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**Studies on the Mechanisms of Vaporization of Analytes and
Matrices in Electrothermal Vaporization Inductively Coupled
Plasma Mass Spectrometry**

by

MUFIDA EL MABRUK BEN YOUNES

M.Sc. (The University of Birmingham, UK)

**A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy**

**Department of Chemistry
Carleton University
Ottawa, Ontario
March 2001**

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acceptance of the thesis,

**Studies on the Mechanisms of Vaporization of Analytes and Matrices in
Electrothermal Vaporization Inductively Coupled Plasma Mass Spectrometry**

submitted by

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M.Sc. (The University of Birmingham, UK)

in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

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ABSTRACT

The mechanism of vaporization of platinum group elements (PGE's) in a graphite furnace was investigated using electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). The results indicated that Ru, Rh, Pd, Ir and Pt were reduced to the metallic state and vaporized by direct sublimation of the metal in the graphite furnace. For Os, two distinct vaporization processes were observed: volatile oxides of Os are released at low temperatures, but some of this oxide was reduced to relatively involatile Os metal, which was vaporized above 2000°C. The addition of a Te chemical modifier improved the analytical figures of merit for Os, but no effect on the other PGE's was observed.

Methods for minimizing isobaric interferences caused by carbon argides for the determination of chromium by ETV-ICP-MS were investigated. Methods compared included (a) use of alternative isotopes (b) optimized temperature (c) use of chemical modifiers. Under optimized conditions, it was possible to achieve improvement of the detection limit for Cr by a factor of 20. Addition of chemical modifiers such as NH_4F and NaOCl caused increased background signals from carbon argides because of additional carbon removed from the surface of the ETV in the presence of these chemical modifiers.

Slurry sampling ETV-ICP-MS was used for the removal of silica for direct analysis of silica-rich solid geological samples. The effect of using HF as a chemical modifier to remove silica as the tetrafluoride was studied. It was found that HF was highly effective in removing silica if sufficient HF was added as a chemical modifier and an adequate reaction time allowed.

Effectiveness of ion-molecule reactions in a Dynamic Reaction Cell (DRC) in reducing or eliminating carbon-based polyatomic ions in ETV-ICP-MS was also studied. The use of a DRC permitted efficient removal of many carbon- and argon-based interferences and had the potential of eliminating other polyatomic interferences, such as, oxides. The results showed that the DRC was effective in reducing carbon-based polyatomic interferences in the determination of ^{52}Cr , ^{53}Cr , ^{24}Mg , and ^{26}Mg . For ^{28}Si and ^{29}Si the use of NH_3 gas was less effective. Interferences at $m/z = 30$ with $^{30}\text{Si}^+$ persisted and might require other gases or mixture of gases for the DRC to remove them.

This thesis is dedicated to the loving memory of my father

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INTRODUCTION

The objective of this work was to study the mechanisms of vaporization of analytes and matrices in electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). The goal of this research was to enhance the present capabilities of ETV-ICP-MS through a better understanding of the mechanisms of various processes involved and through development of new methodologies. A Perkin-Elmer ETV-ICP-MS was employed in this work to study mechanisms of vaporization of analytes and matrices in the ETV-ICP-MS.

This thesis is divided into an INTRODUCTION, followed by six chapters. Chapter 1 presents the current status of the ETV-ICP-MS. Chapter 2 deals with vaporization and determination of platinum group elements. Chapter 3 deals with the determination of chromium. Chapter 4 deals with direct analysis of geological materials by the slurry sampling technique. Chapter 5 presents the spectral interferences caused by formation of polyatomic ions, and the various ways of mitigating the effects of these spectral interferences. Chapter 6 ends this thesis demonstrating the effectiveness of a technique, named "Dynamic Reaction Cell" (DRC) which is based on ion-molecule reactions to reduce/eliminate spectral interferences caused due to formation of polyatomic ions. The analytical significance of the various measures described in the individual chapters, considered together, presents a picture of the ETV-ICP-MS as a promising analytical technique which has removed some of the major shortcomings of

the solution nebulization technique of ICP-MS, while retaining the otherwise great strength (excellent analytical sensitivity) of ICP-MS.

The need for ultra-trace level elemental analysis has been the stimulus for the development and improvement of sensitive analytical techniques. This often leaves the analytical chemist faced with the following challenges: pushing down detection limits, obtaining accurate results, dealing with more difficult matrices, avoiding interferences and optimizing the cost/benefit ratio of analysis. With these incentives in mind, analytical chemists are constantly improving their techniques or adapting them from related fields. This is the case for the techniques using radio-frequency (RF) based plasmas which are better known as Inductively Coupled Plasmas (ICP's) [1,2]. During the past 20 years considerable attention was paid to the development of a powerful analytical technique called Inductively Coupled Plasma Mass Spectrometry (ICP-MS), which attracted a great deal of interest for multi-elemental and isotopic analysis at trace and ultra-trace levels. Methods used to increase the applicability and sensitivity of this technique are of significant interest. The high temperature attainable with these plasmas is used to break down sample matrices, dissociate molecular species and provide enough energy to the atoms to be excited to emit atomic spectra, as in Atomic Emission Spectrometry (ICP-AES), or to form a cloud of ionized atoms which is sampled and analyzed by mass spectrometry; the latter technique is called Inductively Coupled Plasma Mass Spectrometry (ICP-MS). This technique yields considerably lower detection limits than ICP-AES [12]. Moreover, the ability to extract isotopic information makes ICP-MS especially appealing to earth sciences studies [3-7] and allows the analyst to perform isotopic dilutions, one of the most robust calibration strategies currently known.

The plasma is the very heart of the ICP based instrumentation. The initial plasmas appeared with the progressive mastering of electrical discharges, but tremendous advances occurred in the 1950s as a by-product of the effort to produce controlled thermonuclear fusion [8].

The radio-frequency (RF) plasmas commonly used for elemental analysis are considered “condensed-state” plasmas [8]. In fact, they are composed of singly ionized atoms and free electrons which themselves do not amount to more than one tenth of a percent of the total mass of plasma gas [9-12]. Analytical plasmas are often operated at atmospheric pressure, except for special applications [13]. Temperatures generally in the range of 2500-8000 K are commonly reported, depending on the experimental conditions and chemical species being studied [14-18].

In ICP-MS, a volume of the plasma containing analyte ions is extracted and transmitted into a quadrupole mass spectrometer/detector system. The ion extraction from the atmospheric pressure plasma into the vacuum region of the mass spectrometer is achieved in several stages through a differentially pumped interface. A fraction of the positively charged ions produced in the plasma is transported through the orifice of the sample cone (1mm i.d.) in the zone of the plasma containing maximal concentration of analyte ions [9,19]. Here, the plasma beam expands at the speed of a supersonic jet, which is created from the extracted plasma material into an intermediate vacuum (~ 1 torr) on the downstream side of the orifice [20]. The skimmer cone, a second metal cone placed behind the sampler cone and having similar central opening, admits the central part of the jet into the high vacuum spectrometer chamber ($\sim 1 \times 10^{-4}$ torr) and through a

set of electrostatic lenses. The electrostatic lenses extract and focus the ion beam into the quadrupole mass spectrometer.

Sample introduction into the ICP is a critical part of the analytical process and is regarded as “Achilles’ Heel” of the technique, as was pointed out by Browner [21]. Sample introduction continues to play an important role in the successful application of the ICP-MS technique. The sample introduction techniques for solutions were initially directly adopted from flame spectrometry techniques. Solution nebulization which is commonly pneumatic or ultrasonic, represents an attractive form of sample introduction to the analyst even though their use often involves a time-consuming, sample digestion step in the analytical sequence.

Pneumatic nebulization is an attractive approach to liquid sample introduction in ICP spectrometry because of its simplicity and reliability; however, it is a technique that suffers from an inherently low transport efficiency. The situation is even worse for ICPs as the efficiency of the classical tandem nebulizer/spray chamber is rarely above 1% in plasma, as opposed to about 10% in flame atomic absorption spectrometry [21]. The two main classes of pneumatic nebulizers used with ICPs are the cross-flow and the concentric nebulizer. Both types generate aerosol using the shearing action on a liquid flow by a high velocity gas stream. In almost all cases, a spray chamber is interposed between the nebulizer and the plasma to reject the large droplets from the fine mist. Spray chambers come in variety of shapes, but the most widely used is the Scott Double Pass type.

The all-glass concentric nebulizers [22-25] are the most commonly used pneumatic nebulizers in ICP spectrometry. They are inexpensive and can generate

aerosols with sufficient uniformity to yield results with good precision (1% RSD). They are relatively intolerant, however, to high levels of dissolved solids and susceptible to blockage of the very small annular gap by particles (1-35 μm) [26].

Cross-flow nebulizers adapted for ICP spectrometry use the classical design of a gas stream intercepting a liquid stream at right angles [27]. The V-groove, Légère, Babington and Hildebrand (rigid) nebulizers [28-31] can also be considered derivatives of the original cross-flow design. These nebulizers are generally noisier than the concentric counterparts but can accommodate much higher dissolved solids content and most can directly nebulize slurries. However, these characteristics are not particularly advantageous for ICP-MS, since the sample and skimmer cones are prone to blockage by salt build-up which may occur for concentrations typically greater than 0.25% dissolved solids.

In a separate class are the High-Pressure Nebulizers (HPN) [32], where a mist is formed by the interaction of the fast-moving liquid with the surrounding gas atmosphere. A variation of this technique consists in impacting a high-velocity stream on a surface to generate a mist. Other less used nebulizers include the glass frit nebulizer [33] and the thermospray nebulizer [34].

Ultrasonic nebulization (USN) exhibits a higher transport efficiency (30%), but a desolvation stage is required to minimize the increased solvent load of the plasma [35] since the excessive solvent tends to cool or even to extinguish the plasma. With ultrasonic nebulizers, generally, ten times more analytes can be transported to the plasma than with conventional nebulizers. Improvement in detection limits can also be expected to be of the same magnitude. However, possible adverse effects from solid build up at

injector tips or at the sampler and skimmer cones in ICP-MS should be taken into consideration; interferences are also exacerbated. It is not surprising that these drawbacks as well as the higher cost of the instrumentation have limited the popularity of USN. USN exhibits long term stability of typically 1-2% [36,37].

By far the majority of ICP spectrometric applications involve sample introduction by conventional solution nebulization. Some separation techniques such as liquid chromatography and flow injection, in conjunction with solution nebulization can be interfaced with ICP-MS to obtain additional information about the sample. In spite of the numerous advantages of solution nebulization, there are other approaches such as laser ablation (LA) and electrothermal vaporization (ETV) that can provide better performance than solution nebulization, depending on the particular application. Considering the varied nature of applications encountered by today's analysts, most of these sample introduction techniques can be considered to be complementary rather than competitive. For example, ETV can be a useful technique for micro-litre volumes of liquid samples and can also potentially eliminate solvent-related polyatomic ion interferences in ICP-MS. However, in order to realize its full analytical potential as a routine analytical technique for a wider range of applications, further improvements are necessary.

CHAPTER 1

ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ETV-ICP-MS): CURRENT STATUS

Four decades have passed since electrothermal vaporization (ETV) was first introduced [38] as a means of producing analyte vapour for analytical atomic absorption spectrometry. In the intervening period, graphite furnace atomic absorption spectrometry (GFAAS) has become firmly established and has reached maturity as a technique capable of determining about 50 elements at trace and ultratrace levels in a wide variety of sample types. One of the attractive features of GFAAS is the very small sample size requirement where only microlitre volumes are required.

In 1974, Nixon et al. [39] coupled an electrothermal vaporizer (ETV) to an inductively coupled plasma atomic emission spectrometer (ICP-AES). Although a number of papers on ETV for multi-element analysis have been published, the acceptance of this technique and the realization of its full potential has been delayed. The main reason for this is that ETV-ICP-AES conventional spectrometers had difficulty in measuring transient signals accurately, especially when background correction was required. As well, limits of detection for most elements were not competitive with those attainable by GFAAS.

Now, with the advent of ICP-MS, the potential of ETV as a sample introduction device can be more fully realized through the rapid multi-element capability and high sensitivity of mass spectrometry. Since ICP-MS is a fast sequential technique, capable of

scanning spectra on the millisecond time scale, it achieves the accurate measurement of transient signals. The high sensitivity of ICP-MS, which exceeds GFAAS in detection power, also offers the capability of measuring isotope ratios of individual elements. Thus, a new technique has been developed by coupling the ETV with ICP-MS which could significantly extend the reach of the analytical chemist, especially for ultra-trace analysis.

The characteristics of ICP-MS with ETV were first studied by Gray and Date [40]. They have reported that most of the "permanent" background peaks in ICP-MS originate from water and result in high hydrogen and oxygen populations in the plasma which are typically 10^8 times greater than those of analyte ions. The absolute detection limits of 1-12 pg were reported [40]. These authors suggested that ETV could eliminate water from the sample stream and diminish these interferences. They also found the level of oxide ions to be between one and two orders of magnitude lower than with the sample introduction using a solution nebulizer. Gray [41] has demonstrated that the background spectrum of a dry argon plasma creates much less interferences from molecular species than the plasma with high solvent loading does. Especially, the intensities of the ArO- and ArN-species decrease by more than one order of magnitude. The first comprehensive application of ETV-ICP-MS was reported by Date and Cheung [42] for the determination of Pb isotope ratios in geological materials.

Park et al. [7,43-47] have reported on the use of a custom-designed ETV device based on a small flat graphite platform (1.1 cm long and 0.4 cm wide) or a metal (W, Re) filament as the vaporization surface. Based on a previous design, an ETV was constructed [44] with vertical orientation. The centre of the filament had a circular depression to hold about 5 μ L of solution, and argon carrier gas flow was introduced

tangentially. This design of the ETV resulted in analyte mass transport efficiency of 80%, and the analytical potential for this device was demonstrated [7,43,45,47]. A comparison of the Park-design ETV unit [48] with the direct insertion device showed that the ETV was more versatile and amenable to the analysis of samples high in salt content.

Several studies have been reported in the literature on the use of a tungsten electrothermal vaporization device [49-52]. Tsukahara and Kubota [49] completed extensive studies on optimisation of ETV parameters and plasma conditions. Hydrogen gas was mixed with the Ar carrier gas to prevent oxidation of the W surface [51]. Hydrogen gas also produced a rise in the excitation temperature and an increase in the electron number density at the interface, resulting in enhanced ionization of the analyte.

Shen et al. [53] and Carey et al. [54] investigated the use of a modified Heated Graphite Atomizer (HGA)-300 as an ETV for the determination of Pb (L.O.D.= 10 fg), of Fe (L.O.D.= 0.2 pg) and As (L.O.D.= 1.5 pg). The Caruso group [53,54] designed a coolant argon gas flow system to isolate the analyte vapour from the vaporizer walls, thus increasing analyte transport efficiency.

GFAAS and ETV-ICP-MS have been compared and contrasted by Grégoire et al. [55]. These authors pointed out that these two techniques are complementary in nature. By repeating the same experiment using both techniques, the data obtained from both systems can be combined to provide valuable information on the mechanism of analyte vaporization and atomization processes and mechanisms of chemical modification.

Several papers on the advantages of ETV-ICP-MS have appeared in the literature [56-63]. An excellent book chapter on ETV-ICP-MS was written by Grégoire [64], and Carey and Caruso [65] published a literature review on ETV-ICP-AES and ETV-ICP-

MS. Information on ETV-ICP-MS can also be obtained from a book chapter written by Williams [66].

1.1 ETV Instrumentation

The development of an "ideal" ETV device for use in plasma spectrochemistry has proceeded in the same manner as did research on the development of the best atomization device for GFAAS during the early 70's. A number of configurations have been investigated including filament or platform [46,67,68] -based systems as well as tube-type [69-73] devices, ETV systems based on the insertion of a metal wire loop into a tube-type [53] ETV, and an electrically heated wire loop [74] placed directly into the argon plasma. Various metals and graphite have been used as substrates, depending upon the elements determined and the matrix analyzed. A variety of materials have been used in the construction of ETV cells, most are similar to those which have been used for Electro-Thermal Atomizer (ETA)-AAS, i.e. GFAAS. Generally, these are either metals such as Ta [75,73], W [49,73], Re [45,73], Mo [73], or graphite such as pyrolytically coated crystalline graphite [76,77], and glassy carbon [75]. Low-voltage, high-current power supplies are generally used to resistively heat the metal or graphite vaporizer.

Those using metal vaporization surfaces for ETV work have reported that these are less likely (than graphite) to react with analyte to form refractory compounds. However, there are reports [78] on the formation of involatile intermetallic compounds between V [79], Mo [80] and Ni [79] with hot Ta metal. Metal (W) filaments or strips can lose their ductility once heated to incandescence and are prone to contamination.

Metal vaporization surfaces have a major drawback, which is the rate of evaporation of metal at high temperatures. Microgram quantities of metal entering the

plasma can result in loading effects and serious matrix effects, both spectroscopic and non-spectroscopic [50,73]. Studies have been carried out by Grégoire et al. [70] showing no serious effects on plasma loading when carbon is volatilised at 2600°C from a graphite tube resulting in no suppression in analyte signal. One well-known disadvantages of using graphite, lies with elements which form refractory carbides and produce memory effects. However, judicious selection of vaporization temperature along with the use of chemical modifiers can minimize the effects of carbide formation for most elements [81,82].

The ideal ETV system should incorporate characteristics that promote complete analyte vaporization and high transport efficiency (~100%) from the ETV to the argon plasma. Other desirable features include versatile and accurate temperature control, the vaporization surface should be inert, a wide range of operational temperatures, rapid heating rate to high temperatures (3000°C), ease of automation, and low cost.

The first studies in ETV-ICP-MS [40,42,57] were carried out using an ETV system similar to that described by Gunn et al. [83] in which a graphite rod ETV device was employed for the introduction of a 5 µL volume of sample into the ICP. The graphite rod was encased by a 1 L volume quartz glass envelope. Park et al. [46] were the first to attempt using the filament type device (ETV device) as a sample introduction system for ICP-MS. This device was specifically designed to increase sample transport efficiency by the isolation of vaporized sample from cold surfaces. This design facilitates the formation of analyte vapour into micro-particles by the introduction of a flow of carrier argon gas to cool the analyte vapor and cause condensation into micro particles. The carrier gas is introduced tangentially to minimize sample loss on glass and on the walls of the ETV and

transfer line surfaces. As a result, the transport efficiency to the plasma is over 80%. The optimum dead volume of 5 mL in the glass envelope above the filament was designed to minimize dilution of analyte with the argon carrier gas and also served to promote collisions of analyte vapour/aerosol particles during condensation, resulting in the formation of easily transported particulates. A modified Scott-type spray chamber was developed [84] for use with this system capable of changeover from the solution nebulization sample introduction to the ETV mode without system interruption or plasma shut down.

Grégoire [67] used an ETV system with a platform design incorporated with small depression in the centre to prevent spreading of the analyte solution during the drying step. When highly acidic solutions or organic solvents were used as sample solutions, the sample tended to spread quickly to the end graphite contact parts, resulting in memory effects and non-reproducible signal. The problem was controlled by using small sample volumes (5 μL) and relatively low drying temperatures (80°C).

Based on the Park design, commercial ETV systems were developed by two manufacturers. Tsukahara and Kubota [49] have characterized the Seiko Instruments Micro Sampling (ETV) System equipped with tungsten metal ribbon with a 50 μL capacity cavity. The tungsten ribbon was covered with a glass chamber of 300 mL volume.

The EV2000 System presents the second platform-type ETV device [85] and is marketed by Hewlett-Packard Co. This device uses a graphite platform contained in a glass chamber, 90 mL in volume. Gas flows are carefully controlled to provide laminar flow conditions preventing analyte loss on the chamber walls.

Currently, for ICP-MS, commercially available tube-type ETV systems include the Perkin-Elmer HGA-600MS (Fig. 1) and the VG Elemental MicroTherm System. Pyrolytically coated graphite tubes are used by both instruments. These tubes have nearly the same dimensions (28 mm x 8 mm o.d., 6 mm i.d.) and are identical to those which are standard for GFAAS applications.

The commercial VG Elemental MicroTherm System uses an Ar sheath gas which flows between the graphite tube and a quartz envelope surrounding the graphite tube. The sheath gas protects the graphite from air-oxidation at high temperatures. Using either manual or automated pipetting, a sample of up to 100 μL in volume can be deposited into the graphite tube through a hole cut in the quartz envelope which is aligned with the dosing hole. During the temperature pre-treatment steps (dry, pyrolysis) water and other waste vapours are removed from the dosing hole of the graphite tube by an argon carrier flow of about 1 L min⁻¹. During the high-temperature or vaporization step, a graphite rod is placed into the dosing hole of the graphite tube, essentially sealing the tube and thus allowing analyte-containing vapour to be swept into the argon plasma.

The Perkin-Elmer Sciex HGA-600MS (Fig. 1) uses a modified HGA system originally developed for GFAAS. Argon sheath gases continuously flow over the exposed graphite parts to prevent oxidation. During the dry and pyrolysis steps of the temperature program, opposing flows of argon gas (about 300 mL min⁻¹) originating from both ends of the graphite tube remove water and other vapours through the dosing hole of the graphite tube. The argon flow is generally used during the dry and pyrolysis steps. During the high-temperature or vaporization step, a graphite probe is pneumatically activated to seal the dosing hole. Once the dosing hole of the graphite tube is sealed, a valve located

Pre-vaporization

Vaporization

Figure 1. Perkin-Elmer HGA-6000MS Electrothermal Vaporization System

at one end (downstream) of the HGA workhead directs the carrier argon flow (800-1100 mL min⁻¹) (which originates from the far end of the graphite tube) directly to the argon plasma. The HGA-600MS is also equipped with an autosampler which can deliver sample volumes from 2 µL to 100 µL; the latter is the practical maximum capacity of the graphite tube vaporizer.

There are several papers in the literature on the modification of a commercial ETV systems, as reported by Shen et al. [53], Carey et al. [54] and Lamoureux [86] and Lamoureux et al. [87,88]. Caruso's group [53,54] modified a Perkin-Elmer HGA-300 graphite furnace unit. The main feature of this simple modification was incorporating specialized gas flows down stream of the furnace tube to help isolate analyte vapour (leaving the graphite tube) from any surfaces. A tungsten loop [53] or graphite platform [54] set within the graphite tube were used to contain the sample. The HGA system which has been modified by Grégoire's group [86,87,88] is unlike other tube-type configurations. A quartz ring was installed to surround the graphite tube. The quartz ring was fitted with a ball-joint which was connected via a length of PTFE tubing directly to the argon plasma. The opening in the quartz ball joint was aligned directly above the dosing hole of the graphite tube. In this modified ETV system, all vapours produced are carried out through the dosing hole rather than out of one of the ends of the graphite furnace. Argon flows could be carefully controlled and laminar flow conditions were obtained for analyte vapour leaving the graphite tube. This ETV device combines both the vapour isolating conditions characteristic of filament-type systems and the advantages of a graphite tube ETV.

The two above ETV devices were interfaced to the argon plasma via a plastic or a PTFE tube, generally of 1 m or less in length. The diameter of the tubing can be an important parameter, but in general, a diameter equal to the inner diameter of the graphite tube (6 mm) is used to minimize turbulent flow.

No systematic comparison between the various ETV designs has been reported, making it difficult to assess which is optimum for ICP-MS. Since the ETV is only a sample introduction device, reported limits of detection are dependent on the performance of both the ETV and the ICP-MS. A valid comparison of different ETV designs and types can only be done if a single ICP-MS instrument is interfaced with different ETVs and operated under identical experimental conditions.

