	+47
⁶⁹ Ga	+31	+30	+36	+36
⁵⁹ Co	+12	+13	+26	+31
⁵⁸ Ni	+16	+16	+15	+13
⁶⁶ Zn	-36	-29	-20	-32

Figure 26. Effect of the vaporization heating rate on the ETV-ICP-MS signal pulses for 20 pg of Cd with : A) 0 μg of NASS-3 and B) 0.35 μg of NASS-3. Vaporization temperature 2400°C .

Figure 27. Effect of the vaporization heating rate on the ETV-ICP-MS signal pulses for 20 pg of Rb with : A) 0 μg of NASS-3 and B) 0.35 μg of NASS-3. Vaporization temperature 2400°C.

Figure 28. Effect of the vaporization heating rate on the ETV-ICP-MS signal pulses for 20 pg of Cs with : A) 0 µg of NASS-3 and B) 0.35 µg of NASS-3. Vaporization temperature 2400°C.

Figure 29. Effect of the vaporization heating rate on the ETV-ICP-MS signal pulses for 20 pg of Tl with : A) 0 μg of NASS-3 and B) 0.35 μg of NASS-3. Vaporization temperature 2400°C.

Figure 30. Effect of the vaporization heating rate on the ETV-ICP-MS signal pulses for 20 pg of Pb with : A) 0 μg of NASS-3 and B) 0.35 μg of NASS-3. Vaporization temperature 2400°C.

Figure 31. Effect of the vaporization heating rate on the ETV-ICP-MS signal pulses for 20 pg of Ag with : A) 0 μg of NASS-3 and B) 0.35 μg of NASS-3. Vaporization temperature 2400°C.

Figure 32. Effect of the vaporization heating rate on the ETV-ICP-MS signal pulses for 20 pg of In with : A) 0 μg of NASS-3 and B) 0.35 μg of NASS-3. Vaporization temperature 2400°C.

Figure 33. Effect of the vaporization heating rate on the ETV-ICP-MS signal pulses for 20 pg of Ga with : A) 0 µg of NASS-3 and B) 0.35 µg of NASS-3. Vaporization temperature 2400°C.

Figure 34. Effect of the vaporization heating rate on the ETV-ICP-MS signal pulses for 20 pg of Bi with : A) 0 μg of NASS-3 and B) 0.35 μg of NASS-3. Vaporization temperature 2400°C.

Figure 35. Effect of the vaporization heating rate on the ETV-ICP-MS signal pulses for 20 pg of Co with (A) 0 μg of NASS-3 and B) 0.35 μg of NASS-3. Vaporization temperature: 2400 °C.

2

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Figure 36. Effect of the vaporization heating rate on the ETV-ICP-MS signal pulses for 20 pg of Zn with : A) 0 μg of NASS-3 and B) 0.35 μg of NASS-3. Vaporization temperature 2400°C.

Figure 37. Effect of the vaporization heating rate on the ETV-ICP-MS signal pulses for 20 pg of Ni with : A) 0 μg of NASS-3 and B) 0.35 μg of NASS-3. Vaporization temperature 2400°C.

Figure 38. ETV-ICP-MS signal pulses for 20 pg of Rb using a vaporization heating rate of 300 °C/s. A) with 0.1% HNO₃ a) — 0 µg NASS-3 b) ---- 0.35 µg NASS-3, B) with 0.1% HCl a) — 0 µg NASS-3 b) ---- 0.35 µg NASS-3. Vaporization temperature 2400 °C.

during furnace heating. It appears that if the carrier and analyte are more slowly vaporized they will be released later in time and a little more slowly but supersaturation, condensation and efficient transportation is still readily attainable for these larger masses. From such experiments it was found that a decrease in heating rate can improve the enhancements attained using carriers as long as the matrix and analyte are released together.

2.3.6 Effect of Pyrolysis Temperature and Acid Matrix on Temporal Characteristics of NaCl in NASS-3

Figure 39 shows the temporal characteristics of NASS-3 components at pyrolysis temperatures of: 300 °C (curves a-c) and 650 °C (curves d-f). It also shows how these change with increasing concentration of HNO₃. A 2400 °C vaporization temperature with a 7s ramp (heating rate = 300 °C/s) and 10s hold was used. As the HNO₃ concentration was increased, a change in the vaporization characteristics of Na was noted. Sodium vaporized as NaCl when present in 0% HNO₃, as is illustrated in Fig. 39a where Na and Cl signals appear concurrently. Sodium chloride is a non-hydrolysable salt and will vaporize as NaCl. As the nitric acid concentration is increased, two distinct Na peaks appear, as illustrated in Fig. 39c. An investigation of pyrolysis temperatures shows that the first peak disappears when a temperature of 650 °C is used but the second peak remains. The LTV-ICP-MS signal pulses at the 650 °C pyrolysis temperature are shown in Fig. 39 d to f. It can be further seen that the chloride content dramatically drops with the addition of a small amount of HNO₃.

Figure 39. Effect of HNO₃ concentration on ETV-ICP-MS signal pulses for 0.35 μg NASS-3 at a pyrolysis temperature of 300 °C or 650 °C : $\cdots$ $^{35}\text{Cl}^+$ — $^{23}\text{Na}^+$ --- $^{24}\text{Mg}^+$ -.- $^{44}\text{Ca}^+$. Pyrolysis temperature 300 °C: a) with 0% HNO₃, b) with 0.01% HNO₃, c) 0.1% HNO₃, and pyrolysis temperature 650 °C: d) with 0% HNO₃, e) with 0.01% HNO₃, f) 0.1% HNO₃. Vaporization temperature 2400 °C, heating rate 340 °C/s.

These data reveal how pyrolysis temperatures and acid content can affect the temporal vaporization characteristics of carrier components

The temporal release of sodium during vaporization in the HNO_3 matrix was investigated with the use of ^{15}N labelled (99%) nitric acid, necessary to monitor nitrogen containing compounds which cannot usually be studied because of a high ^{14}N background from air entrained in the argon plasma. The same pyrolysis experiments were done using NASS-3 and ^{15}N (99%) labelled 0.1% HNO_3 . The results of these experiments are shown in Fig. 40 where panel A represents a 300 °C pyrolysis and panel B a 650 °C pyrolysis. The first Na peak as well as an overlapping ^{15}N peak remained up to a pyrolysis temperature of 600 °C but disappeared at 650 °C. It is evident that sodium species are released by two separate vaporization mechanisms in an HNO_3 matrix. When nitric acid is added to sodium chloride sodium nitrate is formed [45] as shown by the following reaction

Sodium nitrate decomposes to Na_2O , N_2 and O_2 at ~800 °C [46] as shown below

This reaction will produce gaseous N_2 and O_2 as well as Na_2O , which is known to sublime at 1275 °C [15]. After the addition of sufficient nitric acid, the sodium is present as NaNO_3 which then decomposes into Na_2O at about 650 °C and subsequently vaporizes as the temperature increases. The earlier peak in Fig. 40 A is most probably

Figure 40. ETV-ICP-MS signal pulses for 0.35 μg NASS-3 in 0.1% H^{15}NO_3 (99 % ^{15}N) A) 300 $^\circ\text{C}$ char B) 650 $^\circ\text{C}$ char a) ---- $^{15}\text{N}^+$ b) — $^{23}\text{Na}^+$. Vaporization temperature 2400 $^\circ\text{C}$, heating rate 340 $^\circ\text{C/s}$.

due to loss of some Na O caused by the rapid evolution of N_2 and O_2 gas during the conversion of $NaNO_3$ into products (equation 3). It is clear that a change of acid or pyrolysis temperature can alter the vaporization mechanism of analytes present and thus an understanding of the mechanism of vaporization of carrier elements is also important.

2.4 SUMMARY AND CONCLUSIONS

It was found that seawater functioned well as a physical carrier for a wide range of analytes. The use of reduced heating rates during vaporization can greatly increase the enhancing effect of a physical carrier. The choice of acid and its concentration is also very important as this can have a large impact on how well a carrier functions by affecting its vaporization properties as well as those of the analyte. Since HCl was found to be the most effective carrier studied, the use of a multi-component carrier that hydrolyses at different temperatures could provide an "Ideal" carrier for ETV-ICP-MS work. Such a carrier may allow maximum enhancements to be obtained for analytes of widely differing volatilities.

CHAPTER 3

INVESTIGATION OF VAPOUR CONDENSATION IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY BY THE SHADOW SPECTRAL DIGITAL IMAGING TECHNIQUE

3.1 INTRODUCTION

Chemical modifiers are commonly used in graphite furnace atomic absorption spectrometry (GFAAS) to remove interferences with the primary objective being thermal stabilization of the analyte to withstand higher pyrolysis temperatures and/or increasing the volatility of matrix components [36]. This allows removal of many concomitants prior to the high temperature atomization step without loss of analytes. In addition, chemical modifiers can delay atomization until the temperature in the graphite furnace is higher and more isothermal conditions prevail. Chemical modifiers in GFAAS have been studied by a number of workers in order to understand the way in which they function. In this regard, techniques such as mass spectrometry [47, 48], scanning electron microscopy [49] and temperature-programmed static secondary-ion mass spectrometry [50] have been used to obtain information. Gas-phase chemical modification has been studied by Gilchrist et al [51]. Frech et al [52] studied the effects of the mass of chemical modifiers and tube temperature gradients on analytical sensitivity and performed leaching experiments to study the adsorption of chemical modifiers on cooler ends of graphite tubes.

The effects of chemical modifiers on background absorption have also been studied [53, 54] and problems associated with their use have been reported, such as, unmanageable background levels or depression of the analyte signal when they are used in excess [55]. Condensation of matrix vapours in the graphite furnace is an area of interest since chemical modifiers, usually added to the analyte in quantities of 10 to 200 μg [55], would be expected to condense after supersaturation has been attained [21]. This could result in the appearance of non-specific background absorption due to light-scattering by microparticles. If the distributions of particles causing light-scattering are not temporally and spatially uniform, deuterium arc lamp background correction may give erroneous results. In addition, chemical modifiers are used in graphite furnaces in amounts which could also promote analyte condensation on concomitant elements if they vaporize concurrently. This form of condensation is deliberately promoted in electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) [4, 56] to increase transport efficiency of the analyte. However, if such condensation occurs in GFAAS, it may produce undesirable side effects, such as, reduction in the analyte signal due to trapping of analytes in microparticles as well as increased background absorption.

The condensation of matrix vapours in GFAAS was recently investigated [5, 57, 58]. In a study by Frech et al. [5], it was found that when μg masses of elements were vaporized, non-specific absorbance signals appeared because of the condensation of matrix vapours in both the axial centre of the graphite tube as well as at the ends. A

non-homogenous distribution of particles was determined to exist over the cross-section of the graphite tube. This was determined by moving the tube in vertical and horizontal directions relative to the optical axis. This technique yielded a spatial resolution at the axial centre of the graphite tube of approximately 1 mm [5], insufficient to yield a clear idea as to the spatial condensation of matrix vapours or the dynamic nature of this phenomenon, particularly since only one area can be observed during a single run.

Spatial and temporal imaging of the distributions of atomic and molecular species in the graphite furnace was achieved using a number of approaches [59-66]. Of the systems used, the technique of shadow spectral filming (SSF) introduced by Gilmutdinov et al [64-66] proved to be the most versatile. In these studies [64-66], a cine camera was used as the detector and many images of the atomizer cross-section could be recorded during a single atomization event. Gilmutdinov et al [65] observed a donut-shaped structure in the gas-phase during the vaporization of Al and attributed its formation to condensed-phase aluminium oxide species. Chakrabarti et al [67] used the SSF technique to study atomization processes but replaced the cine camera with a charge-coupled device (CCD). This improvement in the detection system yields quantitative data, makes data acquisition more convenient and provides digital data that facilitate the computer handling of the large amount of data that is collected. This improved technique will be henceforth called shadow spectral digital imaging (SSDI) technique.

The objective of this study was to investigate condensation of vapours of gold and matrices of various salts and chemical modifiers in graphite furnace atomic absorption spectrometry using the shadow spectral digital imaging technique with a charge-coupled device camera. This study reports on the condensation of vapours of matrices of various chemical modifiers encountered in real samples in GFAAS, and imaging of their spatial and temporal distributions with a CCD detector. The effects of heating rate, mass, temperature, gas-flow rate and the presence and orientation of the sample injection hole were investigated. As well, the structures of condensed-phase particle clouds of gold were studied using light-scattering by condensed-phase particles of gold. As gold does not form stable gaseous oxides, the dynamics of cloud formation could be observed without interference from molecular absorption [68].

