EVALUATION OF ELECTROTHERMAL VAPOURIZATION AS A METHOD OF SAMPLE INTRODUCTION FOR THE ICP-MS AND

DETERMINATION OF TRACE LEVELS OF TITANIUM, GALLIUM AND INDIUM IN THE CENTRAL PACIFIC GYRE

by

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SANNY CHAN

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in

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We accept this thesis as confirming to the required standard.

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Department of <u>Chemistry</u>

The University of British Columbia Vancouver, Canada

Date January 13, 1993

Abstract

The analysis of trace metals in the ocean is a relatively new field of study. Since the elements of interest often exist at picomolar levels, this work demands analytical methods with ultra low detection limits. The inductively coupled plasma mass spectrometer (ICP-MS), with its improved detection powers, has proven to be a valuable tool. However, problems resulting from the method of sample introduction, such as low transport efficiency, still prevail.

The first objective of this work was to evaluate an electrothermal vaporization (ETV) device as a method of sample introduction for the ICP-MS. Absolute precisions obtained ranged from 2-10% RSD after modifications to improve the performance of the ETV were made. Once optimized, improvements for both sensitivity and detection limits resulting from increased transport efficiency and matrix separation were found to be more than two orders of magnitude for most of the elements studied. Several elements suffered from isobaric interferences, and therefore exhibited improvements in sensitivity and detection limits of only one order of magnitude. In general, detection limits were in the range of 0.057-72 fmol. Acceptable absolute precision was obtained for multielement determination of three isotopes. Better precision was obtained for isotope ratio measurements. Five or more isotopes may be simultaneously analysed when using isotope ratio techniques. The use of freon to form volatile metal halides was instrumental in the analysis of refractory metals. Signals obtained from refractory metals, previously erratic and poorly defined in graphite furanace atomic absorption spectroscopy (GFAAS), were well defined with large increases in sensitivity as a result of freon addition. Matrix effects were observed using the ETV-ICP-MS in the analysis of seawater samples, thus requiring the use of standard additions or isotope dilution.

The second objective of this thesis was to determine trace levels of Ti, Ga and In in the central Pacific gyre. Little is known about Ti and Ga distributions in the ocean and virtually nothing is known about In behavior in seawater. Dissolved titanium

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exhibited elevated surface values (~100 pM), a subsurface minimum (~50 pM) and a bottom maximum (~230 pM). Enhanced Ti concentrations at 400-1000 m, correlating with the mid-depth oxygen minimum in this region were observed. This Ti distribution, in combination with the limited published data, suggests both atmospheric and bottom sources, removal via scavenging throughout the water column, and a mobilization in the O₂ minimum.

The dissolved Ga distribution shows intermediate surface values (~17 pM), a subsurface increase (~20 pM), an intermediate depth minimum (5-10 pM) and a bottom maximum (~30 pM). On combining the present data with the previous data pool, the observed trends suggest that Ga has an atmospheric input. Sub-surface and intermediate water concentrations may be a result of vertical processes combining scavenging removal and regeneration, or from horizontal advection. The dissolved In distribution was similar to Ga, with intermediate surface values (~0.3 pM), a subsurface maximum (~0.45 pM), a mid-depth minimum (~0.12 pM), and higher concentrations at deep waters (~0.28 pM). Because this is the first reliable profile of indium to be produced, there are no other data to compare with. A comparison of In distribution with Ga show some similarities. The In/Ga ratio, however, changes linearly with depth suggesting that the two elements are controlled by different input and removal processes or rates in the water column. All three elements demonstrate enrichment with respect to AI by comparison with their crustal abundances. Although the Ti/AI enrichment (11 times) may be explained by preferential removal of AI, the degree of Ga/AI and In/AI enrichments (750 and 1500 times) suggest that the source may not be of crustal abundance.

Work to improve the existing chelating resin, a TSK 8-hydroxyquinoline, has afforded a 30-fold improvement of resin capacity. Chelating capacity obtained for this resin is $34 \pm 3 \mu$ mole Cu(II) / g resin. A new resin was synthesized by coupling 5-amino 8-hydroxyquinoline to a new solid support, Affi-Prep®, gave similar chelating capacities.

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List of Abbreviations

ac	alternating current
amu	atomic mass unit
ASV	anodic stripping voltammetry
AV	research vessel "Aleksandr Vinogradov"
CPS	counts per second
CSV	cathodic stripping voltammetry
DC	direct current (plasma)
dc	direct current
DDI	distilled deionized
DIN	direct injection nebulizer
DSI	direct sample insertion
EDTA	ethylene diaminetetraacetate
ETV	electrothermal vaporization
eV	electron volt
FAAS	flame atomic absorption spectroscopy
FAES	flame atomic emission spectroscopy
g	gram
GC	gas chromatograph
GFAAS	graphite furnace atomic absorption spectroscopy
9p ⁺	statistical weight for state p+
9q	statistical weight for state q
h	Planck's constant
HPLC	high performance liquid chromatograph
i.d.	inner diameter
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma atomic emission spectroscopy
ICP-MS	inductively coupled plasma mass spectrometry
К	degrees Kelvin
k	Boltzmann's constant
kg	kilogram
KHP	potassium acid phthalate
kW	kilowatt
Μ	molar
m/z	mass to charge ratio
mA	milliampere

mbar	millibar
MCA	multichannel analyser
m _e	mass of an electron
MHz	megahertz
min	minute
mL	millilitre
μm	micrometer
mm	millimeter
μmole	micromole
mmole	millimole
MS	mass spectrometry
MΩ	megaohm
Ν	normality
n _e	free electron number density
ng	nanogram
nM	nanomolar
nmole	nanomole
NMR	nuclear magnetic resonance
n _p +	species number density in state p+
nq	species number density in state q
o.d.	outer diameter
pg	picogram
PJ	peak jumping
рМ	picomolar
ррb	parts per billion
ppm	parts per million
RF	radio frequency
RSD	relative standard deviation
S	second
SIM	single ion monitoring
SSMS	spark source mass spectrometry
Ti	ionization temperature
V	volt
W	watt
ΔE _{pq}	energy difference between between states p+ and q

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To my Mother and Father

"There may be work without results,

But never will there be results without work."

Unknown

Chapter 1 Introduction

1.1 History of the ICP-MS

The original concept of the inductively coupled plasma mass spectrometer (ICP-MS) can be traced back to A. L. Gray in 1970 at the UK branch of Applied Research Laboratories¹. It had become apparent, especially to geologists, that inductively coupled plasma atomic emission spectroscopy (ICP-AES) suffered from matrix interferences from line-rich elements such as calcium, aluminum and iron. In addition, rare earth elements exhibit complex spectra and generally have poor detection limits in atomic emission spectroscopy. A better method of analysis was clearly needed. The proposed new method of analysis was a mass spectrometric method capable of accepting solid samples and providing multielement analysis at levels down to ng/g levels with an analysis time of several minutes. This criterion was based on the performance of spark source mass spectrometry (SSMS)² which was the technique used in low level, multielement work at the time. However, spectra obtained from SSMS were complicated due to non uniform energy transfer resulting in the formation of molecular fragments. These spectra required time consuming interpretation as well as long sample analysis times. Furthermore, throughput for SSMS was about one to two samples per day. In spite of these drawbacks, SSMS gave uniform and low detection limits across the periodic table.

Atmospheric pressure plasmas appeared to be a good ion source for several reasons. High gas temperatures (~5000 K) could be obtained in the case of a DC plasma. In addition, long analyte residence times of a few milliseconds in the plasma resulted in efficient energy transfer to the analyte. However, the ions produced could not be mass analysed until they were transferred to a high vacuum. A feasibility study of an atmospheric ion source into a high vacuum mass analyser was performed using

a small DC plasma, which had a small tail flame that was easily accessible to ion extraction. This first system gave high sensitivity, 10⁴-10⁵ counts s⁻¹ per ppm Co, with almost no background interference. Sample introduction was facilitated by an ultrasonic nebulizer and gave isotope ratio measurements with <0.5% RSD³.

Unfortunately, the DC plasma suffered from matrix effects and had low ionization efficiencies for elements with high ionization energies (>9 eV). Inefficient ionization was due to the small amounts of sample solution that actually reached the high temperature plasma core. This is a phenomenon common in DC plasmas. High levels of NO, from the acid sample matrix with ionization energies of 9.4 eV dictate the ionization equilibrium for analytes with high ionization energies⁶.

The most attractive answer to the above limitations was the inductively coupled plasma, ICP, first proposed in 1975. In 1977, interest from the Ames Laboratory in the US resulted in a collaboration with the British Geological Survey to further the development of this technique. By June of 1978, Houk et al. (Ames Laboratory) produced the first spectra of the major ions, Ar+, H+, and O+ from the ICP. Later that year, the first spectra of analyte ions (Mg+, Cr+, Mn+, Co+, Cu+, Rb+, Ag+) at 50 µg/mL concentration were produced and resulted in the first publication on ICP-MS³.

The first commercial ICP-MS instrument was introduced at the 1983 Pittsburgh Conference by Sciex with the Elan® followed closely by the VG PlasmaQuad® from VG Isotopes in May of that same year. In 1988, over 175 ICP-MS instruments were in use world wide. This number has risen to over 600 instruments in operation in 1992.

1.2 Operation of the ICP-MS

1.2.1 System Overview

A schematic of the ICP-MS system is shown in Figure 1.1, and the primary method for sample introduction, the Meinhard nebulizer and spray chamber, is shown in Figure 1.2.



Figure 1.1 Overview of the ICP-MS system. (1) channel electron multiplier (2) quadrupole (3) ion lens (4) skimmer cone (5) RF coils (6) ICP torch (7) torch box (8) sampler cone



Figure 1.2 Schematic of the double-pass spray chamber (1) solution up-take (2) nebulizer (3) spray chamber (4) nebulizer gas inlet.

A peristaltic pump pumps the sample into the nebulizer where it is transformed to the aerosol form. Droplets not condensed on the double-pass spray chamber walls are transported to the ICP by the argon carrier gas.

In the ICP, the aerosol droplets are desolvated, vaporized, atomized and ionized. Some of the ions are extracted into a high vacuum region first by a sampling cone, followed by a skimmer cone. The ions then pass through a series of electrodes, or lenses, which focus the ions into the mass spectrometer. Only ions with the selected mass-to-charge ratio are transmitted through the quadrupole mass analyser and subsequently detected by a channel electron multiplier. Pulses from the detection system are fed to a microprocessor-controlled multichannel scaler data acquisition unit. Another microprocessor looks after the overall instrument operation. The overall system is controlled by a personal computer.

1.2.2 Sample Introduction

The most common form of sample introduction is pneumatic solution nebulization, by a Meinhard/concentric nebulizer (Figure 1.2). Gas, typically argon, flows quickly through an opening that concentrically surrounds a capillary tube causing a pressure reduction at the tip. This has the effect of drawing the sample solution from the capillary tube, and due to the high velocity of the gas, causes the formation of droplets with diameters between 1 to 50 μ m.

Sample solution may be introduced in two ways. Sample may be transported to the tip of the nebulizer by a peristaltic pump or at natural rates governed by the speed of the gas flow. Under normal use, the sample is transported by a peristaltic pump to insure signal stability.

Aerosol (10-50 μ m) from the nebulizer is separated according to size in the spray chamber. The most common design of spray chamber is the double-pass spray chamber based on the design of Scott et al.⁴ (Figure 1.2). Aerosol droplets from the nebulizer enter the chamber (approximately 2.5 cm i.d.) and subsequently through a concentric tube of larger diameter at 180° incident to the initial direction of motion. Only the droplets that are not condensed or impacted onto the spray chamber walls (typically <10 μ m) are transported to the ICP. The larger droplets are prevented from reaching the plasma since they may not completely desolvate in the plasma. These larger droplets would only contribute to water loading in the plasma. In this type of system (nebulizer and spray chamber), the unused portion constitutes 99% of the sample solution and is normally pumped away from the spray chamber and discarded.

Solution nebulization is only one of several methods of sample introduction. Alternate methods will be presented later.

1.2.3 The ICP

The ICP torch (Figure 1.3) is made of three concentric quartz tubes surrounded by a copper induction coil. This coil is connected to a high frequency generator typically operating at 27.12 MHz with output powers of 1-2 kW. Argon flows through all three tubes. The gas sheath in the outer quartz tube has functions as both the support gas for the plasma and the coolant gas for the quartz tube.



Figure 1.3 Schematic of the ICP torch.

Sample is introduced through the central channel by the aerosol gas. Once inside the plasma, several processes take place. The analyte aerosol is dried, vaporized, atomized and ionized in the central channel. These processes are made possible by the high gas temperatures (7000-10000 K^{5-8}) of the plasma.

The auxiliary gas in the middle gas channel serves to push the plasma away from the injector tip, thus preventing a torch melt down.

To form the plasma, a spark from a Tesla coil is used to produce seed electrons and ions in the support gas to make the gas electrically conducting. Once this occurs, the plasma forms. The high frequency alternating currents in the induction coil generates magnetic fields with their lines of force parallel to the tube walls. Seed electrons and ions are accelerated in a circular flow. When the current in the induction

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coil reverses direction, the magnetic field and the eddy currents also reverses. The accelerated ions and electrons collide with the support gas to cause further ionization as well as intense heating.

Some characteristics of an ideal ion source are listed below⁷.

- 1. Complete and single ionization of all elements
- 2. Inert chemical environment
- 3. No background interference
- 4. Accept solution, solids, gases
- 5. Reproducible ionization conditions
- 6. Inexpensive

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7. Ease of operation

Unfortunately, no atomic source has yet been developed with all of the above listed characteristics. However, the ICP does possess many of these favorable attributes. Analyte residence time in the ICP is relatively long, approximately 2 to 3 milliseconds. Combined with the high temperature from the plasma, the ICP gives almost complete ionization of the analyte. Argon plasmas provide chemically inert ionization environments, thus, atomic ions generally will not react to form molecular species. These combined properties result in few molecular interferences over most of the mass range. Aqueous and gaseous samples are readily analysed by the ICP while solids may also be analysed with some difficulty. It should be noted that some background interferences are found with the ICP originating from the Ar support gas and the air which is entrained into the plasma. These interferences include ⁴⁰Ar+, $^{41}ArH^+$, $^{56}(ArO)^+$, $^{16}O^+$, $^{32}O_2^+$, $^{17}(OH)^+$, $^{28}(N_2)^+$, $^{29}(N_2H)^+$, $^{80}(Ar_2)^+$. In such instances, alternate isotopes, which do not suffer from interferences can be substituted. Unfortunately, an ICP-MS is quite an expensive technique: the instrument is costly (~\$500,000), and its maintenance and operating costs are substantial. In addition, considerable skill and training is required to become an efficient and knowledgeable user.

1.2.4 Analyte Excitation & Ionization

The function governing the ion population in the ICP is the Saha equation⁵⁶:

$$\frac{n_p + n_e}{n_q} = \frac{2g_p + q_q}{g_q} (2\pi m_e k T_i)^{1.5} h^{-3} \exp\left(\frac{-\Delta E_{pq}}{k T_i}\right)$$
(1.1)

where n_e is the free electron number density, n_p^+ and n_q are the ion and atom concentrations respectively, g_p and g_q are the statistical weights of the two states p and q, m_e is the mass of an electron, h is Planck's constant, ΔE_{pq} is the energy difference between levels p and q (in this case, the ionization energy), T_i is the ionization temperature and k is Boltzmann's constant. Thus, according to the Saha equation, analyte ion density at the sampling aperture in the central channel of the plasma depends locally on:

- i. Analyte atom concentration in the plasma
- ii. Ionization temperature, T_i, of the plasma
- iii. Electron population ne of the plasma
- iv. Ionization energy of the element
- v. Statistical weights between the atom and ion energy states

In addition to the above processes, the analyte atom concentration in the plasma also depends on the sample introduction transport efficiency. Recently, Gray and Date⁸ have determined that the ionization temperature, T_i, is 9000 K in an ICP by monitoring the response (from the mass spectrometer) to known concentrations of elements with a large difference in ionization energies. A curve generated for the Saha equation (Figure 1.4) with T_i at 9000 K shows that for over 75% of the periodic table, the degree of ionization in the ICP is almost 100%.

1.2.5 Ion Extraction

The ion extraction system used (Figure 1.5) consists of two extraction apertures where the analyte ions are taken from atmospheric pressure to a high vacuum

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Figure 1.4 Degree of ionization calculated from the Saha equation for 59 elements between Li - U. Adapted from Ref. 6.

environment where mass analysis may be performed. Ions are extracted from the central channel by the sampling aperture which ranges from 1.0 mm to 1.2 mm. These apertures are drilled to the tips of cones made from metals of high conductivity such as aluminum, copper, nickel or platinum.

Behind the sampling aperture, gas pressures are reduced to about 5 mbar by a rotary pump. The gas expanding into the lower pressure region reaches velocities exceeding the speed of sound in a distance of less than one aperture diameter. In this region, the temperature drops rapidly and reactions which could change the gas composition are effectively frozen out. The free jet formed is bounded by a shock wave known as the barrel shock. A second shock wave, called the Mach disc, occurs about 10 mm behind the sampling aperture. Beyond the Mach disc, the flow becomes subsonic and remixes with the surrounding gas.

The skimmer aperture (typically from 0.7 mm to 1.0 mm) is positioned at a distance less than the Mach disc (~ 6.5 mm) behind the sampling cone. Once past the skimmer aperture, the extracted gas enters a region where the pressure is low enough that the mean free path (distance between collisions) is longer than the system length. At this point, the ions can be focused by the ion lenses.

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Figure 1.5 Ion extraction and ion lens configuration. (1) photon stop (2) skimmer cone (3) sampler cone

1.2.6 Ion Lens and Mass Analyser

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The function of the ion lens is to focus as many ions as possible from the ion cloud behind the skimmer into an axial beam at the quadrupole mass analyser entrance. A photon stop in the ion lens stack prevents photons emitted from the plasma to reach the channel electron multiplier detector.

The quadrupole mass analyser operates as a tunable variable bandpass mass filter where ions are resolved (0.5-1.0 amu resolution) on the basis of the mass-to-charge (m/z) ratio. This method of separation is different from conventional mass spectrometers, such as magnetic sector and time of flight mass spectrometers, where resolution is achieved on the basis of momentum and kinetic energy respectively. The quadrupole resolution is independent of momentum and kinetic energy, therefore, unit mass resolution is retained even when the sampling ion population possesses a wide range of velocities along the quadrupole axis¹¹. Advantages of the quadrupole over magnetic sector mass analysers include lower costs, a more compact size, shorter scan times and higher durability.

Although a thorough, quantitative description of quadrupole operation is beyond to the scope of this thesis, it is useful to understand, in a qualitative manner, the operations of a quadrupole mass analyser.

The quadrupole mass analyser consists of four relatively short, parallel, circular electrodes (Figure 1.6) arranged symmetrically around the ion beam. A combination of dc and ac (RF) potentials are applied to each rod. Rods opposite to each other are electrically connected and are attached to the same side of the dc potential. Thus, one pair of electrodes is connected to the positive side of the dc source while the other pair is connected to the negative terminal. The RF ac potentials are also applied at 180° out of phase with respect to each pair of electrodes. These combined fields cause the ions to oscillate about the central axis.



Figure 1.6 Quadrupole mass analyser and axis orientation.