1.2 ETV-ICP-MS Operating System

Sample introduction by ETV techniques is based on the conversion of solid sample (dried solution, slurry, etc.) to vapour using heat, followed by transport of the sample using an argon stream, to the argon plasma. The heating cycle during which liquid sample is converted to analyte vapour comprises several separate steps. Each of the steps is designed to perform a specific function, but at the same time, other undesirable events may occur.

The lowest temperature step is the drying step which is used to drive off solvents including acids and volatile organics. Loss of sample solution and hence analyte is possible during the drying step if the rate of heating or the maximum temperature is too high. This generally results in explosive boiling of the sample, causing a physical loss or redistribution of sample material within the graphite tube. Low sensitivity, poor reproducibility and broad or multiple analyte peaks indicate too vigorous a drying step.

The pyrolysis step can vary in temperature from 100°C to 1800°C, depending upon the specific element being determined and the composition of the matrix. The pyrolysis step is used to complete solvent removal, to volatilize some of the matrix components especially carbon and volatile salts and to convert the analyte to a form that can be easily volatilized during the high temperature vaporization step. The maximum pyrolysis temperature that can be used for an element is limited by the volatility of the element and/or the volatility of the compound containing the analyte. The maximum pyrolysis temperatures have been obtained from GFAAS studies, and it is likely that many of these will also apply to ETV-ICP-MS work. Measurement of the optimum pyrolysis temperatures is done by determining the temperature beyond which a measurable loss in the analytical signal occurs during the subsequent high temperature atomization step. Since losses occurring during a GFAAS heating step will also occur during an ETV heating step (these are essentially identical except for the internal argon gas flow).

The wide range of maximum pyrolysis temperature imposes a limitation on ETV-ICP-MS when used for multi-element analysis. It may not be possible to determine both volatile and involatile elements during a single ETV run under optimum pyrolysis conditions for a given matrix type.

The high-temperature vaporization step can range from 800°C to a maximum of 2700°C. The maximum temperature is limited by the thermal stability of the vaporization surface. For graphite, temperatures above 2800°C result in the vaporization of large quantities of carbon which can overload the plasma and cause premature wear of the graphite tube. The optimum pyrolysis and vaporization temperatures for many elements

determined by ETV-ICP-MS have been reported in individual papers on the mechanism of vaporization of elements. Generally, the optimum vaporization temperature is the lowest temperature that provides complete vaporization of analyte or analyte-containing compound, while at the same time minimizing unwanted reactions such as carbide formation. When a complex sample matrix is present in relatively large quantities, co-volatilization occurs and the vaporization characteristics of the analyte can take on the vaporization properties of the matrix. Well-defined atomization temperatures are known for GFAAS, but these are not generally transferable to ETV-ICP-MS because for GFAAS, the atomization of analyte is a primary requirement, whereas for ETV-ICP-MS only vaporization of the analyte or the analyte-containing molecules is necessary. Literature reports to date indicate that temperatures significantly lower than those used in GFAAS are optimum for ETV-ICP-MS work.

During the vaporization step, analyte-containing compounds are heated to pre-determined temperatures, resulting in thermal decomposition of these compounds, carbon reduction and volatilization. One of the undesirable chemical reactions that can also occur is the interaction of analyte with the metal filament or graphite tube to form refractory alloys and/or compounds. For graphite-based ETV systems, the formation of carbides is perhaps the most important reaction particularly for elements such as B, U, Th and the rare earth elements (REEs).

The final ETV heating step is the cleaning step which is normally a maximum temperature (2700°C) step. Matrices high in organic compounds such as blood, or those containing refractory compounds such as dissolved zircons require high temperatures to get rid of residual quantities of these materials from the graphite tube. Solid material left

behind in the graphite tube can affect the heating characteristics of subsequent samples injected into the graphite tube or may provide active sites for undesirable chemical reactions. The cleaning step is not always required and should be used only when necessary because this step is tantamount to an additional tube firing and contributes to shortening tube's useful life.

The entire heating cycle takes about 2 minutes to complete. Including the time required to load sample into the ETV, approximately one determination can be completed every 3 minutes or about 20 hr^{-1} . A cooling step is required after the vaporization step to prevent overheating of the graphite tube during the cleaning step. A second cooling step following the cleaning step is needed to allow graphite parts to cool while still being protected by the argon sheath gas. This is done because the graphite sealing probe is heated to incandescence at the cleanup step. Withdrawing the probe before cooling causes rapid air oxidation of the sealing probe and eventual failure of the seal between the probe and the dosing hole. The sealing probe is left in place, sealing the dosing hole during the cleaning step to remove any material that may have condensed onto the tip of the probe during previous heating steps.

Internal gas flows should be relatively low during the drying and pyrolysis steps to prevent expulsion of sample solution or analyte-containing salt crystals and to avoid the excessive build-up of back-pressure within the graphite tube which could blow out the argon plasma or significantly change the effective sampling depth at the interface. The internal gas flow can also be a mixture of gases incorporating air during the pyrolysis step to promote oxidation of organic matrices or added freon during the vaporization step which acts as a chemical modifier. The relative temporal variation in the element's

appearance (of analyte) signal is a reflection of the different volatility characteristics of each element being determined.

1.3 Mechanism of Vaporization

In both GFAAS and ETV-ICP-MS, the sample deposited on the substrate surface volatilizes during the vaporization step. An understanding of the mechanism by which the analyte vaporization takes place is important to the determination of the optimum experimental conditions for quantitative analysis. The GFAAS literature contains much of the data on atomization mechanisms and optimum operating conditions of a number of elements which are applicable to the ETV-ICP-MS studies. Styris and Redfield [89] have provided an extensive review of the various chemical mechanism involved in sample vaporization. In the early 1980s, Sturgeon et al. [90] proposed that the atomic vapour is produced in the graphite furnace through four pathways:

1. The reduction of analyte-containing salt on the graphite surface (C) to produce analyte atoms followed by the volatilization of metal from the graphite surface. An alternative pathway involves the sublimation of metal dimers which further dissociate within the graphite tube into monomeric species.

2. Thermal decomposition of analyte oxide, followed by the sublimation of its decomposition products from the graphite surface.

3. The vaporization of oxide to the gaseous state to produce analyte atoms by thermal dissociation of the vapour-phase oxide.

4. The volatilization of analyte in another chemical form such as a chloride which is thermally dissociated in the gas phase.

Both GFAAS and ETV-ICP-MS techniques have similar interactions of the analyte with the vaporization surface (carbon) which can result in the formation of refractory compounds. Although the GFAAS literature provides some useful insight into sample vaporization mechanism for the ETV, it should be emphasized that there are still some important differences between the two techniques. Grégoire et al. [55] have published a thorough review comparing GFAAS and ETV-ICP-MS.

In GFAAS, when the sample is heated up to high temperature i.e. at the vaporization and atomization step, the argon gas is not allowed to flow within the graphite tube. These stopped-flow conditions increase the gas-phase temperatures of the analyte-containing compounds and help confine atomic vapour within the graphite tube for as long as possible. Achievement of an optimum condition when using GFAAS relies primarily on the success of 100% vaporization and atomization of analyte (efficient

formation of atomic species), and long residence times for analyte atoms within the analytical volume of the graphite tube.

When using ETV-ICP-MS, the conditions are different from those for GFAAS. The continuous argon gas flow conditions are maintained. This means that argon carrier gas of about 1 L min^{-1} is flowing continually through the graphite tube throughout the vaporization step. The requirement for complete vaporization of analyte is the same for ETV-ICP-MS as it is for GFAAS, whereas ETV-ICP-MS is capable of detecting analyte in any form including molecular and atomic form. However, the efficient vaporization of the sample and complete transport of the analyte to the plasma is necessary. All the atomization processes in GFAAS occurs within the graphite tube. In ETV-ICP-MS vaporization occurs in the graphite tube and ionization occurs in the plasma.

The argon stream passing through the plasma during the vaporization step is continuously cooling and removing the vaporized material from the graphite surface. Reduction reactions and solid-state thermal decomposition occurs and atoms released from the surface may quickly re-condense as dimers, clusters or in polyatomic form as oxides and chlorides. As is shown for reactions 3 and 4 (above), the vaporization of analyte oxides and chlorides as well as carbides can become important. Many elements form volatile chlorides and oxides and the vaporization of these within the graphite tube is likely to be the dominant mechanism by which analyte-containing vapour is produced. For ETV-ICP-MS, it is possible that the observed oxide to metal ratios ($<0.2\%$) originate from the mass spectrometer interface region rather than from the undissociated oxide from the plasma.

Because carbides are relatively involatile, the volatilization of these cannot be relied upon as a means of producing useful analyte vapour, but rather the formation of these should be avoided by selecting a vaporization temperature and experimental conditions that favour the production of the more volatile oxide or halide species.

When selecting ETV operating conditions for the determination of any element, guidance should be sought to known vaporization (atomization) pathways and to the element's physical constants (e.g. melting point, boiling point).

A series of papers have been recently published on analyte vaporization mechanisms for more than 30 elements by ETV-ICP-MS [81,82,91-99]. One of the main conclusions that can be drawn from these studies is that it is almost always advantageous to vaporize the analyte in the combined form as an oxide or a halide while at the same time avoiding the production of very refractory compounds such as carbides. A potentially serious problem associated with the ETV-ICP-MS determination of very refractory compounds is that they tend to remain incompletely vaporized from the graphite surface and can also result in a memory or carry-over effect of the analyte from one vaporization cycle to the next.

1.4 Spectral Interferences

When samples are introduced into the ICP-MS by nebulization of aqueous solutions, large quantities of water and water vapour are also introduced into the argon plasma. The addition of water vapour can have a direct influence on the excitation characteristics of the plasma [100]. Moreover, introduction of water causes specific spectral interferences and significant background spectra (polyatomic ions) which may interfere with the determination of certain elements [101] by overlapping with the analyte

at m/z values of interest. The major isotope of iron with a nominal mass of 56 (abundance of 91.52%) has a predominant interference by $^{40}\text{Ar}^{16}\text{O}^+$ [41,68]. In the presence of high chloride concentration matrix, $^{35}\text{Cl}^{16}\text{O}^+$ interferes with the determination of $^{51}\text{V}^+$ (99.76% abundance). Grégoire et al. [70] and Björn et al. [102] have reported on the background spectral features in ETV-ICP-MS and polyatomic ions produced from the vaporization of common matrix components.

A comparison of the background spectra obtained using both solution nebulization (SN) and ETV sample introduction techniques is shown in Figure 2 [103]. By coupling ETV with ICP-MS, water was eliminated and dry plasma was obtained. This results in fewer interferences from polyatomic ions than the plasma with the high solvent loading and the ETV background spectrum is qualitatively simpler than the SN background spectrum. Marked reductions in background signals at $m/z = 19, 32, 33, 34$ and 56 allow for the determination of ^{19}F (100% abundance), ^{32}S (95.02%), ^{33}S (0.75%), ^{34}S (4.22%) and ^{56}Fe (91.52%) by ETV-ICP-MS. The use of dry plasma has allowed the determination of isotope ratios of S, Cl and Se at trace levels and aids in the determination of Br isotopes [4].

Interfering species eliminated or reduced using ETV-ICP-MS compared to SN includes oxygen and hydroxide species as well as oxides and hydrides of Ar which combine to form a fairly large number of well documented polyatomic ions [101].

The background ions found in ETV-ICP-MS, apart from those originating from Ar, are mainly based on oxygen and nitrogen entrained into the plasma from the surrounding atmosphere. When the ETV is heated to a high temperature (e.g. 2700°C), carbon-based polyatomic ions also can make a significant contribution to the

Figure 2. Background spectra for solution nebulization and for electrothermal vaporization sample introduction.

background [70].

The type of graphite used in the ETV, as well as the physical condition of the graphite tube surface control the quantity of carbon vaporized from the graphite tube surface and, at times, the composition of the sample. The temperature of the graphite tube surface makes it the most significant parameter influencing the absolute quantity of carbon reaching the plasma since the vapour pressure of carbon increases by 25 orders of magnitude between 1000 and 3000 K.

Interestingly, another molecular ion which forms in the plasma (and/or interface region of the mass spectrometer) in relatively large concentration is the argon dimer ion ($^{80}\text{Ar}_2^+$). The argon dimer has been used as an internal standard reference isotope [5] for monitoring plasma loading and non-spectral interference effects in multielement analysis. Grégoire et al. [104] used the argon dimer signal to monitor matrix effects for analysis of slurry samples by ETV-ICP-MS. A systematic study was carried out by Vanhaecke et al. [105] on the application of the argon dimer for solid sample vaporization using ETV-ICP-MS.

When the temperature increases, the intensity of most carbon-containing polyatomic ions rapidly increases. The greatest increase occurs for polyatomic ions containing both O and C. The carbon ion count rate increase with temperature closely follows the temperature-time curve of the graphite tube as measured by optical pyrometry. Thus, monitoring the carbon ion intensity during the vaporization step can be useful to assess the repeatability of the heating program and/or the condition of the graphite tube [70]. Furthermore, when the temperature of the graphite tube is increased to 2500°C, the increase in carbon ion count rate was orders of magnitude less than predicted

by the vaporization characteristics. This means that not all the carbon volatilized in the graphite tube is converted to ions and detected by the mass spectrometer. A paper has been published [106] which supports this observation, reporting on the formation and deposition of carbon as soot within the graphite tube or at the contact cones, and the deposition of carbon vapour on the transfer tubing between the ETV and the plasma. The deposition of carbon on the surface of the transfer tubing becomes evident by the gradual build-up of a carbon deposit over several hundred firings.

When applying the optimum analytical conditions for all elements which are interfered by carbon-containing polyatomic ions, one uses the lowest possible vaporization temperature combined with peak-height measurements and chemical modification to increase the analyte volatility.

1.5 Non-Spectral Interferences

In ICP-MS, non-spectral interferences (matrix interferences) are well documented [107]. High levels of concomitant salts in the analyte solution can affect the total electron density in the plasma. When using the ETV as an alternative means of sample introduction technique for the ICP-MS, the same factors that affect matrix interferences in ICP-MS also affect ETV-ICP-MS. In fact, due to the higher sample transport efficiency characteristic of ETV-ICP-MS, the situation may become worse when this technique is used. Grégoire et al. [55] reported that in the presence of NaCl, the loss of the Os (analyte) signal intensity was more severe for ETV than for SN sample introduction, when both systems were operated under optimum experimental conditions. For example, when Os was determined in the presence of $5000 \mu\text{g mL}^{-1}$ NaCl, the ETV

signal was suppressed by 63%, whereas for the SN, Os in the same sample was suppressed by only 17%.

Park et al. [45] studied the effect of 1 µg of Na, Cr, Ca and Se on the determination of As, Cd and Cu (1 ng analyte) by the ETV-ICP-MS. They reported that there was significant analyte signal suppression.

1.6 Chemical Modification

Chemical modifiers are compounds or mixtures of compounds which are used to alter the thermal properties of the analyte, matrix components or the vaporization surface. In the ETV-ICP-MS, chemical modifiers can also be used to alter the analyte vapour transport properties (from the graphite tube to the argon plasma). This means chemical modifiers can have both chemical and physical effects, each improving the conditions for the determination of an analyte in a specific matrix.

Chemical modifiers have been proposed to stabilize analytes, thus, eliminating the more volatile matrix components, to improve the temporal separation of the analyte and the matrix during the volatilization step and to reduce losses prior to the high temperature step by preventing hydrolysis reactions which can expel analyte by co-volatilization with the hydrolysis reaction products. Another benefit of using chemical modifiers is to enhance the volatility of the analyte, to promote the vaporization of analyte before matrix components and to prevent or reduce the interaction of analyte with graphite to form refractory compounds. Also, chemical modifiers can be added to convert the analyte to a single chemical form, eliminating multiple signals which can complicate quantitative analysis.

In general a chemical modifier is used by adding a chemical substance to the sample solution or by the introduction of a gas other than argon gas to the argon gas flow. Chemical modifiers are added to the sample solution just prior to or at the same time as the sample solutions are injected into the graphite tube. The gas-phase chemical modifiers are used during the high-temperature vaporization step. A comprehensive review on the use of chemical modifiers in GFAAS has been published by Tsalev et al. [108]. The amount of chemical modifiers normally used range from 25 to 200 μg , depending on the application. Chemical modifiers which improve the mass transport efficiency of the analyte from the graphite tube to the argon plasma are called physical carriers.

The use of chemical modifiers has been reported in a significant number of papers. Grégoire [67] investigated the use of chemical modifiers with ETV-ICP-MS. Nickel nitrate was used as a chemical modifier in the determination of platinum group metals and resulted in up to 9.4 fold enhancement in the analyte-ion count rate. The sensitivity of Os is improved by 5- to 20-fold when Ni, Se or Te are used as a chemical modifiers [67]. Byrne et al. [77] demonstrated the role of using ascorbic acid as a chemical modifier in alleviating the hydrolysis reactions of magnesium chloride and preventing analyte (Mn) loss by co-volatilization with released hydrochloric acid gas.

Among other applications, chemical modifiers have been applied to convert refractory analytes chemically into more volatile species. Freon has been used as a chemical modifier in the ETV-ICP-AES to enhance the volatility of W vaporized from a carbon surface [109]. Ediger [110] investigated the use of freon for the determination of

refractory elements and reported that there was a significant increase in the sensitivity of REE, Th, and U.

The effect of using Pd/Mg and Na as chemical modifiers for the ETV-ICP-MS has been published by Ediger and Beers [111] and Grégoire et al. [112]. The influence of the condition of the graphite substrate on the analyte signal was reported by Majidi and Miller-Ihli [113]. These authors concluded that the use of an oxygenated pyrolytic graphite surface and chemical modifiers gave the best precision for the ETV-ICP-MS signals. Hughes et al. [114] investigated the use of seawater stripped of trace metals as a universal mixed chemical modifier. The use of halogen-containing compounds has been reported for the determination of Zn, Cd and Pb [115]. Wanner et al. [116] investigated the role of ten chemical modifiers for the determination of B, La and U. Grünke et al. [117] studied the effect of eleven chemical modifiers on the determination of Cd, Cu, Mn, Pb and Zn. The influence of sample matrix components on analyte signals and on the selection of calibration strategy is reported by Fonseca and Miller-Ihli [118], particularly as applied to the analysis of slurries. The use of mannitol for the determination of B has been reported [119]. Polyhydroxy compounds are used as chemical modifiers to facilitate the analysis of B, AS, Se, Sb, Cr and Mo [120].

The very high sensitivity of the ETV-ICP-MS and its use for multi-element analysis places some requirements on the chemical modifiers used. For example, chemical modifiers must be of the highest purity and free of elements that could interfere with the target analytes. The chemical modifier should be of benefit to the largest number of analytes, avoiding the use of several different chemical modifiers for multi-element schemes.

When using chemical modifiers it is very important to take into consideration the quantity of chemical modifiers used. The presence of microgram quantities of matrix components can result in the formation of interfering molecular ions and can contribute to the background spectrum by the formation of polyatomic ions. These ions can take the form of nitride, oxides and argides, and for the ETV (graphite), carbides [70]. The vaporization of chemical modifiers can cause the formation of the polyatomic ions in the plasma [70,102]. Grégoire and Sturgeon [70] studied the most commonly used chemical modifiers in the ETV-ICP-MS. They investigated the use of ascorbic acid, sodium chloride, magnesium nitrate, nickel nitrate and palladium nitrate as chemical modifiers and reported their effect on the determination of different elements. Alternative analyte isotopes free of interferences were suggested for use.

1.7 Analytical Features of the ETV-ICP-MS

Most analytical techniques have associated with them some applications for which no other technique can handle as well or as efficiently. One feature of the ETV is the microsampling capability. The more significant analytical features beside the analysis of small samples (blood, body fluids, and rare materials) is that the ETV can efficiently handle the analysis of radioactive and toxic samples, the analysis of difficult matrices (organic samples, high-salt samples, solids and slurries), and isotope ratio determinations (Br, S, Se, tracer studies, and isotope dilution calibration). Although GFAAS is also an analytical technique that has a microsampling capability and can handle applications in most categories mentioned above only ETV-ICP-MS is practical for the measurement of isotope ratios. This inherent capability of mass spectrometric techniques allows for the measurement of isotope ratios important to geochemical studies [4], human and animal

metabolic studies [121] and the application of isotope dilution calibration [47,67,76] for quantitative analysis.

Another feature of the ETV is the detection power. By comparing the absolute limits of detection obtained by ETV-ICP-MS and GFAAS [122] it can be concluded that limits of detection for all elements determined by ETV-ICP-MS are 2-350 times more sensitive than those reported by GFAAS with the exception of Cr and Zn. The ETV-ICP-MS limits of detection for most elements are in the low femtogram (10^{-15} g) range.

ETV-ICP-MS not only has superior sensitivity when compared to GFAAS, this technique can be used for the determination of analytes, including the rare earth elements, refractory platinum group elements, non-metals and elements such as B, Th, U, W and Zr which are difficult or impossible to handle by GFAAS. The added capability of ICP-MS for multi-element analysis and the determination of isotope ratios of individual elements promise to make ETV-ICP-MS one of the most sensitive and versatile analytical techniques available.

The coupling of ETV to ICP-MS as an alternative sample introduction system to solution nebulization (SN) allows the removal of water and other solvent. This substantially alters the concentration of hydroxide and oxide species in the plasma, thus, reducing spectral interferences from polyatomic ions. As a result, several important elements including Fe and S can be measured using the ETV-ICP-MS. The performance of the microconcentric nebulizer as a small sample volume introduction system is superior to the ETV. However, microconcentric nebulizer still add water to the plasma and is also prone to clogging.

By applying judicious thermal programming one can modify the composition of the sample entering the plasma, and thus, unresolvable (by quadrupole mass spectrometry) spectral interferences can be avoided. The full potential of ETV sample introduction for ICP-MS remains to be explored. The ETV-ICP-MS is a fully quantitative technique which stands ready to take advantage of any developments in the field of mass spectrometry, including instruments having increased sensitivity, resolution, ability to remove (by gas phase collisions and/or reactions) spectral interferences and to measure the entire mass spectrum simultaneously.

CHAPTER 2

VAPORIZATION AND ATOMIZATION OF THE PLATINUM GROUP ELEMENTS IN A GRAPHITE FURNACE INVESTIGATED BY ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

2.1 INTRODUCTION

The platinum group elements (PGE's) comprise a group of six metals (Ru, Rh, Pd, Os, Ir, Pt) which, although relatively rare, have important geochemical and industrial applications. A comprehensive review of the methods for determination of precious metals, including the PGE's, has been recently published [123]. Among the analytical techniques more commonly used for trace-level analysis of these elements are graphite furnace atomic absorption spectrometry (GFAAS) and, recently, inductively coupled plasma mass spectrometry (ICP-MS). The earlier literature on GFAAS methods for determination of PGE's was reviewed in 1989 [124]. Since then, papers describing methods of separation and analysis of these elements by GFAAS have appeared [125-128], as well as a method for the simultaneous multielement GFAAS determination of Ru, Rh, Pd and Ir [129]. Although GFAAS has been established as a routine method of analysis for PGE's, little has been published on the mechanism of atom formation for these elements in a graphite furnace since the early study of Rowston and Ottaway [130].

ICP-MS has provided a powerful alternative method for determination of the PGE's. This technique has been used for their determination in waters and geological

samples, using solution nebulization as the sample introduction technique [67,131-133]. Also, ICP-MS has been used in isotope dilution mass spectrometry [134-136]. Alternative methods of sample introduction have also been used for the ICP-MS analysis of the PGE's. These include slurry sampling [137], flow injection [138,139], laser ablation [140] and vapour generation (OsO_4) for the analysis of Os [75,141]. There are a few reports of the use of electrothermal vaporization (ETV) as a method of sample introduction for PGE's. Grégoire has determined Os [75] and Pt, Pd, Ru and Ir [67] by ETV-ICP-MS using a laboratory-constructed graphite filament electrothermal vaporizer. Recently, automobile exhaust gas has been analysed for some PGE's by collecting particulate exhaust matter on graphite discs from which the sample was then electrothermally vaporized [142]. However, no systematic studies of the mechanism of vaporization or the optimum conditions for vaporization of the PGE's in ETV-ICP-MS have been reported in the literature.