3.1.2 THEORY

Condensation of a vapour occurs when the gas phase becomes supersaturated with the vapour at a given temperature. The supersaturation ratio, S [21], is defined as

$$S = \frac{p_{\text{vap}}}{p_e(T)} \quad (4)$$

where, p_{vap} is the actual partial pressure of the vapour and $p_e(T)$ is the equilibrium vapour pressure at the temperature of nucleation. Kántor [21] has proposed that the equation for the ideal gas law can be used to calculate the partial vapour pressure of the sample evaporating under dynamic heating in an electrothermal vaporizer.

$$P_{\text{vap}} = \frac{N_s T_g R}{V_g t_g} \quad (5)$$

where N_s is the number of moles of vapour from the sample, T_g is the temperature of the gas phase, R the gas constant, V_g the flow rate of the purge gas and t_g the mean evaporation time. Equation 5 can only be used to obtain only an approximate value of the vapour pressure since in using equation 5 it is assumed that the gas behaves ideally, the system is closed, equilibrium exists and all the sample is in the gas phase -all these assumptions are not entirely valid under the experimental conditions usually adopted for GFAAS. The above equations show that the highest supersaturation ratios will be attained using the Gas-Stop mode of operation of the graphite furnace, since the analyte then vaporizes into the minimum volume. Under the Gas-Stop mode the term $V_g t_g$ in equation 5 is replaced by the volume of the graphite tube. However, it should be kept in mind that the actual volume of the gas is much greater than the geometric volume of the graphite tube because the relatively large space between the tube ends and the quartz windows at the ends of the furnace. The use of purge gas-flow during the high temperature vaporization step has the effect of further increasing the volume considered in Equation 5, thereby reducing the vapour pressure of the analyte. It is clear that there are three factors that control analyte vapour pressure and determine its degree of condensation. For a given quantity of an analyte, a change in either the temperature of the gas, the purge gas-flow rate, or the time for vaporization of the analyte will have an effect on the vapour pressure and, therefore, likelihood of its

condensation. An increase in vapour pressure will bring about an increase in the supersaturation ratio, S . Droplets larger than a critical diameter are stable nuclei and will grow rather than evaporate [69 pp.249-254].

If the particles are isotropic and have diameters less than 10% of the wavelength of the incident radiation, then the light-scattering will follow the Rayleigh scattering relationship, which is given by [70]:

$$\frac{I}{I_0} = \frac{9\pi^2 NV^2}{2R^2 \lambda^4} \left| \frac{m^2 - 1}{m^2 + 2} \right|^2 (1 + \cos^2 \theta) \quad (6)$$

where N is the number of particles, V is the volume of the (spherical) particle, m is the refractive index of the particle relative to its surrounding medium, λ is the wavelength of the incident light, I_0 the incident light intensity, θ the angle between the incident and the scattered ray, and R the distance from the centre of the scattering particle to the detector. Rayleigh scattering increases as the particles become larger and the number of particles increases. The intensity of Rayleigh scattering also depends inversely on the fourth power of the wavelength of the incident radiation, with the result that light of shorter wavelength will be very much more severely scattered. As a result of the wavelength dependence of light-scattering and other variables of equation 6, the intensity of light-scattering can provide information on non-specific absorption in a graphite furnace and on the condensed-phase particle clouds which are responsible for light-scattering.

When the wavelength of the incident radiation is 0.2-0.3 μm , the light-scattering by particles larger than 0.03 μm follows the Mie scattering relationship [69, pp.324-329]. The Mie theory treats the scattering of light by a homogenous spherical particle of arbitrary size and refractive index. The solution for the spatial distribution of scattered light for incident unpolarized light is given by [70]:

$$I = I_0 \frac{1}{k^2 R^2} \frac{i_1(\alpha, m, \theta) + i_2(\alpha, m, \theta)}{2} \quad (7)$$

where I , I_0 , λ , R , m and θ are as defined previously, i_1 and i_2 are dimensionless intensity functions, $k = 2\pi/\lambda$ and $\alpha = 2\pi r/\lambda$ (α is the size parameter and r is the particle radius). L'vov [71, pp.230-232] reported that when a considerable amount of a sample is vaporized in a graphite cuvette, the resulting particle diameter was greater than the wavelength of the incident radiation and the scattering intensity was therefore described by the Mie scattering relationship. Sparks et al. [72] studied the particle size distributions of samples transported from an electrothermal vaporizer to an inductively coupled plasma mass spectrometer (internal gas-flow rate of 1.0 to 1.8 L/min used) and found particles of diameter in the range of 0.1 μm to 5 μm . Much lower internal gas-flow rates are used for GFAAS, and hence, it would be reasonable to expect that the diameter of many particles would be much larger than 0.03 μm and they would therefore not follow the Rayleigh scattering relationship except perhaps very early in the vaporization step, when the supersaturation ratio might be expected to be small.

Welz et al. [37] used coherent anti-stokes Raman scattering (CARS) to measure the spatially and temporally resolved gas phase temperature in a Massmann-type graphite furnace (end-heated), fitted with a pyrolytic graphite coated tube. When no platform was used, they found no radial temperature gradient in the gas phase except very close to the graphite tube ends (the temperature gradients had to be greater than the measurement error ($> 50\text{K}$) to be discernible by the CARS technique). However, along the tube longitudinal axis there was a longitudinal temperature gradient in the gas phase. The steady-state gas temperature at the tube ends was 1100-1200 K lower than at that the tube centre heated to 2700 K. However, the gas temperature did not change more than 100 K over a distance of $\pm 6\text{ mm}$ from the tube centre. Gilmutdinov and coworkers [73] developed equation 8 for the velocity $v(x,t)$ of convective expansion of the gas phase in a graphite furnace during heating, encompassing any non-isothermality of the furnace and non-linearity of the heating rate, which are typical of the heating of the end-heated graphite tube furnace used in the study.

$$v(x,t) = \frac{L}{2} \frac{1}{T} \frac{dT}{dt} \frac{D(\alpha, x)}{\alpha} \quad (8)$$

where L is the length of the graphite tube, D is the temperature-dependent diffusion coefficient of the gaseous species, $\alpha = \ln \Delta$, $\Delta = T(x=0)/T(x=L/2)$ is the dimensionless number representing the ratio of the temperature in the furnace centre to that at its ends and is a measure of the degree of atomizer non-isothermality, and T is the temperature

in Kelvin. For linear heating rates ($dT/dt = \text{constant}$) and isothermal conditions ($\Delta = 1$ and $\alpha = 0$), the above equation reduces to a simpler equation (equation 9) developed by Holcombe [74].

$$v = \frac{\beta x}{T} \quad (9)$$

where β is the linear heating rate in K s^{-1} and T is the temperature in Kelvin. Uniform gas heating with symmetrical expansion of the gas from the centre of the tube were assumed. Loss of analyte through the sample injection hole was ignored, as were the effects of forced convection imposed by any sheath gas routed through the furnace. The Holcombe model predicts that thermal expansion of the gas within the furnace volume will contribute significantly to analyte loss when high heating rates and low temperatures are used. At high temperatures and low heating rates diffusive loss will dominate. Since the lowest temperatures in the graphite tube exist at the water-cooled tube ends, vapour farthest from the centre of the tube will be expelled most rapidly, as the average gas expansion velocity will increase towards the ends of the tube.

If the gas-flow is assumed to be laminar [74], maximum flow corresponds to a radial position in the centre of the tube with $v_{\text{max}} = 2v_{\text{av}}$ and the velocity is zero at the tube walls. Substituting some experimental values ($\beta = 2000^\circ\text{C/s}$ and $T = 1800^\circ\text{C}$) into equation 9 and calculating the average velocity close to the graphite tube ends ($x = 1.4$ cm for a Perkin-Elmer HGA standard graphite tube) yields the maximum average velocity of the gas due to expansion at 1800°C , $v_{\text{av}} = 1.45$ cm/s. Along the central axis

of the graphite tube the velocity will reach a maximum value of 2.9 cm/s and drop to zero at the tube wall surface. These values represent the upper velocity limit because the non-isothermal nature of the end-heated graphite furnace was not taken into account.

The velocity due to diffusion can also be calculated. Diffusion coefficients at high temperatures and pressures can be estimated using the relation:

$$D = D_0 (P_0/P)(T/T_0)^n \quad (10)$$

where D_0 is the diffusion coefficient under standard conditions ($P_0=1$ atm and $T_0=273$ K) and n is an exponent that varies between 1.5 and 2 [71, p.205]. Diffusion coefficients D_0 and the values of n for 60 elements have been given by L'vov and Nikolaev [75]. The velocity associated with diffusion, v_d , can be estimated from the relations:

$$\tau_d = \frac{L^2}{8D} \quad (11)$$

and

$$v_d \approx \frac{L}{\tau_d} \quad (12)$$

where τ_d is the residence time of atoms due to diffusion and L is the furnace length ($L=2.8$ cm). Evidence to support the Holcombe model was obtained by Welz et al. [37]. Close to the graphite tube ends a radial gradient in the gas phase temperature was observed, where the gas temperature at the central longitudinal axis of the graphite

tube was found to be some 200 K higher than that close to the tube wall. Welz et al [37] argued that the higher temperature at the central longitudinal axis of the tube was due to thermal expansion of the gas within the furnace during its rapid heating. The longitudinal temperature gradient present in an HGA graphite furnace coupled with thermal gas expansion during heating produces gas phase temperatures higher than the tube wall temperature near the ends of the graphite tube. Additionally, the observed slowing of the heating rate of the gas at the very centre of the tube after 0.3 s, was probably the result of the gas expulsion through the sample injection hole. Gas expands towards the ends of the graphite tube, but pressure builds up because the tube ends are closed by quartz windows, at which point the rate of gas expulsion through the sample injection hole increases.

An additional effect which must be considered is the possibility of ingress of ambient air through the sample injection hole after the graphite tube has reached its preset temperature and the graphite tube ends lose heat through conduction to the water-cooled contact electrodes [76]. Expulsion of the gas through the sample injection hole due to thermal expansion is important during the rapid heating of the graphite tube, whereas ingress of ambient air through the sample injection hole occurs only after the preset temperature is attained and the graphite tube ends begin to cool, resulting in suction of ambient air. These two events are therefore separated in time and, to a first approximation, can be distinguished by measuring the temperature of the graphite tube.

3.2 EXPERIMENTAL

3.2.1 Apparatus. The CCD imaging system has been previously described [67] and is summarized here. Figure 41 shows a schematic diagram of the CCD setup. The charge-coupled device detector was a Photometrics Series 200 CCD Camera System (Photometrics LTD, Tucson, AZ), consisting of a CH250/A passive, air-cooled camera that houses a Thomson Th7883 CCD chip. The CCD was used in the frame transfer mode whereby only half of the chip was illuminated, the image transferred to the dark half and subsequently read out and digitized. A variable-frequency mechanical chopper was used to prevent image blurring wherein timing of the frame transfer was controlled by the frequency output of the chopper connected to the Photometrics AT200 controller. The CCD chip had a Metachrome II coating which allowed it to be used in the ultraviolet region. A plano-convex lens (focal length 15 cm) collimated the emission from the lamp source and a bi-convex lens (focal length 12.5 cm) focused the light passing through the graphite tube onto the CCD chip. Narrow-bandpass interference filters (Andover Corporation) were used to isolate wavelengths of interest and to reduce background emission. The interference filters were mounted in flexible bellows to prevent stray light interference. An iris diaphragm was placed in front of the interference filter to improve the depth-of-field and to reduce the amount of background radiation striking the CCD. Each of the three interference filters used had a different transmission profile; one had a central maximum at 230 nm, another at

Figure 41 Schematic diagram of the CCD imaging apparatus.

240 nm, and the third at 254 nm, each with a full width at half-maximum of 10 nm. The absence of any spectral lines and bands from the lamps (excepting the Au hollow cathode lamp) within the bandpass of the filters, other than the atomic lines and molecular bands being investigated, was verified. Therefore, with the exception of the Au hollow cathode lamp spectral interferences were not expected. Cadmium and Hg electrodeless discharge lamps (Perkin-Elmer) and the Au hollow cathode lamp (Hamamatsu) were used as light sources to back-illuminate the furnace. The lamps were operated in the continuous mode. Imaging of light-scattering by phosphorus compounds was done using a Cd electrodeless discharge lamp and the 230 nm interference filter since the PO molecular band showed strong absorption at the 253.7 nm Hg wavelength [77, pp. 272-276]. Imaging of all other species investigated was performed using a Hg electrodeless discharge lamp. The element, compounds and chemical modifiers investigated were: Au, $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$, $\text{La}(\text{NO}_3)_3$, $(\text{NH}_4)_2\text{HPO}_4$, MgCl_2 and NaCl. With the exception of NaCl [78] and $(\text{NH}_4)_2\text{HPO}_4$ [77], none of the other compounds, Au and matrices investigated produced any molecular species which absorb the 253.7 nm Hg wavelength. The imaging of NaCl was briefly investigated, but since it absorbed over a broad range of wavelengths in the ultra-violet [78] no further work was done on NaCl.

