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**The Direct Determination of Radium in Solids by Electrothermal Vaporization
Inductively Coupled Plasma Mass Spectrometry**

by

Roy St.C. McIntyre, B.Sc.

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

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The undersigned recommend to the Faculty of Graduate Studies acceptance of the thesis:
"The Direct Determination of Radium in Solids by Electrothermal Vaporization Inductively
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partial fulfilment of the requirements for the degree of Master of Science.

Chair, Department of Chemistry

Thesis Supervisor

Thesis Supervisor

Abstract

The mechanism of vaporization of radium from a graphite surface has been investigated using electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). It has been found that, like the other alkaline earth elements, radium volatilizes as an oxide. The optimum pyrolysis (1400°C) and vaporization temperatures (2500°C) and the detection limit (34 fg ml⁻¹) for radium determinations are reported. Diluted seawater (1:500), used as a physical carrier, is effective in improving analytical sensitivity when used in small quantities, but causes significant suppression of Ra signal when quantities of salt in excess of 40 µg are added.

Radium has been determined in four geological reference materials (BL-5, DH-1a, EJB 5-81 and SRM 4353) sampled as slurries using ETV-ICP-MS. Interferences caused by the organic and silica/silicate constituents of the sample matrix are reduced using high pyrolysis temperatures and adding hydrofluoric acid. The method gives a detection limit of 186 fg ml⁻¹.

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Publications

Publications that are a direct result of this research:

1. R.St.C. McIntyre, D.C. Gregoire, C.L. Chakrabarti, **VAPORIZATION OF RADIUM AND OTHER ALKALINE EARTH ELEMENTS IN ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY**, *Journal of Analytical Atomic Spectrometry*, 12, 547 (1997).
2. R.St.C. McIntyre, D.C. Gregoire, C.L. Chakrabarti, **THE DIRECT DETERMINATION OF RADIUM IN GEOLOGICAL SAMPLES ANALYZED AS SLURRIES BY ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY**, in preparation.

Publications that are an indirect result of this research:

3. J.P. Byrne, R.St.C. McIntyre, M. Benyounes, C.L. Chakrabarti, **DETERMINATION OF CHROMIUM BY ELECTROTHERMAL VAPORIZATION-INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY USING MODIFIER ASSISTED VAPORIZATION**, submitted, *Cdn. J. Analytical Sciences & Applied Spectrometry*.

List of Tables

		page
Table 1.	Instrumental operating conditions and data acquisition parameters.	19
Table 2.	Appearance temperatures for the alkaline earth elements.	25
Table 3.	Maximum pyrolysis temperatures for the alkaline earth elements in GFAAS and ETV-ICP-MS.	32
Table 4.	Analytical figures of merit for radium in aqueous solutions.	34
Table 5.	Effects of added NASS-3 on radium signal.	36
Table 6.	Instrumental operating conditions and data acquisition parameters.	49
Table 7.	Isotopic ratios for Si determined from the experimental studies using fluorinating chemical modifiers.	61
Table 8.	Instrumental operating conditions and data acquisition parameters.	69
Table 9.	Results of the determination of ^{226}Ra in three geological standard reference materials.	77
Table 10.	Major components of the four geological standard reference materials, as percent composition.	79
Table 11.	Analytical figures of merit for the determination of radium in slurries of geological materials.	82