It is the purpose of this study to investigate the electrothermal vaporization of the PGE's with a view to (a) determining the optimum conditions for the analysis of these elements by ETV-ICP-MS, and (b) elucidating the vaporization and atomization mechanisms for the PGE's in a graphite furnace. Grégoire's laboratory has made a series of studies of the vaporization and atomization processes for some of the more intractable elements in GFAAS, i.e. B [81], W [82], U [95] and the rare earth elements [93,94] in pursuance of the above objective (b).

2.2 EXPERIMENTAL

A Perkin-Elmer SCIEX ELAN 5000 ICP-MS, equipped with an HGA-600 MS electrothermal vaporizer and AS60 autosampler, was used for the ETV-ICP-MS experiments. Samples were vaporized from the wall of pyrolytically-coated graphite tubes (Perkin-Elmer part No. 091-504). The electrothermal vaporizer was connected to the plasma torch by 80 cm of 0.6 cm i.d. PTFE tubing. The operating conditions used for both the ELAN 5000 and the HGA 600 MS are given in Table 1. During the drying and pyrolysis steps of the furnace program, water and matrix vapours were removed via the furnace dosing hole, by opposing flows of argon gas (300 mL min^{-1}) introduced from both ends of the graphite tube. Five seconds prior to the high temperature vaporization step, the dosing hole was sealed pneumatically with a graphite probe. After the graphite furnace was sealed, a valve located at one end of the furnace workhead directed the argon carrier flow from the far end of the graphite tube to the plasma torch. The plasma and mass spectrometer operating conditions were optimized using solution nebulization sample introduction prior to the changeover to the ETV. The following isotopes (abundances shown in brackets) were chosen for analysis since each is free of any interelement isobaric interference: ^{101}Ru (17.0%), ^{103}Rh (100%), ^{105}Pd (22.3%), ^{189}Os (16.1%), ^{193}Ir (62.7%) and ^{195}Pt (33.8%).

2.2.1 Standards and Reagents

High purity argon gas (99.995%, Matheson Gas Products, Ottawa, Ontario, Canada) was used. All solutions were prepared using ultrapure water obtained from a Millipore Milli-Q water purification system (Etobicoke, ON). The nitric and

Table 1. Instrument operating conditions and data acquisition protocols for ETV-ICP-MS.

<u>ICP mass spectrometer</u>	
R.F. power	1100 W
Coolant Ar flow rate	15.0 L min ⁻¹
Auxiliary Ar flow rate	900 mL min ⁻¹
Carrier Ar flow rate	900 mL min ⁻¹
Sampler and skimmer cones	nickel
<u>HGA-600 MS electrothermal vaporizer</u>	
Sample volume	10 µL
Dry Step	10 s ramp, 100°C for 20 s
Pyrolysis step	5 s ramp, various temperatures for 20 s
Vaporization step	0 s ramp, various temperatures for 5 s
Clean up step	1 s ramp, 2700°C for 4 s
<u>ICP-MS data acquisition</u>	
Scan mode	Peak hop transient
Dwell time	10 ms
Points/spectral peak	1
Signal measurement	Peak area
MS resolution	0.7 u at 10% maximum

hydrochloric acids used were reagent grade (J.T. Baker). The PGE solutions were prepared by serial dilution of 1000 ppm stock solutions (Delta Scientific, Mississauga, ON). The Te chemical modifier stock solution (1000 ppm) was prepared by dissolving Te metal (Matheson Chemicals, E. Rutherford, NJ) in 2 M HCl.

2.3 RESULTS AND DISCUSSION

2.3.1 Vaporization and Thermal Pretreatment Curves

Thermal pretreatment/atomization curves have been used to elucidate atomization mechanisms in GFAAS. In a similar fashion, thermal pretreatment/vaporization curves, determined by ETV-ICP-MS, can be used to elucidate vaporization processes occurring in a graphite furnace [81,82,93-95]. The important distinction between these curves lies in the fact that GFAAS detects only atomic species, so that the atomization curve plots changes in atom concentrations as a function of heating time and furnace temperature, whereas in the case of ETV-ICP-MS atomic and molecular species transported from the furnace to the plasma are dissociated into atomic ions, which are detected along with any other atomic species released in the furnace. Thus, the ETV-ICP-MS vaporization curve plots changes in the concentration with temperature for both the atomic and molecular species which are vaporized in the graphite furnace.

Figure 3 presents the thermal pretreatment/vaporization curves for the six PGE's. These data were obtained using 10 μ L samples containing Rh (100 pg), Ir (100 pg), Pt (250 pg), Ru (500 pg), Pd (500 pg) and Os (500 pg) in 1% v/v HNO₃. The pyrolysis curves were measured using a vaporization temperature of 2500°C, whereas the vaporization curves were measured without any pyrolysis step. Because the pyrolysis and

Figure 3. Thermal pretreatment (pyrolysis) $--\blacksquare--$ and vaporization $--\bullet--$ curves for a 10 μ L sample containing Rh (100 pg), Ir (100 pg), Pt (250 pg), Os (500 pg), Pd (500 pg), and Ru (500 pg) in 1% (v/v) HNO₃.

vaporization curves were not measured on the same day, there was some change in the instrumental response for Pt, Ir and Os. In order to reduce the pyrolysis curve data to the same scale for the above three elements, their integrated counts have been divided by two.

The thermal pretreatment/vaporization curves for five of the elements (Pt, Pd, Rh, Ir, Ru) are very similar. However, the vaporization behaviour of Os, shown in Figure 3, is very different and it will be discussed separately in a later section. Typical ETV-ICP-MS signals for the five PGE's showing similar vaporization behaviour are shown in Figure 4. For these elements, no multiple peaks or shoulders were observed at any vaporization temperature between 1200° and 2600°C. This suggests that, for these five elements, a single species is released from the furnace during the vaporization process. For each of these elements, the temperature for the onset of vaporization also coincides with the temperature at which the pyrolysis curve begins its steep descent (see Fig. 3). This means that the species being lost in the pyrolysis step should be identical to that released in the vaporization step. Some conclusions about the identity of these vaporized species can be drawn by comparing the temperature for the onset of vaporization, i.e. the ETV-ICP-MS appearance temperature, with the melting points, boiling points and decomposition temperatures of likely precursor species of the analyte. Because the samples were introduced as metal nitrates these precursors are most likely to be either free metal or metal oxides.

Table 2 lists the melting and boiling points of the PGE's, along with their appearance temperatures in ETV-ICP-MS. The oxide decomposition temperatures and published appearance temperatures for atomic species in GFAAS are also given. Because

Figure 4. ETV-ICP-MS signals for five platinum group elements: Rh (100 pg), Ir (100 pg), Pt (250 pg), Os (500 pg), Pd (500 pg), and Ru (500 pg). Vaporization temperature 2600°C; no pyrolysis step.

Table 2. Melting points, boiling points, oxide decomposition temperatures (T_d) and appearance temperatures for the platinum group elements.

Element	m.p. ^a °C	b.p. ^a °C	Appearance Temperature (°C)					T _d ^c °C
			ETV-ICP-MS	GFAAS				
Pd	1555	2960	1100	1230 ^b	1250 ^c	1220 ^d	875	
Rh	1963	3700	1500	1630	–	1790	1140	
Pt	1769	3830	1500	1800	1770	1770	650	
Ru	2334	4150	1700	2140	–	1910	930	
Ir	2447	4430	1750	2100	2050	–	1095	
Os	3033	5010	<800	2630	–	–	–	

^aData taken from Ref. [143].

^bRef. [130].

^cRef. [144].

^dRef. [145].

^eRef. [146].

the ETV-ICP-MS appearance temperatures for the five PGE's, excluding Os, are all well in excess of their oxide decomposition temperatures, the species vaporized from the graphite furnace cannot be a metal oxide, but is most likely to be the metal vapour sublimed from the metal deposited on the graphite surface after the oxide decomposition. This deduction is supported by the fact that the ETV-ICP-MS appearance temperatures increase from Pd to Ir, in the same order as the melting points and boiling points of the metals. Moreover, the increase in these ETV-ICP-MS appearance temperatures parallels the increase in the appearance temperature for atomic species in GFAAS, suggesting that no volatile molecular species is generated in the graphite furnace prior to the formation of atomic vapour. These conclusions are in agreement with an earlier study [130] which proposed that the atom formation for the PGE's in the graphite furnace proceeds via sublimation of the free metal.

2.3.2 Vaporization Mechanism for Osmium

It is clear from Figure 3 that the thermal pretreatment/vaporization curves for Os are very different from those of the other PGE's. This indicates a different vaporization and/or atomization mechanism for Os. Conclusions as to the nature of these mechanisms can be drawn, if the thermal pretreatment/vaporization curve for Os is considered in conjunction with the Os ETV-ICP-MS signals shown in Figure 5. These data indicate that two distinct species must be vaporized in the graphite furnace. The vaporization curve indicates that some volatile species is released at temperatures as low as 800°C, whereas the second rising portion of this curve shows that a second, less volatile, species is released when the vaporization temperature is raised above 2000°C. The presence of two species is confirmed by the change in the ETV-ICP-MS signals with increasing

Figure 5. ETV-ICP-MS signals for 500 pg of Os vaporized at (a) 1000°C, (b) 2200°C, (c) 2400°C, (d) 2600°C; with no pyrolysis step

vaporization temperature (see Fig. 5). For vaporization temperatures between 800° and 2000°C, a single ETV-ICP-MS peak is observed with a peak maximum at around 1.2 s. The peak shape and area remains constant over this vaporization temperature range, as reflected in the flat region of the vaporization curve. A typical peak, at a vaporization temperature of 1000°C is shown in Figure 5a. As the vaporization temperature is raised above 2000°C, a second peak with a maximum around 2.8 s appears, first as a shoulder (Fig. 5b), and finally, as a distinct, larger second peak (Fig. 5d), when the vaporization temperature is increased to 2600°C. The release of this second, less volatile, Os species is responsible for the steep rise in the vaporization curve above 2000°C. Because virtually all molecular analyte species vaporized in the ETV are dissociated by the plasma, direct MS identification of these volatile species is not possible. However, some conclusion as to their identity can be drawn from the temperatures at which they are vaporized (< 800°C and > 2000°C) and also from the unusual shape of the Os pyrolysis curve shown in Figure 3.

When samples are introduced into the graphite furnace as metal nitrates, drying and pyrolysis usually results in the formation of a metal oxide. In the case of Os, there are two possible oxides which could form, OsO_4 and OsO_2 . It is unlikely that the more volatile OsO_4 (b.p. 130°C) is formed initially, since if this were the case then all of it should be removed by a 20 s pyrolysis step at 200°C. The pyrolysis curve shows this is not the case. Figure 3 shows that although a small amount of Os is lost with a 200°C pyrolysis, the major initial pyrolysis loss does not reach a maximum until 800°C. The pyrolysis curve for Os is, in fact, very different from those for the other PGE's, with an initial pyrolysis loss between 200° and 800°C, followed by an unusual decrease in this

pyrolysis loss as the temperature is increased from 800° to 1600°C. Further pyrolysis loss then occurs above 1600°C, a temperature comparable with, but slightly greater than, the other PGE's. This unusual pyrolysis behaviour is indicative of pyrolysis loss via two different species, one at low temperatures (200-800°C), and a second above 1600°C.

This behaviour can be explained if OsO_2 is the species formed in the drying/pyrolysis process. OsO_2 is less volatile than OsO_4 , and the solid is known to decompose [146] to form Os(s) and $\text{OsO}_4\text{(g)}$, with decomposition complete at 900°C. The reaction is given by equation (5).

Thus, as the pyrolysis temperature is increased from 200° to 800°C, increasing amounts of OsO_2 are lost from the furnace, explaining the initial decrease in the pyrolysis curve. As the pyrolysis temperature is increased above the decomposition temperature of OsO_2 , i.e. around 900°C, increasing amounts of OsO_2 is converted into $\text{OsO}_4\text{(g)}$ and Os(s) via Eq. (5). The volatile OsO_4 is lost from the graphite furnace, whereas the highly involatile Os metal is left in the graphite furnace. According to Eq. (5), the maximum amount of Os that could remain in the furnace as Os metal should be half of the input amount. The pyrolysis curve of Figure 3 shows that at pyrolysis temperatures above the OsO_2 decomposition temperature (900°C), the maximum amount of residual Os occurs for a pyrolysis temperature of 1600°C, and the signal at this temperature is, in fact, about half that measured for a 200°C pyrolysis. As the pyrolysis temperature is raised above 1600°C, further loss occurs due to pyrolysis, which can be explained by the loss of the refractory Os metal at higher pyrolysis temperatures.

Thus, the unusual shapes of the thermal pretreatment and vaporization curves for Os, as well as the double peaks of Figure 5, can be explained by the sequential vaporization of two separate species in the graphite furnace. At vaporization temperatures between 800° and 2000°C, corresponding to the flat portion of the vaporization curve, a single ETV-ICP-MS peak, with an appearance time of around 0.6 s, is observed. It is proposed that this earlier, low-temperature peak originates from the OsO_4 formed in the graphite furnace by decomposition of the $\text{OsO}_{2(s)}$ precursor.

The second ETV-ICP-MS peak, which appears at a later time and at vaporization temperatures above 2000°C, is attributed to the sublimation of Os metal in the graphite furnace; this metal being formed by the lower temperature decomposition of $\text{OsO}_{2(s)}$.

This vaporization/atomization mechanism can explain the poor sensitivity for determination of Os in GFAAS, which has reported a characteristic mass of 1000 pg [125]. The characteristic mass for Os is much higher than those reported for the other PGE's, which range from around 10 pg for Rh to about 150 pg for Ir [129,144]. This can be explained, in part, by the fact that some of the Os is lost from the graphite furnace as volatile molecular OsO_4 , even if no thermal pretreatment step is included in the heating program. This molecular species which is transported to the plasma, dissociated and detected as the earlier peak in ETV-ICP-MS would not be detected in GFAAS, because it would be lost from the graphite furnace as an undissociated molecular species. The ETV-ICP-MS vaporization curve for Os (Fig. 3) also shows a steeply rising portion between 2400° and 2700°C, with no sign of a plateau at high vaporization temperatures. This means that at the maximum vaporization temperature not all of the Os has been released from the graphite furnace. This is not surprising given that the m.p. and b.p. of Os are

above 3000° and 5000°C, respectively (Table 2). Hence, the poor sensitivity for Os in GFAAS can be attributed to a combination of the loss of volatile OsO_4 , at temperatures below the atomization temperature, and the refractory nature of the Os metal itself.

2.3.3 Effect of the Acid Used in the Sample Preparation

The sensitivity for determination of some PGE's by GFAAS is affected by the type of acid used in the sample preparation. Nitric acid is reported [128,147-149] to cause signal suppression with Pt and Rh. In order to determine if this effect is also observed in ETV-ICP-MS, samples of the PGE's were vaporized from solutions of both HCl and HNO_3 . Figure 6 shows the comparison between the integrated counts for the PGE's vaporized from 1% (v/v) HNO_3 and HCl solutions; for the sake of easier comparison, the Os counts have been multiplied by 4. For these experiments, no pyrolysis step was included and a vaporization temperature of 2600°C was used.

These results show that there is no significant difference between the ETV-ICP-MS signal intensities for Pd, Pt, Ir and Rh, when the matrix is changed from HNO_3 to HCl; some signal improvement is observed for Ru, and a significant (four-fold) enhancement occurs with Os. The enhancements for Os and Ru may be explained in terms of the change in the chemical form of the analyte which would be expected to occur as the matrix is changed from HNO_3 to HCl. With HNO_3 , the osmium and ruthenium nitrates, initially present in the sample solution, would be expected to form oxides during the heating process prior to vaporization, whereas the analyte precursors in the presence of HCl should be chlorides.

Figure 6. Integrated counts for Rh (100 pg), Ir (100 pg), Pt (250 pg), Os (500 pg), Pd (500 pg) and Ru (500 pg) in 1% (v/v) HNO₃; 1% (v/v) HCl. The Os counts are multiplied by 4.

2.3.4 Chemical Modification by Tellurium

In a previous study of the determination of Os by ETV-ICP-MS, Grégoire [75] reported improved analytical sensitivity when TeCl_2 was used as a chemical modifier. In the present work, the effect of addition of Te chemical modifier to all six PGE's was investigated. Sample solutions containing the six PGE's (Ir, Rh 100 pg, Pt 250 pg, Os Ru Pd 500 pg) and 100 ppm of TeCl_2 in 0.2 M HCl were vaporized at 2600°C, with no prior pyrolysis step. The results are shown in Figure 7. For all the elements, the signals obtained with the addition of the Te modifier are larger than those obtained in 1% (v/v) HNO_3 . However, the five to six-fold enhancement for Os is much greater than that for the other PGE's which range from around 1.3 for Pt to 1.9 for Ru. For these five elements there was no significant change in peak shape or appearance time for the ETV-ICP-MS signal when the Te chemical modifier was added; the signal enhancements obtained are typical of carrier effects in ETV-ICP-MS. With Os, however, not only is the enhancement greater, but there is a significant change in the peak shape and the appearance time when the Te chemical modifier is added (see Fig. 8). This suggests that the mechanism of vaporization for Os is significantly changed by the addition of the Te chemical modifier. The addition of the Te chemical modifier results in a single peak at the earlier appearance time of around 0.5 s corresponding to the vaporization of a single species at a low temperature.

In order to elucidate this new vaporization mechanism, the thermal pretreatment/vaporization curves for Os were remeasured in the presence of Te chemical modifier. The results are shown in Figure 9b. In these experiments, 10 μL samples containing 500 pg of Os, with 100 ppm of TeCl_2 in 0.2 M HCl, were vaporized. The vaporization curve was

Figure 7. Integrated counts for Rh (100 pg), Ir (100 pg), Pt (250 pg), Os (500 pg), Pd (500 pg) and Ru (500 pg) in 1% (v/v) HNO₃; 1% (v/v) HCl and 100 ppm TeCl₂ in 0.2 M HCl. The Os counts are multiplied by 4.

Figure 8. ETV-ICP-MS signals for 500 pg of Os in (a) 1% (v/v) HNO₃ (b) 100 ppm TeCl₂ with 0.2 M HCl. Vaporization temperature 2500°C; no pyrolysis step.

Figure 9. Thermal pretreatment $\blacksquare$ and vaporization $\bullet$ curves for 500 pg of Os, (a) without $TeCl_2$ in 1% (v/v) HNO_3 , (b) with 100 ppm $TeCl_2$ in 0.2 M HCl .

measured without any pyrolysis step. The dotted curve (Fig. 9b) between 700° and 800°C represents interpolation because data points could not be measured below 800°C, since with the HGA-600MS vaporizer, the minimum vaporization temperature that could be programmed, using maximum power heating (0 s ramp), was 810°C. No signal could be detected when the vaporization temperature was reduced to 700°C and a heating ramp of 1 s was used in place of the 0 s ramp. The thermal pretreatment/vaporization curve in the presence of the Te chemical modifier (Fig. 9b) is completely different from that obtained in 1% (v/v) HNO₃ (Fig. 9a). With the addition of the Te chemical modifier, the pyrolysis curve (see Fig. 9b) has only one falling portion, at temperatures below 600°C, whereas the vaporization curve has only one rising portion at around 800°C. There was no second steep rising portion above 2000°C as was the case when HNO₃ was present. This result is consistent with the vaporization of a single Os species – a conclusion supported by the fact that no double peaks are observed, in presence of the Te chemical modifier, at any vaporization temperature. The peak shape of Figure 8 (measured at 2600°C) is typical of that obtained with the Te chemical modifier at all vaporization temperatures.

The species vaporized in the presence of the Te chemical modifier cannot be atomic Os; the metal is much too involatile to vaporize at temperatures as low as 800°C. The exact nature of the molecular species vaporized cannot be identified directly by MS because it is dissociated in the plasma. However, the chemical compound most likely to be formed in the presence of a large excess of the Te chemical modifier is OsTe₂. Although no boiling point is listed for this compound, the published [143] melting point of around 600°C means that it is less volatile than OsO₄ (b.p. 130°C) and less prone to vaporization loss from the graphite furnace at very low temperatures. Moreover, its m.p.

suggests its volatility is consistent with the vaporization behaviour exhibited by the thermal pretreatment/vaporization curve of Figure 9b. Here the onset of vaporization is observed at 800°C, and significant pyrolysis loss occurs at temperatures about 600°C i.e. close to the m.p. of OsTe₂.

The addition of the Te chemical modifier causes no obvious change to the vaporization mechanism of other five of the PGE's and provides only modest enhancements of their ETV-ICP-MS signals. In the case of Os, however, the vaporization mechanism is dramatically changed by the addition of the Te chemical modifier. This has practical implications for the determination of Os by ETV-ICP-MS. When Te chemical modifier is used, the double peaks obtained with HNO₃ solutions are eliminated and much lower vaporization temperatures can be used. Figure 9b shows that with 100 ppm TeCl₂, the optimum vaporization temperature for Os is reduced to around 1400°C. Use of this lower vaporization temperature, in conjunction with the Te chemical modifier, has a number of advantages, some of which are illustrated in Figure 10, which shows the ETV-ICP-MS signals for 500 pg of Os both in the presence and absence of 100 ppm TeCl₂ chemical modifier. In the presence of the Te chemical modifier, the ETV-ICP-MS signals are significantly enhanced and, because the Os is more efficiently vaporized from the graphite furnace, blank levels are lower and the signal/background ratio is increased. This results in improved limits of detection, as discussed in the next section. Another advantage of use of the Te chemical modifier is illustrated by Figure 10. In the absence of the Te chemical modifier, not only is the signal suppressed but these signals in 1% (v/v) HNO₃ exhibit a definite dependence on the condition of the surface of the graphite tube. There is a marked suppression of the Os signal after about 100 firings (compare Fig. 10

Figure 10. ETV-ICP-MS signals for 500 pg of Os, (a) 1% (v/v) HNO₃, used tube (about 100 firings), (b) 1% (v/v) HNO₃, new (unused graphite tube), (c) 100 ppm TeCl₂ in 0.2 M HCl old used graphite tube.

(a) and (b)). When the Te chemical modifier is used no deterioration of the ETV-ICP-MS signal with tube age was observed (Fig.10(c)).

2.3.5 Analytical Figures of Merit

Table 3 summarizes the analytical figures of merit for Ru, Rh, Pd, Ir and Pt. For these elements 10 μL samples in 1% (v/v) HNO_3 were vaporized at 2500°C . The analytical sensitivity is given as the blank subtracted integrated counts for 100 pg of each element. The limit of detection (LOD) was calculated from five blank replicates (3σ). In the case of Ru, Pd and Pt measurements were made using the less abundant isotopes which are free from any isobaric interference from other PGE's. These LOD values, when expressed as concentrations (ng mL^{-1}) for a 20 μL drop, are about an order of magnitude improvement over those reported [137] using solution nebulization ICP-MS.

The analytical figures of merit for Os are given in Table 4. These values were determined with a used (> 130 firings) graphite tube, in the manner described above, but at two different vaporization temperatures. The results show that the addition of TeCl_2 chemical modifier (100 ppm in 0.2 M HCl) improves the LOD for Os by about a factor of two at a vaporization temperature of 2500°C . Reducing the vaporization temperature to 1400°C results in a six-fold improvement, in the LOD.