Consider the quadrupole electrodes in the X-Z plane, when only the RF ac potential is applied. These electrodes spend 1/2 of the ac cycle at a positive potential and the other 1/2 of the cycle at a negative bias. During the positive 1/2 cycle, the positively charged ion beam is repelled by the positive bias on the electrodes, and is in essence, focused towards the centre of the Z-axis. Alternately, during the negative 1/2 cycle, the positively charged ion beam is accelerated towards the negatively biased electrodes. Whether the ion will be removed during its time spent in the quadrupole will be governed by the time the ion needs to reach the negatively biased

electrode (during the negative ac cycle) which, in turn, is dependent on the magnitude of the applied potential, the duration of the applied potential, and the m/z ratio of the ion. The ion velocity in the Z-axis is also important. Although the applied fields do not affect the velocity in the Z-axis, and this velocity is not involved in mass resolution, the ion must be traveling slow enough to spend at least one ac cycle in the quadrupole.

Now consider the application of a positive dc potential to the electrodes on the X-Z plane. If an ion is very heavy, it would only feel the effects of the average potential applied, that is, the dc potential. The small periods of time that the electrodes are at a negative bias will have little or no affect on the heavy ions. Conversely, a very light ion will be affected much more by the changing ac potential (in comparison to the heavier ion) and will cause it to collide with the electrode during the negative 1/2 cycle. Thus, ions below a given m/z ratio will be eliminated by the defocusing action of the negative portion of the ac potential. Thus, the electrodes in the X-Z plane act as a high-pass mass filter.

Consider the electrodes in the Y-Z plane whose applied potentials are equal in amplitude by opposite in sign to those on the X-Z plane. In this instance, the ac potential acts to focus the lighter ions onto the Z-axis and prevent them from striking the dc negatively biased electrodes. Since the heavy atoms are affected by the average value of the applied negative potential, they will be eliminated above some critical m/z ratio. In this instance, the electrodes in the Y-Z plane act as a low-pass mass filter.

In order for an ion to travel from the source to the detector, it must be stable in both the X-Z and Y-Z planes. Thus, the amplitude of the RF and dc potential determine the transmitted mass. In addition, it can be shown that the resolution is determined by the ratio of the RF and ac potentials. One of the limitations of the quadrupole mass analyser is that the resolution attainable is about 1 amu which is not enough to separate an isobaric oxide peak from an elemental peak (e.g. ⁴⁰Ar¹⁶O+ from ⁵⁶Fe+).

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1.2.7 Ion Detection

lons transmitted through the quadrupole are detected by a channel electron multiplier. Typically, a continuous dynode channel electron multiplier is used. Channel electron multipliers are made from heavily lead-doped glass and are relatively small (1 mm id x 70 mm). The tube is curved for reasons that will be addressed shortly.

A high voltage is applied (-3000 V to -3500 V) to the multiplier. The applied voltage has two functions. The first is to replenish the charge on the channel wall. The second is to accelerate the secondary electrons, initially with low energy, fast enough such that upon collision with the surface, they will create efficiently secondary electrons. Positively charged ions from the mass analyser are attracted to the negative voltage in the funnel of the multiplier. The multiplier is placed off axis to reduce the chance of detecting stray photons.

Once a positive ion strikes the funnel, at least one secondary electron is emitted. The secondary electrons accelerate down the tube, due to the applied potential, until it impacts with the wall. Collisions with the wall free other secondary electrons and the avalanche builds exponentially. With high electron fluxes, such as those found in the exit of the multiplier, residual gas in the multiplier can be ionized. These gaseous ions have the potential to accelerate back to the input of the multiplier and begin another avalanche of electron. This is called ionic feedback. The curvature of the multiplier allows these positively charged ions to travel only a short distance before encountering the multiplier wall. At this stage of the multiplier, the gain is small and the effects are negligible. The cloud of ~ 10^7 - 10^8 electrons (originating from each positive ion) leaving the multiplier are gathered by a collector electrode.

There are numerous advantages to using a channel electron multiplier including excellent signal-to-noise ratios, low dark counts (<0.5 counts s⁻¹), stable dynode surface that can be exposed to air without degradation, low power

requirements for operation, tolerance to high operating pressure (up to 10⁻⁵ mbar) and a reasonable long life. Linear response is typically 5 to 6 orders of magnitude.

Two modes of operation are possible: pulse counting mode and analog mode. In pulse counting mode, the output pulses above a set discriminator level are counted. In essence, individual ions may be counted giving the highest possible sensitivity. In the analog mode, the applied voltage is only -1500 V. The electrons are collected by the normal collector electrode, but the current is then amplified by a linear amplifier. The response of the amplifier is fast enough that the output accurately reflects the current.

1.3 Advantages and Limitations of the ICP-MS

Some of the advantages of the ICP-MS system includes:

- 1. Low background level
- 2. High sensitivity
- 3. Simple spectra
- 4. Isotope ratio capabilities
- 5. Fast sample throughput (when using nebulizer)
- 6. Multielement capabilities

Background levels obtained on the ICP-MS are very low, ~10-50 counts s⁻¹. Coupled with high sensitivities obtained from pulse counting, the ICP-MS system is able to achieve very low detection limits. The spectra obtained from the ICP-MS are very simple due to the high energy inert ICP ion source, which also effectively desolvates, volatilizes, atomizes and ionizes most elements. Very few molecular species are formed resulting in few isobaric interferences. ICP-MS is a very fast, sequential multielement technique that is capable of isotope measurements. Isotope ratio measurements are important for isotope dilution techniques as well as in stable isotope tracer experiments which are often used in biological uptake studies. The speed of this technique is due mostly to the ability to ionize the sample at ambient

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pressures rather than at low pressures as is common with other mass spectrometric techniques such as SSMS.

With this in mind, some of the limitations of the system are also presented. These include:

- 1. Limited solution introduction
- 2. Matrix induced analyte enhancement/suppression
- 3. High initial and maintenance costs

As with inductively coupled plasma atomic emission spectroscopy, ICP-AES, sample introduction poses one of the greatest limitations to the overall system. The most common form of sample introduction is solution nebulization which suffers from low transport efficiency and the introduction of large quantities of O, N, S, and CI from the water or acid matrix into the ICP. For example, ArO+ and ArN+ interfere with the major isotopes of Fe. Tan and Horlick have studied extensively the molecular interferences that originate from various acid matrices¹⁰. In addition to low transport efficiencies, the nebulization and sampling systems cannot tolerate high salt matrices due to the clogging of the nebulizer and the sampling cone orifice. Concentrated mineral acid matrices are also undesirable as they lead to accelerated cone deterioration. Typically, sample introduction is limited to dilute, well-behaved solutions and gaseous samples. Solid samples require different methods of sample introduction and will be discussed later.

Signal suppression observed in the ICP-MS is higher than that observed in ICP-AES system and has been found to be mass dependent. It has been proposed that the increased analyte suppression is related to space charge effects¹¹. Space charge effects originate from the electrostatic interactions in the ionic beam. Once the ion beam has been extracted, coulombic interactions cause the positively charged ions to repel each other. The lighter ions are repelled from the central ion beam more than the heavier ions, resulting in lower overall extraction

efficiency for lighter elements. High initial investment and the high maintenance costs are other disadvantages of the ICP-MS system.

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1.4 Alternate Methods of Sample Introduction

The method of sample introduction has often been the weak link in elemental analysis. Solution nebulization, the most commonly form of sampling introduction, is plagued with low transport efficiency and molecular oxide interferences. Attempts to remedy these problems, as well as extending the types of samples which may be analysed have been the focus of much recent research effort.

1.4.1 Increased Transport Efficiency

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The transport efficiency of a Meinhard nebulizer and spray chamber system is <1%. Much of the solution is removed in the spray chamber because the droplets formed by the nebulizer are too large.

Wiederin et al. has recently developed a direct injection nebulizer (DIN) that works on the same principle as the pneumatic nebulizer¹². The DIN is capable of producing a very fine aerosol which can be introduced directly into the plasma resulting in very high transport efficiencies. Low flow rates (20 μ L/minute) are used and so only small sample sizes are required. Oxide to ion ratios were found to increase and the system facilitated on-line standard addition to reduce sample preparation time¹³.

A direct sample insertion (DSI) device, developed by Karanassios and Horlick, also gives very high transport efficiencies¹⁴. This device is essentially a small cup made of graphite, Mo or Ta. The analyte is carried by the cup directly to the base of the plasma, through the aerosol injector tube, where it is dried and vaporized, by the heat of the plasma. The analyte vapor is transported directly into the plasma resulting in 100% transport efficiency. Another advantage of this device is that both solution and solid (in the form of a powder) samples may be analysed with this device. An electrothermal vaporization device (ETV), developed by Shen and Caruso, also improves the analyte transport efficiency to the ICP-MS¹⁵. This device is very similar to the graphite furnace used in GFAAS where the sample is dried, ashed and vaporized in a graphite tube. The analyte vapor is then transported to the ICP-MS for analysis. As with the DSI device, both solutions and powdered solid samples may be analysed.

1.4.2 Reduction of Molecular Interference

One of the major sources of interference originates from the acid matrix which is a source of oxygen for the molecular oxide interferences. Advances have been made in this area to modify the method of sample introduction such that the analyte is transferred to the plasma in the absence of oxide interference.

Slight modifications to the normal (nebulizer) mode of instrument operation included a cryogenic desolvation system which is effective in reducing the oxide molecular interferences by several orders of magnitude. This is achieved by "freezing out" the matrix prior to aerosol introduction into the ICP¹⁶. Several studies have shown that introducing small amounts of a molecular gas, such as N₂¹⁷⁻²⁰, Xe²¹ or an organic solvent²⁰ into the plasma gas also reduces molecular oxide and chloride interferences, prevalent interferences in Fe+ (ArO+) and As+ (ArCl+) analyses. For example, addition of Xe (ionization energy 12.1 eV) shifts the ionization energy ~15 eV). In effect, the presence of Xe 'caps' the maximum ionization energy within the plasma and prevents the ionization of molecular species. These modifications maintain the favorable characteristics of the nebulizer, namely high sample throughput and simplicity of operation.

Alternately, changing the method of sample introduction can be used to eliminate oxide molecular interferences. Karanassios' and Horlick's^{14,22,23} direct sample insertion device was shown not only to offer 100% transport efficiency, but also to reduce signals attributed to molecular oxide and hydride interferences. The ETV has been shown to reduce ArO+ interference with ⁵⁶Fe by removing the matrix prior to vaporization. Laser ablation sample introduction have been utilized by several groups to vaporize solid samples directly into the plasma²⁴.

1.4.3 On-Line Matrix Separation

On-line preconcentration and matrix separation have also been studied by several groups. Caruso et al. used on-line anodic stripping voltammetry (ASV) to preconcentrate copper and cadmium²⁵. Samples are passed through the ASV cell where desired analytes are stripped from a predetermined volume of sample at a fixed potential. Output from the ASV cell was directed to waste. Once the sample volume had completely passed through the ASV cell, the cell was washed and the flow then redirected to the ICP and the potential applied was such that the analyte was released. The ASV method of sample introduction has the dual effect of concentration as well as simultaneously eliminating matrix effects such as high concentrations of Na and U.

McLaren et al. has developed an on-line preconcentration system using a chelating resin in micro-columns for simultaneous determination of Fe, Mn, Co, Ni, Cu, Zn, Cd, Pb in seawater such that accurate analyses of these trace metals may be performed in less than ten minutes²⁶. This greatly reduces the sample preparation time and the sample size required for determining these metals in high salt matrices.

1.4.4 Speciation Studies

Typically, analysis with ICP-MS gives information on total analyte concentration without any information on analyte speciation. Combining the separation technology of HPLC with detection by ICP-MS allows speciation studies to be carried out. One element that has been studied using this technique is As. Some species of arsenic (As^{III}, As^V) are highly toxic while others (methylarsonic acid, dimethylarsonic acid, arsenobetaine) are much less toxic. Since normal mode ICP-MS can only

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determination total As content, it cannot accurately produce information regarding the As toxicity of a sample.

Arsenic is monoisotopic and has an isobaric interference from ArCl+ at m/z 75. The use of HPLC as a method of sample introduction also allows one to separate chloride containing species from the As signal²⁷⁻³⁰. High sensitivity of the ICP-MS has allowed these As studies to be performed for samples with very low concentrations or for systems that are sample limited (such as human urine or dogfish analyses). Other elements that have been analysed using HPLC-ICP-MS include Zn³¹ and Cr³².

1.4.5 Electrothermal Vaporization Sample Introduction

One of the approaches to sample introduction that overcomes several of the shortcomings of solution nebulization, such as low transport efficiency and molecular interferences, is electrothermal vaporization (ETV) ICP-MS. Electrothermal vaporization devices have found application in ICP-AES since 1974.³³ In ETV-ICP-AES, the furnace vaporizes the analyte. Analyte vapor is then transported to the ICP where atomization and ionization occurs. This is different from GFAAS where the analyte is vaporized and atomized in the graphite furnace. Until recently, little attention has been paid to the use of ETV as a method of sample introduction for an ICP-MS. The addition of Freon (CHF₃) forms volatile metal halides within the furnace. The metal halides are then introduced to the plasma where they are atomized and ionized. The use of Freon has opened up the use of ETV-ICP-MS for analysis of refractory metals.

To date, only two ETV designs have been used in research. The first is simply a commercial electrothermal device modified from GFAAS to allow for analyte transport to the ICP. The second is a "home-made" design by Park et al. first developed at the University of Toronto³⁴. Both of these systems will be considered in some detail.

The "home-made" system (Figure 1.7) consisted of a Re filament encased in a glass envelope. Temperature control for the Re filament is achieved using a variable

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voltage transformer. An O-ring seals the glass envelop to an Al base. Argon is allowed to flow through the device and carry the analyte to the ICP.



Figure 1.7 Electrothermal vaporization device developed by Park et al.³⁵ (1) nebulizer gas inlet (2)-Teflon® block (3) electrodes (4) metal filament (5) quartz cover (6) aluminum base

It was found that a considerable fraction of the sample was lost as a result of condensation on the glass walls. However, if the analyte vapor was cooled to form microparticles, condensation losses become negligible. Cooling of the analyte vapor may be accomplished by introducing the carrier gas in a tangential fashion. The envelop volume above the filament was optimized to 5 mL. Larger envelop volumes resulted in temporal peak broadening due to excessive dilution. Smaller volumes give rise to high aerosol condensation on the glass envelop.

This device was used to analyse metals, such as Mo, W³⁵, platinum group metals³⁶, Tl³⁷, rare earth elements³⁸, Cu, Cd, and Ni³⁴. Matrix separation of Fe from the oxide interference, ArO⁺, was evident. Using this system, they found that matrix effects found using the ETV was attributed to interelement compound formation on the filament rather than plasma loading effects³⁹ A comparison of ETV with DSI sample introduction system found that although both systems only required small sample
volumes, the ETV provided a more controlled environment for matrix separation⁴⁰. Typically, relative detection limits using the ETV are improved by an order of magnitude over the nebulizer ICP-MS and precision ranges from 8-19% RSD for absolute determinations and 1-2% RSD for isotope ratio measurements³⁵.

Alternately, Caruso and co-workers^{15,41} have modified a commercial Perkin-Elmer HGA-300 electrothermal unit for atomic absorption such that an argon carrier gas may be used to transport the analyte to the ICP (Figure 1.8).



Figure 1.8 Electrothermal device produced by modifying an HGA-300. (1) front adaptor (2)-cooling block (3) temperature sensor (4) graphite furnace (5) L'vov platform (6)-carrier-gas inlet (7) rear adapter (8) drying vent

Sample introduction was achieved by inserting the tip of a pipet into the furnace through the opening for the rear adapter and depositing the required amount of solution onto the platform. This device successfully showed the reduction of isobaric oxide and chloride molecular species for Fe and As respectively. Detection limits of 1.5 pg and 0.2 pg were obtained for As and Fe respectively with absolute precisions between 5-8%¹⁵.

1.5 Trace Metals in the Ocean

1.5.1 Background

The introduction of the GFAAS and, more recently, ICP-MS has provided the chemical oceanographic community with extremely useful methods for the analysis of trace metals. Prior to these analytical methods, detection limit requirements for the analysis of trace metals in seawater could not be achieved by standard instrumental methods, such as flame atomic absorption (FAAS), flame atomic emission (FAES) or inductively coupled plasma atomic emission spectroscopy (ICP-AES). Even with large concentration factors, detection limits of FAAS and FAES spectroscopy were not low enough to detect the trace amounts of analyte present in seawater. GFAAS provides the very low detection limits that are required for trace metal detection after preconcentration, however, this method is limited to relatively volatile elements. Detection limits for refractory metals and metals which formed refractory carbides and oxides remain high. The recent addition of ICP-MS allows analysis of the refractory metals not readily determined by GFAAS. Owing to the high temperatures present in the ICP, most elements are completely ionized. Combined with the increased sensitivity of the MS, the ICP-MS has proven to be a powerful tool for the analysis of trace metals. The much superior detection power of ICP-MS for most of the elements, coupled with recent advances in trace metal clean sampling methodology, permits nearly simultaneous multielement determination with far better precision and accuracy for more metals than those previously obtained using more traditional methods.

Trace metals are defined as those present in sea water at concentrations less than 1 ppm. Trace element behavior can be, in a general sense, divided into three categories. Some trace metals behave conservatively (Figure 1.9 A), that is, the concentration varies only with salinity due to very slow removal from the oceans. Slow removal from the water column leads to concentrations which are high, relative to the crustal abundance. This type of element, therefore, is accumulated in sea water until a steady state is achieved. Conservative elements, usually high in concentration, have long residence times in the oceans and include most alkali metals (such as lithium, caesium) as well as some oxy-anions of Mo and U⁴².



Figure 1.9 Three representative oceanic distributions. (A) Conservative (B) Nutrient (C) Scavenged type profiles

Some trace metals exhibit nutrient type behavior (Figure 1.9 B). These elements are not necessarily nutrients, but they do show a strong correlation with macronutrient distributions. Such distributions typically show surface depletion, due to biological uptake, and increasing concentrations with depth from release during decomposition of the organic material or dissolution of skeletal material. Some elements which show nutrient type behavior include Cd and Zn⁴².

Trace metals can also show scavenged or reactive behavior (Figure 1.9C). These elements are rapidly removed, typically by adsorption onto sinking particles, resulting in spatial and temporal variability as well as short oceanic residence times. Trace metals displaying scavenged behavior have distributions that strongly reflect the location of external sources, with concentrations in waters distant from the source markedly depleted. Such sources originate at ocean boundaries. Thus, scavenged metals are valuable as tracers for elucidating the transport and mixing mechanisms in the oceans.

One example of a good tracer is aluminum. The dominant input of AI in the North Pacific is from aeolian (atmospheric) inputs⁴³. Evidence supporting this premise is the low dissolved aluminum concentration in the low salinity surface waters of the California current (0.3 nmol/kg), where estuarine input is high, and increasing concentrations into the North Pacific subtropical gyre (5 nmol/kg). The observed AI gradient is consistent with decreasing input of aeolian particulate matter from west to east, as atmospheric dust is carried from Asia by the westerlies towards North America. Riverine input of dissolved aluminum has been found to be removed in estuarine and coastal regions, with little or no net input to the open ocean. Aluminum concentrations in the California current range from 0.3 to 5 nmol/kg.

Dissolved Al concentrations vary in the deep waters by 2 orders of magnitude from ocean to ocean. Thus, it is useful for tracing movement and mixing of deep waters. Vertical distributions of Al show a mid-depth minimum with subsequent increases in concentration in deep waters. These observations suggest a deep water source and removal throughout the water column. The proposed removal mechanism is particle scavenging, which is intensified in coastal regions. Aluminum sources to the deep ocean could be from sediment surface remineralization processes and/or diffusion out of the sediments.

1.5.2 Determination of Trace Metals

As mentioned previously, the analysis of trace metals in seawater has been limited by their presence at extremely low levels and the limited instrumental capabilities available. Large improvements in sensitivity and detection limit made possible by the ICP-MS allow many trace metals to be determined with accuracy.