List of Figures

		page
Figure 1.	Uranium radioactive series ($4n+2$).	13
Figure 2.	Effects of pyrolysis ramp and hold times on the Mg signal.	28
Figure 3.	Pyrolysis and vaporization curves for radium.	30
Figure 4.	Pyrolysis curves for the alkaline earth elements vaporized at 2500°C.	31
Figure 5.	Co-vaporization of radium with barium in an AECL sample vaporized at 2500°C with a 1400°C pyrolysis temperature.	38
Figure 6.	Depiction of (a) ideal and (b) non-ideal separation of analyte from matrix components.	48
Figure 7.	Diagram of the Perkin Elmer Ultrasonic Mixer (USS-100).	52
Figure 8.	Monitoring of the ^{13}C signal for the study of the loss of organic material from SRM 4353 as a function of pyrolysis temperature. a) actual signal, b) blank signal, c) blank-subtracted signal.	56
Figure 9.	Effects of reaction times of concentrated hydrofluoric acid (50% HF) on the Si signal from 125 μg SiO_2 vaporized at 2500°C.	64
Figure 10.	Pyrolysis curve for 20 μl ^{226}Ra with the addition of 40 μl of concentrated HF vaporized at 2500°C.	73
Figure 11.	Shift in the appearance temperature of radium signal due to addition of HF for a 2 s ramp to 2500°C; a) without HF and b) with HF.	74
Figure 12.	Suppression of ^{226}Ra signal in standard reference material EJB 5-81 uranium ore matrix vaporized at 2500°C. a) 12.5 mg ml^{-1} , b) 25 mg ml^{-1} , c) 50 mg ml^{-1}	78
Figure 13.	Major elemental components found in standard reference material EJB 5-81 vaporized at 2500°C.	81

Table of Contents

Abstract	iii
Acknowledgements	iv
List of Publications	v
List of Tables	vi
List of Figures	vii

CHAPTER 1. ELECTROTHERMAL VAPORIZATION (ETV) FOR SAMPLE INTRODUCTION INTO AN ICP-MASS SPECTROMETER

1.1	COMPARISON BETWEEN GFAAS AND ETV-ICP-MS	1
1.2	DIFFERENCES BETWEEN GFAAS AND ETV-ICP-MS	4
1.3	ADVANTAGES OF ETV-ICP-MS	7
1.4	DISADVANTAGES OF ETV-ICP-MS	10

CHAPTER 2. VAPORIZATION OF RADIUM AND OTHER ALKALINE EARTH ELEMENTS IN ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

2.1	RADIUM	12
2.2	ETV-ICP-MS AND DETERMINATION OF RADIUM	14
2.3	INTRODUCTION	15
2.4	EXPERIMENTAL	18
	2.4.1 Standards and Reagents	
	2.4.2 Conversion of Units	
2.5	RESULTS AND DISCUSSION	21
	2.5.1 Mechanism of Vaporization of Be, Mg, Ca, Sr, and Ba	
	2.5.2 Mechanism of Vaporization of radium	
	2.5.3 Effects of Ramp and Hold Times on Signal	
	2.5.4 Optimization of Experimental Conditions	
	2.5.5 Analytical Figures of Merit	
	2.5.6 Effects of Physical Carrier and Signal Suppression Due to Matrix Components	

2.6	SUMMARY	37
 CHAPTER 3. SLURRY SAMPLING TECHNIQUES		
3.1	INTRODUCTION	39
3.2	SLURRY AND SOLID SAMPLING FOR ETV-ICP-MS	39
 CHAPTER 4. MATRIX EFFECTS ARISING FROM SLURRY SAMPLES		
4.1	MATRIX EFFECTS: SLURRY SAMPLING OF GEOLOGICAL AND ENVIRONMENTAL MATERIALS	46
4.2	EXPERIMENTAL	47
	4.2.1 Standards and Reagents	
	4.2.2 Preparation of slurries	
	4.2.3 Ultrasonic mixer (USS-100)	
4.3	PRE-VAPORIZATION OF CARBON	54
4.4	PRE-VAPORIZATION OF SILICON	58
4.5	SUMMARY	66
 CHAPTER 5. THE DETERMINATION OF RADIUM IN SLURRY SAMPLES BY ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY		
5.1	INTRODUCTION	67
5.2	EXPERIMENTAL	68
	5.2.1 Standards and Reagents	
	5.2.2 Preparation of slurries	
5.3	RESULTS AND DISCUSSION	71
	5.3.1 Radium Fluoride, RaF_2	
	5.3.2 Method of Standard Additions	
	5.3.3 Analytical Figures of Merit	
5.4	SUMMARY	80