2.4 SUMMARY AND CONCLUSIONS

When the platinum group elements are vaporized in a graphite furnace, the mechanisms of vaporization and atomization are essentially identical for five of the PGE's (Ru, Rh, Pd, Ir and Pt). The results of ETV-ICP-MS experiments were correlated

Table 3. Analytical Figures of Merit for the platinum group elements

Isotope	¹⁰¹ Ru	¹⁰³ Rh	¹⁰⁵ Pd	¹⁹³ Ir	¹⁹⁵ Pt
Counts, s ⁻¹ /100 pg	12660	54340	22520	136700	53770
3 σ blank (n = 5)	21	75	27	21	32
LOD (pg)	0.17	0.14	0.12	0.015	0.059

Table 4. Analytical Figures of Merit for ^{189}Os

Chemical Modifier	Vaporization Temperature/ $^{\circ}\text{C}$	Counts, $\text{s}^{-1}/100\text{ pg}$	3σ blank ($n = 5$)	LOD (pg)
None	2500	4130	64	1.6
TeCl_2	2500	9650	67	0.70
TeCl_2	1400	9270	22	0.24

with the published GFAAS results, and the physical properties of these elements, to conclude that these elements are converted into the metallic state in the graphite furnace prior to vaporization as atomic vapour. There appears to be little change in this mechanism when the sample matrix is changed from HNO_3 to HCl , or when the TeCl_2 chemical modifier is added.

For Os, however, the vaporization mechanism is markedly different and is dependent on the sample matrix present. In HNO_3 solution, Os vaporization and atomization occurs in two distinct stages. Volatile oxides of Os are formed, some of which is vaporized and detected at temperatures as low as 800°C . However, some of these oxides are converted into involatile Os metal which is released in the graphite furnace in a second vaporization process which occurs at temperatures above 2000°C . The addition of the TeCl_2 chemical modifier changes this vaporization mechanism. When Os is vaporized from solutions containing 100 ppm of TeCl_2 in 0.2 M HCl , only a single species, presumably OsTe_2 , is released at relatively low vaporization temperatures. Use of this chemical modifier allows for more efficient vaporization of Os at lower vaporization temperatures (1400°C) and significantly improves the LOD for Os in ETV-ICP-MS.

Only modest signal enhancements are observed when the Te chemical modifier is added to the other five PGE's, and vaporization temperatures above 2000°C are required for their efficient vaporization and determination by ETV-ICP-MS.

CHAPTER 3

DETERMINATION OF CHROMIUM BY ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

3.1 INTRODUCTION

The determination of Cr by electrothermal vaporization inductively-coupled plasma mass spectrometry (ETV-ICP-MS) poses problems from isobaric interferences if vaporizers constructed from graphite are employed. The two major isotopes of Cr at $m/z = 52$ (83.8% abundance) and $m/z = 53$ (9.5% abundance) are both overlapped by carbon argides, $^{12}\text{C}^{40}\text{Ar}^+$ and $^{13}\text{C}^{40}\text{Ar}^+$, formed from carbon which is vaporized from the ETV and transported to the plasma. This problem is compounded by the high vaporization temperature that is required to remove the refractory Cr analyte from the ETV. Grégoire and Sturgeon [70] have shown that the ion counts from $^{12}\text{C}^{40}\text{Ar}^+$ at $m/z = 52$ rose dramatically when the vaporization temperature was increased from 1500° to 2500°C. This high background ion count resulted in a background equivalent mass for ^{52}Cr of around 12 pg [70], resulting in a poor limit of detection (LOD) for this isotope. However, this LOD should be improved if the Cr analyte could be vaporized at a lower temperature and earlier appearance time, when the amount of carbon vaporized from the graphite furnace should be low and there would be some temporal separation of the Cr from the carbon argide signals. This may be achieved by the addition of a suitable chemical modifier which would convert the Cr analyte to a more volatile form.

Chemical modifiers have been used successfully to enhance the volatilization of refractory elements when electrothermal vaporization has been used for sample introduction with GFAAS, ICP-AES and ICP-MS. Matousek and Powell [150] have used Cl_2 as a gaseous chemical modifier to prevent carbide formation in the GFAAS analysis of Cr. Injection of 50 μL volumes of 20% (v/v) Cl_2 during the atomization step reduced the atomization temperature for Cr to 1500°C. Gaseous chemical modifiers such as CHF_3 [109] and freon-23 [58] have been used to improve the vaporization of refractory elements from graphite furnaces and with the direct insertion devices used for sample introduction with ICP-AES. Halide chemical modifiers, both in solution and slurries, have been used to improve sample volatilization in ETV-ICP-AES. Ng and Caruso [151] reported that addition of 7% (m/v) NH_4Cl improved the vaporization of Zr, V, Cr and U from a graphite cup electrothermal vaporizer. Slurries containing 1.8% (m/v) polytetrafluoroethane have been used to lower the vaporization temperature and improve the detection limit for the determination of Cr by ETV-ICP-AES [152].

Recently, an alternative chemical modifier, 8-hydroxyquinoline, has been used to improve sample vaporization for ETV-ICP-AES. Tao and Kumamaru have reported that both Cr [153,154] and V [155] can be vaporized, from a tungsten boat furnace, at much lower temperatures when 8-hydroxyquinoline is used as a chemical modifier. In the case of Cr, addition of 150 μg of this chemical modifier allowed 5 ng of Cr to be vaporized effectively at 950°C.

Halide chemical modifiers have been also used to improve the vaporization of refractory elements with ETV-ICP-MS. Improved sensitivity and peak shapes were obtained for U when 0.3% (v/v) CHF_3 was added to the Ar carrier gas [95]. Wanner et al.

[116] have investigated the vaporization of B, La and U using gaseous chemical modifiers (CHF_3 and CCl_2F_2) as well as halide chemical modifiers added to the analyte in solution (NH_4F , NH_4Cl and NH_4Br). When 0.25% (v/v) CHF_3 was added to the Ar carrier gas La, B and U could be vaporized from a graphite ETV at temperatures as low as 1500°C ; much lower than that normally required for these carbide-forming refractory elements. The use of halide chemical modifiers in solution, although providing some improvements in the sensitivity and the LOD at these low vaporization temperatures, were not as effective as the gaseous freon chemical modifiers.

The objective of this investigation was to determine if a suitable solution phase chemical modifier could be found to improve the vaporization of Cr in ETV-ICP-MS. Such a chemical modifier would be required to release the Cr analyte at a lower vaporization temperature, thus reducing the amount of carbon vaporized from the ETV and hence the amount of background interference from carbon argides formed in the plasma. The chemical modifiers investigated were NH_4F , $\text{NH}_4\text{F-HF}$, NaOCl and 8-hydroxyquinoline.

3.2 EXPERIMENTAL

A Perkin-Elmer SCIEX ELAN 5000 ICP mass spectrometer equipped with an HGA-600 MS electrothermal vaporizer and a Model AS-60 autosampler was used. Pyrolytic graphite coated tubes were used throughout. The experimental conditions for both the ELAN 5000 and the HGA-600 MS are given in Table 5. A PTFE tube of 80 cm and 6 mm i.d. was used to connect the HGA-600 MS to the plasma torch. Optimization of the plasma and mass spectrometer was accomplished using solution nebulization, prior to

Table 5. Instrumental operating parameters and data acquisition protocols of the Perkin-Elmer SCIEX ELAN 5000 ETV-ICP-MS.

<u>ICP mass spectrometer</u>	
R.F. power	1100 W
Coolant Ar flow rate	15.0 L min ⁻¹
Auxiliary Ar flow rate	900 mL min ⁻¹
Carrier Ar flow rate	850 mL min ⁻¹
Sampler and skimmer	nickel
<u>HGA-600 MS electrothermal vaporizer</u>	
Sample volume	10 µL
Dry Step	10 s ramp, 110°C for 30 s
Pyrolysis Step	2 s ramp, 110°C for 10 s
Vaporization Step	0 s ramp, various temperatures for 5 s
Clean up Step	1 s ramp, 2650°C for 3 s
<u>Data acquisition</u>	
Dwell time	20 ms
Scan mode	Peak-hopping
Points per spectral peak	1
Signal measurement mode	Integrated
MS resolution	0.7 u at 10% peak height

switching to ETV mode. The operation of the HGA-600 MS was completely computer-controlled. During the drying and steps of the temperature program, opposing flows of argon (300 mL min^{-1}) originating from both ends of the graphite tube removed water and other vapours through the dosing hole of the graphite tube. During the high-temperature or vaporization step, the dosing hole was sealed by a pneumatically activated graphite probe. 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 at a flow rate of 900 mL min^{-1} .

3.2.1 Standards and Reagents

High purity argon gas (99.995%, Matheson Gas Products, Ottawa, Ontario, Canada) was used. Solutions were prepared with ultra-pure water obtained from a Milli-Q water purification system (Millipore Corp., Mississauga, ON.). The nitric and hydrochloric acids used were analytical-reagent grade (Anachemia). The Cr solutions were prepared by serial dilution of 1000 ppm stock solution (SPEX Industries, Edison, NJ, USA.) in 1% nitric acid. An 8-hydroxyquinoline (Baker Analyzed) solution was prepared in hydrochloric acid. The NH_4F and $\text{NH}_4\text{F-HF}$ (Aldrich Chemical Company, Inc., Milwaukee, WI, USA.) chemical modifier solutions were prepared by dissolving the salts in ultrapure water. Sodium hypochlorite was Baker Reagent Grade (Philipsburg, NJ).

3.3 RESULTS AND DISCUSSION

The extent of the problem posed by isobaric interference from $^{12}\text{C}^{40}\text{Ar}^+$ with $^{52}\text{Cr}^+$ is illustrated in Figure 11, which shows the ETV-ICP-MS background signal of $^{12}\text{C}^{40}\text{Ar}^+$

Figure 11. ETV-ICP-MS signals at $m/z = 52$ for (a) 1% (v/v) HNO₃ blank, (b) 200 pg Cr, both vaporized at 2500°C.

when 10 μL of a 1% (v/v) HNO_3 blank solution is vaporized at 2500°C using the ETV program given in Table 5. Figure 11 also shows the signal for 200 pg of Cr in 1% HNO_3 . Although the appearance time for the $^{52}\text{Cr}^+$ signal is earlier than that for the $^{12}\text{C}^{40}\text{Ar}^+$ background blank, there is significant temporal overlap of the two signals and considerable peak tailing from the background blank $^{12}\text{C}^{40}\text{Ar}^+$, caused by the continuous release of carbon from the ETV during the high temperature vaporization hold time. This results in an unacceptably low signal to background (S/B) ratio, at 2500°C , of around 1.5.

Reducing the vaporization temperature should cause less carbon to be vaporized from the ETV and transported to the plasma, thereby reducing the amount of background $^{12}\text{C}^{40}\text{Ar}^+$. This is illustrated by Figure 12, which shows the ETV-ICP-MS signals for a 1% (v/v) HNO_3 blank and the analyte signal for $^{52}\text{Cr}^+$ at 1800°C . At this vaporization temperature (1800°C), both the background signal of $^{12}\text{C}^{40}\text{Ar}^+$ and the peak tailing are reduced considerably. However, there is also a reduction in the counts for $^{52}\text{Cr}^+$ because not all of the analyte is vaporized effectively at this lower temperature.

In order to investigate the effect of reduced vaporization temperatures on the sensitivity and the S/B ratios for $^{52}\text{Cr}^+$, a vaporization curve was constructed using vaporization temperatures between 1400° and 2500°C . Figure 13 is a plot of the integrated counts for (a) the background blank (1% (v/v) HNO_3), (b) $^{52}\text{Cr}^+$ and (c) the S/B ratio, as a function of the vaporization temperature. Figure 13 shows that the background signal counts (a) for $^{12}\text{C}^{40}\text{Ar}^+$ decrease significantly as the vaporization temperature is reduced from 2500° to 2000°C . The $^{52}\text{Cr}^+$ counts (b), however, do not decrease significantly until the vaporization temperature is reduced below 2000°C . This is reflected by an increase in the S/B ratio which reaches a maximum at 2000°C and then

Figure 12. ETV-ICP-MS signals at m/z 52 for (a) 1% (v/v) HNO₃ blank, (b) 200 pg of Cr, both vaporized at 1800°C.

Figure 13. Effect of vaporization temperature on (a) background signal at $m/z = 52$ for a 1% (v/v) HNO_3 blank, (b) the integrated signal count for $^{52}\text{Cr}^+$ (200 pg Cr), (c) the signal to background ratio (S/B) at $m/z = 52$.

decreases as the vaporization temperature is further reduced. In the absence of any chemical modifier, the optimum limit of detection (LOD), (3σ blank, $n = 3$) of 6.0 pg is obtained at around 2000°C when the optimum S/B ratio occurs. Below this temperature no further improvement in the LOD is obtained as both the $^{52}\text{Cr}^+$ counts and S/B ratio decrease. Two strategies were employed in an attempt to improve this LOD: (a) the addition of chemical modifiers, which could improve the volatilization of Cr at lower temperatures where less carbon should be released from the ETV, and (b) use of the less abundant ^{53}Cr isotope which, though also overlapped by the $^{13}\text{C}^{40}\text{Ar}^+$ argide, should be less affected because of the lesser (x 90) abundance of the ^{13}C isotope.

3.3.1 Effect of Chemical Modifiers on ^{52}Cr

The effect of addition of chemical modifiers was first studied at $m/z = 52$ in order to determine if $^{52}\text{Cr}^+$ could be vaporized at lower temperatures where less concomitant carbon would be released from the ETV. This would result in lower background signals from $^{12}\text{C}^{40}\text{Ar}^+$. Figure 14 is a plot of the change in integrated signal counts for $^{52}\text{Cr}^+$ for (a) Cr without a chemical modifier, and with the addition of three chemical modifiers, i.e. (b) 0.5% (m/v) NH_4F , (c) 0.05% (m/v) 8-hydroxyquinoline (8-HQ) and (d) 0.1% (m/v) NaOCl . In each case 10 μL volumes of a test solution containing 200 pg of Cr, with or without the chemical modifier, were vaporized using the ETV program of Table 5. Blank values for each modifier were also measured at each vaporization temperature. Figure 14 shows that Cr is in fact vaporized at lower temperatures in the presence of the chemical modifiers. With no chemical modifier present, the onset of vaporization occurs at around 1400°C. This temperature is reduced to 1200°C in the presence of either 0.5% (m/v) NH_4F or 0.05% (m/v) 8-HQ, and the temperature is even lower when 0.1% (m/v) NaOCl

Figure 14. Effect of the chemical modifier on the integrated signal counts for $^{52}\text{Cr}^+$ at various vaporization temperatures, (a) no modifier, (b) 0.5% (m/v) NH_4F , (c) 0.05% (m/v) 8-hydroxyquinoline, (d) 0.1% (m/v) NaOCl .

is added. The results obtained with 0.5% (m/v) NH_4F -HF were virtually identical with those for 0.5% (m/v) NH_4F , and for this reason they are not plotted in Figure 14.

On the basis of these results, NaOCl is the chemical modifier which is most effective in promoting the low temperature vaporization of Cr; however, it is also the most effective chemical modifier for enhancing the vaporization of carbon from the surface of the ETV, thus producing higher background signal at all vaporization temperatures than any of the other chemical modifiers. This point is illustrated in Table 6, which gives the integrated blank counts and S/B ratios for each chemical modifier at a vaporization temperature of 1800°C . Table 6 also lists the signal enhancements by each chemical modifier by expressing the counts for $^{52}\text{Cr}^+$ at 1800°C as a percentage of the counts obtained at 2500°C when no chemical modifier is present. Table 6 clearly shows that although both NH_4F and NaOCl enhance the vaporization of Cr at 1800°C they also significantly increase the background counts from $^{12}\text{C}^{40}\text{Ar}^+$. This can be explained by the reported intercalation of halide salts with graphite [156,157] and their detrimental effects in stripping carbon from the surface of the graphite tube. The increase in blank counts, in the presence of both NH_4F and NaOCl , causes a decrease in S/B ratios and a degraded LOD. For this reason these chemical modifiers are rejected as unsuitable for use in the determination of Cr by ETV-ICP-MS. On the other hand, 8-HQ seems to offer more promise because it does not increase the background counts at $m/z = 52$, to the same extent as the halide chemical modifiers and provides a marked signal enhancement at 1800°C , as well as a marginal improvement in the S/B ratio (see Table 6). Addition of 0.5% (m/v) 8-HQ doubles the signal intensity for $^{52}\text{Cr}^+$, but does not increase the signal counts for $^{12}\text{C}^{40}\text{Ar}^+$ to the same extent as either NH_4F or NaOCl . The fact that there is

Table 6. Blank values at $m/z = 52$, signal to background ratios and percentage recoveries for ^{52}Cr with the various chemical modifier additions. Vaporization temperature was 1800°C .

Chemical modifier	Blank (counts)	$^{52}\text{Cr}^+$ (counts, s^{-1})	S/B (ratio)	% Recovery ^a
None (1 % (v/v) HNO_3)	6280	43460	6.9	47
0.05 % (m/v) 8-HQ	8095	60370	7.5	65
0.5 % (m/v) 8-HQ	11400	97000	8.5	104
0.5 % (m/v) NH_4F	17220	65010	3.8	70
0.1 % (m/v) NaOCl	35300	91620	2.6	98

- a. $^{52}\text{Cr}^+$ Counts at 1800°C expressed as a percentage of the $^{52}\text{Cr}^+$ counts (no chemical modifier) at 2500°C .

some increase in background signal counts from 8-HQ can be explained by the fact that this molecule contains 74% (by mass) of carbon. Some of this carbon must be released during pyrolysis of the compound and transported to the plasma resulting in formation of additional carbon argide. However, the results of Table 6 show that less carbon argide is produced from the pyrolysis of 8-HQ than from the graphite released from the furnace by the use of halide chemical modifiers.

Experiments were conducted to determine if increasing the concentration of 8-HQ would further enhance the vaporization of Cr, allowing the vaporization temperature to be further reduced. In these experiments, 10 μL volumes of solutions containing 200 pg of Cr with four different concentrations of the 8-HQ chemical modifier (0.05, 0.20, 0.5, and 1.0% (m/v)) were vaporized at 1400°C. The results are presented in Figure 15, which shows the blank subtracted integrated signal counts for $^{52}\text{Cr}^+$ at each chemical modifier concentration, as well as the S/B ratios. Figure 15 shows that the maximum enhancement for $^{52}\text{Cr}^+$ is obtained at a chemical modifier concentration of 0.5% (m/v); increasing the concentration to 1.0% (m/v) is counter-productive as the analyte signal decreases dramatically at the higher chemical modifier concentration. This is attributed to the space charge and /or ionization suppression effects caused by plasma loading when amounts of the chemical modifier exceeding 0.5% (m/v) are used. Evidence for this effect was obtained by simultaneous monitoring of the argon dimer [104,105], which showed marked disturbance when the chemical modifier concentration was increased to 1.0% (m/v). The optimum concentration of 0.5% (m/v) 8-HQ, which corresponds to 50 μg of the chemical modifier in a 10 μL sample drop, is about three times lower than that used by Tao and Kumamaru [153,154] in their ETV- ICP-AES experiments. This illustrates an

Figure 15. Effect of the concentration of 8-hydroxyquinoline chemical modifier on the integrated signal counts for $^{52}\text{Cr}^+$, at a vaporization temperature of 1400°C . The signal to background ratio (S/B) is also plotted.

important difference in the use of chemical modifiers for ETV-ICP-AES and ETV-ICP-MS, i.e. the amount of chemical modifier that can be used in the optical emission experiments (ETV-ICP-AES), without causing effective plasma disturbance, is generally larger than that in the ETV-ICP-MS.

A comparison of the results of Figure 15 with those of Table 6 shows that lowering the vaporization temperature has a detrimental effect on both the recoveries and the S/B ratios for $^{52}\text{Cr}^+$, when 0.5% (m/v) 8-HQ chemical modifier is present.

When the vaporization temperature was decreased from 1800°C (Table 6) to 1400°C (Fig. 15), the integrated signal counts for $^{52}\text{Cr}^+$ dropped from 97000 (104% recovery) to around 20,000 counts (21% recovery) and the S/B ratio decreased from 8.5 to 2.8. Thus if the optimum concentration of 0.5% (m/v) 8-HQ is used, a minimum vaporization temperature of 1800°C must be used if maximum recovery of Cr is to be obtained.

3.3.2 Limits of Detection for ^{52}Cr

Table 7 summarizes the LOD values (3σ blank, $n = 3$) obtained for ^{52}Cr both with and without the addition of chemical modifiers. Table 7 illustrates two points. First, although the addition of the chemical modifier enhances the volatilization of chromium, the LOD obtained is not necessarily improved by the chemical modifier. For example, when Cr is vaporized at 1400°C, in the presence of 0.1% (m/v) NaOCl, the LOD is 41 pg. This value is higher than the optimum value of 5.9 pg obtained without the chemical modifier at a vaporization temperature of 1800°C. This is because the blank values obtained with the NaOCl chemical modifier are higher and less reproducible because of the carbon released from the ETV in the presence of the chemical modifier. Secondly, the

Table 7. Limits of detection (LOD) for ^{52}Cr , with and without, the chemical modifiers at various vaporization temperatures.

Vaporization Temperature ($^{\circ}\text{C}$)	Chemical Modifier	$^{52}\text{Cr}^+$ (counts, s^{-1})	LOD (pg)
2500	None	93340	9.4
1800	None	43460	5.9
1600	None	17730	6.7
1800	0.5% (m/v) 8-HQ	97000	6.7
1400	0.1% (m/v) NaOCl	34020	41

LOD for ^{52}Cr , in the absence of the chemical modifier, was improved by reducing the vaporization temperature to 1800°C. At this vaporization temperature, addition of 0.5% (m/v) 8-HQ enhanced the analytical sensitivity for $^{52}\text{Cr}^+$ but also increased the blank value by about a factor of two (see Table 6). As a result, no overall improvement in the LOD was obtained. From these data, one concludes that chemical modifiers are of doubtful value if Cr is to be determined using the ^{52}Cr isotope.

3.3.3 Determination of Chromium at $m/z = 53$

Grégoire and Sturgeon [70] have suggested that the isotope of choice for the ETV-ICP-MS determination of chromium is $^{53}\text{Cr}^+$. Although this isotope is interfered with by carbon argide ($^{13}\text{C}^{40}\text{Ar}^+$), the abundance of the ^{13}C isotope (1.1%) is much less than ^{12}C isotope (98.9%). This should mean less interference for $^{53}\text{Cr}^+$ than for $^{52}\text{Cr}^+$. This point is illustrated by Figure 16 which shows the integrated background counts at $m/z = 53$ for $^{13}\text{C}^{40}\text{Ar}^+$ (a) obtained when a 10 μL volume of 1% (v/v) HNO_3 blank was vaporized at various vaporization temperatures between 1400°C and 2500°C. The blank-subtracted counts for $^{53}\text{Cr}^+$ (200 pg of Cr) and the S/B ratios are also plotted (b and c) in Figure 16. When Figure 16 is compared with the similar plot of $^{52}\text{Cr}^+$ (Fig. 13) it is clear that (a) the background signal for $^{13}\text{C}^{40}\text{Ar}^+$ is much lower, and (b) the maximum S/B ratio of 20 obtained for $^{53}\text{Cr}^+$, at a vaporization temperature of 2000°C, is more than twice that obtained for $^{52}\text{Cr}^+$ (8.2). As a consequence, the LOD for this isotope, in the absence of any chemical modifier, was reduced to 1.6 pg compared to 6.9 pg for $^{52}\text{Cr}^+$.