A Perkin-Elmer HGA-500 graphite furnace was used for the imaging experiments and was fitted with pyrolytically coated graphite tubes (Perkin-Elmer part No B0091504) for vaporization from the tube wall. For vaporization from the

graphite platform, pyrocoated grooved tubes (Perkin-Elmer part No 109322) were used in conjunction with laboratory-fabricated platforms made of pyrolytic graphite. These platforms had the same shape as the Perkin-Elmer platforms. The temperature program used for the vaporization of the analytes is shown in Table 6. Light-scattering studies were done using a Perkin-Elmer model 603 atomic absorption spectrophotometer (PE 603 AAS), fitted with an HGA-500 graphite furnace, and a deuterium arc lamp background corrector. The power to the deuterium arc lamp was held constant while the gain on the photomultiplier tube of the PE 603 AAS was adjusted to normalize the measured light intensity over the wavelength range investigated. The spectral bandwidth was 0.2 nm for all light-scattering experiments performed using the Perkin-Elmer 603 atomic absorption spectrometer.

An Ircon Series 1100 (Ircon Inc., Niles, IL) automatic optical pyrometer was used to measure the temperature of the inside tube wall by focusing on the bottom of the inside wall of the graphite tube through the sample injection hole. The output of the pyrometer was collected and stored on a Nicolet Series 4094 digital oscilloscope (Nicolet Instrument Corp.).

3.2.2 Standards and Reagents. High purity argon (99.995 %, Matheson Gas Products, Canada) was used as both purge and sheath gas for the graphite furnace. Solutions were prepared with ultra-pure water obtained direct from a Milli-Q water purification system (Millipore Corp., Mississauga, Canada). Nitric and hydrochloric acid were ULTREX grade (Baker Chemicals, Phillipsburg, NJ, USA). The solutions

Table 6. Temperature Program for Vaporization of the Analytes

Step	Temperature (°C)	Time (s)	Ar Purge Gas Flow (mL/min)
Dry	120	Ramp=10 Hold=60	300
Pyrolysis	400, 900	Ramp=2 Hold=10	300
Pyrolysis	410	Ramp=1 Hold=5	0
Vaporization	Various	Ramp various Hold=10	0-70
Cool Down	20	Ramp=1 Hold=10	300
Clean-up	2650	Ramp=0 Hold=5	300

* The initial pyrolysis temperature for the mixed chemical modifier, $\text{Mg}(\text{NO}_3)_2$ and $\text{Pd}(\text{NO}_3)_2$, was 900 °C, and for all other compounds was 400 °C unless stated otherwise

of the chemical modifiers and salts investigated were prepared as follows lanthanum nitrate (10 000 $\mu\text{g/mL}$) was prepared by dissolving $\text{La}(\text{NO}_3)_3$ (Morton Thiokol Inc., Danvers, M.A.) in ultrapure water, ammonium phosphate (10 000 $\mu\text{g/mL}$) was prepared by dissolving $(\text{NH}_4)_2\text{HPO}_4$ (BDH, Toronto, ON) in ultrapure water, Pd (1000 $\mu\text{g/mL}$) was made by dissolving Pd metal powder (Spex Industries Inc., Edison, NJ, USA) in a minimum amount of concentrated nitric acid with the addition of a few microliters of HCl and then diluting with ultrapure water, magnesium nitrate (1000 $\mu\text{g/mL}$) was prepared by dissolving $\text{Mg}(\text{NO}_3)_2$ (Baker Chemicals) in ultrapure water. The following salt matrices were also studied magnesium chloride (5000 $\mu\text{g/mL}$) was prepared by dissolving high purity Mg metal (Spex, Industries Inc.) in a minimum amount of hot HCl followed by dilution with ultrapure water, sodium chloride (10 000 $\mu\text{g/mL}$) was prepared by dissolving NaCl (BDH, Analar Grade) in ultrapure water. A gold reference standard solution (1000 $\mu\text{g/mL}$) was obtained from Harleco (Philadelphia, PA, USA).

3.2.3 Vaporization of gold. A 5 ms exposure time was used for all imaging experiments except those conducted with the Au hollow cathode lamp, for which a 10 ms exposure time was used because of its lower brightness in comparison with the Hg electrodeless discharge lamp. Images were collected at a rate of 20 Hz with a data transfer time of approximately 44 ms. Absorbance values were obtained with the CCD imaging system as outlined in Reference 67. For all images, the darkest regions inside

the graphite tube represent areas where light-scattering is the greatest and, therefore, probably where the highest concentration of particles is present.

A 20 μg sample (20 μL of the reference standard) of Au was deposited on the inside wall of the graphite tube, dried at 120°C for 60 s, pyrolyzed at 400°C for 10s with a 300 ml/min internal gas-flow, pyrolyzed at 410 °C for 5s with a 0 mL/min internal gas-flow and vaporized at 1800°C with the maximum power heating for 10s under the Gas-Stop mode. The extra pyrolysis step was inserted to ensure that the gas-flow was zero during the high-temperature step, allowing for the response time of the switching valve controlling the internal gas flow. The internal gas inlet tubes were also clamped shut close to the graphite furnace for the duration of the high-temperature step to check if this dead volume had an effect on the formation of condensed-phase structures in the gas phase. The same results were obtained when the inlet tubes were not clamped off, and hence, the extra pyrolysis step was used without clamping the inlet tubes.

3.3 RESULTS AND DISCUSSION

3.3.1 Vaporization of Gold

3.3.1.1 Gas-Stop Mode. Figure 42 shows some of the images which were collected during the high-temperature vaporization of gold, the corresponding absorbance contour plots are shown in Fig. 43. The position of the sample injection hole is indicated by the arrow in Fig. 42. The temperature of the inside graphite tube wall is shown in Fig. 44. The images in Fig. 42 reveal the highly non-uniform nature of the

Figure 42. Vaporization of 20 μg of Au at 1800°C under the Gas-Stop mode. Arrow indicates position of the sample injection hole. Sequence of images obtained with the CCD indicating time elapsed since the start of the vaporization step and measured tube wall temperature.

Figure 43. Absorbance contour maps corresponding to Fig. 42, 20 μg of Au.

Figure 44. Temperature-time heating characteristics of inside tube wall for a final set temperature of 1800 °C with the maximum power heating mode.

light-scattering produced by condensation of the vaporized gold. Light-scattering was minimal early in the heating cycle [Fig. 42 (i) < 650 ms], indicating that condensation was not occurring to a great extent at this point in time. Very soon after the commencement of the vaporization step [Fig. 42 (i) (650 ms)], however, a donut-shaped structure developed inside the graphite tube as a result of the gold vapour reaching a sufficient pressure to attain supersaturation, resulting in condensation.

Particle formation and growth occur at supersaturation ratios of 2-10 for pure materials (homogeneous nucleation) and less than 1.02 for nucleated condensation [69, pp.257-262]. Using tabulated vapour pressure data [79] and equations (4) and (5), the saturation ratio can be calculated for 20 μg of Au at 1800°C (assuming plug vaporization into a furnace volume 0.8 ml under the gas-stop mode (the term V_{gt} in Equation 5 = 0.8 mL)), yielding a value of 16.4. This value is higher than the true value because the graphite tube ends are open and the gas can expand to fill the space between the ends of the graphite tube and the quartz windows. In addition, some gas can also escape out the sample injection hole. Formation of the donut-shaped structure was observed for sample masses as low as 5 μg of gold. However, 20 μg was used for further imaging experiments, thereby eliminating the need for grey-scale manipulation to reveal clearly the structure of the condensed-phase particle clouds of gold. It is evident that condensation occurs away from the tube walls. It is also clear from the images in Fig. 42, and the corresponding absorbance contour plots in Fig. 43, that the optical density of the particles is less along the central axis of the graphite tube,

probably the result of the thermal expansion velocity of the gas being greatest along the central axis and decreasing to zero at the tube wall, and also the result of thermal expansion of the gas from the centre of the tube towards the tube ends which occurs during rapid heating of the furnace. The velocity of the gas is highest along the central axis of the graphite tube, resulting in greatest dilution of the analyte in this region with consequent decrease in the degree of vapour supersaturation. The absence of light-scattering near the tube walls may be the result of the gold vapour initially condensing in the centre of the tube and creating nuclei to promote further condensation in this zone. Also, the gas temperature lags 100-200 K behind the tube wall temperature over most of the rapid heating stage, which means that the tube wall is hotter than the gas [37]; hence, there is no condensation near the tube wall. In addition, aerosol particles will adhere to any surface they contact [69 pp. 127-130], and will then be revaporized if the temperature of the tube wall is high enough. As the vaporization step proceeds, condensation in the tube centre increases; also, light-scattering is observed near the top of the graphite tube. The donut-shaped structure begins to disappear by the time of image (vi) in Fig. 42 (950 ms). At this point in time the graphite furnace has reached a steady-state temperature and thermal expansion effects are no longer present (graphite tube attained its preset temperature at about 850ms [Fig. 44]). It also appears from the images (Figs. 42 and 43) that a cold zone is present near the top of the graphite tube which does not coincide with the sample injection hole. Although there is no direct experimental evidence of the existence of a cold zone near the top of the graphite tube,

the technique used by Welz et al. [37] was only capable of discerning temperatures differences > 50 K. A change of few Kelvin can drastically change the equilibrium pressure of an element and therefore its likelihood of condensation. The graphite contact cylinders contain two holes, one for sample introduction into the graphite tube and the other for monitoring of the graphite tube temperature by the optical sensor. These openings may permit radiative heat loss from the graphite furnace to the ambient atmosphere which is not balanced by radiative heat gain from the other parts of the heated tube walls, and hence may result in a slight cooling of these areas that, by present gas phase temperature measurement techniques, are not discernable. Furthermore, ingress of cold air through the sample injection hole under the Gas-Stop mode might produce cooling in this area. An additional possibility is that expanding gas escaping through the sample injection hole may create turbulences or eddies [80], which could cause more gold to condense in this region, thereby increasing the light-scattering observed near the top of the graphite tube. The condensed-phase particle cloud was greatly reduced by 2000 ms (image (viii)) as most of the gold was removed by this time by expulsion and/or by diffusion. Non-specific absorbance was examined under the same experimental conditions as above but by using the Perkin-Elmer atomic absorption spectrophotometer, model 603, fitted with an HGA-500 graphite furnace. Light-scattering measurements were made using the deuterium arc lamp source. Comparison of data collected with the two different systems (CCD and PE 603 AAS) can only be qualitative because completely different optical and measurement systems

were utilized. Quantitative comparisons between the two set-ups cannot be made but data collected from the two systems can be used to gain a clearer understanding of what is taking place in the furnace. In the case of 20 μg of gold, no condensation and revaporization was observed at the tube ends [Fig. 45, although this was seen for some other compounds which were also investigated. The absence of condensation of gold near the tube ends is not surprising. Smets [81] has concluded that gold atoms do not have a high probability of sticking to graphite and therefore would be removed from a graphite furnace by simple diffusion. Gold microparticles that do adhere to the graphite will be revaporized and will only exhibit light-scattering if the vapour pressure attains supersaturation again.

Gilmutdinov [64] calculated longitudinal diffusion velocities in the manner described by equations (10-12) for several analyte elements. The diffusion coefficient of gold at 2073 K was estimated using equation (10) and data from reference 75 ($D = 3.43 \text{ cm}^2/\text{s}$). Using equations (11) and (12), the velocity of diffusion can be calculated to be approximately 10 cm/s, representing a maximum limiting value. Application of these equations assumes that the vapour consists entirely of monatomic species. This may only be the case very early in the vaporization step if a large quantity of an element is dosed into the furnace. As vaporization proceeds, the vapour can no longer be characterized as monatomic species but will consist of particles formed from many atoms which have coalesced together. The diffusion velocity of microparticles will be reduced as their size increases, but the velocity due to thermal expansion should remain

Figure 45. Non-specific absorbance signals at various wavelengths for vaporization of 20 μg of Au at 1800 $^{\circ}\text{C}$ under the Gas-Stop mode.

relatively unaffected by the masses of the particles. The velocity due to thermal expansion may be more important than diffusion when scattering particles are produced as a result of condensation (when atoms or molecules are present the opposite is true, the diffusion velocities are higher and more important than that due to thermal expansion). The evidence for a great reduction in diffusion can be found in Fig. 42, where the condensed-phase cloud retains its relative structure for an extended period of time. Figure 42 also illustrates how it is possible for the analyte to be trapped in a condensed-phase particle formed from the matrix if the matrix is not removed, or if an improper chemical modifier is used. This problem is especially likely to occur if the analyte and its concomitants in the sample have similar atomization and vaporization temperatures, respectively.