CHAPTER 6.	SUMMARY AND FUTURE WORK	84
References		85

Chapter 1 Electrothermal Vaporization (ETV) for Sample Introduction into an ICP-Mass Spectrometer

1.1 Comparison between GFAAS and ETV-ICP-MS

The use of electrothermal vaporization (ETV) sample introduction for spectrometric determination is not new. L'vov¹ was the first to apply the technique, coupling it with atomic absorption spectrometry (AAS). Electrothermal vaporization is done by ohmic heating to raise the temperature of a substrate through a series of stepwise or ramped temperature increases to a point where a sample deposited on a substrate surface vaporizes.² This not only allows for the vaporization of the sample, but also aids in freeing the analyte element from as many of the matrix components as possible prior to atomization/vaporization. Upon atomization/vaporization the sample is analysed within the tube for atomic absorption studies, or transported to the ICP-MS for mass spectrometric studies.

The techniques of graphite furnace atomic absorption spectrometry (GFAAS) and electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) are very similar with respect to the processes they undergo for sample treatment. The use of a graphite tube links the two techniques. Sturgeon *et al.*³ have shown that there are three processes leading to the production of atoms within the graphite furnace. Since the heating programs used for both GFAAS and ETV-ICP-MS are the same then it can be said that the chemical reactions within the tube should be the same for both techniques. This means that under the same heating conditions, the atomic and molecular species formed and their reactions (atomization, dissociation, conversion to other form, *etc.*) should be the same. This means that all atomization mechanisms applicable for GFAAS should also be applicable to

ETV-ICP-MS. Much of the data used for ETV-ICP-MS research is derived from the extensive literature reported in graphite furnace studies.

Mechanisms and chemical reactions are not the only processes where reactions will be similar. Both GFAAS and ETV-ICP-MS will be equally affected by interactions of the analyte with the vaporization surface, resulting in conversion of the analyte to a non-volatile form.⁴ For example, W forms refractory carbides when vaporized from a graphite surface and Ni forms an intermetallic compound when vaporized from a Ta surface,⁴ resulting in memory effects and degradation of analytical performance.

The validity of comparing these two techniques extends beyond their similarity in the production of analyte vapour and chemical reactions. Both are used to detect elements at ultra-trace concentration levels. Limits of detection for GFAAS and ETV-ICP-MS are in the region of picograms (10^{-12} g) and femtograms (10^{-15} g), respectively.⁴ Typical sample sizes are pg- μ g, but they may be as high as milligrams, depending on the sample matrix. Sample handling is easily facilitated by an autosampler for both techniques. Although ETV-ICP-MS has a linear dynamic range superior to that of GFAAS (7-8 orders as compared to 2-3 orders) and lower limits of detection, there is a considerable amount of overlap between their figures of merit.⁴ As well, some GFAAS instruments can now determine more than one element at a time, making both GFAAS and ETV-ICP-MS simultaneous multi-elemental techniques.

Chemical modifiers are generally applicable to both techniques. The purpose of using chemical modifiers is to improve the analytical performance of GFAAS and ETV-ICP-MS by changing the chemical and physical properties of the vaporization surface, analyte, matrix, or combinations of these.⁴ Chemical modifiers typically act in the following ways: 1)

stabilization of the analyte to allow for a higher pyrolysis temperature for matrix removal, *e.g.*, MgNO_3 on Be; 2) conversion of analyte or matrix to a more volatile form, *e.g.*, addition of halogenating agents to form volatile halides; 3) as a physical carrier. Care must be taken, however, not to add too much of a chemical modifier since this may result in interferences with the analyte signal. The use of large quantities of some chemical modifiers has been known to cause suppression of the analyte signal in ETV-ICP-MS. Grégoire⁵ found that the signal suppression of the analyte was greatest for matrix elements of high atomic mass. He also found that the greater the atomic mass of the analyte, the less susceptible it is to suppression of the signal regardless of the atomic mass of the matrix element. This also applies to large amounts of chemical and physical modifiers.