Experiments were conducted to determine if the analytical sensitivity and LOD for $^{53}\text{Cr}^+$ could be improved by the addition of chemical modifiers. NaOCl could not be used because of the formation of the $^{37}\text{Cl}^{16}\text{O}^+$ ion which caused severe isobaric

Figure 16. Effect of the vaporization temperature on (a) integrated background signal count at $m/z = 53$, (b) integrated signal counts for $^{53}\text{Cr}^+$ (200 pg), (c) signal to background ratio (S/B) at m/z 53.

interference at $m/z = 53$. Both NH_4F and $\text{NH}_4\text{F-HF}$ were found to be unsuitable because of the unacceptably high background counts from $^{13}\text{C}^{40}\text{Ar}^+$ formed from the additional carbon vaporized from the ETV in the presence of these chemical modifiers. However, the small amount of additional carbon produced from the pyrolysis of 0.5% (m/v) 8-HQ gave rise to only marginal increases in the background ion count from $^{13}\text{C}^{40}\text{Ar}^+$ at $m/z = 53$. Both the signal intensity and LOD for ^{53}Cr were improved by the addition of this chemical modifier. These results are summarized in Table 8 which lists the integrated signal counts for $^{53}\text{Cr}^+$, both in the presence and absence of 8-HQ chemical modifier, at various vaporization temperatures. The calculated LOD's (3σ blank, $n = 3$) and percent recoveries for $^{53}\text{Cr}^+$ are also given. These results confirm that, in the absence of this chemical modifier, reducing the vaporization temperature from 2500° to 1800°C will improve the LOD for ^{53}Cr from 4.9 to 1.5 pg, even though the signal response is reduced by a factor of two. Moreover, these LOD's are an improvement over those obtained for the ^{52}Cr isotope (see Table 7). This optimum limit of detection at 1800°C was further improved by the addition of 0.5% (m/v) 8-HQ chemical modifier. At this temperature, there was greater than two-fold signal enhancement for $^{53}\text{Cr}^+$ as the more volatile Cr-8-HQ complex was vaporized. However, the corresponding blank signal was only increased by around 30%, giving rise to an improved LOD of 0.54 pg for ^{53}Cr . This is reflected in the ETV-ICP-MS signals of Figure 17 which shows (a) the background blank and (b) the $^{53}\text{Cr}^+$ signal for 200 pg of Cr in 0.5% (m/v) 8-HQ at a vaporization temperature of 1800°C . If these signals are compared with the $^{52}\text{Cr}^+$ signals of Figure 11 where no chemical modifier and higher vaporization temperatures were used, it is obvious that the

Table 8. Integrated signal counts, percentage recoveries and limits of detection for ^{53}Cr , with and without, the chemical modifier, 0.5% (m/v) 8-hydroxyquinoline

Vaporization Temperature ($^{\circ}\text{C}$)	Modifier	$^{53}\text{Cr}^+$ (counts, s^{-1})	% Recovery ^a	LOD (pg)
2500	without	9600	100	4.9
2000	without	9870	103	1.6
1800	without	4865	51	1.5
1600	without	2076	22	3.0
1800	with	11520	117	0.54
1600	with	5440	57	1.0

- a. ^{53}Cr counts expressed as percentage of the ^{53}Cr counts obtained at 2500°C in the absence of a chemical modifier

Figure 17. ETV-ICP-MS signals at $m/z = 53$ for (a) a blank sample containing 1% (v/v) HNO_3 and 0.5% (m/v) 8-hydroxyquinoline chemical modifier, (b) 200 pg of Cr with 0.5% m/v 8-hydroxyquinoline chemical modifier. The vaporization temperature was 1800°C .

blank signal values are relatively lower, and no significant peak tailing from carbon argide is apparent.

3.4 SUMMARY AND CONCLUSIONS

Although the determination of Cr by ETV-ICP-MS poses problems with isobaric interferences from carbon argides when a graphite ETV is used, these interferences can be minimized if a suitable experimental protocol is employed. This involves: (a) choice of the less abundant ^{53}Cr isotope, (b) use of a reduced vaporization temperature (1800°C) and (c) addition of a suitable chemical modifier (0.5% (m/v) 8-hydroxyquinoline). If these strategies are employed, blank signals are significantly reduced and Cr signals free of peak tailing are obtained. This results in a 20-fold reduction in the LOD for Cr from around 10 pg to 0.54 pg.

Other solution phase chemical modifiers, e.g. NH_4F , $\text{NH}_4\text{F-HF}$ and NaOCl , which have been used to improve the volatilization of refractory elements with ETV-ICP-AES, were found to be less beneficial for ETV-ICP-MS. These chemical modifiers facilitated the vaporization of the Cr analyte at lower temperatures, but they also caused increased interference from carbon argides as additional carbon was released from the ETV in the presence of these chemical modifiers. This point emphasizes the need for caution regarding the choice of chemical modifiers for ETV-ICP-MS. Both the amount and type of chemical modifiers that are used successfully to enhance volatilization of refractory elements in ETV-ICP-AES experiments may prove counter-productive with ETV-ICP-MS, either introducing isobaric interferences or by causing excessive plasma loading.

CHAPTER 4

VAPORIZATION AND REMOVAL OF SILICA FOR THE DIRECT ANALYSIS OF GEOLOGICAL MATERIALS BY SLURRY SAMPLING ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

4.1 INTRODUCTION

Many environmental and geological materials contain high concentrations of Si as SiO_2 or complex silicates. Before analysis of these materials for trace metals can proceed, it is necessary to break up the silicate matrix and to remove it or separate it from the analytes.

The direct analysis of slurries and /or solids has been an important objective for spectrochemical analysis for many years because often the analyst receives a sample in the slurry or in solid state, rather than a liquid. Early pioneers included Kerber [158], who reported on the use of GFAAS for solid sampling and demonstrated the determination of Au in polyester fibres by direct insertion of the sample into the graphite furnace.

Slurry sampling combined with ETV-ICP-MS is an attractive approach to the trace analysis of environmental and geological samples. Bendicho and de Loos-Vollebregt [159] and Miller-Ihli [160] have provided an extensive review of the solid and slurry sampling in GFAAS. Slurry sample introduction combines the advantages of solid and liquid sampling [161]. Slurry sampling has, like all analytical methods, advantages as well as limitations. Slurry sampling offers several advantages including (1) easy and

reproducible introduction into the graphite furnace; (2) reduced sample preparation time; (3) lower risk of contamination; (4) decreased probability of analyte loss through volatilization prior to analysis; (5) reduced loss of analyte related to retention by insoluble residues; (6) capability for analysis of micro amounts of sample. Furthermore, slurry sampling permits the use of conventional liquid sample handling apparatus such as autosamplers. When combined with ETV-ICP-MS, slurry sampling can offer additional advantages. For example, with the ETV system it is possible to use the graphite tube as a chemical reactor. Procedural steps such as the addition of digestion reagents and chemical modifiers can all be done on-line automatically. Thus, it may be possible to complete an entire sample preparation sequence within the graphite tube starting with suitably powdered sample material. However, the limitations of using slurry sampling include: (1) particle size must be small enough to be amenable to slurry sampling; (2) difficulties in maintaining sample homogeneity; (3) difficulties in obtaining representative sample; (4) dilution of the solid sample.

ETV, as a sample introduction technique for ICP-MS, has shown that it is capable of handling solids and slurries of various types of samples [104,162,163,164]. Slurry sampling offers additional advantages for samples that occur naturally in colloidal-like state, such as milk and blood, and for the analysis of large numbers of samples, such as contaminated soils.

Brady et al. [165,166] introduced the technique of slurry sampling to determine Pb in leaves and Zn in marine sediments by applying GFAAS. For these determinations, the standard addition method was used. Calibration for slurry analysis can be accomplished by using the standard addition method as well as the use of aqueous

standards. Analytical calibration curves created by using aqueous and slurry standards were found to be superimposable. This means that in contrast to direct solid sampling, the slurry sampling technique allows aqueous standards to be used for calibration in many instances. However, it may be difficult to use aqueous standards for very complex matrices. In ETV-ICP-MS the presence of matrix can result in enhancement or suppression of the analyte ion signal due to non-spectral interferences (matrix).

A wide range of elements have been determined in slurries of varying matrices, ranging from soils to glass to food [159,160,167]. Literature review by Bendicho and de Loos-Vollebregt [159], Miller-Ihli [160] and Arruda et al. [167] show that a significant amount of research has been done on slurries, especially in GFAAS. In this literature review [159,160,167] they also discussed the benefits of ultrasonic slurry sampling, which has been used successfully in GFAAS. Ultrasonic slurry sampling has also been extended to ETV-ICP-MS [104,164,168-173]. In a recent study, Grégoire et al. [104] demonstrated the feasibility of slurry analysis by ETV-ICP-MS.

Chemical modifiers are used to enhance the vaporization properties of both analyte and matrix components. One approach involves converting relatively refractory compounds into more volatile compounds. Halocarbons introduced into plasma gases have been used to improve the vaporization properties of relatively refractory analytes. Kirkbright and Snook [109] used 0.1% freon-23 for the determination of B, Mo, Zr, Cr and W [174], and CCl₄ and freon-12 to determine trace elements in ceramic powders and SiC [175]. Ren and Salin [176,177] and Alary and Salin [178] used freon-12 to enhance the vaporization of carbide forming elements. Matousek et al. [179] used Cl₂ for the determination of Cr, V, Ti, W, and Zr. Polytetrafluoroethylene was also used as a

fluorinating reagent to promote the vaporization of refractory elements [152,180,181]. Goltz et al. [93] used freon-23 to enhance analyte signals for the rare elements in ETV-ICP-MS and Ng and Caruso [151] added ammonium chloride (7% (m/v)) as a means of vaporizing analytes as chlorides.

It has been reported in GFAAS studies that samples high in silica content caused serious effects on analyte signals. Bendicho and de Loos-Vollebregt [182] reported that when analyzing glass slurries a rapid deterioration in the condition of the graphite tube ensued and a decrease in absorbance signals occurred after 50-100 firings. Eams and Matousek [183] and Müller-Vogt and Wendl [184] attributed the rapid deterioration of the graphite tube when silica was present to the chemical attack of silica on graphite. Bendicho and de Loos-Vollebregt [185] analyzed glass samples and reported that this effect can be minimized by using HF, and thus the deterioration effects of the graphite tube could be reduced and the lifetime of the of the graphite tube extended.

In ETV-ICP-MS, microgram quantities of silicate materials vaporized directly into the plasma result in significant suppression of the analyte signal. For this reason, silicate matrices must be eliminated prior to the vaporization step. McIntyre et al. [173] used NH_4F , $\text{NH}_4\text{F-HF}$, and HF as fluorinating reagents for the removal of SiO_2 . The use of NH_4F and $\text{NH}_4\text{F-HF}$ were ineffective in removing silica; however, HF was able to remove much larger quantities of silica and made possible the direct determination of Ra in silicate reference materials [173]. Although published separately, the work of McIntyre et al. [173] was completed in this laboratory following the research reported here.

The objective of this work was to determine the optimum experimental conditions for the complete removal of silica in geological reference material powders using ultrasonic slurry sampling ETV-ICP-MS.

4.1.1 Characteristics of Slurries

Slurry is a suspension of a finely powdered sample in a liquid medium. Many limiting factors can greatly affect accuracy and precision of the slurry analysis. These factors include: (1) sample homogeneity, (2) grinding and sieving, (3) slurry preparation, (4) mixing and slurry homogeneity, (5) extraction of analyte into the slurry medium, (6) influence of the size of the slurry sub-sample, and (7) the influence of particle size on atomization efficiency.

The mean particle size of a slurry sample is of particular importance to make sure that the test sample is representative of the bulk slurry sample. Sample heterogeneity is a major problem in the analysis of solids. Hence, the degree of heterogeneity must be known or determined by the analyst, e.g. by replicate analysis. Usually, the relative standard deviation (RSD) values are used to determine the degree of homogeneity. Miller-Ihli [186,187] found that 3-5 replicate readings of 3-5 slurry preparations provided sufficient information to determine homogeneity. When the RSD value decreases, this indicates that homogeneity increases. If the degree of homogeneity is not obtained this may suggest that additional determination are needed or conventional acid digestion may be preferred over ultrasonic mixing [187].

Not all the samples to be analyzed are in the form amenable to slurry sampling by graphite furnace or ETV. Therefore, these samples may have to be processed by grinding and/or sieving to decrease particle size and improve homogeneity. The grinding

techniques vary, depending on the properties of the sample matrix. It is also very important that care be taken to minimize contamination from the grinding devices. Biological materials may be ground by using Teflon beads in polyethylene bottles [187]. Mortar grinding or centrifugal mills might be used as alternatives for other samples [187]. Silicon nitride and boron carbide parts showed less contamination problems than stainless steel parts [187] and zirconium beads [188].

The preparation of a slurry consists of adding a liquid diluent to a weighed amount of a solid sample. The diluent may be water, a liquid acid, a liquid stabilizing agent, or any combination of these. The need for stabilizing agents arises from the sedimentation rate of the suspended materials in aqueous solutions. Stabilizing agents such as Viscalex [160] and glycerol [189] which form highly viscous liquids have been used to keep the slurry homogeneous and prevent agglomeration. The stabilization by these agents is highly dependent on the sample characteristics and particle size. Some materials are not dispersed due to their low density or light particles and tend to float on the top of the liquid. For the dispersion of these particles, Triton X-100 [189] was applied. However, the addition of these high viscosity agents might pose problems. The inefficiency of the autosampler when using viscous solutions is due to sample solution adhering to the outside or inside of the autosampler capillary. The sample can also adhere to the outside of the graphite tube around the dosing hole. An additional pyrolysis step will enable excess of the stabilizing agent to be removed.

Important for final homogeneity of the slurry sample and reliable results is effective agitation of the slurry sample just before the introduction of the test sample into the graphite furnace. Numerous approaches have been reported for manual and automated

slurry agitation and introduction into the graphite furnace. Magnetic agitation and vortex mixing were used since the time when early work was carried out investigating slurry analysis [159]. These techniques require manual pipeting of samples. The small opening of the pipet may cause difficulty in picking up large particles, resulting in poor representation of the original sample-composition. Gas mixing by passing an argon stream through a narrow capillary tube introduced into the slurry medium has been reported [185]. Its performance depends on the characteristics and particle size of the sample. The technique which has been used recently and most frequently is the applied agitation technique called the Ultrasonic agitation technique, which has been automated by Miller-Ihli [189,190]. Ultrasonic agitation technique is more effective than other techniques because it aids the extraction of many of the metals of interest into the liquid phase of the slurry, considerably increasing the precision.

The use of acids as diluents, combined with ultrasonic agitation, has proved to be effective in extracting the analyte into the liquid phase. Miller-Ihli [187] demonstrated the utility of 5% (v/v) HNO_3 to extract some metals into the liquid phase. Bendicho and de Loos-Vollebregt [185] have reported on the extraction of metals by HF from slurries of glass samples.

When analyzing solids as slurries the amount of the analyte injected into the graphite furnace becomes an important factor. Calculation of the mass of the sample injected may be done as follows [186]:

$$M_F = M_S \times \frac{V_F}{V_S}$$

where M_F is the mass of the sample injected into the graphite furnace, V_F is the volume of the sample injected into the graphite furnace, M_S is the mass of the sample added to

make the slurry, and V_s is the volume of the slurry (suspension). The more the mass of the sample used to make the slurry (with fixed volume), the more representative will be the determined concentration of the original material. It is important when using ETV-ICP-MS not to overload the plasma.

4.2 EXPERIMENTAL

A Perkin-Elmer SCIEX (Concord, Ontario, Canada) ELAN 5000 ICP mass spectrometer equipped with an HGA-600 MS electrothermal vaporizer, a Model AS-60 autosampler, and a USS-100 ultrasonic mixing probe were used. The ultrasonic mixing probe (constructed of high purity Ti) used a mixing time of 30 s at a power level of 12 W to provide adequate mixing and suspension of slurries. To facilitate analysis of larger particle-sizes samples, the PFA tip provided with the autosampler was replaced with larger thin-walled PFA capillary tube (i.d. 0.81 mm). Pyrolytic-graphite-coated tubes were used throughout. The experimental conditions for both the ELAN 5000 and the HGA-600 MS are given in Table 9. A PTFE tube of 80 cm and 6 mm i.d. was used to interface the HGA-600 MS to the plasma torch. Optimization of the plasma and mass spectrometer was accomplished using the solution nebulization mode, prior to switching to the ETV mode. The operation of the HGA-600 MS was completely computer-controlled. For all experiments, $^{30}\text{Si}^+$ (3.21% abundance) was used to monitor the vaporization of silica. Data in all figures and tables are corrected for any background signal present.

Table 9. Instrument operating conditions and data acquisition protocols of the Perkin-Elmer SCIEX ELAN 5000 ETV-ICP-MS

<u>ICP mass spectrometer</u>	
R.F.power	1100 W
Coolant Argon flow rate	15.0 L min ⁻¹
Auxiliary Argon flow rate	900 mL min ⁻¹
Carrier Argon flow rate	850 mL min ⁻¹
Sampler and skimmer	nickel
<u>HGA-600 MS electrothermal vaporizer</u>	
Sample volume	20 µL
Modifier volume	20 µL
Internal argon flow rate	300 mL min ⁻¹
Digestion step	10 s ramp, 60°C, variable hold time
Drying step	5 s ramp, 100°C for 30 s
Pyrolysis step	1 s ramp, 100°C for 7 s
Vaporization step	1 s ramp, 2500°C for 6 s
Clean-up step	1 s ramp, 2650°C, for 10 s
<u>Data acquisition</u>	
Dwell time	20 ms
Scan mode	Peak hop transient
Points/spectral peak	1
Signal measurement	Integrated counts
MS resolution	0.7 u at 10% peak height

4.2.1 Standards and Reagents

High purity argon gas (99.995%, Matheson Gas Products, Ottawa, Ontario, Canada) was used. Solutions were prepared with ultra-pure water obtained from a Milli-Q water purification system (Millipore Corp., Mississauga, Ontario, Canada.). The nitric and hydrofluoric acids used were analytical-reagent grade (Anachemia, Rouses Pint NY). Finely divided high-purity precipitated silica and high purity silicon carbide were obtained from Spex Industries, Metuchen. N.J., U.S.A. Standard reference materials used were SY-2 syenite rock containing 60.11% SiO₂ and BHVO-1, a basalt containing 49.94% SiO₂.

4.2.2 Preparation of Slurries

The slurries were prepared by accurately weighing the solid sample (e.g. 0.10 g) and placing it into a 10 mL plastic test tube. Water was added as the liquid medium. The slurry was mixed using a vortex mixer from which was removed (during agitation) a 1 mL aliquot. If required, the 1 mL aliquot was diluted further until a 1 mL aliquot was produced which contained the desired mass to volume ratio of solid to diluent liquid.

4.2.3 Ultrasonic Mixer (USS-100)

The system was equipped with a Perkin-Elmer USS-100 ultrasonic mixing probe constructed of high-purity titanium. The system was automated directly from the HGA-600MS and AS-60 autosampler systems. Ultrasonic mixing has been shown to be very effective in the mixing of slurry samples [104,186-188]. The action of ultrasonic mixing should be such that the slurry is vigorously mixed in a rolling manner, while avoiding spillage and loss of slurry due to sputtering [187]. It was found that a mixing time of 30 s coupled with a power level of 30 (12W) provide adequate mixing for slurries. Miller-Ihli

[160] has reported that the power levels are not consistent from unit to unit, therefore making a standard set of settings difficult to find.

The USS-100 consists of two parts: the mixer, consisting of a shaft of high-purity titanium (approx. 26 cm in height and 3 cm max. diameter), and an argon gas driven piston (approx. 23 cm in height and 2 cm max. diameter), which are both attached by a plastic casing (Fig. 18). The total unit occupies a space of approximately 30 cm in height, 5 cm in width and 20 cm in length. The gas piston controls the vertical movement of the instrument into and out of the slurry being mixed. When the mixing probe is down, i.e., in the sample cup, the probe produces its ultrasonic action with the aid of an external power source. When the mixing probe is up, i.e., not in the sample cup, there is no power to the probe. The portion of the probe that does the mixing is approximately 2 mm i.d. and 25 mm in length. A power supply is provided to control the length of time for mixing and the amount of power that controls the mixing, the higher the power, the more vigorous is the mixing.

The USS-100 works in the following manner. The autosampler control moves a cup into position to be sampled. The piston moves down, pulling the mixing probe into the sample and the probe begins the ultrasonic action for mixing. After a preset mixing time, controlled by the user, the piston moves up, removing the probe from the slurry, at which time the autosampler immediately samples the slurry. The autosampler then places the sample in the graphite tube and the heating program begins.

The purpose of high powered ultrasonic application is to cause some permanent change in the material being treated [191]. For slurries, equal distribution of solid particles throughout the liquid portion of the slurry is required for reproducible sampling.

Figure 18. Diagram of the Perkin-Elmer Ultrasonic Mixer (USS-100)

The ultrasonic probe aids the particles in becoming more flocculent and keeps them in suspension longer [192]. The action of ultrasonic, which uses high frequencies, is effective at dislodging mechanically interlocked particles, i.e., particles trapped or entrained within the matrix [191]. This promotes dissolution by freeing analyte from the matrix and by breaking the sample into smaller particles [193,194].

4.3 RESULTS AND DISCUSSION

Freon, used as halogenation agent, has become a popular gas-phase chemical modifier used to enhance the volatility of refractory elements in ETV-ICP-AES [109,176-178] and ETV-ICP-MS [93,116]. In most published work, freon has been mixed with the argon gas during the high-temperature vaporization step. Freon decomposes at high temperatures to give highly reactive chlorine or fluorine radicals. These radicals react with sample and matrix components producing relatively volatile analyte chlorides and fluorides.

In this work, freon-23 was used as a possible fluorinating reagent to remove the SiO_2 by conversion to volatile SiF_4 . The results obtained for these experiments indicated that either large quantities of freon or very long reaction times (minutes) are required to complete the removal of silica. Even when using a pyrolysis temperature of 1000°C , significant quantities of carbon soot were produced as a result of freon decomposition. If either the freon concentration or the reaction time were increased to levels required to remove silica completely, excessive quantities of soot were produced, causing unwanted plasma effects. Because of this, the use of gas-phase chemical modifiers was abandoned in favour of using HF solutions.

4.3.1 Vaporization Curve for Silicon Dioxide

As an initial study on the removal of SiO_2 , a vaporization curve was constructed to determine at which temperature SiO_2 vaporization begins and at which temperature the vaporization is complete. The vaporization curve for SiO_2 (Fig.19) was obtained without using a chemical modifier. Figure 19 was obtained using 20 μL of the SiO_2 slurry containing 125 μg of SiO_2 . The ETV-ICP-MS signal intensity was measured at vaporization temperatures ranging from 810°C to 2600°C. No pyrolysis step was used. The ETV-ICP-MS vaporization curve (Fig. 19) gives an appearance temperature for Si (derived from the vaporization of SiO_2) of approximately 1600°C and reaches a maximum at about 2200°C. These temperatures roughly coincide with the melting point (1610°C) [195] and the boiling point (2230°C) [195] of SiO_2 , respectively. A single Si signal was observed over the entire range of vaporization temperatures studied. Clearly, a pyrolysis temperature of 2200°C cannot be used to remove silica since at this temperature many analyte elements and excessive amounts of C are vaporized as well.

4.3.2 Hydrofluoric Acid Chemical Modifier

The ETV heating program step during which HF is added and the reaction between the sample and HF takes place can best be referred to as the digestion step. The effect of added HF on the removal of SiO_2 in ETV-ICP-MS is shown in Figure 20. For these experiments, a pyrolysis temperature of 100°C and a vaporization temperature of 2500°C were used following a digestion step of 60°C (10 s ramp). The duration of the digestion step (hold time) was varied from 30 s to 300 s. A 20 μL aliquot of 50 % (v/v) hydrofluoric acid was added to 20 μL of the SiO_2 slurry sample in the graphite tube. Following the hold time, the ETV-ICP-MS signal intensity measured during the

Figure 19. Vaporization curve for 20 µL slurry sample containing 125 µg of SiO₂.