Seawater, however, cannot be nebulized directly into the ICP-MS. Trace metals in seawater are present at such low levels that preconcentration is still required. In addition, high salt content (~3.5%) of the sea water matrix can not be

tolerated by the nebulizer or the sampling orifice. Thus, the desired analyte must be isolated from the sea water prior to analysis.

One of the most common methods of preconcentration is via solid-liquid phase extraction. Seawater must be pumped through a chelating resin at optimized conditions. The chelating resin selectively adsorbs the desired analytes, after which the analyte may be eluted using a relatively small volume of strong acid.

Several different chelating resins are used for such extraction and preconcentration processes. These include Chelex-100, silica immobilized 8-hydroxyquinoline and vinyl polymer (TSK) immobilized 8-hydroxyquinoline resin. Chelex-100, a commercially available resin has been utilized in extracting may of the first row transition elements^{44,45}. The advantages of using Chelex include high resin capacities (700 µmol Cu(II)/mL of resin) and commercial availability. However, Chelex suffers from undesirable swelling and contracting with changing pH. Chelex also retains significant amounts of Ca and Mg, major ions present in seawater, even after thorough rinsing.

Another commonly used resin is the silica immobilized 8-hydroxyquinoline resin, first developed by Sturgeon et al. at the National Research Council of Canada⁴⁶. Again, most of the first row transition elements as well as Cd and Pb, have been concentrated and analyzed using this resin. Unfortunately, this resin is not commercially available and has lower chelating capacities than that of Chelex-100. The silica immobilized 8-hydroxyquinoline resin exhibits good physical stability as well as faster exchange kinetics when compared to Chelex-100.

A third resin that has shown promise was first synthesized by Landing et al., where 8-hydroxyquinoline was immobilized onto a vinyl polymer resin⁴⁷. This solid phase is a highly porous, mechanically and chemically stable hydrophillic resin gel. Capacity of this resin has been reported to be as high as 20-30 μ mol Cu²⁺/mL of resin. TSK 8-hydroxyquinoline resin has been previously used to preconcentrate AI, Cd and most of the first row transition elements from organic rich freshwater samples⁴⁷.

1.5.3 Marine Geochemistry of Ti, Ga and In in Seawater

Little is known about the behavior of dissolved titanium, gallium and indium in seawater owing to difficulties in their analysis. Recent studies using adsorptive cathodic stripping voltammetry have shown dissolved titanium concentrations of 0.2-67 nM in estuarine waters⁴⁸. However, the detection limit for this method was 0.03 nM and is inadequate for determination of Ti in open surface ocean waters. Investigations using solid-liquid extraction-preconcentration similar to those described above, followed by ICP-MS analysis, show that titanium exists at concentrations of 5-300 pM in the open ocean with a concentration range in the water column of over 2 orders of magnitude⁴⁹. Dissolved titanium has a vertical distribution similar to that of copper, an element controlled by a complex combination of nutrient type cycling and scavenging, which suggests that Ti may also be controlled by such complex mechanisms. This large variability within the water column could lead to the use of titanium as a valuable tracer of ocean mixing and transport.

Recent studies of gallium by solid-liquid extraction followed by graphite furnace atomic absorption spectroscopy (GFAAS) analysis, suggest complex input and removal mechanisms govern gallium distributions in the oceans^{50,51}. Gallium concentrations found in these studies were between 2-30 pM. Earlier studies using $Fe(OH)_3$ co-precipitation followed by spectrophotometric analysis showed values over an order of magnitude higher than what is now believed⁵².

Early investigations for dissolved indium were carried out with similar solidliquid extraction followed by very time consuming (irradiation was carried out for several weeks) neutron activation analysis⁵³ and thermal ionization mass spectrometry with isotope dilution⁵⁴. Estimate values for indium concentrations in seawater from these studies ranged from 1-35 pM.

1.6 Aims of This Study

The desire to understand the factors that control the distribution of trace metals in the ocean have led to the search for sensitive and accurate techniques for their determination. The presence of these metals at extremely low concentrations as well as the complex seawater matrix in which they exist has proven to be an immense challenge to the analytical chemist. Clean techniques, such as those developed by Bruland and coworkers⁵⁵, have provided contamination control during sampling and storage, so that under proper processing and analysis, accurate and meaningful results may be obtained.

The sensitivities made possible by the ICP-MS have led to significant advancements in trace metal analysis. However, many of the second and third row transition metals and many of the main group elements are still difficult to detect with ICP-MS, even with concentration factors of 1000. Since pneumatic nebulization has a transport efficiency of <1%, an increase in transport efficiency could conceivably increase sensitivity by two orders of magnitude. Changing the sample introduction method to electrothermal vaporization has previously demonstrated increased transport efficiency and, therefore, sensitivity. Chapter 2 of this thesis is devoted to evaluating the capabilities of an ETV device for low level determinations. The increased sensitivity and lowered detection limits should make significant contributions to the determination of trace metals in seawater.

Ultra-trace metal analysis in seawater is a relatively new field of study. Little is known about the behavior of many elements in seawater due to the above mentioned instrumental limitations. Very little is known about the behavior of Ti and Ga and even less is known about In in the oceans. Titanium and Ga distributions in the eastern North Pacific region have demonstrated a bottom source and scavenged behavior in the water column. Gallium is seen to have an atmospheric source in the same region. Chapter 3 will focus on a method for determining of Ti, Ga and In in seawater. This method will be used to investigate these elements in the Central Pacific gyre.

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data, combined with previous studies from the Western Pacific gyre, will be used to further elucidate the control mechanisms of these elements in the Pacific ocean.

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The ability to preconcentrate trace metals from seawater is of vital importance in this work. To date, many of the preconcentrations have been performed by solid-liquid extraction with an 8-hydroxyquinoline immobilized resin that required in-house synthesis. Difficulties encountered in successfully synthesizing this resin led to the third portion of this thesis. Chapter 4 describes attempts to improve the synthetic route as well as the development of a possible new ion exchange resin.

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Chapter 2

Evaluation of Electrothermal Vaporization as a Method of Sample Introduction for the ICP-MS

2.1 Introduction

The introduction of the ICP-MS in 1983 has allowed great advances in trace metal analysis. Detection limits obtained by ICP-MS rivaled those of GFAAS for relatively volatile elements and surpassed GFAAS for refractory elements. Geochemists and chemical oceanographers, require even lower detection limits, reduced isobaric interferences from the acid matrix and reduced sample size requirements. Clearly, modifications to the conventional system are required.

An electrothermal vaporization device, used as a method of sample introduction, appears to be well suited to these demands. The reported increased transport efficiency of this technique should increase sensitivity thereby lowering the detection limits. Controlled drying and ashing steps should allow selective acid matrix removal and the inherently small volumes required by the ETV (10 - 50 μ L) is ideal for use with low level, sample limited analyses.

This chapter describes the optimization and evaluation of an ETV device for the purposes of ultra-trace elemental detection with applications to seawater analysis.

2.2 Experimental

2.2.1 General Instrumentation

The ICP mass spectrometer used for this work was a VG PlasmaQuad® PQ2 Turbo Plus (VG Elemental, Winsford, Cheshire, U.K.). A quartz torch made in the Fassel configuration was used for much of the work in the nebulizer and ETV modes of operation. Coolant, auxiliary and nebulizer gases were controlled by mass flow controllers. The sampling interface consisted of nickel sampling and skimmer cones with aperture diameters of 1.0 mm and 0.7 mm respectively. Vacuum in the intermediate and analyser chambers is maintained by turbo molecular pumps. Detection of the transmitted ions was performed by a channel electron multiplier and subsequent amplifiers. Typical operating parameters are shown in Table 2.1.

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Parameter	Standard Settings Used	
Cool Gas	13.75 L/min	
Auxiliary Gas	0.500 L/min	
Nebulizer Gas	0.800-0.825 L/min	
Incident Power	1350 W	
Reflected Power	~2 W (ETV), ~ 8 W (nebulizer)	
Plate Current	0.69 A	
PA grid	0.22 mA	
PA Volts	0.4 mV	
PA Filament	0.64 mV	
Extraction Lens	-100 V212.5 V	
Collector Lens	-18.49 V	
L1	-2.11 V	
L2	-77.9 V	
L3	10.68 V	
L4	-44.1 V	
Pole Bias	-4.68 V	

 Table 2.1
 Typical operating conditions for ETV and nebulizer modes.

2.2.2 Data Acquisition

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Data acquisition from the ICP-MS was performed using an on-line COMPAQ-386 personal computer equipped with VG Plasmavision® software supplied by VG Instruments. Pulses from the signal handling electronics during an acquisition were counted into memory channels of the multichannel analyser (MCA) and subsequently transferred to the computer once the acquisition had been completed.

Two modes of data acquisition were used in this work. The first mode was peak jumping (PJ) in which ion counts were acquired, sequentially, at specified masses. The second mode was single ion monitoring (SIM) where only one mass was sampled over time.

2.2.3 Solutions

All reagents were prepared using distilled deionized (DDI) water (18 M Ω , Nanopure, Barnstead). The acid used was environmental grade nitric acid (HNO₃) (Anachemia). Standard solutions were prepared by serial dilution of 1000 ppm atomic absorption standards (Johnson Matthey Inc., Seabrook, N.H.) with the appropriate acid matrix in acid leached polyethylene bottles.

2.2.4 Electrothermal Vaporization (ETV) Device

2.2.4.1 ETV Instrumentation

The electrothermal vaporization device was a MicroTherm II, also supplied by VG Elemental (Figure 2.1). The ETV furnace was a Perkin Elmer-type graphite tube (Buck Scientific) mounted between two carbon contact blocks which themselves were recessed in two nickel plated copper contact blocks. Water (15°C) was circulated at 2L/min through channels machined in the blocks. Furnace temperature was regulated by a thermister at temperatures below 650°C and by an optical pyrometer at higher temperatures. A sheath of argon gas maintained around the furnace prevented oxidation of the graphite tube during the heating cycle. This sheath was contained by a quartz ring situated around the graphite tube with the flow of argon at 1-2L/min. A small hole in the quartz ring facilitated sample introduction as well as the insertion of the carbon rod to seal the graphite furnace. A sliding probe carrier housed the nebulizer gas inlet. The system was held together by a pencil spring pack which pushed the sliding furnace block towards the stationary furnace block to facilitate contact between the graphite furnace and the carbon contacts. Analyte vapor produced during the vaporization step is then carried through the quartz tube leading from the furnace, then through Teflon transport tube which leads directly to the injector tube in the ICP torch. Freon-2,3 (CHF₃) gas (Matheson), used for refractory metals, was regulated by a mass flow controller (Edwards 1105).



Figure 2.1 ETV original furnace design. 1) Cooling water inlet 2) Cooling water outlet 3) Screw retaining spring pack 4) Argon gas inlet 5) Support rod 6) Sliding probe carrier 7) Sliding furnace block 8) Quartz shroud 9) Graphite tube 10) Carbon bush/contact 11) Stationary furnace block 12) ETV cabinet 13) Quartz tube

Sample introduction into the graphite furnace was accomplished by inserting the tip of a pipet (Eppendorf[®], NY, USA) into the furnace opening and depositing, typically, 25 μ L of solution onto the furnace wall. A graphite pencil was then used to seal the opening of the furnace in order to prevent sample loss during vaporization.

2.2.4.2 ETV Modifications

Several modifications were made to the ETV device (Figure 2.2 and Figure 2.3). The Swagelock fittings provided by VG Instruments for connecting the quartz tube from the furnace to the Teflon[®] transport tubing leaked. This posed severe air leak problems when trying to light the plasma. A "jam fitting" of a tapered quartz tube (5/32" id, 1/4" o.d.) against the Teflon[®] transport tubing inside a piece of larger ethyl vinyl acetate tubing (1/4" id, 3/8" o.d.) was found to eliminate the air leak.

Other modifications included the addition of a stronger spring to push the heating blocks together. It was found that the pencil spring provided with the ETV was not adequate in applying enough pressure to give good contact between the graphite furnace and the heating blocks. The new spring was used to push the sliding gas housing against the sliding furnace block (Figure 2.3).



Figure 2.2 Modifications to tubing configuration leading from the ETV unit to the ICP-MS.

The general mode of ICP-MS operation was also altered during ETV operation. It was found that the seal in the quartz ball-and-socket joint which connected the tubing to the torch was compromised after threading the stiff Teflon® tubing through the various holes provided in the torch box and the hood to connect the tubing to the ETV device. Again, air leaks were evident which made lighting the plasma very difficult.



Figure 2.3 Modifications to the ETV unit. (14) Additional spring

To remedy this problem, the instrument hood was left open and an aluminum sheet equipped with a welder's shield (to allow viewing of the plasma) was placed in front of the torch box to protect the operator from the UV light emitted from the plasma.

2.2.4.3 ETV Optimization

Univariate optimization parameters included torch position, nebulizer gas flo.v, ash time, ash temperature, vaporization temperature, and acquisition time. Various species were evaluated as a tune species and will be discussed later.

2.2.5 Nebulizer Mode

2.2.5.1 Nebulizer Instrumentation

A four-line peristaltic pump (Gilson) was used to mobilize the carrier flow, sample uptake and waste drainage for the nebulizer mode. The carrier flow rate was 0.6 mL per minute. Sample uptake is manually controlled by a six-way flow injection valve fitted with a 300 μ L flow loop. Typically, the carrier is 1% HNO₃. The carrier bypasses the sample loop during uptake of the six-way valve, and is redirected to transport the sample plug to the nebulizer in the inject position.

2.2.5.2 Nebulizer Optimization

Gas flows and acquisition parameters were recently optimized by a VG technician and were not re-optimized for the nebulizer work in this study. The torch position and the ion lens were tuned by aspirating a solution of 10 ppb indium continuously through the nebulizer. From the SIM mode, the signal from the 300 μ L flow injection loop was determined to be approximately 60 s long. Analyte signal was acquired for the complete duration of this signal.

2.3 Results and Discussion

2.3.1 Electrothermal Vaporization Optimization

2.3.1.1 Modifications To Obtain Better Precision

Initially, extremely poor signal precision was found for the ETV as supplied by the manufacturer. This lack of reproducibility may have been due to several factors; splattering during the drying step, poor contact between the furnace and the electrodes or the transient nature of the signal. Upon inspection of the sample during the drying stage, no splattering was observed. Poor contact between the furnace and the electrodes was ultimately found to be the largest contributor to the lack of precision. The addition of a much stronger spring to push the moveable gas inlet housing, which houses one of the electrodes, against the furnace reduced the relative standard deviation of replicate sample injections from 25 - 50% down to 3 - 8%.

It was thought that precision could again be improved further if the extremely short signal produced by the ETV could be extended to allow for more scans across the signal pulse. Elongation of the ETV signal may be achieved by ramping the vaporization step. Three types of ramping were used (Figure 2.4); a slow ramp (8 s in duration), a fast ramp (1 s in duration) and a step function to vaporization temperature were compared. Initially, an indium signal could be observed at 1200°C, thus this was the vaporization temperature selected for the step function 1

program. To elongate the ETV signal, the profiles ramped "through" the vaporization temperature. Ramp profiles started with a step function to 1000°C from the ash temperature, a ramp portion starting at 1000°C and ended at 1400°C followed by a cleaning step.

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Figure 2.4 Expanded vaporization stage for the various ramping profiles. (1) step function to vaporization temperature (2) 1 s ramp through vaporization temperature (3) 8 s ramp through vaporization temperature

The step function gave best sensitivity and precision. The long temperature ramp afforded signals approximately 1/4 to 1/3 the magnitude of the signals obtained with the step function profile. No improvement in precision was observed with the 8 s ramped vaporization step. Fast ramping afforded sensitivity similar to those observed using the step function profile. However, the level of precision obtained using the fast ramp was still somewhat inferior to those obtained by the step function profile with average RSD's of 9.5% and 5.5% respectively. This difference in precision may not be a result of the difference in the time to reach the vaporization step since a step function still requires a finite amount of time to reach the instrument electronics handle the step function and the sharp ramp gives rise to the difference in precision.

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Since no advantage was gained by ramping the vaporization stage, the step function was used for the majority of the work done.

2.3.1.2 Effects of Ash Temperature

Ashing temperatures that were investigated were 250°C, 600°C, 800°C, and 1000°C. It was found that ashing temperatures of 250°C and 600°C gave sensitivities and precision that were quite similar (3-8%). Ash temperature of 800°C resulted in unacceptably high RSD's (as high as 59%). Low levels of precision obtained at this temperature may be attributed to the temperature regulation switching from the thermister to the optical pyrometer. Ramping of the temperature profile through 650°C has been observed to confuse the electronics, leading to uneven drying or sometimes, no drying at all. Ash temperatures at the low range of the optical pyrometer resulted in poor reproducibility. An improvement in precision at ash temperatures of 1000°C suggests that higher optical emission from the furnace results in better precision than those found at 800°C. However, the precision is still poor at 1000°C (~17%) and analyte losses will increase with increasing ash temperatures. For the moment, it would appear that the limit of the ash temperature is 600°C for this system unless improvements in the hardware and software can be made.

2.3.1.3 Effects of Vaporization Temperature

Vaporization temperature was optimized by varying the temperature and injecting replicate samples of 1 ppb solutions (Figure 2.5). For high boiling or refractory carbide forming elements in which freon was used, the optimal temperatures were identical at ~1950°C.

This lead to the conclusion that the limiting factor was the dissociation of freon to form fluorine radicals. Once formed, these radicals react with the element to form volatile metal fluorides which typically have boiling points that are much lower than 1950°C.



Figure 2.5 Vaporization temperature effects on Hf signal.

For elements that do not require freon, the optimum vaporization temperatures varied from 1950°C for In and Ga to 2200°C for Al. A representative heating profile is represented in Figure 2.6. The drying step is simply a slow ramp to the ashing temperature of 600°C. The ash step is held for 60 s followed by a step function to the vaporization temperature. The vaporization step is held for 5 s followed by a clean step, usually at 2400°C, which is also held for 5 s to expel any residual analyte that may have remained.

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Figure 2.6 Representative of heating profile used in this study.

2.3.1.4 Effects of Nebulizer Gas Flow

Optimization of the carrier flow was accomplished by replicate injections of 1 ppb solutions of Hf and In at varying nebulizer gas flows. Optimum carrier gas flow was found to be the same for both elements. After each change in the gas flow, the extraction and collector voltages were re-tuned. As expected, the extraction voltage decreased as the nebulizer flow rates increased since the analyte region is pushed forward with increasing nebulizer gas flow.

As can be seen from the graph below (Figure 2.7), the optimum gas flow is at 0.8 L/min. At flow rates higher than this, the residence time of the analyte vapor in the cooling block of the ETV may be too short for the efficient formation of microparticulates. This would greatly affect the transport efficiency and thus one observes a decrease in signal. The optimization of hafnium was performed on two different occasions. The results were therefore normalized to the nebulizer flow at 0.8 L/min to account for the differences in sensitivities.

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Figure 2.7 Nebulizer Gas optimization on a 1 ppb solution of Hf.

2.3.1.5 Acquisition Parameters - Effects of Dwell Time

Dwell times between 1 ms and 10 ms were evaluated. Triplicate injections of a 0.7 ppb solution containing 50:50 ²³⁵U:²³⁸U isotopes were performed to determine isotopic accuracy, sensitivity and precision (Table 2.2).

Similar isotope ratio accuracies were obtained for the different dwell times investigated. However, a dwell time of 5 ms was found to give the best isotope ratio precision.

Dwell Time (ms)	Average Isotope Ratio	isotope Ratio Precision	Absolute Signal Precision	Average CPS at m/z 238
1.000	0.97 ₅	3.06%	4.17%	7.7 ₂ x 10 ⁴
5.000	0.980	0.40%	7.17%	8.0 ₂ x 10 ⁴
10.000	0.979	0.53%	14.1%	6.8 ₈ x 10 ⁴

Table 2.2 Effects of dwell time on Isotopic ratio accuracy, precision and sensitivity and absolute precision for a 0.7 ppb solution of 50:50 ²³⁵U/²³⁸U. The expected isotope ratio for ²³⁵U:²³⁸U is 1.