The use of GFAAS and ETV-ICP-MS together has been very effective in elucidating the mechanism of vaporization for elements of interest. Where GFAAS will yield the atomization mechanism, ETV-ICP-MS will allow for the total analysis of analyte, including molecular species that would not be observed in AAS. Because of the extremely hot conditions of the plasma these molecular species are dissociated, ionized and analysed in the plasma. An example of this was shown by Byrne *et al.*⁶ who reported the interferences caused by MgCl_2 with Mn. Losses of Mn were observed in ETV-ICP-MS because of the dissociation of MgCl_2 , resulting in the loss of Mn as the volatile chloride.

As can be seen above there are many reasons why GFAAS and ETV-ICP-MS are usually compared in the literature. A more thorough review of these similarities has been published by Grégoire *et al.*⁴

1.2 Differences between GFAAS and ETV-ICP-MS

Whereas the atomization/vaporization steps are similar for both GFAAS and ETV-ICP-MS, inherent differences between the two techniques exist. In GFAAS, a sample is heated up to high temperatures under stop-flow conditions. This means that there is no removal of analyte from the tube during the signal measurement step. This will reduce interferences caused by the disruption of the thermal equilibrium in the tube due to the flow of cold purge gas.⁷ If the purge gas is in thermal equilibrium with the tube wall at the moment of atomization or volatilization of the sample, no further expansion of the gas takes place, thus avoiding loss of the analyte. Stop-flow conditions of the purge gas also promotes high gas-phase temperatures, which promotes thermal decomposition of the analyte-containing compounds. All reactions, including vaporization and atomization, occur within the graphite tube. This results in both atomic and molecular species existing simultaneously in the graphite tube during the signal measurement step. For GFAAS, complete *in situ* atomization is most desirable.

In electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) continuous flow conditions of the support gas (argon) are maintained. This means that argon is flowing through the graphite tube throughout the vaporization step. During this step, the flow of argon is directed toward the plasma through a PTFE tube, which is at room temperature. This cools the vapour, causing condensation of the components that are volatilized off the graphite tube surface. Once transported into the plasma the components are dissociated, atomized and ionized in the hot ($\sim 8000^{\circ}\text{K}$) argon plasma and analysed by the mass spectrometer.² For ETV-ICP-MS, complete transport of the analyte is desirable.

In GFAAS, all of the atomization processes occur within the graphite tube. In ETV-ICP-MS, vaporization and ionization of the sample are spatially and temporally separated; vaporization occurs in the graphite tube and ionization occurs in the plasma. This allows for the optimization of both the vaporization and the ionization to improve the results. If the heating program of the graphite tube is optimized to provide maximum volatilization and transport of the analyte material and the plasma gives the optimum dissociation and ionization of the materials, the instrument will show higher sensitivity than the GFAAS. Separation of the vaporization and ionization are especially important for multi-elemental determinations, as the instrument can be configured for the optimum response to a wide variety of elements simultaneously. Only the atomization of the element, *via* the heating program, can be controlled in GFAAS. No other parameters can be optimized since the whole signal is dependent on the atomization process. As techniques, ICP-MS is inherently more sensitive than GFAAS.

Another difference that exists between GFAAS and ETV-ICP-MS is the temperature at which a signal may first be observed for a given element. Since atomization/vaporization mechanisms are the same for both techniques, the difference is a result of the relative volatilities of the compounds of the analyte. For GFAAS, if the analyte is present in a compound that is volatile at a low-temperature and does not dissociate (meaning it will not atomize) then that compound is lost from the graphite tube by diffusion. This means that some of the analyte of interest is lost from the graphite tube. Determinations using a lower temperature would not yield better results since the analyte must be in atomic form to be detected. However, in ETV-ICP-MS, atomization of the analyte containing compound is not