Imaging of the interior of the graphite furnace was also performed using a Au hollow cathode lamp at the 242.8 nm Au resonance line. A 240 ± 5 nm interference filter was used. All other conditions were as before for 20 μ g of Au except that a 10 ms exposure time was used instead of a 5 ms exposure time because of the lower brightness of the Au lamp. Surface plots of CCD images obtained with both lamps are shown in Fig. 46, where (a) presents the absorption measured with the Hg electrodeless discharge lamp and (b) presents the absorption measured with the Au hollow cathode lamp. The same pattern of condensation was visible in the CCD images except that the "background absorption" was uniformly elevated. The low atomic absorption observed when the Au hollow cathode lamp was used was due to

Figure 46. Surface plots of CCD images for 20 μg of Au vaporized at 1800 $^{\circ}\text{C}$: (a) imaged with the Hg electrodeless discharge lamp ($\lambda=253.7$ nm) (b) imaged with the Au hollow cathode lamp ($\lambda=242.8$ nm).

the filter having a 10 nm bandpass and passing non-absorbable lines to the detector

Figure 45 reveals that this light- scattering phenomenon exhibits a definite wavelength dependence (light-scattering increases as the wavelength of the incident radiation decreases). Rayleigh scattering would show a $1/\lambda^4$ dependence whereas Mie scattering is a complex function of many parameters. In the present case, the light-scattering intensity does not follow the Rayleigh scattering relationship. According to the Mie scattering theory, when the scattering particles are much larger than the wavelength of the incident radiation, the light-scattering cross-section becomes independent of the wavelength [82]. When 20 μg of gold was used, a definite wavelength dependence was observed, where the light-scattering intensity varied closely with $1/\lambda^2$. From these results it appears that the particles produced had diameters within an order of magnitude of the wavelength of the incident radiation used to measure the light-scattering. Very early in the vaporization step, the particles would be smaller and would probably follow the Rayleigh scattering relationship. As the particles grow in size, they approach the wavelength of the incident radiation and then pass into the Mie scattering region for particles larger than 10 % the wavelength of incident radiation. For the D_2 arc lamp source, significant continuum radiation exists in the range of 200 - 300 nm (the wavelength range investigated in this study) Therefore, the particles in observed in Fig. 45 must be $< 3 \mu\text{m}$ to produce the observed wavelength-dependent scattering. Frech et al.[5] found that the light-scattering recorded during the vaporization of 6.9 μg of gold at 1800 $^\circ\text{C}$ followed a $1/\lambda^4$

relationship only when the rising parts of the signals were used for evaluation. As a larger mass of gold was used in this study, it is not surprising that this relationship was not followed

Non-specific absorbance signals were measured for various masses of gold vaporized at 1800 °C. Figure 47 shows the non-specific absorbance increased in intensity and began earlier as the sample mass was increased. Condensation and light-scattering in the gas phase was clearly much more intense in the centre of the graphite tube (the first absorbance peak) than near the ends (second absorbance peak) even for large sample masses. As the sample mass was increased, the intensity of scattered light initially increased dramatically. When the sample mass exceeded 60 µg, the light-scattering reached a maximum limiting value. Frech et al. [5] also observed such a phenomenon for Cu and proposed that the surface coverage might reach a maximum limiting value such that further increases in the mass might not enhance transport of Cu atoms to the colder zone, but evaporation was simply prolonged. Similar observations were also made when using the chemical modifier $\text{La}(\text{NO}_3)_3$, but not NaCl , MgCl_2 or $(\text{NH}_4)_2\text{HPO}_4$, even though the sample masses were increased to 280 µg. It is possible that for the latter compounds, saturation surface coverage was not achieved even with these larger sample masses.

Vaporization of 20 µg of Au from a graphite platform was also investigated under the same experimental conditions as above (except that the drying temperature was increased to 150°C). When a graphite platform was used, the light-scattering was

Figure 47. Non-specific absorbance signals for various masses of Au, vaporized at 1800°C.

greatly reduced and only very slight light-scattering was observed just above the platform. No donut-shaped structure was found and the signal only persisted for about 200 ms. The presence of the graphite platform produced a radial temperature gradient in the gas phase [37], where the lowest temperatures were found closest to the platform, which was where the light-scattering was observed. The use of a graphite platform delayed the vaporization of the analyte until more isothermal conditions prevailed, and therefore, gas expansion was greatly reduced, eliminating the driving force for formation of the hole in the donut-shaped structure. The sample mass was increased as high as 80 μg , but light-scattering was still quite minimal under these experimental conditions in contrast to what was observed when no graphite platform was used.

3.3.1.2 Gas-Flow Mode. When 20 μg of gold was vaporized at 1800 $^{\circ}\text{C}$ with the maximum power heating and with a mini-flow of argon (20 ml/min), the light-scattering images obtained (Figs. 48 and 49) were different from those shown in Figs. 42 and 43 obtained under the Gas-Stop mode. The light-scattering recorded under the small gas-flow mode (Fig. 48) was less intense than that recorded under the Gas-Stop mode. However, in Fig. 48 the donut-shaped structure was more well-developed, especially early in the vaporization step [images (iii) 750 ms and (iv) 900 ms]. The time resolution of the CCD system used is 50 ms, which limited the minimum time required for an event to be recorded. However, it is clear from figure 48, frames i (650 ms), ii (700 ms) and iii (750 ms), that the events occurring in the graphite furnace are faster

Figure 48. Vaporization of 20 μg of Au at 1800°C under the gas-flow mode (20 mL/min). Sequence of images obtained with the CCD indicating time elapsed since the start of the vaporization step and measured inside tube wall temperature.

Figure 49. Absorbance contour maps corresponding to Fig. 48, 20 μg of Au.

than the resolution of the CCD system used, and this time resolution limits our ability to record faster events in GFAAS. Initial formation of the particle cloud appears to be very similar for both purge gas-flow modes. One difference, readily noted from the images in Figs. 42 (the Gas-Stop mode) and 48 (the Gas-Flow mode), is that under the Gas-Flow mode the donut-shaped structure did not disappear and form a ball-shaped structure as was evident under the Gas-Stop mode. Light-scattering near the top of the graphite tube was also not observed with a mini-flow of argon. When the mini-flow of argon was used, the donut-shaped structure simply faded away with time (Fig. 48 (vii) 1500 ms). Dissipation of the donut-shaped structure began at the lower portion (Fig. 48 (vi)), whereas the last part of the condensed-phase cloud to disappear was near the top of the graphite tube, closer to the sample injection hole. A small internal purge gas-flow (50 mL/min) has only a relatively minor effect on the gas phase temperatures inside the graphite tube without a graphite platform [37]. However, the forced convective flow of purge gas from the ends to the centre of the tube, counteracts the thermal expansion of the gas towards the tube ends [37] and serves to dilute the gold vapour even more along the central axis of the tube, resulting in a more spread-out, and hence larger donut-shaped structure which persists longer in the gas phase. This structure does not contract in diameter as vaporization progresses. It appears that the mini-flow of purge gas defines a zone within the centre of the graphite tube where very little analyte condenses because of the dynamics of the gas flow. The early formation of the donut structure in the presence of the Ar purge gas flow further supports the

argument that these condensation clouds occur near the centre of the graphite tube and not at the ends of the tube. However, in the case of aluminium which requires a much higher atomization temperature than gold and which readily forms a refractory oxide (Al_2O_3), donut-shaped structures observed during its atomization in a Massmann-type graphite furnace may be also due to condensation of Al_2O_3 at the water-cooled tube ends which have much lower temperatures than the tube centre [68, 83].

The results of studies of non-specific absorbance as a function of Ar purge gas flow rates in the vaporization of 20 μg Au at 1800 °C are presented in Fig. 50. A mini-flow of purge gas during the high temperature vaporization step resulted in a decrease in the peak-height of light-scattering signal; at very low gas flow rates (10 mL/min) the light-scattering signal persisted longer than at higher gas-flow rates. The purge gas-flow reduced the analyte vapour pressure by dilution with the purge gas. The donut-shaped structure cannot be detected at a purge gas-flow rate of 70 mL/min. The non-specific absorbance signals measured with the Perkin-Elmer model 603 clearly revealed that light-scattering was still occurring, but discernable structures were too faint to be recorded with the CCD. Microparticles were therefore produced at a 70 mL/min flow rate of Ar purge gas, but the number of microparticles produced was not high enough to result in a measurable signal-to-noise ratio with this CCD detector.

3.3.1.3 Effect of sample injection hole and the location of sample deposition. The effect of the sample injection hole on the formation of condensed-phase particle clouds of gold was studied. The absence of the sample injection hole eliminates the possibility

Figure 50. Non-specific absorbance signals as a function of Ar purge gas-flow rates for vaporization of 20 μg of Au at 1800°C.

of gas expulsion through the sample injection hole, as well as ingress of ambient air. A normal Perkin-Elmer pyrolytically coated graphite tube but which had no sample injection hole was used rather than one closed with a graphite plug because a plug could present a cold spot onto which analyte vapour could condense. In addition, it would have been difficult to ensure that a perfect seal was formed with the plug. The analyte (gold) solution was carefully pipetted into the graphite tube through one of the ends of the tube and deposited at the centre. The internal gas inlet tube had to be modified with a T-junction and an extra length of tygon tubing to allow venting during drying and charring since the sample injection hole was no longer present. In addition, the first pyrolysis temperature was increased to 500 °C and the hold time for this step increased to 300 s. These changes did not affect the formation of the donut-shaped structure in the gas phase (this was confirmed by repeating these experimental conditions using a regular Perkin-Elmer pyrolytically coated graphite tube which contained the usual sample injection hole). The increase in the pyrolysis temperature and time was necessary because the water vapour produced during the drying step otherwise condensed at the end of the graphite contact cylinder and on the quartz window. The CCD images obtained by using the graphite tube with no sample injection hole are shown in Fig. 51 (a). The same condensed-phase structures were generally observed even when no sample injection hole was present, indicating that the sample injection hole had a relatively minor effect on the formation of the condensed-phase structures. The mass of gold, however, had to be increased to 40 µg since no

Figure 51.

(a) Vaporization of 40 μg of Au at 1800 $^{\circ}\text{C}$ under the Gas-Stop mode. The graphite tube had no sample injection hole. Sequence of images obtained with the CCD indicating time elapsed since the start of the vaporization step and measured inside tube wall temperature.

(b) Vaporization of 20 μg of Au at 1800 $^{\circ}\text{C}$ under the Gas-Stop mode. The graphite tube with the sample injection hole facing downward. Sequence of images obtained with the CCD indicating time elapsed since the start of the vaporization step and measured inside tube wall temperature.

(c) Vaporization of 20 μg of Au at 1800 $^{\circ}\text{C}$ under the Gas-Stop mode. The graphite tube with the sample injection hole facing upwards (normal position). 10 μg of Au deposited at each end of the tube. Sequence of images obtained with the CCD indicating time elapsed since the start of the vaporization step and measured inside tube wall temperature.

light-scattering was observed with 20 μg . With increasing time of heating, the condensed-phase structure was found to extend towards the top of the graphite tube, again suggesting condensation of gold which was however, not produced by ingress of air through the sample injection hole. Probably, the formation of the donut-shaped structure in this case was due to the effects of thermal expansion of gas within the graphite tube and these effects were probably enhanced when gas expansion through the sample injection hole was free to occur.

The effect of the orientation of the sample injection hole (facing upwards or downwards) was studied by rotating the graphite tube on its horizontal axis so that the sample injection hole faced downwards and was no longer aligned with the sample injection port through the outer graphite contact cylinder. The analyte (20 μg of gold) solution was deposited into the graphite tube in the usual (facing-upwards) position and then dried. After the drying step the graphite tube was rotated and the normal temperature program was run. Some of the CCD images collected are presented in Fig. 51 (b). The donut-shaped structure formed as usual, but in frame (iii) the particle cloud was found to be extending towards the sample injection hole, which (in the facing-down position) was located in the lower right-hand corner of the image. The presence of the condensation cloud extending in a plume-like structure towards the sample injection hole in Fig. 51 (b) (iii) and its absence in Fig. 42 may be rationalized by suggesting that when the graphite tube is oriented with its sample injection hole facing downward, the external Ar sheath gas flow grazes against the sample injection

hole, resulting in some of the Ar gas entering into the graphite tube, thereby cooling the expanding vapour to supersaturation before it is expelled through the sample injection hole, and resulting in formation of condensed-phase particles in this area. This explanation is supported by the fact that the plume-like structure appeared only after the graphite tube reached its preset temperature [Fig 44, 1000 ms], ending thermal expansion of gas and allowing cold Ar sheath gas to enter through sample injection hole. The absence of the plume-like structure extending towards the sample injection hole when the graphite tube with its sample injection hole in its normal (facing-upwards) orientation is probably the result of the external Ar sheath gas in its exit through the sample injection port (in the graphite contact cylinder) not grazing against the sample injection hole because it is located at a distance of a few mm. Lamoureux et al [83] also postulated that the plume-like structures observed in their investigation into Al spike formation were due to condensation of finely-dispersed Al_2O_3 . Both the formation and condensation of Al_2O_3 was due to the ingress of atmospheric oxygen through the sample injection hole of the graphite tube under the Gas-Stop mode. The cold oxygen both reacted with Al atoms forming Al_2O_3 , and lowered the vapour temperature, resulting in condensation of Al_2O_3 .