Figure 20. Effects of the digestion step hold time on the integrated signal for Si (125 μg) using 20 μL 50% (v/v) HF. The vaporization temperature was 2500°C.

vaporization step for Si decreased with increased hold time for the digestion, indicating that most of the silica was removed with a hold time of about 150 s. For the digestion step hold times greater than 150 s, little additional SiO_2 is removed. This observation is in agreement with the work of McIntyre et al. [173], who used HF for the removal of silica from geological materials analyzed for Ra using slurry sampling ETV-ICP-MS.

The actual Si signals obtained during the digestion step corresponding to the data given in Figure 20 are shown in Figure 21, which shows that both curves a and b display two distinct signals (one large and the other small) widely separated in time. The first signal appears at about 1 s, reaching a maximum at about 2 s, and the second, smaller signal appears at about 5 s with a maximum at approximately 6 s into the high temperature vaporization step. This suggests that probably two different Si species are released during the vaporization step and that these two species have very different volatilities. Increasing the hold time above 60 s (Figs. 21c-21g) shows no change in the Si signals with the exception that the second signal persists and is somewhat variable, indicating that some residual, unreacted silica remained in the graphite tube.

4.3.3 Origin of the Si Signals in ETV-ICP-MS

To investigate the nature of the above two Si species observed, the effect of changing the ramp time (time to reach maximum vaporization temperature) or graphite tube heating rate was studied. For these experiments, an HF digestion step of 60°C with a hold time of 30 s, a pyrolysis temperature of 100°C (7 s hold time) and a vaporization temperature of 2500°C was used. The effect of changing the graphite tube heating rate during the vaporization step is shown in Figure 22. The ramp time was varied between 1 s and 10 s, giving a heating rate of between 2400°C s⁻¹ and 240°C s⁻¹, respectively. At a

Figure 21. ETV-ICP-MS signals for 125 µg SiO₂ using 20 µL 50 % (v/v) HF at hold time of (a) 30 s, (b) 60 s, (c) 90 s, (d) 120 s, (e) 150 s, (f) 180 s, (g) 300 s. The vaporization temperature was 2500°C

Figure 22. ETV-ICP-MS signals for 125 μg SiO_2 using 20 μL 50 % (v/v) HF at various vaporization ramp time, (a) 1 s, (b) 5 s, (c) 10 s. Hold time at the digestion step was 30 s. The vaporization temperature was 2500°C.

ramp time of 1 s, the first signal (Fig. 22a) appeared at 1 s with a signal maximum at about 2 s. The second signal occurred at about 5 s, reaching a maximum at 7 s. As the ramp time was increased, there was a large shift in the appearance time and also in the signal maximum time of the second signal, and a correspondingly small shift in the signal times for the first signal. The higher the ramp time (slower heating rate) the greater the shift in the second signal. Figure 22c shows the ETV-ICP MS signal for Si at a ramp time of 10 s. The appearance time for the first signal was 2 s and for the second signal between 12 and 19 s. The fact that a radical change in the heating rate of the graphite tube results in almost no change in the signal position, height and width of the first Si signal while resulting in a very large change in the shape and size of the second signal suggests that the two Si species are not only different but also have WIDELY different vaporization characteristics.

Since the first larger signal appeared at 2 s using a 10 s ramp time, it can be calculated that the appearance temperature of this Si species is about 480°C. The melting point and boiling point of SiO₂ is 1610°C and 2230°C, respectively, indicating that the first signal cannot be due to SiO₂, but could be due to SiF₄ (b.p.-86°C) [195], which was formed by the addition of HF as a chemical modifier in the digestion step. Both fluorine and HF are known to intercalate in graphite [196], and it is possible that SiF₄ is also thermally stabilized through intercalation. From this, it can be surmised that although most of the SiF₄ was lost during the reaction and pyrolysis steps, some SiF₄ remained and perhaps became intercalated into the graphite tube only to be released later at higher temperatures during the vaporization step. In a separate study, Grégoire et al. [197]

reported that small quantities of HCl were retained within the graphite tube by intercalation even after pyrolysis at 400°C.

Figure 23 shows ETV-ICP-MS signals for Si obtained from the vaporization of (a) SiO₂ and (b) SiC, both without a chemical modifier. A ramp time of 1 s was used for the vaporization step. Figure 23a shows that the signal for SiO₂ occurred between 3.5 and 10 s with the maximum occurring at about 5.9 s, which was coincident with the second Si signal shown in Figure 22a. Figure 23b shows that the signal for SiC occurred between 3.5 and 12 s with the maximum at about 7.3 s. This may suggest that the small, second signal in Figure 22a, which appeared at a later time, could be due to unreacted SiO₂ remaining following the digestion step and then released at a later time during the vaporization step. It may also be attributed to the release of a mixture of SiO₂ and SiC or SiC alone, which may be formed at high temperatures.

4.3.4 Optimization of the Chemical Modification by HF for Silica Removal

In Figure 21g it was shown that for a digestion step with hold time of 300 s, the first larger Si signal essentially disappeared and that only a small decrease in the second Si signal was observed. This indicated that using only 20 µL HF possibly did not convert all of the SiO₂ to SiF₄. To investigate the effect of increasing amounts of HF on the ETV-ICP-MS signal intensity for Si, the volume of 50 % (v/v) HF used was increased from 20 µL to 70 µL. To ensure adequate reaction time, a digestion step hold time of 300 s was used. Figure 24 shows that the second signal (in Fig. 21) appeared at slightly earlier times with increasing amounts of HF and that the second signal was almost completely removed when 70 µL of HF was used. This suggests that there was enough HF and a sufficient holding time for the SiO₂ to react completely with HF to produce SiF₄ and that

Figure 23. ETV-ICP-MS signals for (a) SiO₂ and (b) SiC, without HF as a chemical modifier. Vaporization step ramp time of 1 s and vaporization temperature of 2500°C were used.

Figure 24. Effect of HF volume on the ETV-ICP-MS signals for SiO_2 , (a) 20 μL , (b) 40 μL , (c) 60 μL , (d) 70 μL of HF. Hold time at the digestion step was 300 s. Vaporization temperature was 2500°C.

there was also enough time to volatilize SiF_4 during the digestion and pyrolysis steps.

To obtain the most practical conditions for removing silica, we also determined the reaction step holding time required to eliminate SiO_2 when using 70 μL of 50 % (v/v) HF. The results in Figure 25 show that the Si signal intensity decreases as the digestion step hold time is increased and essentially disappears at a hold time of 150 s. This result is similar to that obtained when using 20 μL of 50 % (v/v) HF (Fig. 21) with the exception that virtually no second Si signal is apparent. This may mean that the second signal observed earlier was due to the presence of unreacted silica or silica that had escaped contact with the HF.

An important finding resulting from this study was that at a hold time of 180 s (using 70 μL 50 % (v/v) HF) the graphite tube failed catastrophically with the end of the graphite tube downstream from the dosing hole (end nearest to plasma) completely breaking off. To determine whether this effect was due to the presence of silica or hydrofluoric acid, the experiment was repeated using only 70 μL of 50 % (v/v) HF and 20 μL H_2O . When using only HF, the tube also failed, indicating that tube fracture was the result of the corrosive effect of HF on graphite. From this we conclude that using a 20 μL of 50% (v/v) HF and a reaction hold time of 150 s at the digestion step are optimal for the removal of silica while maintaining the integrity of the graphite tube. The small quantities of silica remaining when using 20 μL of HF were not significant and did not prevent the determination of Ra in silicate materials using slurry sampling ETV-ICP-MS [173].

Figure 25. ETV-ICP-MS signals for 125 μg SiO_2 using 70 μl 50 % (v/v) HF at hold time of (a) 30 s, (b) 60 s, (c) 90 s, (d) 120 s, (e) 150 s, (f) 180 s. Vaporization temperature was 2500°C.

4.3.5 Removal of Silica from Geological Reference Materials

Silica is, of course, the simplest of silicate materials and so it is possible that the removal of Si from more complex silicates may be more difficult relative to pure silica. The method developed above was applied to two geological reference materials: syenite SY-2 (60.11% SiO₂) and basalt BHVO-1 (49.94% SiO₂). Figure 26 shows the ETV-ICP-MS signals for Si obtained when 125 µg BHVO-1 basalt reference material was vaporized (a) without using a chemical modifier and (b) using 20 µL of 50% (v/v) HF as a chemical modifier with a reaction time of 150 s. Figure 26a shows a single large Si signal appearing at about 3.9 s, reaching maximum at about 5.8 s. This signal can be attributed to SiO₂. Figure 26b shows a smaller signal appearing at about 1.6 s with a maximum at about 2.9 s. with a very small shoulder appearing at about 4 s. The first signal can be attributed to the release of SiF₄, as discussed earlier. The shoulder may be due to a very small quantity of unreacted silica. This result demonstrates that almost all the silica was removed by using 20 µL of 50% (v/v) HF (150 s reaction time) and that complex silicate materials can be successfully digested using HF. The results obtained for SY-2 (Fig. 27) were identical to those reported above for BHVO-1.

4.4 SUMMARY AND CONCLUSIONS

The removal of silica in direct analysis of solid geological samples high in silica has been investigated by using slurry sampling in ETV-ICP-MS. The vaporization curve for SiO₂, sampled as a slurry has been run at a temperatures ranging from 810° to 2600°C. This curve shows an appearance temperature for Si at approximately 1600°C, and that silica is completely vaporized at a temperature of 2200°C.

Figure 26. ETV-ICP-MS signals for SiO₂ from 125 µg of basalt (BHVO-1), (a) without using HF as a chemical modifier, (b) using 20 µL of 50% (v/v) HF chemical modifier. Digestion step hold time: 150 s.

Figure 27. ETV-ICP-MS signals for SiO₂ from 125 µg of syenite (SY-2), (a) without using HF as a chemical modifier and (b) using 20 µL of 50% (v/v) HF chemical modifier. Digestion step hold time: 150 s.

The studies on the effect of using HF as a chemical modifier to remove silica as silicon tetrafluoride was first conducted, by varying the duration of the digestion step (hold time), and secondly, by varying (increasing) the amount of HF. It was found that any Si attributed to silica could be completely removed if the chemical modifier (HF) was added in a sufficient amount and an adequate reaction time was allowed.

Two Si signals were observed at reaction times less than optimal. The ramp time at the vaporization step was changed to investigate the nature of the two Si species corresponding to the two Si signals.

The first signal which at an earlier time, was attributed to the volatilization of silicon tetrafluoride since it is appeared at a temperature less than 480°C. At a temperature of about 2500°C, the second signal appeared at a later time and this was attributed to the residual, unreacted SiO₂ remaining in the graphite tube and released later at the vaporization step, or to the partial vaporization of a mixture of SiO₂ and SiC.

For effective and complete removal of 125 µg of SiO₂ twenty microliters of 50 % (v/v) HF was required. Over the lifetime of the graphite tube, which exceeded 200 firings, no adverse effects including corrosive degradation of the graphite tube was observed.

CHAPTER 5

POLYATOMIC IONS

Inductively coupled plasma mass spectrometry (ICP-MS) offers extremely high sensitivity for the determination of a wide range of elements [198]. However, the technique is subject to specific spectral interferences, which can limit detection power for few elements [198]. Since the high-temperature atomizes samples very efficiently, it follows that there will be large population of reactive atomic and ionic species, which can combine, in the interface region of the ICP-MS to form polyatomic clusters, with a frequency proportional to their abundances. Thus, spectral interferences can arise from species associated with the normal operation of the plasma, and from components of the sample matrix.

Argon, hydrogen and oxygen are the dominant species present in the plasma as well as nitrogen. These may combine with each other or with other elements from the sample matrix. Some of the more obvious and serious spectral overlap problems include $^{28}\text{Si}^+$ (N_2^+) and ^{56}Fe (ArO^+). The major elements present in the solvents or acids used during sample preparation (e.g. N, S, and Cl) also participate in these reactions.

Many of polyatomic ion interferences include O and H. The interference of O and H arises as a result of interaction from the dissociation of water, and Ar from the plasma support gas in the mass spectrometer interface behind the sampling cone.

When using an ETV system the release of carbon from the graphite tube especially at high temperature poses a problem with some elements. The polyatomic ions that can originate because of the presence of carbon and other species are listed in Table 10 [70].

As described below, elements such as Mg, Si, and Cr are interfered with by carbon-containing polyatomic ions [70]:

Magnesium: Two Mg isotopes are isobaric with carbon-containing ionic species, leaving ^{25}Mg (10.11%) available for analytical purposes.

Silicon: All three Si isotopes are interfered by carbon-containing polyatomic ions, making silicon difficult to determine at trace levels using ETV-ICP-MS. Note that a significant proportion of the background equivalent mass is due to nitrogen containing-polyatomic ions which interfere with the determination of Si by all modes of sample introduction.

Chromium: ^{52}Cr (83.3%) and ^{53}Cr (9.6%) are both interfered by carbon argides, leaving only ^{54}Cr (2.38%), which is free of carbon argide, but isobaric with ^{54}Fe (5.9%) and $^{40}\text{Ar}^{14}\text{N}^+$.

The elements Mg, Si, and Cr are relatively involatile and will be vaporized from the graphite surface only at high temperatures. Therefore, the seriousness of interferences by carbon-containing polyatomic ions will be dependent on the actual appearance-- and peak-temperatures of the analyte, and hence, it is important to consider the temporal characteristics of the background species [70]. The resolution of the quadrupole mass spectrometer is insufficient to separate direct spectral coincidences of this type.

Table 10. Spectral interferences arising from graphite electrothermal vaporizer heated to 2500°C and other polyatomic ions not originating from carbon.

Mass	Background Ion(s)	Analyte (% abundance)
24	$^{12}\text{C}^{12}\text{C}^+$	Mg (78.6)
26	$^{12}\text{C}^{14}\text{N}^+$	Mg (11.3)
28	$^{14}\text{N}^{14}\text{N}^+, ^{12}\text{C}^{16}\text{O}^+$	Si (92.2)
29	$^{14}\text{N}^{14}\text{N}^1\text{H}^+, ^{12}\text{C}^{16}\text{O}^1\text{H}^+, ^{13}\text{C}^{16}\text{O}^+$	Si (4.7)
30	$^{14}\text{N}^{16}\text{O}^+, ^{13}\text{C}^{16}\text{O}^1\text{H}^+$	Si (3.1)
52	$^{12}\text{C}^{40}\text{Ar}^+$	Cr (83.8)
53	$^{13}\text{C}^{40}\text{Ar}^+$	Cr (9.6)

5.1 ATTENUATION OF POLYATOMIC IONS

A number of methods have been proposed in the literature for the attenuation or correction of such interferences. These include (1) stripping the spectrum of the blank from that of the analyte, mathematical correction methods, (2) adjusting plasma conditions, (3) introducing sample as dry aerosol, (4) the use of alternative gas to replace totally or partially the usual argon plasma gas, (5) use of high-resolution MS and (6) the use of gas-phase collisions (reactions) cells. Many of these approaches have been reviewed by Evans and Giglio [199].

5.1.1 Mathematical Correction

The use of equations or multivariate correction methods are one of the simplest methods to correct for spectral interferences. For example [200], the interferences caused by $^{40}\text{Ar}^{35}\text{Cl}^+$ with $^{75}\text{As}^+$ can be corrected for by measuring the $^{40}\text{Ar}^{37}\text{Cl}^+$ at $m/z = 77$ and back-calculating the contribution from $^{40}\text{Ar}^{35}\text{Cl}^+$ at $m/z = 75$, assuming that the sample does not contain $^{77}\text{Se}^+$. These corrections can be implemented with appropriate software. However, if many samples with similar matrices are to analyzed, then such an approach, even in its simplest form, would prove invaluable.

5.1.2 Adjusting Plasma Conditions

The reduction of polyatomic ion species can be achieved by optimization of instrument parameters, particularly the carrier gas flow rate and the forward rf power. These parameters can have a significant effect on the level of polyatomic ion species produced and the signal response [201,202]. Jiang et al. [202] investigated the effect of changing the position of the sample cone orifice relative to the load coil on the measurement of K isotopes, using high nebulizer gas flow rates and low forward power.

These conditions resulted in suppression of nearly all Ar^+ and ArH^+ ions. NO^+ dominated the background spectrum.

5.1.3 Introducing Sample as a Dry Aerosol

In general, any technique which removes solvents, typically water from the sample solution to form a 'dry' aerosol, should lead to a reduction in the level of polyatomic and oxide species which involve O and H in their formation. This means reduction in spectral interferences by polyatomic interferences. The ETV technique efficiently accomplishes this process during the sample drying stage. Some workers [54,58] indicated that both ArO^+ and ArCl^+ levels were reduced, allowing for almost interference-free determination of $^{56}\text{Fe}^+$ and $^{75}\text{As}^+$.

5.1.4 Alternative Gas and Mixed Gas

A series of papers have been published on the use of alternative and mixed-gas plasmas. All currently available plasma source mass spectrometry instruments use an argon ICP as the ion source. However, a number of studies have investigated the use of alternative gases. Montaser et al. [203] has reported on the use of He gas. Polyatomic ion interferences by Ar can be substantially reduced using a He ICP [204]. However, a number of alternative interferences from polyatomic ions were reported. These involved polyatomic ions resulting from recombinations of O, H, etc. with He. The lower gas temperature of the ICP operated with He gas has restricted its application.

Altering the composition of the plasma gas can have a dramatic effect on the level of certain spectral interferences. The addition of nitrogen [205], hydrogen [51], xenon [206], and methane [207] has been explored and, in general, found to have an attenuating effect on specific interfering species. Beauchemin and Craig [205] investigated the use of

mixed gases to reduce interference effects in ICP-MS. A small addition of H_2 or N_2 can lead to a reduction in the size of the argon dimer in some instances. Evans and Ebdon [208,209] reported on the use of oxygen and nitrogen additions to suppress the formation of ArCl^+ and ArAr^+ and thus reduce the interferences with As and Se by these species. The addition of Xe showed substantial reductions in many polyatomic ions. The lower excitation and ionization energy of Xe compared with that of Ar was suggested as a reason for the decrease in polyatomic ion levels. However, although the introduction of an additional gas may result in a decrease in specific polyatomic ions as the equilibrium changes, it normally results in a corresponding increase in species related to the added gas. For example, the addition of N_2 to the coolant gas may reduce $^{40}\text{Ar}^{16}\text{O}$ interference with ^{56}Fe , but $^{14}\text{N}_2$ and $^{40}\text{Ar}^{14}\text{N}$ ions are enhanced, compromising the determination of ^{28}Si and ^{54}Fe , respectively.

5.1.5 High-Resolution MS

One of the most effective methods of overcoming spectral interferences is by coupling ICP source to a high resolution mass spectrometer. For example, Bradshaw et al. [210] used a double focusing magnetic sector mass spectrometer that was capable of achieving a resolution of 50000. However, a resolution of 3000 was sufficient to resolve OCl^+ at m/z 50.964 from V^+ at m/z 50.944. It is likely that a trade-off in sensitivity will result if an extremely high resolution is required. The main drawback of using high resolution instruments is the expense and added complexity compared with quadrupole ICP mass spectrometry.

5.1.6 Gas-Phase Collision (Reaction) Cells

Recent developments in ICP-MS technology have introduced ‘collision’ or ‘reaction’ cells for ion focusing [211-213] and for filtering of selected ions by reactions with gases during transmission from plasma to analyzer [207,214-216]. H_2 , Xe, N_2 , O_2 , NH_3 , and various other gases have been introduced into the rf-only multi-pole ‘reaction’ cell in small volumes to promote ion-molecule reactions. Ion traps, multi-pole collision cells and dynamic reaction cells have been used.

The ion trap has been coupled to an Ar ICP by Barinaga and Koppenaal [217]. Molecular hydrogen reacted with Ar^+ and certain other plasma ions, greatly reducing their intensities [218]. The typical and problematic polyatomic ion interferences found in conventional Ar ICP-MS were nearly eliminated. No ArO^+ , ArCl^+ , ArN^+ , ArC^+ , ArAr^+ , or other polyatomic ions were even observable. Polyatomic species were decomposed by collisional dissociation reactions.

Fieldmann et al. [219] reported on the use of a hexapole collision cell in ICP-MS. Helium was used as a buffer gas and H_2 as a reaction gas. The later was found to be effective in reducing typical Ar polyatomic species by up to 4 orders of magnitude. Shakra [220] described accurate determination of As in RM NASS-3 using hexapole technology and the removal of ArCl^+ .

In a series of reports, Tanner and co-workers have described the dynamic reaction cell (DRC) for ICP-MS [221-225]. The cell is pressured with a gas or a mixture of gases to reduce or eliminate the interfering polyatomic species by collisional dissociation and/or gas phase chemical reactions. More details on DRC will be presented in Section 5.2.

5.2 DYNAMIC REACTION CELL (DRC)

Douglas [226] and Rowan and Houk [207] were the first to report on the application of quadrupole collision cells for ICP-MS. Douglas [226] reported that, in collision cells scattering loss rates exceeded collisional fragmentation rates, and that the reactive conversion process was more attractive. Also, it has been shown that reaction cells for ICP-MS could take advantages of the specificity of near-thermal ion-molecule reactions [207].

The DRC is an enclosed quadrupole introduced between the ion lens and mass analyzer pre-filter (Fig. 28). The DRC is a controlled environment for the promotion of desirable ion-molecule reactions and collisions (chemical resolution) [224]. This is achieved by introducing a reactive gas into a pressurized cell at pressures ranging from 5 to 20 mTorr [222]. The DRC can then convert polyatomic interferences to different ions which do not interfere with the analyte and enhance sensitivity with collisional focusing of ions.

The DRC has some characteristics such as: (1) reduces/eliminates plasma and sample based interferences; (2) automatic switching between standard (open cell, with no reaction gas) and DRC (with reaction gas) modes; (3) lower background noise, (4) lower detection limits; (5) always uses normal temperature plasma, even for elements such as K, Ca, and Fe; (6) reaction cell has a dynamic bandpass which is scanned with the analyzer quadrupole [223].

Figure 28. Schematic Diagram of Perkin-Elmer Elan 6100 DRC

5.2.1 Ion-Molecule Reactions

The specific chemistry and collisions are dependent on the chemical and physical characteristics of the reaction gas. A reaction gas is selected based on its ionization potential (IP), which should be lower than the IP of the interfering species, but higher than the IP of the analyte [222]. The reaction gas enters the cell and reacts more quickly with the polyatomic interfering species than with the analyte. Removal of interference depends on the reaction rate constants and thermodynamics [222]. The gas flow is optimized to maximize the removal of the interfering species while maintaining adequate sensitivity for the analyte.

The common reaction mechanisms for ion-molecule chemistry between the interfering argon-containing polyatomic species and the cell gas include:

1. Charge transfer $\text{Ar}^+ + \text{NH}_3 \longrightarrow \text{NH}_3^+ + \text{Ar}$
2. Proton transfer $\text{ArH}^+ + \text{NH}_3 \longrightarrow \text{NH}_4^+ + \text{Ar}$
3. Hydrogen atom transfer $\text{Ar}^+ + \text{NH}_3 \longrightarrow \text{ArH}^+ + \text{NH}_2$

which result in elimination of interferences by neutralization, dissociation or an increase by one mass unit from the mass unit in the m/z value of interest [219,221,222].