required; only complete vaporization and transport of the analyte or compound containing the element of interest is required. Since the argon plasma does all of the dissociation, atomization and ionization, the chemical form of the analyte reaching the plasma does not matter. Volatile compounds can be directed toward the plasma and the analyte can be determined. An example of this was shown by Byrne *et al.*⁸, who reported observing a signal for boron at 800°C using ETV-ICP-MS as opposed to 2200°C for GFAAS. A highly volatile, non-dissociating oxide of boron was observed at low temperatures in the ETV-ICP-MS because atomization and ionization occur in the plasma. In GFAAS, no signal was observed until a very high temperature was attained, at which time boron carbide thermally dissociated to form atomic boron. At lower atomization temperatures, gas-phase temperatures are too low to dissociate the oxide and the analyte is simply lost from the graphite tube. Using ETV-ICP-MS, boron can be determined at a temperature low enough to vaporize all of the boron oxide without forming the carbide. No analyte losses or memory effects occur. The elimination of these losses and memory effects improve limits of detection of the ICP-MS technique.

During any ETV-ICP-MS heating cycle several separate heating steps are used. In the presence of liquid samples, slurries or samples of high water content, a drying step ranging from 80°C to 110°C is used to remove the solvent. A second intermediate temperature, or the pyrolysis step, is used to remove volatile matrix components and to activate chemical modifiers. Temperatures for this step could be as high as 1500°C, depending upon the volatilities of the matrix and analyte(s). The third and final step for ETV is a high-temperature vaporization step that converts the analyte to a vapour. This step is the signal

measurement step and can be as high as 3000°C, although typically temperatures of 1500-2600°C are used. Loss of carbon from the graphite tube occurs at all temperatures, with graphite subliming rapidly at temperatures near 3600°C. The graphite surface degrades less quickly if lower temperatures are used and memory effects are not usually prominent above 2600°C. Finally, a clean-up step, which may be placed at the beginning or at the end of the heating program, is commonly used at a higher temperature than the signal measurement step to prevent the buildup of materials and eliminate memory effects.

1.3 Advantages of ETV-ICP-MS

Electrothermal vaporization has many advantages over other methods of sample introduction into an inductively coupled plasma mass spectrometer (ICP-MS). Sample transport efficiency is greatly improved over conventional methods such as solution nebulization (SN). Typical solution nebulizers result in an absolute maximum of 15% transport efficiency, although it is usually much lower (1-2%). The transport efficiency of the ETV unit is usually 80%-100%. A high speed flow of argon gas ($\sim 1 \text{ l min}^{-1}$) takes the vaporized analyte and samples it directly into the plasma. This results in a lower detection limit for most elements with the ETV technique compared with the solution nebulization technique.

Efficiency of sample transport is not the only advantage that ETV has over SN sample introduction. When using SN, approximately 20% of the energy of the plasma is used in the vaporization and decomposition of water.² This means that there is less energy to ionize analyte and to prevent the formation of polyatomic ions. More polyatomic ions are formed

when using SN than in ETV. This is because of the presence of solvents (especially water) which add large quantities of other elements to the plasma. Oxide formation is one of the biggest problems caused when solutions are nebulized. Large quantities of oxygen are introduced from the dissociation of water in the plasma. The result of this is excessive formation of oxide with argon and many other elements present in the sample solution. One problem occurs with the determination of Fe^+ at $m/z=56$, where ArO^+ is the interfering ion. As well, oxides of the lighter rare earth elements overlap with some of the heavier rare earth elements. These interferences can often be eliminated when using ETV. The removal of solvent during the drying and pyrolysis steps reduces the amounts of oxygen and other elements that enter the plasma from the sample. This in turn decreases or eliminates the spectral interferences caused by these polyatomic ions. Analysis of Fe^+ at low levels becomes possible only when water has been removed prior to its determination.