The CCD images shown in Fig 51 (c) are for vaporization of 10 μg of Au which was deposited at each end of the graphite tube instead of the usual central site. A donut-shaped cloud did appear during the high temperature heating step, but its structure was significantly different from that which developed when the analyte was

introduced into the usual central site through the sample injection hole. Formation of the donut-shaped cloud is probably the result of nucleation occurring in the vapour phase after vaporization of the analyte from the point of deposition when it is deposited into the usual central site of the graphite tube. The early appearance of the donut-shaped structure under these conditions (Fig. 42 (i) 650 ms), as well as the difference in the images when the analyte was deposited at the ends of the graphite tube (Fig. 51 (c)), indicates that this structure was not the result of condensation and revaporization from the tube ends because analyte could not have travelled to the tube ends and revaporized in this period of time (650 ms). The tendency for the condensed-phase particle cloud to develop at the top of the central zone of the graphite tube, irrespective of the presence of the sample injection hole or its vertical orientation, must be related to the temperature and/or the gas flow patterns which develop in the end-heated Massmann-type graphite furnace.

3.3.2 Effect of heating rate on condensation of MgCl_2 matrix vapour. The effect of the heating rate on the condensation of the MgCl_2 matrix vapour was studied by vaporizing 50 μg of MgCl_2 at 2400°C using slow and fast heating programs. The sample (10 μL) was deposited at the usual site in the graphite tube and dried at 120°C for 60s, pyrolyzed at 400°C for 10s, pyrolyzed again at 410°C for 5s with 0 mL/min Ar internal gas flow and then vaporized at 2400°C . For the experiments with a fast ramp, the maximum power heating rate of 2000°C/s and the Gas-Stop mode were used. For the slow-heating experiments, the heating rate was 300°C/s . The pyrometrically-

measured temperatures of the tube wall for the two heating programs are shown in Fig 52. Representative images obtained with the fast-heating rate are shown in Fig 53 and the corresponding absorbance contour maps in Fig 54. Images obtained using slow heating (300 °C/s) are shown in Figs 55 for the Gas-Stop mode (corresponding absorbance contour maps in Fig. 56), and 57 for the Ar purge gas flow of 20mL/min (corresponding absorbance contour maps shown in Fig 58). It can be seen from Figs. 53 and 55 that the heating rate has a large effect on the condensation of vapours. Although the CCD images (Figs 53, 55 and 57) shown are for 50 µg MgCl₂, similar images were also observed for gold, silver, lanthanum and palladium, for the same heating rates (figures not shown), but these patterns were most clearly seen with MgCl₂. This is therefore a general effect of the heating rate. It is clear from Fig. 53 that the same donut-shaped structure is formed as is observed in Fig 42 for gold vaporized under the Gas-Stop mode and the fast heating rate.

When the heating rate is much slower (300 °C/s), rapid thermal expansion of gas in the furnace is greatly reduced and diffusion for removal of analytes may dominate. In addition, end-heated graphite furnaces develop greater axial temperature gradients at lower heating rates [76] which also decrease the thermal expansion velocity [73]. Reduction in the thermal expansion of gas results in reduction in the disturbance caused by thermal expansion, which allows the vapour to condense in the centre of the graphite tube (Fig. 55) when the vapour pressure reaches saturation. The particle density remains highest in the centre of the particle cloud at all times. The

Figure 52. (a) Temperature-time heating characteristics of inside tube wall for a final set temperature of 2400 °C with the maximum power heating mode.

(b) Temperature-time heating characteristics of inside tube wall for a final set temperature of 2400 °C with a heating rate of 300 °C/s.

Figure 53. Vaporization of 50 μg of MgCl_2 at 2400°C under the Gas-Stop mode. Heating rate 2000°C/s. Sequence of images obtained with the CCD indicating time elapsed since the start of the vaporization step and measured inside tube wall temperature.

Figure 54. Absorbance contour maps corresponding to Fig 53, 50 μg of MgCl_2 .

Figure 55. Vaporization of 50 μg MgCl_2 at 2400°C under the Gas-Stop mode. Heating rate 300°C/s. Sequence of images obtained with the CCD indicating time elapsed since the start of the vaporization step and measured inside tube wall temperature.

Figure 56. Absorbance contour maps corresponding to Fig. 55, 50 μg of MgCl_2 .

(i) 1850 ms, 1350 °C (ii) 1900 ms, 1370 °C (iii) 1950 ms, 1380 °C

(iv) 2000 ms, 1400 °C (v) 2100 ms, 1420 °C (vi) 2200 ms, 1440 °C

(vii) 2250 ms, 1460 °C (viii) 2300 ms, 1480 °C

Figure 57. Vaporization of 50 μg MgCl_2 at 2400 °C under the Gas-Flow mode (20 mL/min). Heating rate 300 °C/s. Sequence of images obtained with the CCD indicating time elapsed since the start of the vaporization step and measured inside tube wall temperature.

Figure 58. Absorbance contour maps corresponding to Fig. 57, 50 μg of MgCl_2 .

particle cloud can be seen to extend to the top of the graphite tube and remains less dense near the bottom. It appears to reach a maximum density in Fig. 55 image (iv) 2350 ms, after which dissipation begins. It is therefore reasonable to conclude that at a heating rate of 300 °C/s, thermal expansion of gas is too gentle to perturb the gas much, and as a result, the structure of the condensed-phase particle cloud looks like a filled circle, instead of a ring (when viewed from the front as a two-dimensional structure).

When 50 µg MgCl₂ was vaporized under the same slow heating rate (300 °C/s) but with the addition of an internal Ar gas-flow of 20 mL/min during the high temperature vaporization step, the donut-shaped structure was again observed (Fig. 57). These images show that a small internal gas-flow with a slow heating ramp causes enough disturbance in the gas phase in the axial and radial centre of the graphite tube to reduce significantly condensation in this zone. The particle cloud formed is quite similar to that produced under fast heating conditions with no internal Ar purge gas flow. An internal purge gas flow rate of 20 mL/min (0.33 cm³/s) should produce an average internal purge gas flow velocity through the graphite tube of 1.18 cm/s (internal radius of the graphite tube is 0.3 cm). The average thermal expansion velocity in the graphite tube would be 1.05 cm/s if the heating rate was 2000 degrees per second and the final set temperature was 2673 K. The above results further support the hypothesis that thermal expansion effects in the graphite tube are responsible for the donut-shaped structure. Some aspects of thermal expansion (disturbance) of gas

produced by rapid high-temperature heating can be simulated by the use of a small internal purge gas flow.

A decrease in the heating rate reduces the condensation (and hence, light-scattering) which occurs later in the vaporization cycle, probably near the cold ends of the tube. The change in the light-scattering due to heating rate can be seen in Figs. 59 (a) and (b), which show the non-specific absorbance signals measured at 254 nm using the deuterium arc lamp with the Perkin-Elmer AAS model 603. The light-scattering with the slow heating rate is greatly reduced later in time, probably because of reduced thermal expansion of gas and analyte transport due to thermal expansion (when microparticles are present). When low sample masses (50 μg) were used diffusion did not appear to transport as much of the analyte to the tube ends as thermal expansion. When sample masses were significantly increased (200 μg MgCl_2), light-scattering, even at a later time, was observed. When a slow heating rate was used, light-scattering early in the vaporization step was found to be much greater than that observed at later times. With a fast heating ramp, the light-scattering observed for MgCl_2 in the tube centre and at the tube ends was of comparable magnitude.

3.3.3 Vaporization of ammonium phosphate, lanthanum nitrate, palladium nitrate, and magnesium nitrate.

Condensation of ammonium phosphate was investigated because it is often used as a chemical modifier in the determination of Cd, Pb, Zn, Sn and Ag [55]. The elements that are determined with the phosphate modifier, however, are volatile

Figure 59. Non-specific absorbance signals for 50 μg MgCl_2 vaporized at 2400 $^\circ\text{C}$ under the Gas-Stop mode (a) Heating rate 2000 $^\circ\text{C/s}$ (b) Heating rate 300 $^\circ\text{C/s}$.

themselves and often low vaporization temperatures are used. Usually, 200 μg of ammonium phosphate is used as the chemical modifier in combination with relatively low vaporization temperatures (such as 1600 $^{\circ}\text{C}$ for Cd [84]). When 200 μg of ammonium phosphate was vaporized at 1600 $^{\circ}\text{C}$, light-scattering was not severe at 228 nm. When the temperature was lowered to 1400 $^{\circ}\text{C}$, the light-scattering became pronounced, and at 1300 $^{\circ}\text{C}$ the CCD images revealed a distorted donut-shaped structure. Images of the condensation of 200 μg $(\text{NH}_4)_2\text{HPO}_4$ vaporized at 1300 $^{\circ}\text{C}$ are shown in Fig. 60 and the corresponding absorbance contour maps are shown in Fig. 61

Figure 60 reveals that condensation initially occurred near the top of the graphite tube and not in the centre, unlike that observed for other compounds. Following initial condensation at the top, a ring-shaped structure later formed, but it disintegrated at longer times. When the temperature was increased to 1400 $^{\circ}\text{C}$, the ring-shaped structure no longer formed, but condensation near the top of the tube persisted (Fig. 62 (b)). However, if the mass of $(\text{NH}_4)_2\text{HPO}_4$ was decreased from 200 μg to 150 μg or less and vaporization was done at 1300 $^{\circ}\text{C}$, condensation at the top of the tube was observed, but ring formation was again absent, (figure not shown). Additionally, condensation at the top of the tube during vaporization of 200 μg $(\text{NH}_4)_2\text{HPO}_4$ disappeared when the temperature was raised to 2000 $^{\circ}\text{C}$ (figure not shown). Condensation later in the vaporization step, which probably originated near the tube ends, was completely eliminated only when the temperature was increased to

Figure 60. Vaporization of 200 μg $(\text{NH}_4)_2\text{HPO}_4$ at 1300°C under the Gas-Stop mode and with the maximum power heating mode. Sequence of images obtained with the CCD indicating time elapsed since the start of the vaporization step.

Figure 61. Absorbance contour maps corresponding to Fig. 60, 200 μg $(\text{NH}_4)_2\text{HPO}_4$.

Figure 62. Vaporization of $200\ \mu\text{g}$ $(\text{NH}_4)_2\text{HPO}_4$ under the Gas-Stop mode and with the maximum power heating mode: (a) Vaporization temperature $1300\ ^\circ\text{C}$, sequence of images obtained with the CCD indicating time elapsed since the start of the vaporization step. (b) Vaporization temperature $1400\ ^\circ\text{C}$, sequence of images obtained using the CCD indicating time elapsed since the start of the vaporization step. (c) Vaporization temperature $1600\ ^\circ\text{C}$, sequence of images obtained with the CCD indicating time elapsed since the start of the

2600 °C (figure not shown). The effects of temperature on the condensation of 200 µg of ammonium phosphate can be seen in the images presented in Figs. 62 (a),(b) and (c).

These figures present images collected with the CCD at the same time in the vaporization step but at different temperatures. Somewhat similar images were recorded in a study by Masera et al. [85] on the matrix effects of silver on the atomization of gold. It is clear that condensation is greatly reduced by a relatively small increase in the vaporization temperature. A small purge gas flow (a few mL/min) also greatly reduced light-scattering, especially later in time, which probably originated near the tube ends (figure not shown).

The combination of palladium with magnesium nitrate has been reported to be an excellent mixed chemical modifier for most volatile elements [36]. CCD images were obtained for the vaporization of a mixture of 15 µg Pd + 10 µg Mg(NO₃)₂, which had been pyrolyzed at 900 °C for 10 s and vaporized at 2400 °C for 10 s under the maximum power heating. The experimental conditions used for obtaining images of La(NO₃)₃ were pyrolysis at 400 °C for 10 s and vaporization at 2600 °C for 10 s, with the maximum power heating. This chemical modifier was found to produce very little light-scattering with or without a graphite platform when used at the usually recommended temperatures and mass (15 µg Pd + 10 µg Mg(NO₃)₂ [86]; however grey scale manipulation was necessary to enhance the images because of the faintness of the condensed-phase structures. However, the same condensation pattern as observed for gold was again evident. One chemical modifier which was found to

produce severe light-scattering was 50 μg of $\text{La}(\text{NO}_3)_3$. Although normally used at lower levels, typically 10 μg [87], as much as 200 μg of $\text{La}(\text{NO}_3)_3$ was used for complex samples [88]

One consequence of the severe light-scattering which occurs at low temperatures is that deuterium arc lamp background correction may give erroneous results. This problem may be alleviated by using higher vaporization temperatures or a small purge gas flow during the vaporization step. Using the Perkin-Elmer AAS, model 603, fitted with a Cd hollow cathode lamp, it was verified that the $(\text{NH}_4)_2\text{HPO}_4$ was free of cadmium. When 200 μg $(\text{NH}_4)_2\text{HPO}_4$ was vaporized at high temperatures ($> 2000^\circ\text{C}$) and the deuterium arc lamp background corrector was used, a flat baseline was obtained, indicating accurate correction. When the ammonium phosphate was vaporized at low temperatures ($< 1600^\circ\text{C}$) in the Gas-Stop mode, overcorrection resulted, which became more severe as the temperature was decreased. Correct alignment of the deuterium arc lamp with that of the Cd hollow cathode lamp was verified, using the procedure suggested by Welz [89], but the overcorrection persisted. A small gas-flow (20 mL/min) was found adequate, however, to enable a good baseline to be obtained. The overcorrection was probably the result of the dynamic nature of the scattering particles, i.e., they rapidly change their spatial distributions and optical densities during the course of a measurement, making the results of deuterium arc lamp background correction uncertain. The background and total absorption measurements were time offset and therefore if the background was changing faster than the time

offset then incorrect correction would result. Good background correction with the deuterium arc lamp background corrector was obtained only by increasing the temperature, or by using a mini-flow of Ar purge gas to reduce light-scattering significantly.