Charge transfer is the most simple and common process, which often takes place when the ionization potential (IP) of the neutral reactant is less than that of the neutral corresponding to the ion. The reaction is exothermic and rapid because the IP of NH_3 (10.2 eV) is less than that of Ar (15.8 eV) [222]. On the other hand, the reaction of Ca^+ with NH_3 is endothermic and extremely slow according to:

because the IP of NH_3 is greater than that of Ca (6.11 eV) [222]

Ammonia is usually favoured as an effective reaction gas for the removal of most argide ion interferences. This is because Ar^+ and its polyatomics generally have IP's greater than that of ammonia, and most analyte ions have IP's that are lower. However, some analyte ion may also react with the reaction gas. For example, As^+ reacts relatively rapidly with NH_3 . In this case an alternative reaction gas, such as, CH_4 or H_2 [222] is used. It is also important that the mass of the reaction gas should be less than mass of the analyte ion. This is because scattering losses of the analyte ion might otherwise become the limiting factor. The high purity of reaction gas is very desirable, since trace impurities might contribute to the spectral background through ionization in the reaction cell. In general, it is favourable to use a reaction gas that reacts slowly (or not at all) with the analyte ion and reacts very fast with interfering ions.

5.2.2 Stability of Ions in Quadrupole Mass Spectrometers

If the ions can be confined and transmitted through the multi-pole it means they are stable. The stability of the ions are affected by (1) the amplitude and frequency of the applied rf, (2) the mass of the ion, (3) the size of the multi-pole array, and (4) the dc voltage applied between pole pairs [222].

The stability and instability regions in the quadrupole are normally expressed in terms of the Mathieu parameters, **a** and **q**:

$$a_n = 2n(n-1) \frac{eV_{dc}}{m\omega^2 r_0^2}$$

$$q_n = n(n-1) \frac{eV_{rf}}{m\omega^2 r_0^2}$$

where n is the order of the multi-pole, e is the electronic charge, V_{dc} is the dc voltage pole-to-pole, m is the ion mass, ω is the rf angular frequency, r_0 is the field radius of the multi-pole array, and V_{rf} is the peak-to-peak rf amplitude [222]. The parameter a influences the high mass cutoff of the quadrupole bandpass and q influences the low mass cutoff of the quadrupole bandpass. Mathieu parameters can be plotted to give a stability diagram for ions in a linear quadrupole (Fig. 29) [222].

The ion must have stable trajectories in both directions, x and y , in order to pass successfully through the quadrupole. In the rf mode of operation, the quadrupole acts as a high pass filter. Ions having masses such that $q > 0.908$ do not have stable trajectories and are ejected from the device. The bandpass of the DRC is adjusted by setting the parameters a and q , restricting the range of ion masses that are trapped, and scanning this bandpass range in concert with the mass analyzer, thereby, suppressing any unwanted secondary reaction products within the reaction cell. The superior bandpassing capabilities of the quadrupole permits the use of complex reaction gases, giving control over secondary and sequential reactions [222].

Figure 29. Ion Stability Diagram

CHAPTER 6

EFFECTIVENESS OF A DYNAMIC REACTION CELL FOR REDUCTION OF POLYATOMIC ION INTERFERENCES IN ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

6.1 INTRODUCTION

In spite of several advantages of ETV-ICP-MS, its full analytical potential cannot be realized for determination of certain analytes because of spectral interferences caused by polyatomic ions due to the presence of vaporized carbon in the argon plasma. In particular, the determination of Mg, Cr and Si, can be severely affected by such spectral interferences. Table 10 in chapter 5 summarizes possible polyatomic ion interferences for these elements arising from the presence of carbon containing ionic species, as well as other polyatomic ions not originating from carbon.

Some studies were reported by Horlick et al. [101,227] and by Grégoire and Sturgeon [70] on the major signal background features of ICP-MS using solution nebulization and ETV sample introduction systems. ETV-ICP-MS, when compared with solution nebulization, exhibited significant reduction of background signals due to oxygen and hydrogen polyatomic ions. However, an increase in background signals due to carbon-containing ions was also observed, especially at high temperatures.

Basically, there are two main approaches for minimizing or eliminating spectral interferences caused by the formation of polyatomic ions when using ETV sample

introduction. One approach used to avoid such interferences is to use a mass spectrometer with a resolving power high enough for spectral separation of analyte ions from the polyatomic ions. However, high-resolution mass spectrometers can be expensive and are not capable of resolving all polyatomic ion interferences. The other approach is to reduce or eliminate the presence of interfering polyatomic ions, by using a reaction cell which is incorporated into the ICP-MS system.

Reaction cells exploit gas-phase ion-molecule reactions to suppress selectively the interfering polyatomic ions before the ions are transferred to the quadrupole mass analyzer. Such a system is commercially available with the Perkin-Elmer SCIEX ELAN, and is called "Dynamic Reaction Cell" (DRC) [228-232].

The use of a Dynamic Reaction Cell makes possible the reduction of individual polyatomic ion interferences by several orders of magnitude. Neubauer and Vollkopf [231] have studied the benefits of using a DRC for the removal of carbon and chloride based spectral interference in simulated carbon matrix solutions. For this study, they used solution nebulization sample introduction and reported that major interferences on $m/z = 52, 53, 55$ (Cr) and 75 (As) resulting from $^{40}\text{Ar}^{12}\text{C}^+$, $^{35}\text{Cl}^{16}\text{OH}^+$, $^{40}\text{Ar}^{13}\text{C}^+$, $^{37}\text{Cl}^{18}\text{O}^+$, and $^{40}\text{Ar}^{35}\text{Cl}^+$, respectively can be reduced.

The DRC in combination with ETV can be used to reduce carbon-based polyatomic interferences, taking advantages of the best features of both ETV and the DRC. The characteristics of a Dynamic Reaction Cell used in conjunction with the ETV have not yet been investigated. The purpose of this study is to evaluate the effectiveness of the Dynamic Reaction Cell in reducing polyatomic ion interferences for the determination of Mg, Cr and Si by ETV-ICP-MS. Also, to be investigated are the

optimum operating parameters of the DRC-ETV-ICP mass spectrometer for providing the greatest analyte sensitivity and lowest limit of detection for selected analytes. A second goal was to determine if it is possible to optimize the performance of the DRC using solution nebulization (SN) sample introduction and to use these same conditions for ETV sample introduction.

6.2 EXPERIMENTAL

A Perkin-Elmer SCIEX ELAN 6100 DRC ICP mass spectrometer, equipped with an HGA-600 MS electrothermal vaporizer and a Model AS-60 autosampler, was used in this work. Pyrolytic graphite coated tubes were used throughout. The experimental conditions for both the ELAN 6100 DRC and the HGA-600 MS are given in Table 11.

A PTFE tube of 80 cm and 6 mm i. d was used to connect the HGA-600 MS to the plasma torch. The instrument was controlled by the ELAN 6100 DRC software, which permitted full control of all Dynamic Reactions Cell parameters such as gas type, gas flow, and power settings. The instrument can be sequentially operated in the standard ICP-MS mode and the DRC mode in a fully automated manner using the software. The DRC is an adjustable bandpass quadrupole. The DRC permits ion-molecule reactions to take place in order to de-activate interfering polyatomic and atomic ions. The bandpass of the DRC can be used to eliminate unwanted precursors of interfering ions produced within the DRC and to limit the transmissions of (only) desired ions to the analyzing mass spectrometer. As discussed in Chapter 5, the bandpass is determined by the rf frequency and the dc voltage applied between the quadrupole rods. By proper selection of the parameters a and q , the width of the bandpass of the DRC can be

Table 11. Instrumental operating parameters and data acquisition protocols of the Perkin-Elmer SCIEX ELAN 6100 DRC ETV-ICP-MS.

<u>ICP mass spectrometer</u>	
RF power	1100 W
Coolant Ar flow rate	16.0 L min ⁻¹
Auxiliary Ar flow rate	1000 mL min ⁻¹
Carrier Ar flow rate	900 mL min ⁻¹
Sampler and skimmer	Platinum
<u>Dynamic Reaction Cell parameters</u>	
Quadrupole rod offset	-5 V
Cell rod offset	-10 V
Cell path voltage	-20 V
Ammonia flow rate	Variable (0.05-2.2 mL min ⁻¹)
<u>HGA-600 MS electrothermal vaporizer</u>	
Sample volume	20 µL
Dry Step	10 s ramp, 100°C for 30 s
Pyrolysis Step	5 s ramp, 100°C for 7 s
Vaporization Step	0 s ramp, 2500°C for 6 s
Clean up Step	1 s ramp, 2650°C for 3 s
<u>Data acquisition</u>	
Dwell time	20 ms
Scan mode	Peak-hopping
Points per spectral peak	1
Signal measurement mode	Integrated
MS resolution	0.7 u at 10% peak height

specifically adjusted for every analyte isotope. When $a \approx 0$ the quadrupole is in rf only operation; in this case, q defines the low mass boundary of the stability region. Changing the rf-frequency allows the variation of q . Thus, with decreasing frequency, the low mass cut-off is increased. The application of a dc-potential between the rod pairs introduces a high mass cut-off. The operation of the HGA-600 MS was completely computer controlled.

6.2.1 Standards and Reagents

High purity argon gas (99.995%, Matheson Gas Products, Ottawa, Ontario, Canada) was used. Solutions were prepared with ultra-pure water obtained from a Milli-Q water purification system (Millipore Corp., Mississauga, ON.). The glacial acetic acid used was high purity grade (Seastar Chemicals Inc., B.C. Canada). The Cr solutions were prepared by serial dilution of 1000 $\mu\text{g/mL}$ stock solution (Delta Scientific, Mississauga, ON). The Mg (Delta Scientific, Mississauga, ON) and Si (SPEX Industries, Metuchen, NJ, USA) solutions were prepared by serial dilution of 10 mg/mL stock solution. Ammonia gas used was high purity gas (Praxair Products Inc., Mississauga, ON).

6.3 RESULTS AND DISCUSSION

6.3.1 Optimization of DRC Operating Parameters

The selection of an appropriate reaction gas is important (as discussed in Chapter 5) especially since one of the criteria is that the reaction gas reacts faster with interfering polyatomic ions than with the analyte isotope of interest. The reaction gas selected for this study was ammonia. As previously discussed, the stability of the ions in the quadrupole is related to the a and q parameters. After the selection of the reaction gas, the

appropriate DRC bandpass should then be determined. This was done by scanning the ion signal as a function of the q parameter for the blank and the analyte solution. The scan range was between $q = 0.05$ and $q = 0.9$. The blank solution and the standard solution for SN were prepared using 1% (v/v) acetic acid (HOAC) to obtain a solution containing a carbon matrix which, when nebulized into the plasma will produce carbon-based polyatomic ions identical to those produced by the ETV. The optimization for q was done for both SN and ETV sample introduction systems. For both SN and ETV, using the standard mode (i.e. DRC off), the signal was obtained using $q = 0.25$ and $a = 0$. When using ammonia gas in the reaction cell it is important to optimize a and q in order to minimize and suppress reactions which may lead to new unwanted interferences [224]. The value of q was optimized using the DRC mode (for Mg, Cr and Si isotope ions), with a value of $a \sim 0.005$. As has been mentioned in Chapter 5, the ions are normally stable in the range $0 < q < 0.908$ [222]. Figure 30 shows the normalized signals for (a) Mg, (b) Cr and (c) Si isotopes ions (Mg and Cr at 5 ng mL^{-1} , Si at 50 ng mL^{-1} in 1% v/v HOAC) as a function of the q parameter using SN sample introduction. The ammonia gas flow rate used was 0.9 mL min^{-1} . For $^{24}\text{Mg}^+$ and $^{26}\text{Mg}^+$ the optimum stability parameter q obtained was about 0.5. The optimum q value obtained for $^{52}\text{Cr}^+$ and $^{53}\text{Cr}^+$ was approximately 0.5. For $^{28}\text{Si}^+$, $^{29}\text{Si}^+$ and $^{30}\text{Si}^+$, $q = 0.4$ was obtained. Figure 31 shows an example of the normalized signals as a function of the q parameter: (a) blank, 1% (v/v) HOAC, and (b) 5 ng mL^{-1} Mg in 1% (v/v) HOAC. The $^{26}\text{Mg}^+$ analyte ion shows a maximum signal at about $q = 0.5$. The blank signal shows a maximum at about $q = 0.25$. This suggests that operating with $q > 0.25$ obviously suppresses the chemical reaction which creates the

Figure 30. Optimization of q (with $a = 0.005$) using SN for (a) Mg (5 ng mL^{-1}), (b) Cr (5 ng mL^{-1}), (c) Si (50 ng mL^{-1}) isotope ions in a mixed solution. The solution was prepared in 1% (v/v) acetic acid (HOAC). The flow rate of NH_3 gas used was 0.9 mL min^{-1} .

Figure 31. Optimization of q (with $a = 0.005$) using SN ICP-MS. Ion signals at $m/z = 26$ for blank (1% (v/v) HOAC), standard solution of Mg (5 ng mL⁻¹) in 1% (v/v) HOAC. The flow rate of NH₃ gas used was 0.9 mL min⁻¹

interference. This means that it is important to optimize q for maximum analyte ion signal transmission. For the blank solution (1% v/v HOAC), the q values for $^{24}\text{Mg}^+$, $^{52}\text{Cr}^+$, $^{53}\text{Cr}^+$, $^{28}\text{Si}^+$, $^{29}\text{Si}^+$ and $^{30}\text{Si}^+$ were 0.35, 0.2, 0.25, 0.25, 0.3, and 0.3, respectively.

Using ETV sample introduction, the q parameter was also optimized. Figure 32 shows the normalized analyte signals obtained for (a) 100 pg Mg (at $m/z = 24, 26$), (b) 100 pg Cr (at $m/z = 52, 53$), (c) 0.5 ng Si (at $m/z = 28, 29, 30$) as a function of the q parameter. The NH_3 gas flow rate used for q optimization was 0.9 mL min^{-1} . The analyte solutions were prepared using ultra-pure water. The maximum q parameter value obtained for $^{52}\text{Cr}^+$ and $^{53}\text{Cr}^+$ was about 0.5. For $^{24}\text{Mg}^+$ and $^{26}\text{Mg}^+$, and $^{28}\text{Si}^+$, $^{29}\text{Si}^+$ and $^{30}\text{Si}^+$ the maximum q value obtained was near 0.45.

6.3.2 Effect of Ammonia Gas Flow Rate at $m/z = 52$ and 53

After choosing the operating q for the DRC mode, it is important to optimize the NH_3 gas flow rate which corresponds to the pressure of the reaction cell. In general, for intense polyatomic ion interferences or slow reactions, a high gas flow rate is required [222]. The reactivity of ammonia gas with background species and analyte ions was investigated using SN and ETV techniques. Figure 33 shows the effect of ammonia gas flow rate on reducing the interference of polyatomic ions from $^{12}\text{C}^{40}\text{Ar}^+$ with $^{52}\text{Cr}^+$ using SN. The signals at $m/z = 52$ were monitored as a function of the reaction gas for the 1% (v/v) HOAC (the blank), the standard in ultra-pure water and the standard in 1% (v/v) HOAC. The signal for $^{12}\text{C}^{40}\text{Ar}^+$ at $m/z = 52$ in the blank solution was proportionally reduced as the NH_3 gas flow rate was increased, suggesting a fast reaction of the NH_3 gas with the $^{12}\text{C}^{40}\text{Ar}^+$ argide. The results show that the blank signal decreased from 10^4 counts per second (cps) to less than 100 cps at the NH_3 gas flow rate of 0.95 mL min^{-1} .

Figure 32. Optimization of q (with $a = 0.005$) using ETV-ICP-MS for (a) Mg (100 pg), (b) Cr (100 pg), (c) Si (0.5 ng) isotope ions. The solutions were prepared in ultra-pure water. The flow rate of NH_3 gas used was 0.9 mL min^{-1} .

Figure 33. Effect of NH_3 gas flow rate using SN ICP-MS on background signal (1% (v/v) HOAC), the analyte signal for $^{52}\text{Cr}^+$ (5 ng mL^{-1}), the analyte signal for $^{52}\text{Cr}^+$ (5 ng mL^{-1}) in 1% (v/v) HOAC, and the signal to background ratio (S/B) at $m/z = 52$. The q value was 0.45 and a was 0.005.

The analyte signal for Cr 5 ng mL⁻¹ in aqueous solution (i.e. standard) and for Cr 5 ng mL⁻¹ in HOAC showed an initial rapid decrease since the predominant component of the signal is from ¹²C⁴⁰Ar⁺. The signal then showed an increase due to collisional focusing of the analyte mass in the DRC [229]. This means that significant amounts of axial kinetic energy are lost, corresponding to the energy losses predicted from the collision cross-section, and ions are focused towards the centre of the quadrupole device. The number of ions transmitted by the quadrupole will therefore increase as the flow rate of ammonia gas increases until maximum is reached and ion transmission starts to decay again. The analyte signal slowly started to decrease as the NH₃ gas flow rate was increased to 2.2 mL min⁻¹. The slow decrease of this signal could be due the scattering of the analyte or perhaps due to the slow reaction of the NH₃ gas with the analyte. Figure 33 shows a nearly 2.5 orders of magnitude suppression of ¹²C⁴⁰Ar⁺. This is reflected by an increase in the signal to background (S/B) ratio as the NH₃ gas flow rate was increased to 0.95 mL min⁻¹. The S/B then decreased as the gas flow rate was further increased.

For the blank (1% (v/v) HOAC), the ¹³C⁴⁰Ar⁺ signal at m/z = 53 showed (Fig. 34) a fast decrease as the NH₃ gas flow rate was increased. Figure 34 illustrates that ¹³C⁴⁰Ar⁺ ion counts apparently decreased at a nearly the same rate as that of ¹²C⁴⁰Ar⁺ (Fig. 33). This is reasonable since the argides of both carbon isotopes should react similarly with ammonia. The analyte ion signals at m/z = 53 due to a solutions containing the 5 ng mL⁻¹ Cr standard alone and in the presence of 1% (v/v) HOAC are presented in Figure 34. The response curves (Fig. 34) initially showed a fast decrease because ¹³C⁴⁰Ar⁺ ion predominated the composition of the signal at m/z = 53. The same response curve showed a faster decrease for the ¹²C⁴⁰Ar⁺ ion signal at m/z = 52 (Fig. 33). This is reflected

Figure 34. Effect of NH_3 gas flow rate using SN ICP-MS on the background signal (1% (v/v) HOAC), the analyte signal for $^{53}\text{Cr}^+$ (5 ng mL $^{-1}$), the analyte signal for $^{53}\text{Cr}^+$ (5 ng mL $^{-1}$) in 1% (v/v) HOAC, and the signal to background ratio (S/B) at $m/z = 53$. The q value was 0.45 and a was 0.005.

in the S/B ratio of 99 for $^{52}\text{Cr}^+$ and 22 for $^{53}\text{Cr}^+$. These results showed that $^{13}\text{C}^{40}\text{Ar}^+$ ion counts were decreased by about three orders of magnitude at an ammonia flow rate of 0.95 mL min^{-1} . The S/B ratio reached maximum at a flow rate of 0.95 mL min^{-1} for NH_3 gas.

The effect of using the DRC with the ETV-ICP-MS was also investigated. Figure 35a shows the extent to which the interference of the $^{12}\text{C}^{40}\text{Ar}^+$ polyatomic ion affects $^{52}\text{Cr}^+$ when the ETV sample introduction was used. Figure 35a shows the ETV-ICP-MS background signal for $20\text{ }\mu\text{L}$ of blank solution (ultra-pure water) and the signal for 100 pg of Cr vaporized at 2500°C at the standard mode. The appearance time for the $^{52}\text{Cr}^+$ signal was earlier than that for the $^{12}\text{C}^{40}\text{Ar}^+$ background; however, there was significant temporal overlap of the two signals caused by the continuous release of carbon from the ETV during the high temperature vaporization step. This resulted in a very low signal to background (S/B) ratio (at 2500°C) of about 0.9 for 100 pg Cr .

The attenuation of the $^{12}\text{C}^{40}\text{Ar}^+$ polyatomic ion by ammonia gas in the DRC is shown by Figure 35b which shows the ETV-ICP-MS signals for the blank and the $^{52}\text{Cr}^+$ signal at an NH_3 gas flow rate of 0.9 mL min^{-1} . At this NH_3 gas flow rate, the $^{12}\text{C}^{40}\text{Ar}^+$ signal was reduced considerably; there was also some reduction in the counts for $^{52}\text{Cr}^+$ may be due to analyte scattering or slow reaction of analyte with the ammonia gas.

The effect of the NH_3 gas flow rate on the integrated ETV-ICP-MS $^{12}\text{C}^{40}\text{Ar}^+$ ion signal showed a very similar effect to that obtained with the solution nebulization. Figure 36 shows that the analyte signal (100 pg Cr) first decreased rapidly because the predominant signal was from the $^{12}\text{C}^{40}\text{Ar}^+$ ion. The signal then showed a small increase due to collisional focusing. Finally with increasing gas flow rates the signal slowly

Figure 35. ETV-ICP-MS signals at $m/z = 52$ (a) standard mode, (b) DRC mode for ultra-pure water (blank), and 100 pg Cr. Vaporization temperature was 2500°C. NH_3 flow rate with DRC mode was 0.9 mL min⁻¹.

Figure 36. Effect of NH₃ gas flow rate on the integrated ETV-ICP-MS signals: background signal (ultra-pure water), the analyte signal for $^{52}\text{Cr}^+$ (100 pg), and the signal to background ratio (S/B) at $m/z = 52$. The q value was 0.45 and a was 0.005.

decreased as a result of scattering of the analyte by the DRC gas at higher pressures. The $^{12}\text{C}^{40}\text{Ar}^+$ ion signal counts (Fig. 36) shows an optimum S/B ratio at 0.9 mL min^{-1} NH_3 gas corresponding to a decrease in the $^{12}\text{C}^{40}\text{Ar}^+$ counts of about three orders of magnitude. This demonstrates a fast reaction of ammonia gas with carbon-argides.

The effect of using DRC-ETV-ICP-MS at $m/z = 53$ was also investigated. Figure 37 showed the integrated ETV-ICP-MS signal as a function of NH_3 gas flow rate. The ion counts for the $^{13}\text{C}^{40}\text{Ar}^+$ (blank) shows a faster decrease than the analyte ion signal (100 pg Cr). At the optimum flow rate of 0.9 mL min^{-1} , the ion counts for $^{13}\text{C}^{40}\text{Ar}^+$ decreased by about three orders of magnitude, giving a S/B ratio of 29.

The limits of detection (LOD) for Cr isotope ions ($^{52}\text{Cr}^+$ and $^{53}\text{Cr}^+$) using ETV-ICP-MS at a vaporization temperature of 2500°C are summarized in Table 12. The LOD values were obtained for $^{52}\text{Cr}^+$ and $^{53}\text{Cr}^+$ in both the standard and the DRC mode (3σ blank, $n = 7$). The NH_3 gas flow used in the DRC mode was 0.9 mL min^{-1} . The sensitivity is given as the blank (ultra-pure water) subtracted integrated counts for 100 pg of Cr. The LOD values, when expressed as concentration (ng mL^{-1}) for a $20\text{ }\mu\text{L}$ solution volume, show an improvement in the LOD values. Even though when using the DRC mode the signal intensity for $^{52}\text{Cr}^+$ was reduced by 30%, the LOD values for $^{52}\text{Cr}^+$ improved by a factor of 50. The LOD value (0.74 pg) for $^{53}\text{Cr}^+$ using the DRC mode is about five orders of magnitude better than that obtained with the standard mode. Table 12 shows that using the $^{52}\text{Cr}^+$ isotope gives a better LOD (0.23 pg) than that obtained using $^{53}\text{Cr}^+$ (0.74 pg). Under certain ETV conditions, it may even be advantageous to use $^{53}\text{Cr}^+$ in spite of its lower sensitivity [70]. For the analysis of chromium by ETV-ICP-MS, Grégoire and

Figure 37. Effect of NH₃ flow rate on the integrated ETV-ICP-MS signals: background signal (ultra-pure water), the analyte signal for ⁵³Cr⁺ (100 pg), and the signal to background ratio (S/B) at m/z = 53. The q value was 0.45 and a was 0.005.