The effects of dwell time on precision may be explained when the method of acquisition is considered. In the peak jumping mode, which is the mode used here, the time needed per sweep is given by the following:

sweep = number of peaks [quadrupole settle time + (points per peak)(dwell time)]

The quadrupole settle time is the amount of time the quadrupole waits after 'arriving' at a peak prior to acquiring. This helps to clear the signal from the previous peak and prevent carry-over or memory effects from the previous isotope. The 'points per peak' is the number of points to be sampled in a peak. Dwell time is the time that the quadrupole will spend acquiring at the desired mass. So, the number of sweeps across the signal is not linearly dependent on the dwell time. That is, decreasing the dwell time by 1/2 will not increase the number of sweeps by a factor of 2. So, when the dwell time is decreased, there is an overall decrease in the amount of time the quadrupole actually spends acquiring even when there is an increase in the number of sweeps.

On the other hand, increasing the dwell time would decrease the number of sweeps during the signal pulse. Since the ETV signal is very short and intense, the number of scans over this transient signal is very important. As shown in Figure .-

2.8, the majority of the signal intensity from an ETV acquisition is very short, ~200-300 ms.



Figure 2.8 Representative signal obtained from the ETV for Th.

If only a few scans are obtained over this very short period of time where a signal of high intensity exists, this would result in lowered sensitivity (since the signal is averaged over the 3 s integration period) and decreased precision. In using the ETV as a sample introduction method, care should be taken to optimize the dwell times to give optimum sensitivity and precision.

2.3.1.6 Acquisition Parameters - Effects of Acquisition Time

In the SIM mode, the transient signal observed from the ETV was approximately 1.0-1.5 seconds in duration depending on element and concentration. The sensitivity that could be obtained using the peak jump mode would be optimal if a minimal acquisition time could be used. Unfortunately, the signal was found to migrate over a window ranging from 0.5-1.0 s from the time of vaporization. Thus an acquisition time of 2.0 s starting from 0.5 s after the step function was required. Because the integration time was limited by the software to start and acquire in whole second intervals from the point of vaporization, 3.0 s was the minimal acquisition time possible to encompass the transient signal.

2.3.1.7 Optimization of Torch Position and Ion Lens Tuning

Tuning the ion lens and the torch position for the ICP-MS in the ETV mode requires a continuous strong and steady signal. Since the signals obtained from the ETV are transient, it would be very cumbersome to tune the ion lens to the particular mass of interest. In order to optimize the mass of interest, multiple ETV runs would be required while changing the lens settings each time until a maximum was obtained. Since the length of time required to complete this operation would be so time consuming as to be impractical (estimated to be 6 - 8 hours), it was thought that the ion lenses and the torch position could be optimized using a species already present in the plasma or using an element which has a high vapor pressure, and could be continuously introduced to the system.

To avoid contamination of the ICP-MS system, the minor isotope of the argon dimer, Ar_2^+ - 76 was initially chosen¹,². It was found that tuning to this dimer did not give consistent results. The lens tuning, especially the extraction voltage, changed quite drastically over short periods of time. In addition, the sensitivity varied by a factor of 2 to 3 from day to day when using Ar_2^+ - 76 to optimize the system. It is thought that by tuning to a molecular species such as Ar_2^+ we may be tuning to the "wrong" part of the plasma. The site of maximum molecular ion formation may be different from that of atomic ions. Tuning to Ar_2^+ - 76 was ultimately abandoned and alternate species for tuning were sought.

The ideal species needed to tune the ICP-MS ion lens in the ETV mode had to possess several properties:

- 1. has volatility for ease of introduction
- 2. exhibits no memory effects
- 3. does not interfere with elements of interest
- 4. forms only elemental ions
- 5. has m/z close to the mass of interest

Using this criterion, iodine was thought to be a good candidate for use as a tune element. lodine is a volatile species, monoisotopic, and does not isobarically interfere with any elements. An aqueous solution of iodine was prepared from which 25 µL was injected into the ETV and dried at 200°C. The ion lens and the torch position were then tuned to the I-127 signal. After the lenses were tuned, the ETV was fired up several times to drive off any residual iodine. Unfortunately, although iodine made it possible to tune to a non-interfering volatile species, the chemical interaction of the iodine with the analyte in subsequent sample runs was detrimental. Precision of the In signals obtained following the use of iodine to tune were poor. Precision degraded to 61% RSD for a 10 ppb solution of In. After 4-5 hours of operation, when most of the iodine had dissipated, the precision of the same solution dropped to 3.0% RSD. Similar degradation in precision has been observed when using Freon with indium. The use of iodine for tuning the ion lens when running hafnium was more successful. Precision of three replicate measurements were similar to the normal levels obtained, 3 to 8% RSD, for solutions of 0.1 ppb to 10 ppb.

One possible explanation for these observations is that hafnium does not form iodides easily by simply reacting with elemental iodine. Hfl₄ can be formed by reacting with elemental iodine in a sealed tube at temperatures higher than 700°C - conditions somewhat more drastic than those present in the ETV during drying and ashing stages³. However, indium monohalides may be prepared at temperatures as low as 350°C⁴. These halides have relatively low boiling points of 711-715°C⁵. Thus ashing temperatures would be limited to lower than 350°C. Ashing at higher temperatures would lead to loss of analyte. Since the amount of iodine available to form halides was not constant, the amount lost should vary from sample to sample leading to the degradation of precision for In. Other elements that were considered as tune elements include Xe and Kr. These elements are present in trace amounts in the argon gas and have high ionization potentials, 12.13 eV and 13.999 eV for Xe and Kr respectively⁴. It was thought that due to their high ionization potential, they would be ionized most efficiently at the hottest part of the plasma. One drawback to using Xe and Kr was that signals derived from these contaminant species were quite weak. Tuning the ion lens to Xe and Kr did not result in very good sensitivities and it was thought that, again, the wrong regions of the plasma were probed. Similarly, ²⁹Si⁺ signals could be used if the source of Si in the plasma originated only from the injector tube. If this was true, tuning to ²⁹Si⁺ should represent the analyte region. Unfortunately, as with Xe and Kr, the Si tune gave sensitivities lower than those obtained from tuning to Ar_2^+ - 76 thus indicating that there are other sources of Si⁺ in the plasma.

Finally, a volatile metal was chosen as a tune species. Several microlitres of a 1000 ppm mercury solution were injected into the ETV furnace and dried at ~200°C. The resulting mercury signal was used to tune the torch and ion lens settings. No effect on precision was found for the metals of interest and tuning was found to be stable for the duration of the run. Unfortunately, analysis of trace levels of mercury could not be performed on this instrument for a long (approximately 1-2 weeks) period of time owing to system contamination.

2.3.1.8 Effects of Freon Addition

Freon was used for refractory metals such as Ti, Hf, Zr, Th and U. Shown below, in Figure 2.9, are mass spectra of 1 ppb injections of Th with and without freon gas. The erratic and poorly defined signals were probably a result of carbide formation due to the refractory nature of the metal. Freon introduction gave rise to well defined, discrete signals, with little to no memory effects and a higher transport



efficiency. Freon flow was optimized by varying the flow rate and measuring the response of triplicate measurements.

Figure 2.9 Thorium signals obtained by the ETV with and without Freon. (A) without Freon (B) with Freon

In the case of Hf, Th and U, the optimum freon flows were found to be the same (≥ 0.7 mL/min). Analyte signal levels off at higher flow rates. No interferences were observed with the introduction of freon.

Unfortunately, in the case of Ti and Zr, an increase in background was found with freon use. The interference for Ti at masses 47, 48, 49 and 50 was found to be the SiF+ species (discussed later). Thus, the analysis of Ti was performed using

the lowest freon flow that could be obtained with the mass flow controller. Unfortunately, even with the introduction of small amounts of freon, the peaks



Figure 2.10 Freon effects on Hf Signal for a 1 ppb solution. Signals were normalized to a freon flow rate common to both days. In this case, the common freon flow was 0.4 mL/min. Error bars are one standard deviation of the measurements.



Figure 2.11 Freon effects on Hf background. Error bars are one standard deviation of the measurements.

obtained with Ti are still quite broad and ill-defined. The origin of the background interferences for Zr is unclear. The magnitude of the interference is not as severe

as that for Ti and a slightly higher freon flow rate (0.25 mL/min) was possible without much of an increase in the background (Figure 2.12).



Figure 2.12 Zirconium background as a result of Freon Flow(s) Zr - 91, (m) Zr - 90.

Optimum sensitivity for Zr was also found at high flows (>0.5 mL/min) of freon. Freon was required for Zr analysis because of the refractory nature of Zr. However, the negative effects of an increased background on detection limits, the flow rate of freon was confined to ≤ 0.25 mL/min.

2.3.2 Analytical Figures of Merit

2.3.2.1 Evaluation of Sensitivity and Precision

The analytical figures of merit for this study are presented in Table 2.3. The detection limits were evaluated based on $3\sigma_{N-1}$ of five replicate injections of a 2.3 N HNO₃ blank solution.

Sensitivity for the ETV mode of sample introduction was found to be consistently higher than that of the nebulizer mode. The sensitivities obtained have been shown in terms of absolute concentration (signal/pg and signal/fmole) rather than in relative concentration (signal/ppb). It is more valid to compare the sensitivities at the absolute level since relative sensitivity is volume dependent. For example, relative sensitivity for the ETV mode can easily be multiplied by injecting a larger volume or by multiple injections. Nebulizer sensitivity can be increased by increasing the volume of the injection loop. However, there is an upper limit for nebulizer sensitivity. This upper limit is obtained through continuous sample introduction.

	Sens	itivity	Detection Limits		Detection Limits	
Element	Neb	ETV	Neb	ETV	Neb	ETV
	(CPS/pg)	(CPS/pg)	(pg)	(pg)	(fmol)	(fmol)
In	4.7	5.5 x 10 ³	5.7	0.016	49	0.14
TI	4.9	1.4 x 10 ³	14.7	0.0054	72	0.027
AI	.4.2	1.4 x 10 ³	36.2	1.9	1340	72
Hf	3.1	2.5 x 10 ³	2.90	0.020	16.5	0.117
Zr	3.4	1.5 x 10 ³	2.72	0.019	30.2	0.21
Ga	1.7	1.8 x 10 ³	5.2	0.0041	73	0.057
Fe	4.3	2.6 x 10 ²	1370	2.1	24500	36
Th	11.1	8.8 x 10 ³	0.102	0.0035	0.440	0.015
Ti	3.4	4.8 x 10 ²	6.8	0.98	141	20
U	10.2	4.5 x 10 ³	0.559	0.0045	2.35	0.019

Table 2.3 Comparison of absolute sensitivity and detection limits for pneumatic nebulizer and ETV modes.

Upon examination of the values obtained, it is clear that the sensitivity in most cases was increased by two to three orders of magnitude. This is due to the increased transport efficiency afforded by the ETV over the nebulizer, where over 99% of the sample is lost as large droplets in the spray chamber as described in the introduction. Some enhancement effects are suspected for the very large (greater than 2 orders of magnitude) improvements in sensitivity. These effects may stem from matrix effects as a result of using a dry plasma or to chemical

contributions from the graphite furnace. The rationale for these observations is still unclear.

As a result of the large increase in the sensitivity, detection limits were improved. For elements which do not suffer from high background or isobaric interferences, the detection limits were lowered by over two orders of magnitude. However, for the elements which have very high backgrounds in the ETV mode, such as Ti and AI, absolute detection limits were typically lowered by only one order of magnitude. Although the detection limits were improved, Ti was found to suffer from memory effects. Lengthy and repeated tube firings to remove residual Ti makes this element very cumbersome to analyse by ETV.

Precision obtained using the ETV were found to be comparable to that found with the nebulizer mode at low concentrations (<1 ppb) though inferior for higher concentrations. Typical RSD values obtained for In by both methods of sample introduction are shown in Table 2.4. Similar results were observed for most of the elements studied.

In Concentration	ETV Precision	Nebulizer	
(ppb)	(% RSD)	Precision (% RSD)	
0.010	9.58	7.82	
0.100	5.82	4.80	
0.500	1.90	6.64	
1.00	5.37	3.78	
5.00	4.37	0.80	

 Table 2.4
 Precision obtained for In by ETV and Nebulizer modes.

Day-to-day variation in instrument performance may cause some of the above precision estimates to deviate from the overall trend. At low levels, the signals from the nebulizer mode are close to the detection limit. Any changes in background noise level will have a large effect on the signal. The signals obtained using the ETV mode are well above the detection limits at these concentrations. A portion of the %RSD obtained may be traced to the method of sample injection. The precision found using manual injection of 25 μ L of sample by pipet has been found to be ~4% (i.e. ±1 μ L). Instrumental factors, pipeting error and imprecision due to the short transient signal may combine to give the observed 2 - 10% RSD values. At higher levels, the precision improves for the nebulizer mode since the S/N is high. RSD values for the ETV remain similar to those obtained for low levels for the same reasons mentioned above.

2.3.2.2 Evaluation of Linearity

Linear dynamic range for most of the elements (Table 2.5), spanned over 3 orders of magnitude with the exception of Al and Ti. Again, high background counts for these elements resulted in a reduction of linear dynamic range. An example of this linear range is shown in Figure 2.13 for Hf.

Element	Nebulizer	ETV	r ²
In	10 ³	10 ³	1.0000
ΤI	10 ³	10 ³	0.9980
AI	10 ⁴	101	0.9958
Hf	10 ⁴	10 ³	0.9973
Zr	10 ⁴	10 ³	0.9998
Ga	10 ⁴	10 ³	0.9997
Fe	<10 ¹	NE	NE
Th	10 ³	10 ³	1.0000
Ti	10 ³	>10 ¹	0.9982
U	10 ⁴	10 ³	0.9997

Table 2.5 Linear dynamic range obtained with pneumatic nebulizer and ETV. NE - not evaluated

2.3.2.3 Comparison of Sample Throughput

As with graphite furnace atomic absorption spectroscopy, the ETV mode of sample introduction is slower than the nebulizer mode. The approximate time per sample, including sample injection; drying, ashing and vaporization stages; and



Figure 2.13 Optimized Log-log calibration curve for Hf using ETV sample introduction. Error bars are one standard deviation

cool down, was three minutes per sample (20/hr). This rate of sample throughput was one-half of the rate of the nebulizer mode, which was about 1.5 minutes per sample (40/hr).

2.3.2.4 Evaluation of Multielement Capabilities

Multielement analysis on the ETV is more difficult than that of the nebulizer for several reasons. Primarily, the optimum heating parameters often vary from element to element. For example, very low ashing temperatures would be required if Hg analyses were desired. It may be necessary to compromise freon flows if simultaneous determinations were desired. For example, if Hf was analysed simultaneously with Zr, freon flows would have to be adjusted so that the isobaric interferences for Zr are at a reasonably low level without losing too much sensitivity for Hf.

Indium could not be measured simultaneously with refractory elements since the introduction of freon would form halides with In at low ashing temperatures
resulting in the loss of In. Gallium also could not be measured simultaneously with the refractory metals since freon also contributes to isobaric interferences at m/z 69 from the formation of ${}^{12}C^{19}F_{3}^{+}$. Great care and some compromise must be made when trying to perform multielement analyses using the ETV.

Elements chosen for evaluating the multielement capabilities of the ETV were Zr, Th, and Hf. A freon flow of 0.7 mL/min was used, which resulted in an increase in the ⁹⁰Zr background. This increase in the background was reflected in the increased detection limits for ⁹⁰Zr.

A slight decrease in the sensitivity and more significant decreases in precision was observed in the multielement mode. Relative standard deviations for five replicate injections of a 1 ppb solution ranged from 14-18%. However, the isotope ratio precision obtained for the five isotopes monitored were comparable to precision obtained with monitoring fewer isotopes. The RSD value obtained for the Zr (90:91) isotope ratio was attributed to high backgrounds from freon use which significantly affected the minor isotope. Results from this study are summarized in Table 2.6.

	Sens	itivity	Detection Limits		Abs Precisi	olute on (%)	Isotope Ratio* Precision (%)	
Element	Neb	ETV	Neb	ETV	Neb	ETV	Neb	ETV
	(cps/pg)	(cps/pg)	(pg)	(pg)	(%)	(%)	(%)	(%)
Zr	3.4	4.9 ₃ x 10 ²	4.75	0.69 ₆	2.34	13.2	1.97	18.0
Hf	4.2	6.7 ₇ x 10 ²	1.94	0.020 ₅	2.02	18.2	1.58	1.50
Th	11.7	3.1 ₅ x 10 ³	1.15	0.0157	1.91	15.8	1.30	2.93

Table 2.6Results of multielement analysis for five isotopes by ETV and nebulizer modes.*Isotope Ratios for Zr - 90:91, Hf - 177:178, Th - 232:178

The loss of precision and sensitivity was attributed to the short signal pulse which, with five isotopes monitored, allowed only 48 scans across the desired masses in

the 3 s acquisition. Since the signal pulse is only 1s in duration from baseline to baseline, only 16 sweeps were made across the peak.

A similar evaluation for the nebulizer mode was performed on a 10 ppb solution of the same elements as those introduced to the ETV. The changes in the sensitivity, detection limits and precision found in the ETV were not matched in the nebulizer mode. This may be explained by the extended signal pulse of 60 s which allows 600 sweeps for the same five isotopes monitored. The larger number of sweeps should average any random noise spikes and give a better representation of the analyte signal than the 16 sweeps could for the ETV mode.

Even with the above mentioned degradation in absolute precision, the absolute sensitivity and detection limits obtained using the ETV were still, with the exception of Zr, two orders of magnitude better than those obtained using the nebulizer mode. The increase in Zr background, due to the increased freon flow, leads to the reduction in detection limits by one order of magnitude, still somewhat better than the detection limits obtained using nebulizer mode. In order to maintain good absolute precision, it would appear that only 2 - 3 isotopes may be analysed simultaneously. Since good isotope ratio precision could be obtained, it would appear that isotope ratio techniques, such as the method of internal standard or isotope dilution, should be incorporated for multielement analysis.

2.3.2.5 Isotope Ratio Accuracy and Precision

Isotope ratio precision using the ETV were evaluated by triplicate injections of each solution (Table 2.7). Natural isotopic abundance's were used for Ga, Zr and Hf. Precision at concentrations higher than 1 ppb are comparable to those obtained using the nebulizer mode. However, due to the increased sensitivity of the ETV mode, isotope ratio precision was much improved over those of the nebulizer mode for lower concentrations. Typically, good precision (3%) can be expected for levels ~ 0.1 ppb in the ETV mode while similar precision in the nebulizer mode would require concentrations greater than 1 ppb for most metals.

The difference between the expected isotope ratio and the measured isotope ratio (accuracy) obtained using the ETV were better than values obtained using the nebulizer for concentrations below 1 ppb. This was thought to be due to the increased sensitivity of the ETV over the nebulizer mode. At concentrations below 1 ppb, the S/N ratios in the nebulizer mode are low. Therefore any variations in the noise would have a large effect on the minor isotope, and thus, the isotope ratio. In the ETV mode, the S/N ratios are significantly higher for the same concentrations, thus any variation in noise would affect the isotope ratio to a much lesser extent. Typically for concentrations at the 0.05 ppb levels, ETV isotope ratio accuracy of 4% or lower may be achieved. At concentrations over 1 ppb, the S/N increases for the nebulizer mode and the minor isotopes are less affected by variations in the background noise. Accuracy of isotope ratios between the ETV and nebulizer modes is comparable at higher concentrations.