3.4 SUMMARY AND CONCLUSIONS

In view of the extreme light-scattering produced by some chemical modifiers, the amount of chemical modifiers added should be the minimum possible. The use of a graphite platform and/or a small internal purge gas flow during the high temperature vaporization step can greatly reduce light-scattering. When a large amount of a chemical modifier is necessary for thermal stabilization of analyte species, Zeeman effect background correction should be used to provide more accurate results.

The radially non-uniform nature of vapour condensation is probably the result of changes in the purge gas-flow velocity and/or temperature within the graphite tube during heating. Condensation of vapours in GFAAS is undesirable, but is of great benefit in electrothermal vaporization inductively coupled plasma mass spectrometry, where such effects promote efficient transport of the analytes to the ICP torch. Results obtained from this study suggest that the heating rate and the internal purge gas flow through the electrothermal vaporizer are important for optimization of analyte condensation on the physical carriers used in ETV-ICP-MS for enhancing transport of analytes to the ICP torch, and hence, the analytical sensitivity.

CHAPTER 4

VAPORIZATION OF PHOSPHORUS COMPOUNDS AND USE OF CHEMICAL MODIFIERS FOR DETERMINATION OF PHOSPHORUS BY ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

4.1 INTRODUCTION

Phosphorus is an element which is difficult to determine accurately at very low levels by most analytical techniques. Molecular spectrophotometry has been used extensively because of its simplicity and low cost. Molybdophosphoric or molydovanadophosphoric heteropolyacid chromophores [90] yield detection limits in the $\mu\text{g/mL}$ range [91]. However, this method is time consuming and requires oxidation of P compounds to orthophosphate. Flame spectrophotometry for atomic emission and molecular emission using the HPO and PO absorption bands [90] have also been used for the determination of P giving detection limits in the $\mu\text{g/mL}$ range [92, 93]. Phosphorus has also been determined using graphite furnace atomic absorption spectrometry (GFAAS) but detection limits are poor. One of the main problems with the determination of this element by GFAAS is the fact that its resonance lines are in the vacuum ultraviolet between 167.2 and 178.8 nm. Phosphorus has been determined using the ultraviolet resonance lines with a specialized spectrophotometer using a graphite cell [94] giving a detection limit of 3 pg. The equipment necessary for measurements in the vacuum ultraviolet is

relatively complex and expensive, and not practical for routine analysis. Phosphorus has later on been determined by atomic absorption spectrometry using the 213.5-213.6 nm non-resonance doublet [6, 95]. Manning et al. [95] used a nitrous oxide-acetylene flame and obtained a sensitivity ($\mu\text{g/mL}$ giving 1% absorption) of 290 $\mu\text{g/mL}$ using water dilutions of phosphoric acid. The analytical sensitivities of Na and K phosphate salts for atomic absorption spectrometry were found to be about the same as for phosphoric acid, and a detection limit of 0.2 ng was obtained [6]. The use of non-resonance lines for the determination of P is not practical because at the temperatures attainable in a graphite furnace or flame, most of the P is in the ground state and thus the analytical signal obtained is derived only from a small fraction of the P present [6, 95].

The determination of P by GFAAS is complicated by the formation of gaseous compounds of high thermal stability [96]. Persson and Frech [96] proposed that the determination of P would best be carried out in a graphite furnace in which the heating rate, final temperature and atmosphere inside the graphite tube were controlled or if the sample were inserted into a graphite tube preheated to a high temperature. L'vov and Pelieva [97] determined P in an HGA atomizer by introducing the sample (placed on a tungsten probe) into a preheated graphite tube. A detection limit of 2 ng was obtained [97] which was 30-fold lower than that obtained using wall atomization. The use of chemical modifiers [88] and/or platform atomization [98] in GFAAS has been investigated. Ediger et al. [88] reported that most P compounds, except for Ca phosphate, produced no

signal unless La was used as a chemical modifier. Uncoated polycrystalline electrographite forms thermally stable phosphorus compounds by a condensed-phase reaction between the electrographite and P because of the existence of a large number of active carbon sites on electrographite compared to pyrolytically coated graphite tubes [98]. Although the nature of the graphite surface can have a profound effect on the determination of P, it cannot produce the desired effect (stabilization to high temperature) in the same way a chemical modifier can [98]. Lanthanum has been used as a chemical modifier because of its ability to form thermally stable phosphorus compounds [54, 99-103], although it is corrosive and can attack the graphite surface [87, 104]. Other elements have been studied for their suitability as chemical modifiers for the determination of P [87, 105-108]. Curtius et al. [87] suggested that Pd used alone or with Ca are good chemical modifiers for GFAAS allowing for a maximum pyrolysis temperature of 1400 °C for P. Lanthanum, Y and Ni used as chemical modifiers gave almost the same maximum pyrolysis temperatures for P, but GFAAS signals were not stable

Other spectroscopic techniques used for the determination of P include graphite furnace atomic non-thermal excitation spectrometry (FANES) [109] and molecular non-thermal excitation spectrometry (MONES) [110] which gave detection limits of 90 pg and 700 pg, respectively. The FANES source is not practical for routine analysis as it requires low pressure operation. Furnace atomization plasma emission spectrometry (FAPES) [111, 112] gave a detection

limit of 29 pg for P [111] and laser-excited fluorescence spectrometry of P and P oxide using an electrothermal atomizer [113] gave a detection limit of 8 pg.

More recently, ICP-MS has been used for the determination of P, an element with only one isotope at m/z 31. Unfortunately, this isotope is not free of polyatomic interferences since NOH^+ ions formed in the plasma from water and atmospheric gases produce a relatively high background signal when the solution nebulization sample introduction technique is used [114]. Electrothermal vaporization sample introduction (ETV) allows for the removal of water and can greatly reduce polyatomic ion interferences as well as improve detection limits relative to solution nebulization sample introduction. The 100-fold improvement in the detection limit for P was achieved using ETV sample introduction [115] was largely due to substantial reduction (50-fold) in the background signal, and increased sensitivity and signal stability [115]. A detection limit of 0.3 $\mu\text{g/L}$ corresponding to an absolute detection limit of 15 pg (50 μl) was reported.

This research was undertaken as a part of a program to develop a method for determination of P at trace levels in steels and high-purity iron. The objective of this study was to investigate the mechanism of vaporization of various P compounds in a graphite tube (ETV) using ICP mass spectrometry. The role of chemical modifiers was investigated to determine their ability to form thermally stable compounds with P which remain stable at high temperatures, allowing for the removal of interfering matrix species.

4.2 EXPERIMENTAL

4.2.1 Apparatus

A Perkin-Elmer Elan 5000 ICP mass spectrometer equipped with an HGA-600 MS electrothermal vaporizer and a model AS-60 autosampler were used. Tube wall vaporization with pyrolytically coated graphite tubes (Perkin-Elmer Part No. 091504) was used. For some experiments uncoated polycrystalline electrographite tubes were used. The experimental conditions for both the Elan 5000 and HGA-600 MS are summarized in Table 7. During the dry and pyrolysis steps of the operation program, opposing flows of argon gas (300 mL/min) originating from both ends of the graphite tube removed water and other vapours through the sample injection hole of the graphite tube. For some experiments signal acquisition (read step) was initiated during the dry step and thus any vapours produced were sent to the ICP rather than being expelled out of the sample injection hole. During normal operation a graphite probe is pneumatically activated which seals the sample injection hole during the high-temperature vaporization step. Once the graphite tube was sealed, a valve located at one end of the HGA workhead directed the argon carrier gas flow originating from the far end of the graphite tube directly to the argon plasma

4.2.2 Standards and Reagents.

High purity argon gas (99.995%, Matheson Gas Products, Canada) was used. The test solutions were prepared with ultra-pure water obtained from a Milli-Q water purification system (Millipore Corp., Mississauga, ON). The nitric acid used was analytical grade (Ultrax) and the phosphoric acid was reagent grade

Table 7: Instrumental operating conditions.**ICP mass spectrometer.**

Rf power	1050 W
Coolant argon flow rate	15.0 L/min
Auxiliary argon flow rate	900 mL/min
Carrier argon flow rate	1150 mL/min

HGA-600 MS electrothermal vaporizer.

Sample volume	20 μ L
Internal argon flow rate	0 mL/min
Dry step (10 s ramp)	130°C for 40 s
Pyrolysis step (2s ramp)	400°C for 10s
Vaporization step (variable ramp)	variable for 10s
Clean-up step (0s ramp)	2650°C

Data acquisition.

Dwell time	20 ms
Scan mode	peak hop transient
Points/spectral peak	1
Signal measurement	Signal maximum and area
MS resolution	0.6 u at 10% peak height.

Solutions containing various P compounds were prepared by dissolving the compounds (Baker Analyzed, J.T. Baker Co., Toronto, ON) in ultra-pure water (Milli-Q System, Millipore Corp., Mississauga, ON). The chemical modifier solutions were prepared as follows: lanthanum nitrate was prepared by dissolving $\text{La}(\text{NO}_3)_3$ (Morton Thiokol Inc., Danvers, M.A.) in ultra-pure water, the Ni and Zr solutions (the nitrate form) were prepared from 1000 $\mu\text{g/ml}$ Spex AA standards (Spex Industries, Edison, NJ).

For all experiments, a 20 μL volume of sample was pipetted onto the inner wall of the graphite tube. The total volume was maintained at a constant 20 μL for the various chemical modifier masses by the automatic addition of diluent water by the autosampler.

4.3 RESULTS AND DISCUSSION

4.3.1 Polyatomic Spectral Interference of $^{14}\text{N}^{16}\text{O}^1\text{H}^+$ on $^{31}\text{P}^+$

The sensitivity for P is not as good as for most elements determined by ICP-MS largely because of its high ionization energy (10.486 eV), resulting in only partial ionization in the Ar plasma (29 %) [116]. Introduction of P into the plasma using ETV not only reduces the background signal (relative to solution nebulization) produced by the NOH^+ ions [115] but also promotes the ionization of P in the plasma by making available the energy that would have been otherwise consumed by the vaporization of water in the solution nebulization sample introduction technique.

In a study by Grégoire et al. [31], it was reported that mineral acids were retained by the graphite tube until high temperatures. For nitric acid, virtually complete removal was possible at temperatures well below the vaporization temperature of P. However, under certain circumstances, it is possible that some of the nitric acid could condense on the cooler graphite contact of the graphite furnace housing and be vaporized along with P [31].

In order to study the vaporization of water and nitric acid and their possible effects on the determination of P, 1 ng of P (as $(\text{NH}_4)_2\text{HPO}_4$) was vaporized in the presence of 0.02% HNO_3 . The signals of the analyte and of possible concomitants were monitored during both the drying and vaporization steps. The sample was dried at 130°C for 30s using a 10 s ramp time and then vaporized at 2500°C . Signal pulses shown in Figure 63 A and 63 B are those arising from $^{40}\text{Ar}^{16}\text{O}^+$, $^{40}\text{Ar}^{40}\text{Ar}^+$ and $^{38}\text{Ar}^+$ as well as P. The argon dimer and argon signals were recorded and used as a diagnostic probe of plasma conditions as was done by Grégoire et al. [8] who used these ions to study signal suppression in ETV-ICP-MS resulting from the use of chemical modifiers. Both the $^{40}\text{Ar}^{16}\text{O}^+$ and $^{14}\text{N}^{16}\text{O}^1\text{H}^+$ signals shown in Figure 63 rise together during the drying step indicating that the majority of oxygen and nitrogen containing species vaporize at about 35s. At the same time both the $^{38}\text{Ar}^+$ and $^{40}\text{Ar}^{40}\text{Ar}^+$ signals drop indicating loading of the plasma caused by the evaporation of the solvent or a change in the sampling depth resulting from the rapid expansion of gases. The signal at m/z 31 obtained during the drying cycle probably originates from $^{14}\text{N}^{16}\text{O}^1\text{H}^+$ rather than $^{31}\text{P}^+$ because

Figure 63. ETV-ICP-MS signal pulses for A: 1 ng of P $((\text{NH}_4)_2\text{HPO}_4)$ in 0.02% HNO_3 and B: for 0.02% HNO_3 . Drying temperature 130 °C with a 10 s ramp and 30 s hold time, vaporization temperature 2500 °C with a 0 s ramp and 10 s hold time.

phosphoric acid does not boil at this temperature while the boiling point of nitric acid is 83°C [15]. No loss of P was observed at the low temperatures (130°C) used in this study. The second peak at m/z 31 in Figure 63 A corresponds to the vaporization of P as the graphite tube is heated to 2500°C. No P signal is observed (Fig. 63 B) during the vaporization step when only water and 0.02% nitric acid are vaporized. This result demonstrates the importance of thoroughly removing solvent to avoid polyatomic interferences with P. Also shown in Figure 63 B is the high background level at m/z 56 (ArO^+) and 31 (NOH^+), which are absent when the solvent vapors are vented through the sample injection hole during the drying step. These background signals are probably due to the vaporization of solvent and analyte species condensed on the cooler graphite cones during the evaporation of solvent during the drying step when the sample injection hole was plugged.