Table 12 Limits of detection for ^{52}Cr and ^{53}Cr at the standard and the DRC mode. The NH_3 gas flow rate at the DRC mode was 0.9 mL min^{-1} .

	^{52}Cr			^{53}Cr		
	no DRC	with DRC	I F*	no DRC	with DRC	I F*
	(standard)			(standard)		
Net counts/100pg	47676	33419		5184	4064	
n	3	3		3	3	
% RSD	9	1.1		4.6	1.3	
Sensitivity (cps/pg)	476.8	334.2	0.70	51.8	40.6	0.78
Blank (cps)	53445	327		933	248	
n	3	7		3	7	
σ (counts)	1816	26		63	10	
LOD (pg)	11	0.23	50	3.6	0.74	4.9

*Improvement Factor

Sturgeon [70] have suggested that the $^{53}\text{Cr}^+$ is the isotope of choice since the abundance of the ^{13}C isotope (1.1%) is much less than that of ^{12}C isotope (98.9%). This may be true also when using chemical modifiers because in this case the analyte signal could be enhanced but the carbon argide was also increased [92]. This is not the case when using DRC-ETV-ICP-MS where the main purpose is to attenuate the carbon-argide ion. This shows that carbon argide interferences can be attenuated at both $m/z = 52$ and $m/z = 53$ which allows low levels of chromium to be successfully determined.

6.3.3 Determination of Magnesium at $m/z = 24$ and 26

The determination of magnesium in the presence of a carbon matrix is problematic due to the formation of $^{12}\text{C}^{12}\text{C}^+$ and $^{12}\text{C}^{14}\text{N}^+$ whose signals interfere with magnesium isotopes at $m/z = 24$ and 26, respectively. In order to investigate if these interferences could be reduced by reaction with ammonia gas, the signals at $m/z = 24$ and 26 were monitored for a 1% (v/v) HOAC blank (carbon matrix) solution, a standard solution ($5 \text{ ng mL}^{-1} \text{ Mg}$) in ultra-pure water, and a standard solution ($5 \text{ ng mL}^{-1} \text{ Mg}$) containing 1% (v/v) HOAC. Figure 38 shows response curves for SN-ICP-MS signals as a function of NH_3 gas flow rate using solution nebulization (SN) sample introduction. The background signal ($^{12}\text{C}^{12}\text{C}^+$) at $m/z = 24$ showed a decrease with increasing ammonia flow rate. The signal from the Mg standard alone decreased as the flow rate of NH_3 gas was decreased. The signal of the standard in a carbon matrix initially showed a rapid decrease in $^{12}\text{C}^{12}\text{C}^+$ ion counts (Fig. 38); then, the signal increased due to collisional focusing of the analyte ions in the DRC [229]. However, the signal then showed a slow decrease as the NH_3 gas flow was increased. Figure 38 shows that the S/B ratio reached maximum at an ammonia flow rate of 0.8 mL min^{-1} .

Figure 38. Effect of NH_3 gas flow rate using SN ICP-MS on background signal (1% (v/v) HOAC), the analyte signal for $^{24}\text{Mg}^+$ (5 ng mL^{-1}), the analyte signal for $^{24}\text{Mg}^+$ (5 ng mL^{-1}) in 1% (v/v) HOAC, and the signal to background ratio (S/B) at $m/z = 24$. The q value was 0.45 and a was 0.005.

The signals at $m/z = 26$ for the standard alone (5 ng mL^{-1}) and the standard (5 ng mL^{-1}) in 1% (v/v) HOAC (Fig. 39) decreased at about the same rate as the signal at $m/z = 24$, suggesting that $^{24}\text{Mg}^+$ and $^{26}\text{Mg}^+$ may be scattered or perhaps reacted at about the same rate with ammonia. However, Figure 39 shows that the ion count signal due $^{12}\text{C}^{14}\text{N}^+$ at $m/z = 26$ decreased more rapidly as did ion counts for $^{12}\text{C}^{12}\text{C}^+$ (Fig. 38) as the ammonia flow rate was increased. This suggests that the $^{12}\text{C}^{14}\text{N}^+$ polyatomic ion is more reactive with ammonia gas than $^{12}\text{C}^{12}\text{C}^+$. The results in Figure 39 also show that $^{12}\text{C}^{14}\text{N}^+$ ion counts were decreased by about two orders of magnitude at ammonia flow rates of 0.85 mL min^{-1} , giving a maximum S/B ratio at this flow rate.

The reduction of $^{12}\text{C}^{12}\text{C}^+$ and $^{12}\text{C}^{14}\text{N}^+$ ion counts (signals) at $m/z = 24$ and 26, was also investigated using DRC-ETV-ICP-MS. A $20\text{ }\mu\text{L}$ solution of blank (ultra-pure water) and analyte (100 pg Mg) were vaporized at 2500°C . Figure 40 shows the change in the integrated counts at $m/z = 24$ as a function of ammonia gas flow rate. The ion count signal of the analyte (Fig. 40) decreased slowly with increasing ammonia flow rate, whereas the ion counts of $^{12}\text{C}^{12}\text{C}^+$ decreases more rapidly, resulting in the attenuation of polyatomic interferences from $^{12}\text{C}^{12}\text{C}^+$. The ion counts for $^{12}\text{C}^{12}\text{C}^+$ decreased by about 1.5 orders of magnitude at the optimum flow rate (0.5 mL min^{-1}), at which the greatest S/B ratio was obtained. The ion count signals at $m/z = 26$ is shown in Figure 41. As in SN (Figs. 38 and 39), magnesium at $m/z = 24$ (Fig 40) and $m/z = 26$ (Fig. 41) scattered or may be reacted essentially at the same rate with ammonia gas. The signal at $m/z = 26$ (Fig 41) shows that $^{12}\text{C}^{14}\text{N}^+$ reacts more rapidly with ammonia than $^{12}\text{C}^{12}\text{C}^+$. Both $^{24}\text{Mg}^+$ and $^{26}\text{Mg}^+$ showed maximum S/B at flow rates of about 0.5 mL min^{-1} .

Figure 39. Effect of NH_3 gas flow rate using SN ICP-MS on background signal (1% (v/v) HOAC), the analyte signal for $^{26}\text{Mg}^+$ (5 ng mL^{-1}), the analyte signal for $^{26}\text{Mg}^+$ (5 ng mL^{-1}) in 1% (v/v) HOAC, and the signal to background ratio (S/B) at $m/z = 26$. The q value was 0.45 and a was 0.005.

Figure 40. Effect of NH₃ gas flow rate on the integrated ETV-ICP-MS signals: background signal (ultra-pure water), the analyte signal for ²⁴Mg⁺ (100 pg), and the signal to background ratio (S/B) at m/z = 24. The q value was 0.5 and a was 0.005.

Figure 41. Effect of NH₃ gas flow rate on the integrated ETV-ICP-MS signals: background signal (ultra-pure water), the analyte signal for ²⁶Mg⁺ (100 pg), and the signal to background ratio (S/B) at m/z = 26. The q value was 0.5 and a was 0.005.

The use of ammonia gas improved the LOD for $^{24}\text{Mg}^+$ and $^{26}\text{Mg}^+$. These results are summarized in Table 13, which also lists the integrated counts for $^{24}\text{Mg}^+$ and $^{26}\text{Mg}^+$, obtained both in the standard and the DRC mode. These results show that the LOD for ^{24}Mg improved from 23 pg to 7.8 pg. For $^{26}\text{Mg}^+$ there was an improvement in the LOD from 18.6 pg to 7.4 pg. The improvements in LODs for Mg isotopes are relatively small compared to that for Cr. However, these results clearly show that ammonia gas reduces the background signal intensities at $m/z = 24$ and 26 , which indicates that the polyatomic ions $^{12}\text{C}^{14}\text{N}^+$ and $^{12}\text{C}^{12}\text{C}^+$ are attenuated within the DRC.

6.3.4 Effect of Ammonia Gas on the Determination of Silicon

The measurement of silicon is also interfered by carbon and nitrogen containing polyatomic ions. In this study, the effectiveness of ion molecule reactions in reducing polyatomic interferences using ammonia as the DRC gas was investigated. As for previous studies, the DRC was coupled with both SN and ETV sample introduction devices.

The first study in this series involved SN sample introduction and the effect of ammonia gas flow rates on the determination of the three silicon isotopes at m/z 28, 29 and 30. For the SN experiments, a 1% (v/v) HOAC was used to provide for the production of carbon-containing polyatomic species, a standard Si solution containing 50 ng mL⁻¹ of Si prepared in ultra-pure water, and a 50 ng mL⁻¹ Si standard solution prepared in 1% (v/v) HOAC.

Figure 42 shows response curves for Si and polyatomic ion intensities at $m/z = 28$ as a function of ammonia gas flow rate. The $m/z = 28$ signal derived from the 1% (v/v) HOAC showed a steep and rapid decrease as the flow rate of ammonia gas was increased.

Table 13. Limits of detection for ^{24}Mg and ^{26}Mg at the standard and the DRC mode. The NH_3 gas flow rate at the DRC mode was 0.5 mL min^{-1} .

	^{24}Mg			^{26}Mg		
	no DRC	with DRC	I F*	no DRC	with DRC	I F*
	(standard)			(standard)		
Net counts/100pg	14452	8618		5930	1373	
n	3	3		3	3	
% RSD	16.4	7.7		8.7	3.6	
Sensitivity (cps/pg)	144.5	86.2	0.60	59.3	13.7	0.23
Blank (cps)	15657	3576		3607	584	
n	3	7		3	7	
σ (counts)	1124	223		367	34	
LOD (pg)	23	7.8	2.9	19	7.4	2.5

*Improvement Factor

Figure 42. Effect of NH_3 gas flow rate using SN ICP-MS on background signal (1% (v/v) HOAC), the analyte signal for $^{28}\text{Si}^+$ (50 ng mL^{-1}), the analyte signal for $^{28}\text{Si}^+$ (50 ng mL^{-1}) in 1% (v/v) HOAC, and the signal to background ratio (S/B) at $m/z = 28$. The q value was 0.45 and a was 0.005.

The ion counts for $^{14}\text{N}^{14}\text{N}^+$ and $^{12}\text{C}^{16}\text{O}^+$ at $m/z = 28$ (Fig 42) were decreased by about five orders of magnitude at flow rate of 1.1 mL min^{-1} . The signals corresponding to the standard alone and the standard in 1% (v/v) HOAC showed a slow and steady decrease while the ammonia gas flow was increased. A maximum S/B ratio was obtained at an ammonia gas flow rate of 1.1 mL min^{-1} . The effect of ammonia gas on $^{14}\text{N}^{14}\text{N}^+\text{H}^+$, $^{12}\text{C}^{16}\text{O}^+\text{H}^+$ and $^{13}\text{C}^{16}\text{O}^+$ at $m/z = 29$ was also investigated. Figure 43 shows that the ion count response curve for $^{14}\text{N}^{14}\text{N}^+\text{H}^+$, $^{12}\text{C}^{16}\text{O}^+\text{H}^+$ and $^{13}\text{C}^{16}\text{O}^+$ at $m/z = 29$ decreased more slowly than the ion counts at $m/z = 28$. This can be attributed to the fact that at this m/z , nitrogen-containing polyatomic ions are present at the same time that we are introducing more nitrogen into the system in the form of ammonia. Clearly, at the same time, carbon-containing polyatomic ions are dramatically reduced since the background signal was reduced by about five orders of magnitude at the optimum ammonia flow rate of 1.2 mL min^{-1} . At this flow rate, the maximum S/B ratio was achieved. Figure 44 shows the effect of ammonia gas on ion intensities at $m/z = 30$. The ion signals due to 1% (v/v) HOAC, (blank) standard alone and standard in 1% (v/v) HOAC, all initially increased when the ammonia gas flow rate was increased from 0.1 to 0.4 mL min^{-1} . At higher flow rates, all three response curves started decreasing. The ion counts for $^{14}\text{N}^{16}\text{O}^+$, and $^{13}\text{C}^{16}\text{O}^+\text{H}^+$ at $m/z = 30$ were higher than those due to the standard alone and the standard in 1% (v/v) HOAC. This suggests that there is no reduction in the interfering polyatomic ions or there are new polyatomic ions produced which also interfere at $m/z = 30$. This effect is probably not due to the reaction of Si with the ammonia since the same effect was not observed at $m/z = 28$ and 29 under the same experimental conditions. This may be attributed to the combination of nitrogen and oxygen ($^{14}\text{N}^{16}\text{O}^+$) resulting in increased

Figure 43. Effect of NH_3 gas flow rate using SN ICP-MS on background signal (1% (v/v) HOAC), the analyte signal for $^{29}\text{Si}^+$ (50 ng mL^{-1}), the analyte signal for $^{29}\text{Si}^+$ (50 ng mL^{-1}) in 1% (v/v) HOAC, and the signal to background ratio (S/B) at $m/z = 29$. The q value was 0.45 and a was 0.005

Figure 44. Effect of NH_3 gas flow rate using SN ICP-MS on background signal (1% (v/v) HOAC), the analyte signal for $^{30}\text{Si}^+$ (50 ng mL^{-1}), the analyte signal for $^{30}\text{Si}^+$ (50 ng mL^{-1}) in 1% (v/v) HOAC. The q value was 0.45 and a was 0.005.

concentrations of interfering polyatomic ions.

When using ETV-ICP-MS, the determination of Si becomes a problem, especially at elevated ETV vaporization temperatures where excessively high concentrations of carbon-based polyatomic ions are formed in the argon plasma. Figure 45a shows the extent of interferences by $^{14}\text{N}^{14}\text{N}^+$ and $^{12}\text{C}^{16}\text{O}^+$ ions with $^{28}\text{Si}^+$. Figure 45a shows the ETV-ICP-MS background signals for 20 μL of ultra-pure water (blank), and for 0.5 ng of Si vaporized at 2500°C in the standard mode (without using ammonia gas). Figure 45a clearly shows that there is a significant spectral interference between the $^{28}\text{Si}^+$ signal and the $^{14}\text{N}^{14}\text{N}^+$ and $^{12}\text{C}^{16}\text{O}^+$ background blank signal. Applying the ammonia gas reduced the extent of the interference by reducing the background (Figure 45b) signal. However, there was also a reduction in the counts for $^{28}\text{Si}^+$ probably due to the scattering of the analyte or could be that some of the analyte reacted with the ammonia gas.

The effectiveness of the DRC with ETV-ICP-MS in reducing polyatomic interferences with Si was investigated. For these experiments a 20 μL Si solution containing 0.5 ng Si was used. Figure 46 shows that the ion counts for $^{14}\text{N}^{14}\text{N}^+$ and $^{12}\text{C}^{16}\text{O}^+$ at $m/z = 28$ are not rapidly decreasing as the ammonia flow rate was increased. At the optimum flow rate of 0.9 mL min^{-1} of NH_3 gas, the ion count rate for the blank decreased by about three orders of magnitude (Fig 46). The effect of ammonia gas on the signals at $m/z = 29$ are shown in Figure 47. The rate of reaction of $^{14}\text{N}^{14}\text{N}^+\text{H}^+$, $^{12}\text{C}^{16}\text{O}^+\text{H}^+$ and $^{13}\text{C}^{16}\text{O}^+$ at $m/z = 29$ is apparently similar to that of $^{14}\text{N}^{14}\text{N}^+$ and $^{12}\text{C}^{16}\text{O}^+$ with ammonia gas. The analyte ion signal was only slowly decreasing under the same experimental conditions. A maximum S/B ratio was obtained at 0.9 mL min^{-1} NH_3 gas flow rate (Fig. 47). At $m/z = 28$ and 29, the optimum flow rate for the ETV was less than

Figure 45. ETV-ICP-MS signals at $m/z = 28$ (a) standard mode, (b) DRC mode for ultra-pure water (blank), and 0.5 ng Si. Vaporization temperature was 2500°C. NH_3 flow rate at the DRC mode was 1.1 mL min⁻¹.

Figure 46. Effect of NH_3 gas flow rate on the integrated ETV-ICP-MS signals: background signal (ultra-pure water), the analyte signal for $^{28}Si^+$ (0.5 ng), and the signal to background ratio (S/B) at $m/z = 28$. The q value was 0.45 and a was 0.005.

Figure 47. Effect of NH_3 gas flow rate on the integrated ETV-ICP-MS signals: background signal (ultra-pure water), the analyte signal for $^{29}Si^+$ (0.5 ng), and the signal to background ratio (S/B) at $m/z = 29$. The q value was 0.45 and a was 0.005.

that for the SN. This may be attributed to the dry plasma of the ETV system, where the amount of hydrogen and oxygen introduced to the plasma was reduced substantially. Combinations of hydrogen and oxygen with carbon or nitrogen are source of polyatomic ion interferences. Figure 48 shows the effect of ammonia gas flow rate on ion signals at $m/z = 30$ when using ETV-ICP-MS. The response curves obtained were very similar in nature to those obtained when using the SN sample introduction. The analyte ion signal intensity was less than the blank. The ion counts for $^{14}\text{N}^{16}\text{O}^+$, and $^{13}\text{C}^{16}\text{O}^+\text{H}^+$ are plotted as function of NH_3 gas flow rate on a linear scale (Fig. 49). The gas flow rate was varied between 0.05 and 1 mL min^{-1} . This clearly shows the behaviour of the background signal.

The effect of ammonia on the reduction of polyatomic interferences at $m/z = 28$, 29 and 30 is reflected in the LOD values which are summarized in Tables 14 and 15. The LOD using the DRC mode for ^{28}Si and ^{29}Si and ^{30}Si were obtained at an ammonia gas flow rate of 0.9 mL min^{-1} . These results show that $^{28}\text{Si}^+$ gave better LOD than for $^{29}\text{Si}^+$ and $^{30}\text{Si}^+$ when using ammonia as a reaction gas. The LOD for ^{28}Si (Table 14) was 24.2 pg with the DRC mode which is an improvement factor of 16.1. Table 14 also shows that the LOD for ^{29}Si was 70.6 pg even though the improvement factor in LOD was 15.1, which is almost the same as for ^{28}Si . When using NH_3 gas for DRC-ETV-ICP-MS, the LOD for ^{30}Si suggests that $^{30}\text{Si}^+$ is not an appropriate isotope selection for the ETV-ICP-MS determination of Si. The LOD for ^{30}Si was very high and the improvement factor was only 1.4.

Figure 48. Effect of NH₃ gas flow rate on the integrated ETV-ICP-MS signals: background signal (ultra-pure water), the analyte signal for ³⁰Si⁺ (0.5 ng). The *q* value was 0.45 and *a* was 0.005

Figure 49. Effect of NH_3 gas flow rate on polyatomic ions ETV-ICP-MS signals for $^{30}Si^+$ (0.5 ng). The q value was 0.45 and a was 0.005.

Table 14. Limits of detection for ^{28}Si and ^{29}Si at the standard and the DRC mode.

The NH_3 gas flow rate at the DRC mode was 0.9 mL min^{-1}

	^{28}Si			^{29}Si		
	no DRC	with DRC	I F*	no DRC	with DRC	I F*
	(standard)			(standard)		
Net counts/1000pg	51300	1736		1835	272	
n	3	3		3	3	
% RSD	18.6	4.7		22.7	2.2	
Sensitivity (cps/pg)	51.3	1.7	0.03	1.8	0.3	0.17
Blank (cps)	325967	552		11252	204	
n	3	7		3	7	
σ (counts)	6663	14		653	6.4	
LOD (pg)	390	24.2	16.1	1070	70.6	15.1

*Improvement Factor

Table 15. Limits of detection for ^{30}Si at the standard and the DRC mode. The NH_3 gas flow rate at the DRC mode was 0.9 mL min^{-1} .

	^{30}Si		
	no DRC (standard)	with DRC	I F*
Net counts/1000pg	4688	24445	
n	3	3	
% RSD	111.4	24.4	
Sensitivity (cps/pg)	4.7	24.4	5.2
Blank (cps)	86736	91939	
n	3	7	
σ (counts)	1031	3898	
LOD (pg)	660	478	1.40

*Improvement Factor

6.4 SUMMARY AND CONCLUSIONS

The results obtained in this work demonstrate the effectiveness of using a Dynamic Reaction Cell in reducing carbon-based polyatomic ions when ETV sample introduction is used. The NH_3 gas was effective in reducing interferences by $^{40}\text{Ar}^{12}\text{C}^+$ and $^{40}\text{Ar}^{13}\text{C}^+$ ions with $^{52}\text{Cr}^+$ and $^{53}\text{Cr}^+$, respectively. The LODs obtained for Cr indicated that both ^{52}Cr and ^{53}Cr isotopes can be used for DRC-ETV-ICP-MS determinations.

The application of the DRC for the ETV-ICP-MS determination of Mg was also proven to be advantageous. Polyatomic ion interferences from $^{12}\text{C}^{12}\text{C}^+$ ion with $^{24}\text{Mg}^+$ and $^{12}\text{C}^{14}\text{N}^+$ ions with $^{26}\text{Mg}^+$ were substantially reduced and both isotopes can be used equally well for determination of Mg.

The use of NH_3 as a reaction gas for the reduction of polyatomic ion interferences by $^{14}\text{N}^{14}\text{N}^+$, $^{12}\text{C}^{16}\text{O}^+$ with $^{28}\text{Si}^+$; by $^{14}\text{N}^{14}\text{N}^1\text{H}^+$, $^{12}\text{C}^{16}\text{O}^1\text{H}^+$ and $^{13}\text{C}^{16}\text{O}^+$ with $^{29}\text{Si}^+$ was not fully successful. However, the LODs for $^{28}\text{Si}^+$ and $^{29}\text{Si}^+$ were greatly improved over conventional ICP-MS. Ammonia gas was not effective in reducing polyatomic interferences by $^{14}\text{N}^{16}\text{O}^+$ and $^{13}\text{C}^{16}\text{O}^1\text{H}^+$ with $^{30}\text{Si}^+$. It is possible that the use of another reaction gas or mixture of gases may be more effective in reducing polyatomic ions at $m/z = 28, 29$ and 30 ; however, that research was beyond the scope of this work.

The results for the S/B studies indicate that the experimental conditions required to optimize the DRC are the same for SN and ETV for Cr only. For Mg and Si, the S/B studies show that optimization must be completed separately, indicating that the process of attenuation of polyatomic ions interfering with these elements is different in dry and wet plasmas.

One of the limitations of the DRC is the shortage of fundamental information available on specific ion-molecule reactions. The level of knowledge in thermodynamics required makes it difficult for casual users to develop their own strategies for attenuating interference by polyatomic ions.

The DRC was initially developed to address problems associated with polyatomic ion interferences in the low mass range. However, there are other spectral interferences that also need to be studied using the DRC technology. For example, the production of analyte oxide polyatomics can make difficult the determination of some of the rare earth elements. Also, isobaric interferences such as that of $^{187}\text{Re}^+$ with $^{187}\text{Os}^+$ cannot be resolved even by using high-resolution mass spectrometer. A resolution in excess of 60 million is required to resolve these two ions. At present, chemical separations are required prior to analysis.

Clearly, the application of a Dynamic Reaction Cells in ICP mass spectrometry is in its infancy. Further developments and research on collision gas compositions may yield at some time in the future an ICP mass spectrometer free of polyatomic ion interferences of all kinds.

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