In general, good isotope ratio precision, 3% RSD, was obtained for the ETV with concentrations ~0.1 ppb. Similar levels of precision using the nebulizer would require concentrations of an order of magnitude higher. Again, this observation is due to the increased sensitivity in the ETV.

The utilization of an internal standard also looks very promising for the ETV (Table 2.8). The precision of the Ga/In isotope ratio (~44 amu apart) ranged from 0.17% to 4.49% for three replicate injections of solutions with concentrations between 0.05 - 0.5 ppb. This is superior to the 15-159% precision obtained for the same concentrations in the nebulizer mode. It should be noted that 0.05 ppb is at about the detection limit of Ga in the nebulizer mode.

Hf (ppb)		Nebulizer				ETV	
	measured	Isotope	measured/		measured	Isotope	measured/
	177:178	Ratio RSD	natural		177:178	Ratio RSD	natural
0.010	0.7 ₈	29%	1.15		0.774	7.74%	1.14
0.050	0.5 ₉	20%	0.86		0.71 ₂	8.36%	1.05
0.100	0.54	5.7%	0.8 ₀		0.71 ₀	3.33%	1.04
1.00	0.679 ₁	0.75%	0.9967		0.679 ₁	0.75%	0.9967
5.00	0.674	1.91%	0.989		0.680 ₂	0.52%	0.998 ₃

Zr (ppb)	Nebulizer			ETV		
	measured	Isotope	measured/	measured	Isotope	measured/
	90:91	Ratio RSD	natural	90:91	Ratio RSD	natural
0.020	-2	608%	-0.3 ₈	4.7 ₇	10.5%	1.04
0.100	5. ₀	36.2%	1. ₁	4.8 ₁	3.60%	1.04
0.459	4.4 ₈	8.27%	0.97 ₇	4.27 ₂	0.33%	0.930 ₈
1.001	4.72 ₇	1.42%	1.03 ₀	4.48 ₆	0.50%	0.977 ₆
4.667	4.577	0.31%	0.9974	4.50 ₅	0.57%	0.981 ₆
9.8	4.51 ₈	0.78%	0.984 ₅			

Ga (ppb)		Nebulizer				ETV	-
	measured	Isotope	measured		measured	Isotope	measured
	69:71	Ratio RSD	/natural		69:71	Ratio RSD	/natural
0.010	0. ₃	745%	0. ₂		1.9 ₀	22.7%	1.2 ₆
0.050	0.4	698%	0.з		1.539	1.95%	1.02 ₂
0.100	1.7 ₇	29.8%	1.18		1.55 ₁	3.09%	1.03 ₀
0.500	1.5 ₀	9.05%	0.99 ₃		1.46 ₂	1.94%	0.970 ₇
1.00	1.457	5.73%	0.967 ₃		1.461 ₃	0.62%	0.9702
5.00	1.404	1.80%	0.932 ₂		1.452 ₇	0.57%	0.9644
10.00	1.465	1.44%	0.972 ₃		1.45 ₃	1.11%	0.9645

Table 2.7Precision and accuracy for Hf, Zr and Ga for nebulizer and ETV modes. Natural isotope ratios
are Zr (90/91) - 4.589, Hf (177/178) - 0.681, Ga (69/71) - 1.506.

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Isotope	Concentration	ETV RSD	Neb RSD
ratio (Galin)	(000)	(%)	(%)
71:115	0.050	4.50	160
	0.100	1.57	39.7
	0.500	0.17	14.9

Table 2.8 Ga/In Isotope ratio precision obtained using the ETV and nebulizer modes.

2.3.3 Isobaric Interference - Problematic Elements

2.3.3.1 Titanium

The purpose of introducing freon into the nebulizer gas stream was to promote the formation of more volatile halide species, such as TiF₄⁶, during vaporization. Upon adding freon, an increase in background was observed (Table 2.9 and Figure 2.14) at m/z 47-49. Isotopic abundance's for masses 47, 48 and 49 were found to be $90.2 \pm 0.5\%$, $5.4 \pm 0.5\%$ and $4.4 \pm 0.1\%$, which strongly suggest that the interference originated mostly from the SiF+ species. Isotopic ratios expected for SiF+ were 92.2%, 4.7% and 3.1%, stemming from the natural abundance of silicon.

Freon Flow Rate (mL/min)	CPS 47	CPS 48	CPS 49
0.15	79973	5567	3072
0.25	115682	7667	4309
0.50	1009326	56806	37579

 Table 2.9
 SiF+ interfering species with increasing Freon.

In an effort to avoid freon (and the resulting high background at mass 48) while still gaining the advantages of a more volatile titanium halide, treatment with HF was studied. It was hoped excess HF would be removed during the drying and ashing stages leaving the only source of fluoride contained in the TiF_n compounds.



Figure 2.14 Blank spectra for m/z 45 - 50 in ETV mode. (A) Without Freon (B) With Freon.

This would greatly reduce the fluoride content in the plasma. The halide formed may be titanium tetrafluoride⁷, TiF₄, titanium oxide difluoride⁸, TiOF₂, or the titanium oxide hydroxyfluoride, [TiO(OH)F]⁸. During the drying and ashing stage, an increase in the signal for mass 48 was detected. It was thought that TiF_n may be lost at this stage. However, it was found that the isotopic ratios during this stage were $92 \pm 1\%$, $5.0 \pm 0.2\%$ and $3\pm1\%$ for m/z 47, 48 and 49 respectively, indicating that the signals were due to SiF+ formation and not loss of the analyte. Unfortunately, it appeared that the Ti compound formed with HF in the graphite

furnace was the TiO(OH)F compound that loses HF during the drying and ashing stages to form TiO₂. The dioxide form is undesirable as it is refractory, and forms titanium carbides with the graphite furnace at elevated temperatures, thus leading to high memory effects. Little enhancement in sensitivity over the nebulizer mode of operation was observed and severe memory effects were evident under these conditions.

Since fluorine is required to efficiently volatilize Ti and prevent carbide formation, perhaps the source of silicon could be reduced or removed, lowering the SiF+ interference. One possible source of silicon is the quartz transport tube leading from the furnace. A Teflon® insert was made to fit inside the quartz tube with approximately a centimeter allowance on the end closest to the furnace. This allowance was a precaution taken to avoid the melting of the Teflon during the vaporization stage. The purpose of this insert was to minimize the fluoride contact with the quartz. Unfortunately, SiF+ signals were not reduced with this modification.

Another source of SiF+ may be in the torch itself. For the freon to react with the quartz, high temperatures are required (>1700°C). Thus the torch, specifically the injector gas tube which is in close proximity to the plasma, could very easily contribute to the isobaric interference. A corrosion resistant torch, which has a removable alumina insert as the injector tube, may be used to reduce the amount of interference (Figure 2.15). However, as shown in Figure 2.16, SiF+ signals increased dramatically with increasing Freon flow even with the corrosion resistant torch. Again, isotopic abundance's strongly support that the interference was due to SiF+. The source of this Si may be the outer concentric tubes of the torch where scorching have been observed. Similar increases in SiF+ signals were observed in the nebulizer mode when HF is used with corrosion resistant components (torch, spray chamber, nebulizer).



Figure 2.15 Corrosion resistant torch.; (A) Teflon® ball and socket joint (B) Aluminosilicate injector tube (C) Normal quartz tube on torch (D) & (E) Cool and Auxiliary gas input.



Figure 2.16 Effect of Freon flow rates on SiF+ signal at m/z 48 with a corrosion resistent torch.

This is evidence that the source of SiF+ in the ETV mode originated from the torch since it is the only common component in both modes of sample introduction.

Replacement of the normal torch with a corrosion resistant torch did reduce the background from that observed with a normal torch by approximately 6000 CPS on a blank solution at the lowest freon flow possible. However, this is still significantly higher than that observed using the nebulizer. The gain in sensitivity by a factor more than 200 over the nebulizer mode compensated for the increased background giving detection limits which were an order of magnitude lower (based on signals three times the standard deviation of the blank solution). This set up was used for all experiments reported unless other specified.

2.3.3.2 Aluminum

High background signals at m/z 27 were observed for 25 μ L injections of 2.3 N HNO₃ blank solution for aluminum. These high counts were much higher than those observed in the nebulizer mode. Similar signals were found when no liquid was introduced into the graphite furnace. Typical signals obtained for masses 23 to 27 in the peak jumping mode are shown Table 2.10.

Description	CPS 24	CPS 25	CPS 26	CPS 27
no freon (HNO ₃ blank)	71273	10146	26281	51020
with freon (HNO ₃ blank)	29589	6756	63178	208406
with freon (dry)	2688	1312	14964	224689

Table 2.10 Signals observed for m/z 24 - 27 in ETV mode with and without Freon.

It is thought that the vaporization of the carbon from the graphite furnace contributed to the increased signal. If some carbon from the furnace was vaporized during the vaporization stage, strong candidates for the interferences observed are carbon containing species. Some of the possibilities are listed in Table 2.11.

It was first thought that the increased interference for m/z 27 originated from CN+ species. The origin of the carbon could be from the graphite tube and the nitrogen from air entrained into the plasma.

m/z	Possible interference			
27	12 _C 15 _N +			
	13 _C 14 _N +			
	¹² C2 ¹ H3 ⁺			
	12 _C 14 _N 1 _H +			
26	12 _C 14 _N +			
	12C21H2+			
25	12 _{C2} 1 _H +			
24	12 _{C2} +			

Table 2.11 Possible carbon-containing interferences for aluminum. Natural isotopic abundances of minor isotopes: ¹³C - 1.1%, ¹⁵N - 0.36%.

When 0.15 mL/min of freon was added, significant increases in signals were observed, which agrees with the theory that the isobaric interference contains carbon. If CN⁺ was the dominant interferent, then the isotope ratio for m/z 26: m/z 27 that would be expected is 66:1. However, the observed m/z 26: m/z 27 isotope ratio was 0.23 ± 0.03 . Thus CN⁺ was not the major interferent for Al.

It was found that the background interference at m/z 27 remained the same when comparing the response obtained from a 25 μ L injection of 2.3 N HNO₃ acid blank and a dry tube. However, for masses 24-26, the background was lower for the dry tube firing. Thus, the interference for m/z was not contained within the acid blank.

Thompson and Houk proposed that $C_2H_n^+$ species may mask the Al⁺ signals⁹. The signals observed for m/z 24 and 25 show a decrease when freon was introduced. This would not be expected to occur if $C_2H_n^+$ species were the major interferent since the introduction of carbon from freon should increase these signals. In addition, Lamoureux has reported low backgrounds for Al in the ETV-ICP-MS system¹⁰. It was not clear at this point, whether or not the interference at m/z 27 originates from carbon containing species. Other possible interferences are described below.

The increases in background for masses 26 and 27 may be a result of an increase in the doubly charged species. Some possible doubly charged interferents are listed below (Table 2.12).

m/z	Interference
27	54 _{Cr} ++
	54 _{Fe} ++
	40 _{Ar} 14 _N ++
	38 _{Ar} 16 _O ++
26	40 _{Ar} 12 _{C++}

Table 2.12 Possible doubly charged interferences for m/z 26 and 27.

The atomic doubly charged interferents, Cr++ and Fe++, were easily eliminated as possible interferents. Although the signal at m/z 54 was high, the signal at m/z 53 remained at background levels even with the introduction of freon. This indicated that little chromium was present in the system. When ⁵⁶Fe, the major isotope of iron, was monitored, it was found that it was present at trace levels and so, from natural abundance, any contribution to ⁵⁴Fe would be very small and could not account for the increases observed at m/z 27. The molecular ion, ³⁸Ar¹⁶O+ may also be eliminated. Again, the increase in signal as a result of freon addition was small for ⁴⁰Ar¹⁶O+ is small so that any contribution it may have on ³⁸Ar¹⁶O+, and subsequently ³⁸Ar¹⁶O++ (m/z 27). is negligible. Thus, the majority of the signal intensity at mass 54 may be attributed to the molecular ion, ⁴⁰Ar¹⁴N+. The ArN+ signal did not increase with the addition of freon. Therefore, the doubly charged species ³⁸Ar¹⁴N++ was not expected to increase to give in an enhanced isobaric interference for m/z 27.

At this point, the origin of the AI interference is not conclusive. Some possible interferent such as CN⁺, double charged molecular and atomic species, were not found to be the source of high isobaric interference in this system. Aluminum contamination from the graphite tube, mobilized by the introduction of freon, may be the origin of high backgrounds. Further studies are required to elucidate the identity of the Al interference.

2.3.3.3 Zirconium

An increase in background levels was observed as the flow of freon allowed to increase (Table 2.13). It was soon evident that the species affecting m/z 91 was not the same as those which affected m/z 90 since the ratios of 90:91 varied with freon flow rates. This observation is also evidence that the contamination is not due to Zr contamination in the graphite tube.

Freon Flow Rate (mL/min)	CPS m/z 90	CPS m/z 91	CPS m/z 92	CPS m/z 93
0.07	268	258	205	128
0.70	1379	6361	629	922

Table 2.13 Effect of Freon on Zr m/z 90 - 93. Zr 90 - 51.4%, Zr 91 - 11.2%, Zr 92 - 17.1%

Tube contamination would result in constant isotope ratios with values similar to those of natural isotopic abundances. Possible interferences may be various NiSi+ and CuSi+ species (Table 2.14).

Mass	Possible Interferences		
90	62Ni ²⁸ Si+		
	61 _{Ni} 29 _{Si} +		
	⁶⁰ Ni ³⁰ Si+		
91	⁶² Ni ²⁹ Si+		
	⁶¹ Ni ³⁰ Si+		
	⁶³ Cu ²⁸ Si+		
	⁶⁰ Ni ¹² C ¹⁹ F+		
92	⁶³ Cu ²⁹ Si+		
	⁶¹ Ni ¹² C ¹⁹ F+		
	60 _{Ni} 13C19F+		
93	⁶³ Cu ³⁰ Si+		
	⁶⁵ Cu ²⁸ Si+		
	62 _{Ni} 12C ¹⁹ F+		

Table 2.14Possible NiSi and CuSi interferences.Natural isotopic abundances for minor isotopes:60Ni - 26.1%, 61Ni - 1.13%, 62Ni - 3.59%, 29Si - 4.7%, 30Si - 3.1%

The source of Ni and Cu may be from the erosion of the nickel extraction cones and the copper plated cooling blocks respectively. The isotope ratios expected when NiSi+ species are the only interferences are shown in Table 2.15.

Dominant	Isotope Ratio	Expected Value	Isotope Ratio
		Value	Talue measured
NiSi+	90:91	20	0.18 ± 0.02
	90:92	20	2.6 ± 0.1
CuSi+	91:92	19.6	14 ± 3
	91:93	2.09	7.7 ± 0.5
NiCF+	91:92	18.75	14± 3
	91:93	7.27	7.7 ± 0.5

 Table 2.15
 Comparison of isotope ratios expected for various interferences and the isotope ratios observed for masses 90-93.

Clearly, the isotope ratios obtained using the ETV did not agree with the values expected for NiSi+. Therefore, we can rule out NiSi+ as a major source of interference in Zr determination.

The measured 91:92 isotope ratio suggests that CuSi⁺ may be a major interferent. However, the isotope ratio for 91:93 is somewhat higher than the value expected for CuSi⁺. Instead, it is possible that the interference at m/z 91 could be the molecular ion ⁶⁰Ni¹²C¹⁹F⁺. The isotope ratio obtained for 91:93 was 7.7 ± 0.5 which is in good agreement with the expected value of 7.27 calculated from isotope abundances. However, the isotope ratio measured for 91:92 was 14 ± 3. The large error was to due, in part, to the low signal counts obtained for m/z 92. This ratio was slightly lower than the expected 91:92 ratio of 18.75 if NiCF⁺ was the only interferent present at mass 92.

Clearly, the addition of freon results in increases in isobaric interferences for Zr. The interference at mass 91 may be due to NiCF+, CuSi+ or a combination of these two species. It is unclear what species are responsible for the increase in background for m/z 90. Some sources of interference, such as tube contamination

and NiSi+, have been eliminated but further studies will be needed to determine conclusively the interfering species at masses 91 and 90.

2.3.3.4 Iron

The most predominant isobaric interference for Fe is the ArO+ ion which overlaps the most abundant isotope for Fe at mass 56. The primary source of this interferent originates from the aqueous sample matrix, which is the major supply of oxygen. As can be seen from Figure 2.17 and Table 2.16, the background in the nebulizer mode is quite high at over 300000 counts per second for a blank solution. Thus separating the sample matrix from the analyte can greatly reduce the background.

Analysis Mode	CPS 56	Standard Deviation (CPS)	
Neb	328618	1959	
ETV	2948	193	
ETV-dry	2563	119	

 Table 2.16
 Comparison of ArO signals obtained by nebulizer and ETV modes

Separation of the matrix from the analyte was accomplished by thermally drying the sample in the ETV. As can be seen in Table 2.16 the background at mass 56 can be reduced by two orders of magnitudes. Unfortunately, the background could not be reduced to the near zero levels found by Evans¹¹ and Hutton¹. The levels obtained in this work were approximately 3000 counts per second. Thus, only a small portion of the background signal coul d be attributed to any Fe contamination in the acid blank. The ArO⁺ signal was also monitored for a dry plasma during the ashing stage. The signal obtained was similar in magnitude as that during the vaporization stage with a dry tube. Thus, little, if any, contamination was attributed



Figure 2.17 Representations of Fe blank solutions obtained with the nebulizer and ETV modes; (A) Nebulizer mode (B) ETV with 25 µL blank solution (C) ETV with no blank solution

to contamination in the graphite tube. So it appears that the most probably source of interference was due to oxygen containing species in the argon supply gas or due to air entrainment into the plasma.

In the initial stages of this work, it was found that although the drying and ashing stages were very lengthy, higher backgrounds at mass 56 were still found during vaporization. This was later thought to originate from any moisture which may have condensed on the cooler edges of the furnace or on the quartz tube. This particular problem was perhaps a result of the furnace design (Figure 2.18).



Figure 2.18 Drawing of furnace and quartz tube.(1) Quartz tube (2) Cooling block (3) Graphite furnace (4) proposed site of condensation

The cooling block is designed such that, during the vaporization step, the analyte vapor was cooled to form microparticulates and prevent analyte condensation on the transport tube¹¹. However, this system was found to also condense water on the quartz tube during drying and ashing stages. When the vaporization stage is

reached, the sudden rush of hot air carries some of the water vapor with it and in this way, contributes to the ArO+ signal.

To circumvent this problem, the drying and ashing stages were completed with the carbon pencil removed and the nebulizer gas reduced to 0.4 mL/min. The omittance of the carbon pencil insertion allowed the water vapor to escape through the hole thereby preventing the vapor from entering to the cooling block and condensing on the transport tube. Back pressure from the plasma would "push" back and force the nebulizer gas to exit through the hole. The nebulizer gas was reduced to insure that the nebulizer gas would not push the vapor forward and to maintain a positive pressure to prevent condensation on the "gas inlet" side of the system. By taking these precautions, the ArO+ background could be reduced significantly. However, the low backgrounds obtained by Evans¹¹ could not be reproduced in the present work.

2.3.4 Analysis of Seawater Samples

Seawater samples were processed in a similar procedure as that described in chapter 3. The eluents were analysed by ETV and by nebulizer. Using an external calibration curve gave results that clearly did not agree (Table 2.17).

Method	Calibration Curve	Standard Additions	
	(ppb)	(ppb)	
ETV	1.27 ± 0.04	0.194 ± .008	
Nebulizer	0.14 ± 0.01	0.23 ± 0.03	

Table 2.17 Comparison of Ga concentrations obtained by calibration curve and standard additions for both methods of sample introduction.