4.3.2 Effect of Graphite Surface on Vaporization of Phosphorus.

It is reported [98] in GFAAS studies that an uncoated electrographite tube gives a 10-fold greater signal for P than does a pyrolytically coated graphite tube. This increase in sensitivity is attributed to the higher porosity and the greater number of reactive carbon sites available on an electrographite surface. The effect of using various graphite vaporization surfaces on ETV-ICP-MS signals was therefore studied. Phosphorus (500 pg) as $(\text{NH}_4)_2\text{HPO}_4$ was vaporized from a pyrolytically coated graphite and an uncoated polycrystalline electrographite tube. Phosphorus signal maxima and peak areas as a function of vaporization temperature are shown in Figures 64 and 65, respectively. Signal maxima and

Figure 64. ETV-ICP-MS vaporization curves (peak heights) for 500 pg of P ((NH₄)₂HPO₄) using a pyrolytically coated graphite tube, an uncoated polycrystalline electrographite tube, and a pyrolytically coated graphite tube, with 1 μg of La.

Figure 65. ETV-ICP-MS vaporization curves (peak areas) for 500 pg of P ((NH₄)₃HPO₄) using a pyrolytically coated graphite tube, an uncoated polycrystalline electrographite tube, and a pyrolytically coated graphite tube, with 1 μg of La.

peak areas were normalized to account for small sensitivity changes obtained on different days. These two figures show that the graphite surface and presence of a chemical modifier have a significant impact on the P signal and its appearance temperature. When $(\text{NH}_4)_2\text{HPO}_4$ was vaporized from the pyrolytically coated graphite tube no signal was detected until a temperature of 950°C was reached and no loss of P was observed below this temperature. This was surprising since Curtius et al. [98] recorded loss of P at pyrolysis temperatures greater than 200°C when vaporizing $1\text{ }\mu\text{g}$ of $(\text{NH}_4)_2\text{HPO}_4$ was vaporized. In a study by Liang et al [113] a significant loss of P signal (20 ng P was taken as $\text{NH}_3\text{H}_2\text{PO}_4$) was reported when the pyrolysis temperature was greater than 600°C . Disagreement between our results and those reported in the literature for GFAAS may be due to the sample mass used in this study compared to that used in other studies in GFAAS. Curtius et al. [98] used $1\text{ }\mu\text{g}$ of P which was 2000 times greater than the sample mass we used. In that study no signal was obtained when $1\text{ }\mu\text{g}$ of P as $(\text{NH}_4)_2\text{HPO}_4$ was atomized from the wall of a pyrolytically coated graphite tube at a temperature of 2650°C , following pyrolysis at 200°C for 30 s . A P signal however was obtained when atomization took place from an uncoated graphite tube or if a platform was used. Another interesting effect noted by Curtius et al [98] was that due to the sample volume. When the same mass of sample ($1\text{ }\mu\text{g}$ of P) was delivered in $20\text{ }\mu\text{L}$ rather than $5\text{ }\mu\text{L}$, the peak area increased. This indicated that the graphite surface was interacting with the analyte in the condensed phase. Further evidence for the interaction of P with the carbon surface

were provided by thermal pre-treatment curves [98], which show the analyte signal obtained at a constant atomization temperature as a function of a changing pyrolysis temperature. Often, thermal pre-treatment curves exhibited a second maximum such that the sensitivity decreased up to a pyrolysis temperature of about 1000°C and then increased again to a maximum at about 1500°C. It was proposed that the formation of the “metallic” carbide P_2C_6 contributes to the prevention of P losses at high pyrolysis temperatures and that the stabilization of P on the graphite surface is primarily a condensed-phase reaction that leads to the formation of lamellar and/or residue compounds [98]. Thus, the difference in the stabilization of P for this study when compared to Curtius et al. [98] is probably due to the greatly different P masses used. One μg of P which corresponds to 4.29 μg of ammonium phosphate would not form a surface monolayer once evaporated from a 10 μl droplet. Such a large amount of sample would likely exhibit bulk properties such as melting point, boiling point and decomposition temperatures. When working with analytes present in nanogram quantities, it is often difficult to account for vaporization mechanisms based on bulk properties especially if the analyte is reactive toward graphite. For example, the thermal properties of ammonium dihydrogen phosphate crystals in the temperature range of 25-600°C have been studied by thermal analysis [117] using a 38 mg sample heated at a rate of 5°C min^{-1} . It was reported that at 210°C, ammonium dihydrogen phosphate decomposed to orthophosphoric acid, H_3PO_4 , with the evolution of ammonia gas. At about 350°C, pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$, formed which in turn was

transformed into metaphosphoric acid [117]. The same decomposition scheme is probably valid for diammonium hydrogen phosphate and is shown below

At temperatures up to 600°C there was a steady weight loss corresponding to release of ammonia and water [117]. The low temperature losses of P during pyrolysis observed by Curtius et al. [98] could be due to loss of P by co-volatilization during the evolution of ammonia and water during decomposition. This phenomenon has been observed during the pyrolysis of microgram quantities of nickel nitrate [118], magnesium chloride [34] and sodium nitrate [56]. A much smaller analyte mass, as is used for ETV-ICP-MS, would be deposited in much thinner layers upon the graphite surface allowing decomposition gases to escape without physically removing any of the remaining analyte-bearing residue.

4.3.3 Thermal Stabilization of Phosphorus by Lanthanum

In GFAAS, lanthanum is perhaps the most popular chemical modifier used to form thermally stable phosphorus compounds, allowing for vaporization of P into a hotter graphite tube promoting atomization. This stabilization effect where 1 µg of La shifts the appearance temperature of P from about 950°C to 1400°C is shown in Figures 64 and 65. The formation of La phosphide is probably responsible for this effect. Curtius et al. [87] reported on the thermal stabilization

of P and proposed compound formation to explain this. In a study by Welz et al. [104] it was reported that La produces serious pitting and corrosion of the graphite surface, but there was no evidence for the formation of a dense coating of lanthanum carbide. It was found that when P was atomized in the presence of 10 μg of La, there were no significant differences in the thermal pretreatment curves between an electrographite tube and a pyrolytically coated graphite tube [87]. Ediger et al. [88] found that while most P compounds produced no signal in GFAAS, these same compounds gave good signals when La was added as a chemical modifier.

Metal phosphides can be produced by the reduction of a phosphate with carbon [90, 119, 120]. Metal phosphides generally have high melting points which tend to increase with increasing metal content [90]. Lanthanum reacts with P to form lanthanum monophosphide [120]. Lanthanum can also form the phosphide LaP_3 [90], however formation of this compound would not be favoured when La is present in a huge excess over P. Many metal phosphates can be prepared by heating a mixture of a metal salt and a phosphate [90]. It is possible that La and ammonium phosphate together would react to form lanthanum phosphate which in turn would react with carbon to form a lanthanum phosphide. Any excess La would probably be present as an oxide and/or carbide. Lanthanum oxide (La_2O_3) has a melting point of 2307°C , whereas lanthanum phosphate (LaPO_4) has a melting point of 2072°C . When a large quantity (μg) of both La and P are present in the graphite tube, not all of the sample will be in contact with the graphite

surface to facilitate the formation of a metal phosphide and therefore a mixture of compounds might result. The mechanism proposed by Dittrich et al. [110] is consistent with our observations and with the data presented below. The formation of lanthanum phosphate probably takes place during the drying step as shown below:

Then, during the pyrolysis step and the first part of the vaporization step, lanthanum phosphide is probably formed as previously discussed [110]

Finally, during the vaporization step, lanthanum phosphide vaporizes and dissociates as shown below [110]:

In GFAAS, the mass of the chemical modifier can sometimes be increased to quite high levels without detrimental effects, but in ETV-ICP-MS the mass of chemical modifier can only reach several μg before causing signal suppression effects [8].

An equally important consideration which effects the detection limit in ETV-ICP-MS is the signal to background ratio obtained for vaporization under different experimental conditions. The vaporization of 500 μg of P as $(NH_4)_2HPO_4$ using pyrolytically coated graphite and electrographite tubes are shown in Figures 66 and 67, respectively. The same experiment repeated using a pyrolytically coated

graphite tube but with the addition of 1 μg of La is shown in Figure 68. Pyrolytic graphite (Fig. 66) gives the best signal to background ratio (with peak height signals) reaching a value of about 170 at a temperature of 1200 °C. The signal to background ratio is poorer for peak areas because more counts arising from NOH^+ are collected whereas these are temporally separated to a larger extent for peak height signal measurement. Grégoire et al. [8] measured the background equivalent analyte masses for spectral interferences in ICP-MS arising from a graphite electrothermal vaporizer at 2500°C and found that the background due to NOH^+ was equal to the signal of 2 pg of phosphorus.

Significantly greater background signals were obtained when electrographite was used (Fig. 67). In fact, blank levels increased over repeated vaporizations of P; the increase could be due to the partial desorption of P intercalation compounds formed during previous firings. Although electrographite did form a thermally stable phosphorus compound (relative to pyrolytic graphite), memory effects made it impractical for use as a vaporization surface in ETV-ICP-MS.

The poorest signal to background ratios were obtained when La was used as a chemical modifier (Fig. 68). These low signal to background ratios cannot be accounted for by the poorer sensitivity (cf. Fig. 71), and thus must be the result of a higher background signal. High P background levels as well as memory effects were also reported by Welz et al. [104] when La was used. These authors [104] proposed that La attacks the graphite surface, creates active carbon centres and

Figure 66. Signal to background ratio for 500 pg of phosphorus ($(\text{NH}_4)_2\text{HPO}_4$) as a function of vaporization temperature. A pyrolytically coated graphite tube was used.

Figure 67. Signal to background ratio for 500 pg of phosphorus ((NH₄)₂HPO₄) as a function of vaporization temperature. An electrographite tube was used.

Figure 68. Signal to background ratio for 500 pg of phosphorus ($(\text{NH}_4)_2\text{HPO}_4$) as a function of vaporization temperature. A pyrolytically coated graphite tube with 1 μg of La was used

promotes the formation of intercalation compounds. The memory effect observed is an indication that residual La is retained in the graphite lattice and plays a role in the stabilization of phosphorus [104], a view supported by our observation using ETV-ICP-MS that large La signals persist even after many blank vaporization cycles

Signal profiles for P (500 pg as $(\text{NH}_4)_2\text{HPO}_4$) vaporized at various temperatures from pyrolytically coated and electrographite tubes and from a pyrolytic graphite tube in the presence of La (1 μg) are shown in Figures 69, 70 and 71, respectively. For P vaporized from a pyrolytic graphite surface (Fig. 69), signals are well defined at lower temperatures. As the vaporization temperature was increased, a shoulder appeared on the P signal which became more pronounced at 2650°C. This shoulder was probably due to the vaporization of a second P compound, or the release of P intercalated within the graphite surface. Phosphorus signals obtained from an electrographite (Fig. 70) surface were broader, and at 2650°C showed severe tailing, indicating interaction of P with the graphite surface. When La was used (Fig. 71), a significant shift in the appearance temperature occurs and the signals are quite broad relative to those produced on pyrolytic graphite without La chemical modifier (Fig. 69). The shift in the appearance temperature indicates compound formation, probably lanthanum phosphide.

Figure 69. ETV-ICP-MS signal pulses at various vaporization temperatures for 500 pg of phosphorus ($(\text{NH}_4)_2\text{HPO}_4$) vaporized using a pyrolytically coated graphite tube.

Figure 79. ETV-ICP-MS signal pulses at various vaporization temperatures for 500 pg of phosphorus ((NH₄)₂HPO₄) vaporized using an electrographite tube.