There are two possibilities that can explain these observations; isobaric interference or matrix suppression/enhancement. Isotope ratios obtained from both methods produced 69:71 isotope ratios expected from the natural abundance of Ga. It may be concluded that the discrepancy was not due to isobaric interference.

For example, if chloride interference was present, the 69:71 isotope ratio would deviate significantly from the natural Ga isotopic abundance.

Matrix effects can be corrected by the method of standard additions. As demonstrated (Table 2.17), the method of standard additions gave results which were in much better agreement between the two methods. The matrix effects may be a result of organics in the eluent from the resin, the reagents used or something species the seawater sample. Further investigations into the origin of the matrix effect in the nebulizer mode will be discussed in chapter 3.

2.4 Conclusions

The ETV is a useful alternative to the Meinhard nebulizer as a method of sample introduction. Its increased transport efficiency has demonstrated increases in sensitivities of over two orders of magnitude for most of the elements studied when compared to the nebulizer mode. Significant improvements in detection limits were found for many of the elements investigated. Detection limits obtained in this study ranged from 0.019 - 72 fmole. Elements with high atomic masses were found to be quite interferent free and had detection limits of 0.019 - 0.14 fmole. Elements at the middle and lower end of the mass scale, such as Ti, Al and Zr, suffered isobaric interferences, especially with the introduction of freon. Detection limits for these elements were 20 - 72 fmole. Freon was found to be very effective for forming volatile fluorides with high boiling or refractory carbide forming metals such as Hf, Th and U. The linear dynamic range was ~3 orders of magnitude for most elements. However, the maximum concentrations in the linear dynamic range are normally found to be less than 10 ppb, thus making the ETV a complementary method of low level detection method for the pneumatic nebulization system. Precision obtained using the ETV is 2-10%, somewhat inferior to the precision obtained using the nebulizer. Significant reduction in the RSD may be obtained

using an autosampler, since manual injections were found to have approximately 4% RSD.

It is concluded that the most efficient way to utilize the ETV would be by employing isotope dilution techniques. The ETV shows comparable precision in isotope ratio measurements to the nebulizer method. Analysis by external calibration or by standard additions (required since matrix enhancement was found from the analysis of seawater eluents) is lengthy and cumbersome.

2.5 References

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Chapter 3

Determination of Trace Levels of Titanium, Gallium and Indium in the Central Pacific Gyre

3.1 Introduction

Trace metals exist in very low concentrations in seawater due their rapid removal from the oceans. Removal mechanisms, such as particle scavenging and biological uptake, result in large temporal and spatial variability in the oceans. By determining such variabilities in the ocean, we can elucidate the biogeochemical controls on these elements and evaluate their potential to act as tracers of ocean processes. Titanium, gallium and indium are the elements that will be focused on in this study.

There have been few published papers on titanium in natural waters. Orians et al. measured Ti in the northeastern Pacific and the north Atlantic using ICP-MS after seawater preconcentration with a chelating resin¹. They found Ti concentrations of 5-300 pM, with a distribution similar to Cu in the subarctic regions of the north Pacific. Titanium exhibits surface depletion and concentrations increasing linearly with depth. This similarity suggests that Ti, analogous to Cu, is controlled by a complex combination of input and removal mechanisms. Titanium concentrations in the North Atlantic are higher than the Pacific, but with similar depth dependence which supports a scavenging-type distribution for Ti. Titanium in estuarine waters was recently studied by Uehara et al using HPLC after evaporative preconcentration² and Skrabal et al using cathodic stripping voltammetry (CSV)³. They discovered Ti concentrations were higher in these waters (0.2-67 nM) than those of the open ocean and that Ti removal was due mainly by particle or colloidal scavenging.

Early studies by Culkin and Riley estimated that the average gallium concentration in seawater near the English Channel was ~430 pM⁴. More recent

studies using clean methods and advanced instrumentation has shown average seawater gallium concentrations to be much lower¹³. Gallium has recently been studied as a potential analog of Al^{5,6}. Shiller found gallium concentrations in the northwest Atlantic ocean to be 10 - 45 pM⁶ while Orians and Bruland determined open north Pacific ocean Ga concentrations to be 2-30 pM⁵. The lower concentration seen in the older waters of the deep north Pacific, relative to the newly formed deep north Atlantic waters, shows a scavenged-type interocean fractionation. Comparisons of dissolved Ga to Al showed that Ga is enriched with respect to AI in seawater relative to their crustal abundance^{5,6}. This enrichment was found for both the Atlantic and Pacific oceans. Several proposed theories to try to account for this enrichment include preferential removal of Al, preferential dissolution of Ga from the atmospheric dust or the presence of a Ga source not yet identified. An increasing gradient of dissolved Ga concentration with longitude towards the Asian dust in the North Pacific and towards Saharan dust in the North Atlantic supports an aeolian input for dissolved Ga⁵. No fluvial input of dissolved Ga to the open ocean was found to either the eastern north Pacific or the western north Atlantic. Generally, vertical distributions of dissolved Ga in the Pacific Ocean show low surface values, a subsurface maximum, an intermediate minimum and a bottom maximum which suggests a variety of addition input and removal mechanisms. These mechanisms include intermediate and bottom water sources as well as scavenging removal and possibly nutrient type cycling in the upper waters. Further studies into gallium distributions in other oceanic regimes may help elucidate its chemistry in the ocean.

There are no recent publications regarding the oceanic behavior of indium. Early studies using very expensive and time consuming neutron activation analysis found average indium concentrations in seawater to be 1-35 pM^{20,21}. Clearly, insufficient data is available to accurately deduce the oceanic behavior of indium.

3.2 Experimental

3.2.1 Study Site

Seawater samples were collected on board the Russian research vessel, "Aleksandr Vinogradov" in April 1991. Samples used for this study were from the Pacific central gyre at the station labeled AV 10 (27° 46.5'N, 174° 59.4'E) in Figure 3.1. Also included on this map are the sites from previous studies that will be utilized later for comparison.

3.2.2 Seawater Sample Collection

Seawater samples were collected at AV 10 (174 59.4' E, 27 46.5' N) using Teflon® lined General Oceanics "Go-Flo" bottles. These 30 L samplers were suspended on a Kevlar line. The "Go-Flo" bottles, sealed prior to entering the ocean, were opened by a pressure sensor at 5-10 m depth, once they have left the surface region where potential contaminants are higher. Bottles were then lowered to the desired depths, and termination of sampling was triggered by a Teflon® messenger. Once retrieved, all seawater samples were filtered through 0.45 µm Poretics® polycarbonate membrane filters on board the ship in a make-shift clean area. This was followed by acidification to pH 1.5 - 2.0 with 6 M double distilled hydrochloric acid (Seastar Chemicals) and storage in acid-cleaned polyethylene storage bottles.

3.2.3 Reagents and Solutions

All reagents were prepared using distilled deionized (DDI) water (18 M Ω , Nanopure, Barnstead). The acids used were environmental grade nitric acid (HNO₃) (Anachemia), quartz double distilled hydrochloric acid (HCI), ammonium hydroxide (NH₄OH), and acetic acid (HOAc) (Seastar Chemicals). Concentrated (0.2 M) reagent grade potassium acid phthalate (KHP) (Baker) was cleaned prior to use by passing the solution through 1 mL gravity packed vinyl polymer (TSK)



Figure 3.1 Map indicating study site for this study and sites that will be used for comparison. Exact locations for each site are listed below. Each location will be referred to their abbreviation in the discussion that follows. Aleksandr Vinogradov station 10 (AV10) 174 59.4' E 27 46.5' N, Vertex IV (IV) 155° 07'W 28° 15'N, Vertex VA (VA) 139° 34'W 33° 06'N, Vertex VC (VC) 122° 38'W 36° 06'N, Vertex V7,T7 (V7,T7) 145° 00'W 50° 00'N.

immobilized 8-hydroxyquinoline resin, synthesized in house following published methods⁷. Modifications to the synthetic route will be discussed in Chapter 4.

Standards of Ti, Ga, and In were prepared by serial dilution of 1000 ppm atomic absorption standards (Johnson Matthey Inc.) with the appropriate acid matrix. An isotopically enriched ⁴⁹Ti standard solution (⁴⁹Ti - 96.25%, ⁴⁸Ti - 2.71%) was prepared previously from an enriched solid standard of ⁴⁹TiO₂ (Oak Ridge National Laboratories). The TiO₂ was dissolved with a 4 mL acid mixture of 25% HF, 25% HCl and 50% HNO₃ followed by digestion by microwave⁸. After 100-fold dilution with water, the concentration of this solution was determined by reverse isotope dilution with a known solution of ⁴⁸Ti of natural abundance.

3.2.4 Column Preparation

Teflon® columns and fittings were acid washed prior to use. Approximately 1 mL of gravity packed TSK 8-hydroxyquinoline resin was placed in each of these columns. The resin was cleaned by gravity eluting (~0.2 mL/min) 20 mL of 2.3 N HNO₃ through each column. At this point, column blanks are collected from each column. Water adjusted to pH ~3.8 was passed through the columns to pH adjust the resin prior to pumping seawater.

3.2.5 Seawater Sample Processing

All sample processing was performed in a Class-100 filtered air clean room to avoid air borne contamination.

Acidified seawater samples (4 L) were used for these analyses. A 100 mL aliquot was removed from a number of the samples, prior to any further processing, for the purposes of a spike recovery test. The preconcentration procedure used here is similar to one previously developed⁸. Modifications to the procedure will be discussed further in Section 3.3.1. The final procedure is presented in this section. Each 4 L sample was spiked with an amount of ⁴⁹Ti which would result in

isotope ratios of ⁴⁹Ti to ⁴⁸Ti approximately equal to unity. Estimates were based on preliminary studies performed without isotopic dilution and assuming similar Ti distributions with those previously reported¹. After allowing the samples to equilibrate for a minimum of three hours, the seawater samples were pH adjusted to 3.8 ± 0.2 with NH₄OAc and NH₄OH. Samples were then pumped using a variable speed MasterFlex L/S pump (Cole Parmer) at a rate of 2.5-3.5 mL/min through the 8-hydroxyquinoline resin. Pumping rates were closely monitored during the first 8 hours to insure that pumping rates were within the desired limits. Columns were then resuspended with 1 mL of DDI water, and washed sequentially with 2 x 500 µL of 0.1 M KHP (to remove sulphate interferences), 8 x 1.0 mL 5% NH₄OAc (pH ~6) (to remove Ca interference), and 5 x 3 mL of DDI water. The desired metals were eluted from the resin into 4 mL acid clean polyethylene bottles by passing 7 x 500 µL aliquots of 2.3 M HNO₃.

3.2.6 Spike Recovery Tests

Spike recovery experiments were performed to determine the efficiency of the concentration technique. Two resins were used: the TSK 8-hydroxyquinoline resin and the Chelex-100 (Bio-Rad). For the conditions described above, the recoveries of 50 ng spikes of Ga, In and Ti were evaluated to be $95\pm9 \%$ (69 Ga), $98\pm3 \%$ (115 In) and $100\pm3 \%$ (47 Ti) respectively with the TSK 8-hydroxyquinoline resin. Chelex recoveries were similar to those obtained for TSK 8-hydroxyquinoline resin at $100\pm7 \%$ for Ga and $98\pm4 \%$ for In. Titanium results were not obtained for Chelex due to high Ca interferences. It should be noted that Ca interference for 48 Ti was also found to be relatively high for the TSK 8-hydroxyquinoline resin. Due to the slow exchange kinetics, Chelex required over 20 mL of 2.3 M acid to attain the above recoveries while the TSK 8-hydroxyquinoline resin can be eluted completely with less than 4 mL of acid. Although the volume of eluent can be reduced by evaporation with subsequent re-

dissolution for Ga and In, Ti cannot be treated by this method. Titanium requires the use of HF for dissolution. Not only is HF corrosive, but as discussed previously (Section 2.3.1.7), the use of fluoride-containing eluent results in SiF+ interference with Ti isotopes of interest. Thus, the analysis of seawater samples was carried out using the TSK 8-hydroxyquinoline resin.

3.2.7 ICP-MS Operating Conditions

Column eluents were analysed by solution nebulization ICP-MS in the peak jumping mode. Sample solution was introduced using a 300 μ L flow injection sample loop with uptake rates of 0.6 mL/min. Signal duration, determined with single ion monitoring (SIM) mode, under these conditions was approximately 60 seconds. Data acquisition began three seconds after the sample had reached the ICP and continued for 45 seconds to truncate the tailing of the signal resulting in better sensitivity without sacrificing reproducibility. From the SIM mode, it was estimated that over 90% of the signal was measured with the 45 second acquisition time.

3.3 Results and Discussion

3.3.1 Attempts to Remove Isobaric Interferences

It was discovered that the source of calcium interference was not only from the sea water, but also from the KHP solution used in this study. This interference persisted even though the KHP solution had been cleaned by passing it through the 8-hydroxyquinoline resin prior to use. To remedy this problem, the eluents from the columns could be collected, diluted with 750 mL distilled deionized water and reprocessed according to the procedure described in Section 3.2.5. With no KHP rinse used during the second elution sequence, this led to significant removal of the calcium interference. The level of Ca removal was inconsistent, however, and ⁴⁸Ca⁺ interference was evident periodically. These additional procedures also led to extended processing time.

In an attempt to reduce the Ca interference without additional processing, the 5% NH₄OAc solution wash was added to the processing sequence after the KHP wash. Some removal of Ca was observed. Again, Ca removal was not consistent, thereby affecting the signal of ⁴⁸Ti. Complete removal of the Ca interference has, as of yet, not been achieved. Further work is needed to develop better methods of Ca removal. Reagents, such as the KHP solution, could be cleaned more efficiently by passing them through a higher capacity resin, such as Chelex, or by using a larger amount of the TSK 8-hydroxyquinoline resin. Alternately, by monitoring the ⁴⁴Ca isotope a correction could be made for the interference from calcium at m/z 48. By using this method of correction, satisfactory results for Ti were obtained. Thus the final seawater processing procedure used is this study is as described in Section 3.2.5.

3.3.2 The Method of Isotope Dilution

Isotope dilution techniques were used for the analysis of Ti. The principle of isotope dilution analysis (ID) is that, by altering the natural ratio between two isotopes in the sample with an amount of an accurately known quantity of an isotopic spike (usually a minor isotope), the concentration of the analyte present in the original sample may be determined from the measured isotope ratio. A major advantage of ID analysis is that ratios, rather than absolute sensitivities are measured. Thus, once the isotopic spike has been added and equilibrated, loss of analyte or incomplete recovery is not important since the isotope ratio will not change. Also, ID analysis corrects for instrumental drift and matrix effects since both isotopes are affected equally. It should be noted that ID techniques do not account for isobaric interferences. The only instrumental requirement of ID analysis is that mass bias between isotopes must remain constant.

The amount (moles) of the minor isotope in the sample, ${}^{b}X_{s}$, can be calculated from the formula⁹:

$${}^{b}X_{s} = \frac{{}^{b}X_{t}(R_{m} - R_{t})}{(R_{s} - R_{m})}$$
 (3.1)

where ${}^{b}X_{t}$ is the number of moles of the minor isotope in the spike added, R_{m} is the isotopic ratio for the mixture, R_{t} is the isotopic ratio of the spike solution, R_{s} is the isotopic ratio of the sample. By incorporating the isotopic abundance of the minor isotope, f, the total amount of analyte, X_{s} , may be determined.

$$X_{s} = \frac{{}^{b}X_{t}(R_{m} - R_{t})}{f(R_{s} - R_{m})}$$
(3.2)

It has been shown that, in theory, the most accurate results for ID analyses are obtained when the measured ratio, R_m , equals the square root of the ratios of the spike and natural isotope product¹⁰. For Ti, with abundances in the spike solution of ⁴⁹Ti - 96.25%, ⁴⁸Ti - 2.71%, this optimum spike ratio is ⁴⁹/₄₈ = 1.6. However, in practice, counting statistics dictate that maximum precision is obtained for isotope ratios of unity. In these studies, isotope ratios between 1 and 1.3 were used.

3.3.3 Method of Standard Additions

The method of standard additions as well as the calibration method were used to determine Ga and In concentrations. Standard additions provide a monitor and a correction for signal suppression/enhancement caused by the sample matrix which would not be detectable by the method of external calibration. Due to sample limitations, one point standard additions were used in this study once linearity in this concentration range had been verified. To minimize extrapolation error, the added standard resulted in concentrations approximately five times that of the original sample¹¹.

3.3.4 Matrix Effects

It was found previously that both indium and gallium suffered some form of matrix suppression at low concentrations (Section 2.3.4.5). There are three possible origins of the matrix effects; the seawater, the resin, or the reagents. To evaluate the latter two possibilities a standard solution of 0.2 ppb Ga, Ti and In in 2.3 M HNO₃ was passed through the resin. Since this acid matrix is used to elute the columns in the seawater studies, no metal retention is expected. Any deviation in instrumental response from the standard solution that was not passed through the column should therefore be a result of the resin or resin-reagent effects.

Nine columns were used. Each column was cleaned with 20 mL of 2.3 M HNO₃, and pH adjusted with 25 mL pH adjusted DDI water. The columns were then divided into three groups and the various reagents were passed through as shown in Table 3.1.

Column #	KHP	5% NH ₄ OAc	DDI water
	(2x500 µL)	(8x1 mL)	(5X3 mL)
1 - 3	-	-	4
4 - 6	4	-	4
7 - 9	4	4	4

Table 3.1 Column washes for matrix effect experiment.

All columns were washed with $5 \times 3 \text{ mL}$ of DDI water followed by elution with $4 \times 1 \text{ mL}$ the standard solution. The eluent was collected and then analysed by nebulizer ICP-MS and compared with the signal obtained from the original standard solution.

All eluents displayed similar degrees of signal suppression (~20 - 30%) for In. Thus, it would appear that no signal suppression originated from the reagents, KHP and NH₄OAc. Matrix suppression is thought to be a result of the residue from the 8-hydroxyquinoline resin. Little or no signal suppression was observed for gallium in this experiment. Thus, perhaps part of the matrix suppression for Ga found for the nebulizer mode in section 2.3.4 originated from the seawater obtained from the Halifax Harbour. It should be noted that the matrix effects for In were not observed with high concentrations, such as the levels used for recovery studies. It is not clear why matrix effects should only be observed only for low concentrations, however, it is obvious that care must be taken to correct for these effects during analysis. Only the nebulizer mode was used in these experiments. The use of ETV-ICP-MS, especially when employing the method of standard addition, was too cumbersome. It was not necessary to use the ETV in these experiments since sufficient signal was obtained in the nebulizer mode of operation for all elements.

3.3.5 Titanium Distribution

The distribution of titanium found in the central gyre (Figure 3.2) shows a surface maximum (~100 pM), a sub-surface minimum (~50 pM) and increasing concentrations with depth to a bottom maximum (~230 pM). Slightly elevated dissolved Ti levels are observed at ~400-1000 m. This type of behavior suggests that titanium distribution in the central Pacific gyre is governed by a combination of external inputs and removal mechanisms.

The observed surface maximum with a subsurface minimum suggests an atmospheric input (aeolian source) with removal at mid-depth by scavenging onto particles. Results of this study are somewhat different from those found previously¹ where no surface maximum was observed. This discrepancy is likely to be due to the difference in atmospheric fluxes to the high latitude eastern North Pacific vs the central gyre. AV 10 is significantly further west and south of the previously studied sites (VA and VII). Since atmospheric input is carried by the westerlies, the aeolian



Figure 3.2. Titanium distribution at AV 10. No error bar for the Ti concentration at 400 m since only two determinations were performed.

signature would be expected to be much more pronounced in western regions, closer to the Asian dust sources. The vertical distribution of dissolved Ti in the upper waters resembles that of dissolved AI where there is a rapid decrease in concentration in the top 300m. Dissolved AI has been found to have a surface maximum from aeolian input with rapidly decreasing concentrations at mid-depth due to rapid scavenging removal.

The Ti distribution also exhibits slightly elevated levels at mid-depth (~400-1000 m). This observed increase may be correlated to the oxygen minimum observed at this station (Figure 3.3). Although Ti itself will not be reduced under suboxic conditions, Ti may be released by association with Mn oxide particles. Manganese is known to be reduced and transported in suboxic environments¹².

Dissolved Ti concentrations below 1500 m were found to increase almost linearly with depth to ~230 pM. This type of distribution would suggest a bottom water source such as a pore water flux or sediment surface remineralization. At this point, the exact nature of the bottom source of dissolved Ti is not known. Further studies of pore waters are needed to elucidate the dissolved Ti bottom source.



Figure 3.3 Titanium and O₂ distribution at AV 10. No error bar for the Ti concentration at 400 m since only two determinations were performed. Collection of the oxygen data was performed by the Institute of Ocean Science (Sidney, BC). No error estimates were supplied.

3.3.6 Gallium Distribution

The distribution of gallium (Figure 3.4) shows intermediate concentrations at the surface (~17 pM) with a slight subsurface maximum at 200 - 300m (~20 pM), a minimum at ~1000 m (5-10 pM) followed by increasing concentration with depth to a maximum at bottom waters (30 pM). The values found here are much lower than those reported in an earlier study by Culkin and Riley⁴ (~500 pM), but similar to those found more recently by Orians and Bruland¹³ and Shiller⁶. This profile shows subsurface and bottom sources of dissolved gallium as well as scavenging removal in the water column.

The source of dissolved gallium to the surface has been proposed to be from dissolution of atmospheric dust^{5,6}. This data supports aeolian input, in that higher

surface values (~17 pM) are found in this study than those found further east⁵ (<10 pM). Aeolian input from the Asian dust sources would predict that dissolved gallium concentrations increase towards the west.



Figure 3.4 Gallium distribution at AV 10. The data points are a combination of the values obtained using the external calibration method and the method of standard additions. No matrix effects were observed for Ga in these samples.

The subsurface maximum and the mid-depth minimum may be a combination of two processes, horizontal advection and/or a vertical process involving exchange with sinking particles. Gallium taken up at the surface may be released in this region to give the subsurface maximum, which might be expected if biological uptake into soft tissues is occurring in surface waters. After release, gallium may then be scavenged by sinking particles resulting in the minimum observed at 1000 m as was suggested previously⁵.

An alternate subsurface source may be due to lateral advection. Contours generated by combining this data with previous values help to visualize the possible horizontal processes (Figure 3.5).



Figure 3.5 Contours generated by combining data obtained in this study with those previously obtained⁵. Numbers on the contour lines have units of pM.

The subsurface maximum may be due to horizontal advection from the west where the isopycnal surfaces outcrop. This far western region of the Pacific is a region of high dust input and thus a high Ga signal is expected. At this point, the source of the subsurface maxima is not clear. Additional data for sites further west are required to further investigate this theory.

Dissolved gallium concentrations below 1000 m increase almost linearly with depth to a bottom maximum. This is indicative of a bottom water source such as diffusion from sediments or a surface sediment remineralization.

3.3.7 Indium Distribution

There are no other reliable data that may be used for comparison with this In data. The behaviour of indium (Figure 3.6) is similar to that of gallium, with intermediate surface values (~0.3 pM), a subsurface maximum at ~500 m (0.45 pM), a mid-depth minimum at ~1500 m (0.16 pM) and some increase in concentration with depth to 0.3 pM in deep waters. The subsurface maximum is somewhat deeper than that observed for Ga, and the deep water values are lower relative to surface waters. A more detailed discussion of In will follow in Section 3.3.9.1.



Figure 3.6 Indium distribution at AV 10. Due to sample limitations, only two replicate determinations were performed. The average values of the duplicates are presented here.

3.3.8 Vertical Advection-Diffusion Model

A simple vertical advection-diffusion model may be used to approximate the deep-water scavenging times for non-conservative elements with bottom sources.
The model may be expressed as¹⁴:

$$0 = D_z \left[\frac{\partial^2 [C]}{\partial z^2} \right] - v_z \left[\frac{\partial [C]}{\partial z} \right] + J$$
(3.3)

where D_z is the turbulent mixing coefficient, [C] is the concentration of the element, z is the depth, v is the rate of seawater advection and J is the term that accounts for scavenging removal. It can be shown that, by rearranging the solution to the above differential equation, the advection-diffusion model may be expressed by¹⁴:

$$[C] = \alpha + \frac{J}{v_z} z + \beta \theta \qquad (3.4)$$

where α and β are constants, and θ is the potential temperature. Alternately, potential temperature may be replaced by a conservative tracer such as salinity. By using multiple linear regression, α , J/v_z and β can be determined, and thus, J, the scavenging term may also be determined assuming an upwelling rate of 4 m/yr.

Temperature - salinity plots (Figure 3.7) at depthes below 1000 m at the study site show a linear relationship which allows application of a vertical, one-dimensional, advection-diffusion model¹⁴.

Dissolved titanium data from below 1000 m, plotted with respect to salinity demonstrates a concave contour indicative of scavenging removal (Figure 3.8). Residence times for dissolved titanium in this region are estimated at 500 - 600 years, somewhat longer than the 100-200 years previously reported for dissolved Ti in the Subarctic current¹. Longer residence times may be due to the reduced production in this central gyre location, leading to decreased particle flux in the water column, and thus, decreased scavenging.



Figure 3.7 Temperature vs. salinity plot for depths below 1000 m at AV 10. Data was obtained from other scientists. Data provided did not contain uncertainties.



Figure 3.8 Titanium vs. Salinity in the deep Pacific ocean.

A plot of dissolved Ga in deep water with respect to a conservative tracer, salinity, also demonstrates evidence of scavenging behaviour (Figure 3.9). Using the simple advection-diffusion model, the scavenging residence times are estimated to be approximately 600±100 years. This is in agreement with previous values of 750±100 years¹³ reported for station IV, also in the central gyre.

Again, a plot of salinity with respect to In at depths greater than 1500 m indicate that indium is, similar to Ga and most other hydrolysis dominated species, possibly removed by particle scavenging. Unfortunately, the sparsity of data available in the deep waters for In does not allow for an estimate of residence times at this point.



Figure 3.9 Gallium - Salinity and Indium - Salinity Plots for the deep Pacific Ocean. Note: Indium - Salinity plot was obtained by curve fitting.

3.3.9 Interelement Comparisons

From the distribution of dissolved Ga and In (Figures 3.2 and 3.3), it would appear that both elements are governed by similar inputs and removal mechanisms. To be able to rigorously compare the oceanic chemistry and uptake/removal rates of the two elements, one must know their initial relative sources and concentrations. To date, such information is not available for the actual Ga and In source. However if we consider only atmospheric dust sources and assume average crustal abundance for these elements in the atmospheric input, then the expected Ga/In ratio would be approximately 250. Variations from this ratio would indicate, if our source estimate is correct, that removal rates for these two elements vary.

The dissolved Ga/In ratios plotted vs depth (Figure 3.10) demonstrate a relatively linear decrease in the Ga/In ratio with depth down to 1000 m. This change in ratio suggests that the controls for dissolved In and Ga are different since similar input and removal processes and rates would result in constant Ga/In ratios. This change in ratio may be a result of Ga depletion by preferential scavenging relative to In. In surface waters, closer to the atmospheric source, ratios are closer to crustal values. As the effects of scavenging increase with depth, the Ga/In ratio decreases. Another possible explanation is that In is more involved in nutrient



Figure 3.10 Plots of Ga/In ratios vs. depth at AV 10. The expected Ga/In ratio for crustal abundance is 250.

cycling than Ga. Nutrients are depleted in surface waters and enriched at middepth. If In was controlled to a significant degree by nutrient cycling, it would experience depletion at surface waters (increased ^{Ga}/_{In} ratio) and In enrichment at mid-depth (decreased ^{Ga}/_{In} ratio). It is interesting that this decrease is linear.

In deep waters, using the limited data available, the Ga/In ratio is closer to the crustal than the upper water column. This increase in Ga/In ratio may be a result of the closer proximity to the sediment source and would have a closer value to the crustal abundance. At this point, based on the only available In profile, it is difficult to draw many conclusions about the factors controlling In distributions in the ocean.

3.3.10 Comparison of Ti, Ga and In with Aluminum

It is often useful to compare the concentrations of hydrolysis-dominated trace metals against those of aluminum. Aluminum is the most abundant metal in the earth's crust and has been shown have a high atmospheric input in the surface oceans. Aluminum is also one of the most reactive species in the oceans. Dissolved Al is rapidly removed from the surface waters to give a minimum at 1000 m¹⁵. Slightly higher dissolved Al concentrations found in deep waters suggest the possibility of a bottom source.

Since AI values were not available for this study site, values obtained in a neighboring site (IV) were used. Since dissolved AI levels have been previously found to be relatively uniform in the central Pacific gyre¹⁶, it is thought that AI levels and distributions at AV 10 and (IV) should be similar. It is likely, however, that AI levels at AV 10 would be slightly higher in the surface waters, since it is situated west of (IV) (elevated surface concentrations for Ga are found at AV 10 vs IV). If this was the case, then the calculated ^{element}/_{AI} ratios in the surface waters may be slightly over estimated, but still useful for comparison. A comparison of $Ga/_{AI}$, $In/_{AI}$,

and ^{Ti}/_{Al} ratios in seawater with those expected from crustal abundance (Table 3.2) is useful since much more is known about Al behavior in seawater.

Element Ratio ¹⁷	Expected Ratio (^{mmol} / _{mol})	Surface Enrichment	Deep Water Enrichment
Ga/AI	.067	90	750
In/Al	2.67x10 ⁻⁴	450	1500
Ti/ _{Al}	36.5	0.9	11

Table 3.2 Table of estimated enrichment factors of Ti, Ga and In with respect to Al for surface (<500 m) and deep (1500-4500 m) Pacific waters. Enrichment is defined as observed/expected.

3.3.10.1 Surface Waters

In surface waters of the central north Pacific, the Ti/AI ratio was found to be close to that expected in the crust. If the Ti and Al sources were similar to that expected from crustal abundance and both elements encounter similar degrees of dissolution, then this ratio suggests that the residence times of Ti and Al are similar (1-4 years)¹⁵. This short residence time is also consistent with the observed horizontal concentration gradient between the present study site and the high latitude North Pacific (V7,T7)¹. Element surface residence times much longer than the surface water residence time (>50 years) would result in mixing of input and output signals and thus a conservative surface distribution would be expected. Gallium-aluminum ratios show an enrichment factor of ~90. This enrichment in the surface waters could suggest that Ga would have a residence time of approximately 100-350 years (90 times that of Al). This estimate is not reasonable since a surface concentration gradient has been observed for Ga in the eastern central Pacific gyre. Several possible explanations may be invoked in an attempt to account for the additional Ga. These include preferential scavenging of Al in surface waters, an additional Ga source not yet identified, a greater abundance of Ga in the atmospheric source relative to the average crust or an enhanced

dissolution of Ga from aeolian materials. The vertical advection-diffusion model for deep ocean waters at this station has predicted that Ga has a longer residence (~600 years) time than Al (~100-200 years at IV) which suggests that Al may be preferentially scavenged in comparison to Ga. A possible surface source, in addition to crustal dust, is atmospheric Ga emissions related to coal burning⁶ that could enter into the surface waters. Ga has been reported to show nutrient type cycling in the upper water column which could also contribute to increase d Ga residence time. The fraction of Al that dissolves from atmospheric sources was evaluated to be 5-10%¹⁸. It is possible that a larger fraction of Ga dissolves in seawater⁶ A combination of the above mentioned factors may contribute to the Ga enrichment over Al in surface waters.

Many of the arguments used to explain Ga enrichment in the upper waters, such as increased dissolution, may be applied to try to unravel the large In enrichment. The In/AI ratio demonstrates an enrichment over the Ga/AI ratios. Perhaps In is less particle reactive than Ga and thus would have a longer residence time. Other factors, such as an additional source, may account for the In enrichment as well. At this point, not enough data is available to accurately postulate many theories on what processes control In in the surface waters.

3.3.10.2 Deep Waters

The enrichment of Ti/AI in deep waters (11 times) may be a result of preferential scavenging of AI over Ti. Scavenging times of Ti in the deep waters are estimated at ~600±100 years, considerably longer than the ~50-150 years previously estimated for AI¹⁵. This 4-10 fold difference in residence times, combined with the prominent bottom input observed for Ti, is likely to explain the 11-fold enrichment of Ti in deep waters.

Gallium-aluminum enrichment is ~750 times the expected ratio from crustal abundance. Again, the presence of a significant Ga bottom source combined with

reduced particle reactivity compared to AI may partly contribute to such an observation. However, since deep water residence times for Ga and Ti are similar and Ti is only enriched by one order of magnitude, preferential scavenging is not expected to be the dominant cause of Ga enrichment. An additional source of Ga to the whole ocean appears to be needed to explain the observed Ga enrichment throughout the water column. It is not thought that the Ga emissions from coal use, which might be invoked to explain surface enrichment, could have penetrated the deep Pacific waters. The Pacific deep ocean waters are roughly 500-1000 years old. The use of large amounts of coal, enough to emit significant amounts of Ga, has only occurred within the last 300 years or less. Thus deep Pacific waters predate this era. At this point, the origin of the large ^{Ga}/_{AI} enrichment is still uncertain.

The enrichment of ^{In}/_{AI} ratio in deep waters determined to be over three orders of magnitude higher than those predicted by natural crustal abundances. In order for variations in scavenging intensity to explain this observation, a residence time of a hundred thousand years for In would be required. This residence time is clearly unreasonable since oceanic mixing times are on the order of thousands of years, thus, allowing the oceans to completely mix the external input and output signals. Spatial distribution would not be observed with depth for such long residence times unless internal cycles dominate the In distribution. Though some internal cycling may be involved, the distribution of In does not follow any of the known nutrients. This large enrichment thus suggests that our estimate of the atmospheric input is incorrect. That is, the abundance of In in the atmospheric source is not of crustal abundance.

It has previously¹³ been argued that AI was preferentially scavenged relative to Ga due to its speciation in seawater. From a thermodynamics point of view, it can be shown that AI, Ga, In and Ti primarily exist in seawater as various hydroxide species (Table 3.3)¹⁹.

Element Species	Abundance (%)	
AI(OH)3	39	
AI(OH)4 ⁻	61	
Ga(OH)3	1	
Ga(OH)4 ⁻	99	
TiO(OH) ₂	100	
in(OH)3	97	
In(OH)4⁻	3	

Table 3.3Speciation of elements in seawater at pH 8.2.

It had been hypothesized that Ga enrichment is due to the dominance of the negatively charged $Ga(OH)_{4}$ species. Since oceanic particles have a net negative charge¹³, $Ga(OH)_{4}$ is not as likely to be scavenged as a neutral specie, such as $AI(OH)_{3}$. Indium is also predicted to exist predominantly as the neutral specie $In(OH)_{3}$. Extension of the above theory predicts that the Ga/In ratio should be enriched due to increased scavenging of In. However, this was not observed in this study. In fact, Ga/In ratios were found to be lower than the ratio that would be expected from crustal abundance. Thus, preferential scavenging does not appear to depend on molecular charge.

It must be stated, however, that until better measures of Ga and In sources are available, it will be difficult to determine whether enhanced input or decreased removal is responsible for their enrichments in seawater.

3.4 Conclusions

The concentrations of titanium, gallium, and indium have been determined in seawater by first preconcentrating with a TSK 8-hydroxyquinoline resin followed by analysis with ICP-MS.

The range of dissolved Ti concentrations found was 50 - 230 pM consistent with previous observations. Dissolved Ti showed elevated surface values (~100

pM) decreasing to a minimum at ~250 m (~50 pM) and subsequently increasing with depth to a bottom maximum (~230 pM). The distribution of Ti in surface waters strongly supports an atmospheric source for titanium. Previous studies have found Ti surface concentrations to be much lower (< 10 pM) at a site (V7,T7) that was situated much further from the Asian dust sources. The subsurface minimum observed here suggest particle scavenging removal. A slight increase in Ti concentration between ~400-1000 m may be correlated to the oxygen minimum observed at this site (AV 10). This suggests that Ti may be associated with Mn oxide cycling. The increasing concentration with depth strongly suggests a bottom source, details of which are still unknown. A vertical advection-diffusion model predicts that residence times for Ti in deep waters to be approximately 500 - 600 years.

Gallium distributions found at AV 10 showed intermediate surface concentrations (~17 pM) with a slight subsurface maximum at 200-300 m (~20 pM), a minimum at ~1000 m (5 - 10 pM) and an increase with depth to a maximum at bottom waters (30 pM). This type of distribution suggests a subsurface and a bottom water source with scavenging removal throughout. Correlating this data to previous Ga data obtained in the eastern North Pacific shows an increase in dissolved gallium surface values towards the west, and strongly indicates an atmospheric source of gallium. Latitudinal contours generated with the combined data set may indicate that the subsurface maximum is due to horizontal advection from surface sources further west. Additional profiles obtained at study sites further west would more clearly demonstrate the feasibility of the theory. Application of a vertical advection-diffusion model to the data is this study predicts that dissolved Ga has a residence time of 600±100 years and is in agreement with previous studies.

Dissolved indium distribution at AV 10 was found to be similar to that of Ga, suggesting that the two elements may be governed by similar processes.

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Dissolved In concentrations are ~0.3 pM at the surface with a subsurface maximum at 500 m of 0.45 pM, decreasing to a minimum at 1000 - 1500 m of 0.12 pM and increasing slightly at bottom waters to 0.28 pM. The Ga/In ratios are lower than expected from crustal sources and decrease with depth in the upper water column. One explanation may be that Ga is preferentially scavenged with respect to In in the upper 1000 m. Alternately, if In undergoes more internal cycling than Ga, the Ga/In ratio would be expected to be depleted at mid-depth.

Comparison of Ti, Ga and In concentrations with Al concentrations at (IV) showed enrichment for all three elements. Titanium enrichment over Al was found to be 11-fold by comparison with crustal abundances. This enrichment may be explained by preferential scavenging of Al and an increased bottom source for Ti. Comparing ^{Ga}/_{Al} and ^{In}/_{Al} ratios show that both elements are significantly enriched (750- and 1500-fold respectively) over the crustal abundance. These large enrichment factors may be attributed to a variety of sources. These may include preferential dissolution of Ga and In; Ga and In sources not yet identified from atmospheric aerosols; additional nutrient type cycling causing a regenerative input; and significant bottom water inputs. Variable scavenging removal rates do not appear to be able to explain these enrichments. Further studies are needed to advance our understanding of behavior exhibited by these trace elements.

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Chapter 4 Resin Development

4.1 Introduction

Ion exchange resins have a wide range of applications in analytical chemistry, including the separation of ions from solution matrix and preconcentration of trace metals from aqueous samples. Several resins have been described earlier for this type of work; Chelex¹, silica gel immobilized 8-hydroxyquinoline² and TSK immobilized 8-hydroxyquinoline³. Chelex is a commercially available imide diacetate chelating resin. Although it has a high chelating capacity, Chelex swells and shrinks with changing pH, and is therefore cumbersome to work with. The functional chelating group in the latter two resins is 8-hydroxyquinoline. 8-Hydroxyquinoline is a widely used chelating agent in liquidliquid extraction for trace metal preconcentration and has a high affinity for both transition group and heavy metals. This property may be transferred to a solid phase by immobilizing 8-hydroxyguinoline on a solid support. Two of the solid supports used are silica gel and TSK resin. The silica gel solid support exhibits good mechanical strength, and resistance to swelling and shrinking; however, silica gel is not stable and dissolves at high pH. Dissolution exposes fresh silica gel surfaces from which trace metals may be leached. Clearly, this potential source of contamination greatly inhibits the use of this material for trace metal analysis. Fractogel TSK is a highly cross-linked polymer containing methacrylic, ether and secondary alcohol groups. The physical properties of the TSK resin are quite similar to those of silica gel. Unlike silica gel, this resin is stable under both in acidic and basic conditions, making the TSK gel resin an excellent support for ion exchange applications.