Figure 71. ETV-ICP-MS signal pulses at various vaporization temperatures for 500 pg of phosphorus ($(\text{NH}_4)_2\text{HPO}_4$) vaporized using a pyrolytically coated graphite tube with 1 μg of La

4.3.4 Vaporization of Phosphate Compounds.

The thermal characteristics of Na_2HPO_4 , K_2HPO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and H_3PO_4 was studied by ETV-ICP-MS. The samples (1 ng of P in 0.02 % HNO_3) were deposited onto the pyrolytic graphite tube wall, dried at 130°C using a 10 s ramp time and a 40 s hold time and vaporized using a 1 s ramp time and a 10 s hold time. No pyrolysis step was used. The vaporization curves given in Figure 72 show that phosphoric acid is not vaporized until 1000°C . Whereas this temperatures seems high in comparison to other mineral acids, P is an element whose compounds form condensed species, which is a term used to describe all phosphates whose acids have less water than orthophosphate (H_3PO_4) [121]. Poly, linear, or chain phosphates are derived from the parent orthophosphoric acid by the elimination of water between hydroxyl groups. These polyphosphates are referred to as di, tri, tetra, etc. phosphates. However the term pyrophosphate is still often used for the diphosphate. When a dilute solution of orthophosphoric acid is heated, water evaporates and the solution becomes more concentrated in orthophosphoric acid [122]. The boiling point increases slowly until a composition of 87.7 % H_3PO_4 (65% P_2O_5) is reached [122]. The boiling point then rises rapidly and pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$) is formed. On further heating, water continues to evaporate and a mixture of polyphosphoric acids is produced [122]. Condensation occurs according to the following reaction [122]:

Figure 72. ETV-ICP-MS vaporization curves for 1 ng of phosphorus in the form of various phosphates. Vaporized using a pyrolytically coated graphite tube and a 1s vaporization ramp time.

where n represents the number of P atoms. The vapours above boiling orthophosphoric acid do contain some P_2O_5 (0.02% P_2O_5 by weight at 255°C) [122] and the amount of P in the vapour increases as the acid becomes more concentrated. An azeotropic mixture is reached at 92.4 % P_2O_5 , which boils at 864°C and at this point the liquid and the vapour have the same composition [122]. It is evident from Figure 72 that the graphite surface is able to retain these phosphate species quite well until 1000°C.

The thermal vaporization characteristics of Na_2HPO_4 and K_2HPO_4 , also shown in Figure 72, indicate that these two salts have similar vaporization properties and that the Na salt is slightly more volatile. The appearance temperature for Na and K phosphates were 1150°C and 1200°C, respectively. For these experiments, the heating ramp rate during the vaporization step was slowed down to 10 s to give better temporal resolution of the signal profiles. Both salts vaporized in a similar manner, and the K and Na signals were coincident with the P signal. A single clearly defined peak was obtained for P, indicating that a single P species was vaporized or that if more than one species existed, they possessed the same vaporization properties. Since these salts were present in dilute nitric acid as they were deposited in the graphite tube, probably hydrolysis occurred during the heating, resulting in the formation of the dihydrated Na and K orthophosphate, as well as their nitrates. Thermal analysis of dihydrated Na orthophosphate [123] and K dihydrogen phosphate [124] showed that the metaphosphate was formed as the end product and a pyrophosphate as an intermediate [123, 124]. Dittrich et

al [110] have proposed that NaPO_3 is formed in a graphite tube during the heating of NaH_2PO_4 . The overall reaction [123, 124] can be shown as

where M represents Na or K. The alkali metaphosphates can also form long chain structures [90]. The metaphosphates or further reaction products (if they react with carbon as proposed by Dittrich et al [110]) would then vaporize or be decomposed at higher temperatures. Potassium and Na oxides could also vaporize in the presence of nitric acid.

The dehydration scheme for the last compound studied, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, is complex and not well understood [90]. In GFAAS studies, it was reported that Ca promotes thermal stabilization of P to higher vaporization temperatures [88, 96]. In ETV-ICP-MS, Ca is vaporized only at temperatures above 1150°C. Under slow heating (10 s ramp) conditions, the P signal had two peaks with Ca volatilizing at the same time as the second P peak, indicating the presence of a mixture of P species on the graphite surface. A study of the condensation of $\text{Ca}(\text{F}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} - \text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ during thermal treatment has been reported [106], but a very complex reaction scheme was proposed. It is probable however, that some Ca metaphosphate ($\text{Ca}(\text{PO}_3)_2$) would form [106] along with some Ca phosphide because it is known that tricalcium phosphate ($\text{Ca}_3\text{P}_2\text{O}_8$) reacts with carbon to form tricalcium diphosphide (Ca_3P_2) [120]. Alternatively, it is also possible, as suggested by Saeed et al [106], that Ca phosphate could react with carbon to form CaO , P_2 and CO.

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4.3.5 Interference due to the Presence of Iron.

Iron is a common matrix element encountered in analytical chemistry and is present in many samples such as geological materials and steels. Iron does not produce a spectroscopic interference in the determination of P by ICP-MS, but the presence of large quantities of Fe reaching the plasma could lead to P signal suppression. The effect of Fe on P signals was investigated by vaporizing 1 ng of P as H_3PO_4 in the presence of 1 μg of Fe as FeCl_3 . The vaporization curve for P vaporized in the presence of Fe (Fig. 73) gives an appearance temperature of 1300°C for P. The large shift in the appearance temperature compared to P vaporized alone indicates compound formation, probably a Fe phosphate or phosphide. Also, the presence of Fe at the 1 μg level caused suppression of the P signal, and the magnitude of this suppression was dependent on the vaporization ramp time and increased as the heating rate was increased (Fig. 74). The maximum power heating mode produced a 43% reduction (cf. Fig. 74 A and B) in the P signal; a 1 s ramp time a 29 % reduction (not shown), whereas a 10 s ramp time produced no decrease in the P signal area (cf. Fig. 74 A and B). It should be noted that whereas the interference from Fe decreased on going to a slower heating rate, P signals also decreased so that while there was a reduction in the interference from Fe there was also a reduction in the P sensitivity. As mentioned earlier, the argon dimer at m/z 80 can be used as an indicator of plasma loading and possible matrix interference effects [8]. In this study, it was found that the argon dimer was very stable when P was vaporized alone using the maximum power heating mode

Figure 73. ETV-ICP-MS vaporization curve for 1 ng of phosphorus (as H_3PO_4) with 1 μg of Fe (as FeCl_3), vaporized using a pyrolytically coated graphite tube and a 1s vaporization ramp.

Figure 74. ETV-ICP-MS signal pulses for the vaporization of 1 ng of phosphorus (as H_3PO_4) at 2600 °C. A: With 0 μg of Fe using the maximum power heating mode. B: With 1 μg of Fe using the maximum power heating mode. C: With 0 μg of Fe using a 10 s vaporization ramp. D: With 1 μg of Fe using a 10 s vaporization ramp.

However, the argon dimer signal decreased significantly when 1 μg of Fe was also vaporized with P, indicating that the Fe reaching the plasma would probably also suppress the P signal. The stability of the argon dimer in the presence of Fe improved as the heating rate was slowed and was unaffected when a 10 s ramp time was used. Clearly, as the heating rate was decreased, the quantity of Fe reaching the plasma at any given time was less and thus at some point, insufficient Fe was reaching the plasma to cause signal suppression.

4.3.6 Chemical Modifiers.

In order for a chemical modifier to be effective in removing the interference produced by Fe, it must form a more thermally stable compound with P, allowing for the removal of Fe at a low temperature prior to the vaporization of P. For these experiments, several chemical modifiers including Ni, Zr and La were investigated to determine their ability to form thermally stable compounds with P. The effects of these chemical modifiers were first investigated using a slow vaporization ramp rate to allow sufficient time for the compound formation to occur, and also to take advantage of any temporal separation achieved in the vaporization of Fe and P.

The effect of adding each of the three chemical modifiers to the P and argon dimer signals is shown in Figure 75 (Fig. 75 A shows the effect when no chemical modifier was used). For these experiments, a 400°C pyrolysis step, a vaporization temperature of 2600°C and a 10 s ramp time were used. The earlier appearance time of P (as H_3PO_4) shown in Figure 75 A compared to that in Figure

74 C was the result of adding a 400°C pyrolysis step which was included immediately prior to the vaporization step whereas no pyrolysis step was used for experiments shown in Figure 74. All of the chemical modifiers (Fig. 75 B: Ni, C, La and D: Zr) produced thermal stabilization of phosphorus when present at the 1 µg level. Higher masses of the chemical modifiers were also investigated as it had been reported in GFAAS that the integrated absorbance increases with increased mass of chemical modifiers [87]. This increase in the peak area in GFAAS was most probably the result of greater extent of thermal dissociation of phosphorus compounds in the gas-phase. The chemical modifiers at higher temperatures, the larger mass of the chemical modifiers probably formed phosphorus compounds of greater thermal stability, which resulted in their vaporization and thermal dissociation at higher temperatures. The effect of using 10 µg of the chemical modifiers on 1 ng of P is shown in Figure 76. The presence of 10 µg of Ni or La (Figs. 76 B, 76 C) caused strong suppression of both the argon dimer and the P signals, whereas 10 µg of Zr (Fig. 76 D) did not. The suppression of analyte signals is due to the vaporization of a relatively large mass of modifier, an effect previously reported by Grégoire et al. [8]. The use of up to 20 µg of Zr, resulted in no P signal suppression and stabilized P to even higher temperatures. This is probably because Zr is a relatively involatile element and the bulk of the metal vaporizes only after the phosphorus signal appears. On the other hand Ni gives the greatest suppression of the P signal probably because Ni is relatively volatile and is co-volatilized with P.

Figure 75. ETV-ICP-MS signal pulses for the vaporization of 1 ng of phosphorus (as H_3PO_4), pyrolysis at 400 °C for 30 s, vaporization at 2600 °C using a 10 s vaporization ramp. A: 1 ng of P. B: 1 ng of P with 1 μg of Ni. C: 1 ng of P with 1 μg of La. D: 1 ng of P with 1 μg of Zr.

Figure 76. ETV-ICP-MS signal pulses for the vaporization of 1 ng of phosphorus (as H_3PO_4), pyrolysis at 400 °C for 30 s, vaporization at 2600 °C using a 10 s vaporization ramp. A: 1 ng of P. B: 1 ng of P with 10 μg of Ni. C: 1 ng of P with 10 μg of La. D: 1 ng of P with 10 μg of Zr.

Lanthanum allowed the use of slightly higher pyrolysis temperatures when used at the 2 μg level (1300°C compared to 1200°C for Zr). The blank signals for Zr, however, were much lower than those obtained when La was used instead. The effects of the chemical modifiers on the P signals when iron is present is shown in Figure 77, which shows that 2 μg of Zr (Fig. 77 D) or La (Fig. 77 B) thermally stabilized P effectively even when 1 μg of iron was present. Iron essentially vaporized and was removed from the graphite furnace before P vaporized and thus Fe matrix suppression was avoided. The removal of Fe interference using the Zr chemical modifier was effective up to a mass of 4 μg of Fe. At higher Fe masses, the chemical modifier was no longer effective, and hence it would be necessary either to dilute the sample prior to the addition of the chemical modifier or to remove the iron by some technique such as solvent extraction. The use of higher graphite tube heating rates (Fig. 74) for the vaporization of P when the chemical modifiers were used resulted in greater suppression of the P signal, as was observed in the Fe vaporization studies. The absolute detection limit for the determination of P by ETV-ICP-MS was 4 pg when 2 μg of Zr was used as a chemical modifier in a pyrolytically coated graphite tube heated to 2600°C.

4.4 SUMMARY AND CONCLUSIONS

The determination of P using ETV-ICP-MS essentially eliminates the polyatomic interference of NOH^+ with P; NOH^+ is a major interfering species in the solution nebulization sample introduction technique. Pyrolytically coated

Figure 77. ETV-ICP-MS signal pulses for the vaporization of 1 ng of phosphorus (as H_3PO_4), pyrolysis at 400 °C for 30 s, vaporization at 2600 °C using the maximum power heating mode. A: 1 ng of P. B: 1 ng of P with 1 μg of Fe and 2 μg of La. C: 1 ng of P with 1 μg of Fe. D: 1 ng of P with 1 μg of Fe and 2 μg of Zr.

graphite tubes provided the most trouble-free vaporization surface for the determination of P, by ETV-ICP-MS. Clearly, studies involving the porous electrographite show that the presence of active carbon sites is detrimental to the determination of P. This suggests that P may be difficult to determine by ETV-ICP-MS in highly organic materials such as blood, etc., unless carbon is removed prior to the volatilization of P using air or oxygen ashing techniques. The use of chemical modification is effective in removing matrix interference caused by the presence of Fe, with Zr being the best chemical modifier since it does not itself suppress the P signal even when present at relatively high masses. The choice of a chemical modifier and experimental conditions will likely be very dependent upon the sample being analyzed. It will therefore be important for analysts to consider the relative volatility (compared to P) of the sample matrix components when selecting instrumental operating conditions such as the heating rate of the graphite tube, and the chemical modifier.

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