Fractogel®, the original TSK resin is reported to have good capacities (~300 μ mol Cu(II)/g of resin)³. However, using a resin manufactured by Toyopearl®

(reported to be identical to Fractogel® which is no longer available), a reduced and variable capacity was obtained (<1 μ mol Cu(II)/g of resin). Extensive research efforts by our group over the last few years has not been fruitful in elucidating the cause of this reduced capacity and problematic synthesis. A portion of this thesis has therefore been devoted to investigating this problem, since access to a reliable ion exchange resin is of fundamental importance to this type of trace analysis. In addition, the potential of a new ion exchange resin, using a new solid support to immobilize a derivative of 8-hydroxyquinoline, has also been investigated.

4.2 Experimental

4.2.1 Reagents

All reagents were analytical grade and were used as received unless otherwise indicated. All water used was analytical grade type I distilled deionized which was made using a Barnstead Nanopure water purification system.

4.2.2 Synthesis of TSK 8-Hydroxyquinoline Resin³

Approximately 30 mL of the Toyopearl[®] TSK-Gel HW-75 (Supelco) resin slurry was washed sequentially with the following: 2 x 100 mL aliquots of 0.5 M NaOH; 3 x 100 mL aliquots of distilled deionized water; 2 x 100 mL aliquots of 1.0 M HCl; 3 x 100 mL aliquots of distilled deionized water; 2 x 100 mL aliquots of 95% ethanol; 2 x 100 mL aliquots of acetone; and 2 x 100 mL of chloroform. All filtering took place under vacuum conditions using a sintered glass funnel. The resin was filtered, then dried under vacuum (~0.1 torr) at ~60-70°C overnight. The dried resin (3.08 g) was then added to a mixture of 6.18 g (0.033 mol) p-nitrobenzoyl chloride (Aldrich) and 15 mL (0.11 mol) of triethylamine (BDH) in 195 mL of chloroform and refluxed under nitrogen for 48 hours. The reaction mixture

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was filtered and washed with chloroform. The resulting faint yellow product was dried under vacuum at ambient temperatures overnight.

A solution of 2.13 g (0.027 mol) of Na₂S (Fisher) in 20 mL 0.1 M acetic acid at pH ~7, was added to the esterified resin to reduce the nitro moiety. The reaction mixture was allowed to stir for several hours to give the yellow amine product. The product was filtered and washed with 4 x 10 mL of acetone to remove any elemental sulfur which may have formed, followed by 3 x 20 mL of distilled water to remove the acetone.

The resin was transferred to a clean reaction vessel with 5-8 mL of distilled water. A cold solution of 5.0 g (0.072 mol) sodium nitrite (Eastman) in 1.0 M acetic acid was added to the resin. The reaction proceeded at 0°C for 45 minutes, then the diazotized resin was filtered and washed with cold water. The cold resin was transferred to the reaction flask with 5 mL of cold water. A cold solution of 4.0 g (0.027 mol) 8-hydroxyquinoline (BDH) in 200 mL of 95% ethanol was added to the resin. If the coupling was successful, the resin turns dark orange to dark red at this point. The reaction was allowed to stir for two hours. The product was then filtered and rinsed with: 2 x 75 mL 0.5 M NaOH; 3 x 100 mL water; 2 x 75 mL 1.0 N HCI; and 3 x 100 mL water. The resulting resin was stored in water. A summary of the reaction sequence described is shown on the following page in Figure 4.1.

4.2.3 Affi-Prep® Coupling

Approximately 25 mL of the cold (-20°C) Affi-Prep® (Bio-Rad) resin was slurried and filtered through a sintered glass filter. Care was taken such that the resin did not filter dry. After washing the resin with 8 x 100 mL of cold (3°C) 10 mM sodium acetate at pH ~4.5, the moist resin was transferred to a cold (0°C) 500 mL flask with 250 mL of 20 mM sodium acetate (BDH) at pH 7.

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Resin.

eaction sequence for the coupling of 8-hydroxyquinoline to the TSK-Ge

A 100 mL solution of 0.03 M 5-amino-8-hydroxyquinoline dihydrochloride (Aldrich) at pH ~6 was added to the reaction vessel. The reaction sequence for the Affi-Prep® coupling is shown in Figure 4.2. After 2 hours of stirring, the reaction mixture was allowed to warm to room temperature. The coupled resin was stirred overnight before filtering through a sintered glass funnel. The resin was then washed with 5 x 200 mL distilled deionized water and stored in 60 mL distilled deionized water.

4.2.4 Capacity Test: Affi-Prep® Resin

Approximately 0.5 mL of the coupled Affi-Prep resin was gravity packed in a 0.8 x 4 cm Poly-Prep Chromatography column (Bio-Rad, Richmond CA) shown in

Figure 4.3. Due to the instability of the 5-amino-8-hydroxyquinoline linkage to acid, acidic solutions were not used to clean the columns prior to loading the copper solution. Column blanks were evaluated by eluting a column which had not been exposed to the copper solution. After washing with 10 mL of water, the resin was loaded with 3 x 10 mL aliquots of 20 μ g/g copper solution at pH ~6. Interstitial copper was removed with 10 mL of distilled deionized water. Chelated copper was eluted with the appropriate solution.



Figure 4.2 Affi-Prep® coupling reaction sequence.



Figure 4.3 Poly-Prep Chromatography column. 1) End cap 2) 10 mL reservoir 3) 20 μm frit to prevent the resin from escaping

Two neutral solutions, ethylenediaminitetraacetic acid (EDTA, Mallinckrodt) and 8-hydroxyquinoline, were evaluated in addition to the acid eluents. Because these solutions are neutral, they were passed through the resin for the purposes of cleaning the resin, and to obtain a column blank. Copious amounts of water were passed through the resin to remove interstitial 8-hydroxyquinoline solution prior to Cu loading. Washing and eluting procedures for these neutral solutions were similar to those used for the acid eluent.

Analysis of copper content, using matrix matched standards, was performed by flame atomic absorption spectroscopy (Perkin Elmer 560).

4.2.5 Capacity Tests: TSK 8-Hydroxyquinoline Resin

Capacity tests performed on the TSK immobilized 8-hydroxyquinoline resin were very similar to those of the Affi-Prep resin. Approximately 0.5 mL of resin was gravity packed in the Poly-Prep Chromatography column. Each column was washed with 20 mL of 2.3 N HNO₃ to displace any previously chelated metals. Resin loading was accomplished by passing 3 x 10 mL aliquots of 20 μ g/g copper solution at pH~6 through each column. Interstitial copper was removed with 10 mL of distilled deionized water. Chelated copper was eluted with 2.3 N HNO₃.

4.3 Results and Discussion

4.3.1 Studies on 8-Hydroxyquinoline Immobilization onto TSK

The synthetic sequence for the coupling of 8-hydroxyquinoline to the solid support consisted of four steps (Figure 4.1). Elucidation of the step responsible for the decreased chelating capacity (compared to the immobilization onto Fractogel® as reported by Landing et al.³) was desired. It was not possible to isolate the coupling step since the intermediate diazonium salt is unstable and may decompose explosively. The study was accomplished by the diazotization and coupling of a model compound, ethyl p-amino benzoate (1), with 8-hydroxyquinoline under the same conditions as those used to immobilize 8-hydroxyquinoline onto the Toyopearl TSK resin. These simple compounds were used as models to simplify the spectral analysis of the resulting product. Compound 1 was treated with NaNO₂ and HOAc followed by 8-hydroxyquinoline (1.1 equivalent) in a similar manner to the resin coupling.



Figure 4.4 Model compound (ethyl p-amino benzoate) reaction sequence.

A strong color change from pale yellow to bright red occurred upon the addition of 8-hydroxyquinoline to the diazonium salt, which suggests that this coupling was quite facile and that failure at these two steps was not the source of reduced capacity. Typically, in an unsuccessful resin coupling, little or no color change was observed denoting little 8-hydroxyquinoline coupling. The color change in the model compound is due to the formation of the azo product and not other byproducts. A ¹H NMR of the crude reaction mixture showed that starting materials were present. However, the appearance of new peaks at 7.3-7.4, 8.6-8.7, and 9.0-9.1 ppm, which were expected for coupled product, were also observed. The product was separated by flash column chromatography (methylene chloride followed by ethyl acetate), and preliminary characterization was performed. Gas chromatography (GC) of the isolated material showed that the material decomposes on heating to give starting materials. The GC integrations showed that approximately 99% of the product decomposed within the GC, but the remaining 1% gave retention times consistent with those expected for the desired product. ¹H NMR spectra of the purified material had new peaks consistent with the predicted structure of the product.

The work with the model compound indicates that the diazo coupling reaction was successful (albeit in low yield ~30%). The low yield may be due to the use of only 1.1 equivalents of 8-hydroxyquinoline in the model compound coupling reaction sequence. This is not expected to result in a low yield in the resin coupling since the 8-hydroxyquinoline is present in 3-5 fold excess. Thus, the problem was due to one of the earlier two steps in the resin reaction sequence. The second step was not likely to be the limiting step since Na₂S is a strong reducing agent, and should easily reduce the nitro moiety into an amine. The esterification of the secondary alcohol on the resin must therefore be the limiting step. Esterification efficiency could be reduced by the presence of water reacting

with the acyl chloride to convert it to the unreactive carboxylic acid. Although methylene chloride is not hygroscopic, precautions were taken to perform the reaction under nitrogen with freshly-distilled solvent, in addition to using excess acid chloride. These precautions did not overcome the low-capacity problem.

Since the reagents were not the cause of failure, perhaps it was the resin itself. The procedure required that the resin be dried overnight in an oven prior to use, however, any water hydrogen-bonded to the secondary alcohol groups would not be removed under these conditions. Hydrogen bonding with water would prevent any reaction of the hydroxyl moiety with the acid chloride since the latter reagent would be hydrolyzed before esterification could occur. Drying the resin under vacuum gave inconsistent results, as the resulting capacities obtained were low and variable. Finally, the resin was dried under heat (60°C) and vacuum overnight prior to use. The resulting capacities were significantly higher than those previously found (~30 μ mol Cu(II)/g of resin). The capacity achieved with the Toyopearl® resin was still lower than that reported with the Fractogel® resin, even though both resins should have the same structure and functional groups. Clearly, further work is needed to optimize the capacity of this resin. However, the capacity obtained through these studies was sufficient for use in the preconcentration of trace metals from seawater.

The capacity of this new 8-hydroxyquinoline immobilized resin ($30\pm2 \mu$ mol Cu(II)/g of resin) is 30 times greater than the previously synthesized resin. This increase was probably due to the increased esterification efficiency resulting from thorough drying of the resin under vacuum oven conditions prior to use. From the work on the model compound, it was evident that the 8-hydroxyquinoline coupling efficiency in the last step needs to be increased. The yield in the coupling reaction may be improved by adjusting the pH more carefully during the coupling step, or by substituting hydrochloric acid, a more commonly used acid media for this type of reaction⁴, for acetic acid in the diazotization step.

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4.3.2 Studies on Affi-Prep® Resin

Capacity tests on the Affi-Prep® resin were performed using several different eluents. The linkage of either the extensor arm or the 5-amino-8-hydroxyquinoline group were unstable and as a result, some of the 5-amino-8-hydroxyquinoline groups were cleaved each time the resin was eluted with 2.3N HNO₃. The columns were not washed with acid prior to Cu(II) loading. Instead, a column packed with the same amount of resin was eluted without Cu(II) loading and used as the blank. A more dilute acid eluent, such as 1% (0.14N) HNO₃ was used. Similar degradation of the 5-amino-8-hydroxyquinoline immobilization was observed. The capacity obtained with acid eluents are shown in Table 4.1.

Eluent	Calculated Capacity	
2.3 N HNO ₃	34 ± 3	
1% (0.14 N) HNO ₃	34 ± 3	
EDTA	22 ± 1	
8-hydroxyquinoline	5 ± 1	

Table 4.1 Resin capacities obtained from Affi-Prep® resin.

The resin capacity was indicative of quantitative coupling of the 5-amino-8hydroxyquinoline to the solid support. The active ester content of the Affi-Prep® quoted by the manufacturer was ~30 μ mole/g or resin. It was found that the unreacted resin possessed some chelating properties (~3 μ mole / g or resin). Thus a capacity of 34 ± 3 is indicative of the combined resin and coupled 5-amino-8hydroxyquinoline capacity. Acid blanks were passed through the resin exhibited signals below detection limits for the FAA.

Neutral eluents, such as aqueous solutions of 8-hydroxyquinoline or EDTA, were used in an attempt competitively remove the Cu from the resin. Unfortunately, even with the large volumes used (50 times the resin volume), only a fraction of the copper may be removed by this method when compared to the acid elution method

(Table 4.1). Competitive ion exchange was not found to be effective with EDTA and 8-hydroxyquinoline for reasonable eluent volumes.

4.4 Conclusions

Resin capacity of the TSK immobilized 8-hydroxyquinoline has been improved over 30-fold by the thorough drying of the resin under vacuum oven conditions prior to use.

A new resin has also been developed by the coupling of 5-amino-8hydroxyquinoline to a solid support called Affi-Prep®. Although good resin capacity was obtained, the weak linkages of either the extensor arm or the chelating agent resulted in decoupling of the 5-amino 8-hydroxyquinoline under acidic conditions from the Affi-Prep® resin. Some eluting abilities were observed with 8-hydroxyquinoline and EDTA solutions. However, the solutions were not as effective at elution as acids. In light of the matrix effects observed in the ICP caused by the presence of organic compounds, the Affi-Prep® resin is not viable for trace metal preconcentration without subjecting the eluent to evaporation and digestion to remove the organic residue eluted from the resin after the preconcentration step.

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Chapter 5 Summary

The method of sample introduction has been the weak link in elemental analysis. Solution nebulization suffers from low transport efficiency and molecular interferences. The ETV has been shown to be a useful alternative to the nebulization as a method of sample introduction. Its increased transport efficiency has demonstrated sensitivities more than two orders of magnitude higher than the nebulizer mode. Subsequently, significant improvements in detection limits were found for many of the elements investigated. Signals from high mass elements were found to be interferent free and possessed detection limits in the range of 0.019 -0.14 fmole. Elements at the middle and lower end of the mass scale, such as Ti, Al and Zr, suffered isobaric interferences in the ETV mode. These interferences were enhanced with the introduction of freon into the nebulizer gas. Detection limits for these elements were in the range of 20 - 72 fmole. When it did not contribute to isobaric interferences, freon was found to be very effective for forming volatile fluorides with high boiling or refractory carbide forming metals such as Hf, Th and U. The linear dynamic range was ~10³ for most elements. The maximum concentrations in the linear dynamic range are normally found to be less than 10 ppb, thus making the ETV a complementary method of ultra-low level detection method for the pneumatic nebulization system. Precision obtained using the ETV is 2-10%, somewhat inferior to the precision obtained using the nebulizer. Significant reduction in the RSD may be obtained using an autosampler, since manual injections were found to have approximately 4% RSD. Matrix effects were found for the ETV mode for the analysis of processed seawater samples.

It is concluded that the most efficient way to utilize the ETV would be by employing isotope dilution techniques. The ETV shows comparable precision in isotope ratio measurements to the nebulizer method. Analysis by external calibration or by standard additions is lengthy and cumbersome but is required since matrix enhancement was found from the analysis of seawater eluents.

The concentrations of titanium, gallium, and indium were determined in seawater collected in the central Pacific Gyre (174° 59.4'E, 27° 46.5'N). The analysis procedure involved a solid-liquid extraction using a TSK immobilized 8-hydroxyquinoline resin followed by analysis using ICP-MS in nebulizer mode using both the method of external calibration as well as standard additions. The range of dissolved Ti concentrations found was 50 - 230 pM consistent with previous observations. Dissolved Ti showed elevated surface values, a minimum at ~250 m, and a bottom maximum. Combined with previous studies, the distribution of Ti in surface waters strongly supports an atmospheric source for titanium. The observed subsurface minimum suggests scavenging removal in the water column. A slight increase in Ti concentration at depths between ~400-1000 m may be correlated to the oxygen minimum observed at this site. The increase in concentration with depth strongly suggests a bottom source. A vertical advection-diffusion model predicts that residence time for Ti in deep waters to be approximately 500 - 600 years.

Gallium distributions found at this site showed intermediate surface concentrations, a slight subsurface maximum at 200-300 m, a minimum at ~1000 m and a bottom maximum. This type of distribution suggests a subsurface and a bottom water source with scavenging removal throughout. Correlating this data to previous Ga data obtained in the eastern North Pacific shows an increase in dissolved gallium surface values towards the west, and strongly indicates an atmospheric source of gallium. Latitudinal contours generated with the combined data set may indicate that the subsurface maximum is due to horizontal advection from surface sources further west. Additional profiles obtained at study sites further west would more clearly demonstrate the feasibility of the theory. Application of a vertical advection-diffusion model to the data is this study predicts that dissolved Ga has a residence time of 600 ± 100 years.

Dissolved indium distribution at this station was found to be similar to that of Ga, suggesting that the two elements may be governed by similar processes. Dissolved In distributions show intermediate surface values, a slight subsurface maximum at 500 m, a minimum at 1000 - 1500 m and a slight increase at bottom waters. The ^{Ga}/_{In} ratios are lower than expected from crustal sources and decrease with depth in the upper water column which suggests that Ga and In are controlled by different processes or by similar processes at different rates.

Comparison of Ti, Ga and In concentrations with AI concentrations at (IV) showed enrichment for all three elements. Titanium enrichment over AI may be explained by preferential scavenging of AI and a Ti source for bottom waters. Comparing Ga_{AI} and In_{AI} ratios show that both elements are significantly enriched (750- and 1500-fold respectively) over the crustal abundance. These large enrichment factors may be attributed to preferential dissolution of Ga and In; Ga and In sources not yet identified from atmospheric aerosols; additional nutrient type cycling causing a regenerative input; and significant bottom water inputs. Variable scavenging removal rates do not appear to be able to explain these enrichments. Further studies are needed to advance our understanding of behavior exhibited by these trace elements.

In recent years, the synthesis of the TSK immobilized 8-hydroxyquinoline has produced resins with low chelating capacities. Thus, efforts to improve the coupling sequence or to find a suitable new resin were merited. The failure of the coupling synthesis was discovered to be due to water hydrogen-bonded to the resin. Resin capacity of the TSK immobilized 8-hydroxyquinoline has been improved over 30-fold by the thorough drying of the resin under vacuum oven conditions prior to use. Further improvements to the chelate capacity may be achieved by changing the acid media from acetic acid to hydrochloric acid, a more commonly used acid in the diazotization step.

A new resin has also been developed by the coupling of 5-amino-8hydroxyquinoline to a solid support called Affi-Prep®. Although good resin capacity was obtained, the weak linkages of either the extensor arm or the chelating agent resulted in decoupling under acidic conditions. 8-hydroxyquinoline and EDTA solutions had some eluting abilities, but these were not as effective as the acid eluents. In light of the matrix effects observed in the ICP caused by the presence of organic compounds, the Affi-Prep® resin is not viable for trace metal preconcentration without subjecting the eluent to lengthy evaporation and digestion procedures to remove the organic residue eluted from the resin after the preconcentration step.