In the drying step, normally from 80-110°C, water is removed from aqueous solutions. A second, higher-temperature step below the pyrolysis maximum for the analyte is used to remove other matrix components, such as salts, acids and organics, that may not otherwise be removed by the drying step. These components are removed through the dosing hole, which is left open throughout these two heating steps. This results in an effective separation of the analyte from volatile components of the sample matrix. Many analytes can be subjected to higher temperatures, in the hundreds of degrees Celsius range, with no loss of the analyte. This enables many of the possible matrix components to be eliminated.

Another advantage of the ETV comes in the sample handling. Many samples require some form of chemical pretreatment prior to analysis. The ETV offers the ability to perform

in situ treatment of samples by adding a chemical modifier on top of the sample in the graphite tube or directly to the sample in the sampling cup. This reduces the sample preparation time. As well, sample sizes are usually no larger than 50 μl , meaning that a 1 ml representative sample would provide a minimum of 20 determinations. Solution nebulization sample introduction usually requires a few millilitres or more per determination, although some microconcentric nebulizers have reduced the amount of sample required.

Aside from the removal of interferences caused by the sample solvent, the effects of other interfering species can also be eliminated from the matrix through selective volatilization. If a sample contains a species that will interfere with the determination, the interfering species could be volatilized before or after the analyte species. If the nature of an interfering compound is changed (*e.g.*, from an oxide to a halide), the compound could be removed from the graphite tube prior to vaporization of the analyte, removing the interference. Likewise, the analyte could be treated (*e.g.*, stabilized by Pd or MgNO_3) to vaporize after the interfering compound. One example for both of these cases is the elimination of interference with $^{75}\text{As}^-$ by $^{40}\text{Ar}^{35}\text{Cl}^-$ when the As is present in a chloride matrix. Arsenic is mono-isotopic, meaning that no other isotope is available for determination if there are interferences. Ediger⁹ showed that the addition of ammonium nitrate to sodium chloride produced volatile ammonium chloride, which can be removed from the graphite tube at temperatures below 500°C. Carey *et al.*¹⁰ showed that the addition of nickel nitrate to form a stable Ni-As complex and the addition of ammonium nitrate to remove chloride greatly reduced interferences of $^{40}\text{Ar}^{35}\text{Cl}^-$ with $^{75}\text{As}^-$.

The direct analysis of solids and slurries is yet another advantage of the ETV. Solids

need only to be in a powdered form so that they can be easily facilitated by the autosampler or directly weighed and placed into the graphite tube. Most samples require mixed acid digestions or fusions and separation of the analyte from the rest of the sample. As stated previously, this type of chemical pretreatment can often be avoided when using the ETV. As well, samples that normally exist as slurries, such as blood and milk, can be analysed directly.

1.4 Disadvantages of ETV-ICP-MS

Whereas ETV sample introduction greatly reduces the problems caused by SN sample introduction, it is not without its drawbacks. The sample is placed in a graphite tube heated up to temperatures of 2000-3000°C during the vaporization step. The sample is then quickly sent through a tube that is at room temperature before reaching the argon plasma. Potential exists for some analyte vapour to condense on the much cooler tubing and thus not reach the plasma. This would result in less than 100% sample transport efficiency. Sparks *et al.*¹¹ showed that approximately 10% of the sample is retained in the transport tubing. However, this is a great improvement over the low transport efficiency of SN.

Another problem is the formation of polyatomic ions. While ETV reduces or eliminates the problems associated with many oxides, the presence of large amounts of carbon creates polyatomic carbides. The formation of ArC^+ at $m/z=52$ creates a problem when determining chromium since the major chromium isotope (83.8%) is found at the same m/z value. Application of the $m/z=53$ isotope of chromium (9.5%) generally results in a degraded limit of detection because of the lower signal resulting from its lower abundance. Recently, Byrne *et al.*¹² have attempted to reduce the effects of ArC^+ formation by vaporizing Cr at

lower temperatures and by using chemical modifiers.

Speed is also a problem when analyzing samples using ETV-ICP-MS. One complete analytical cycle with ETV requires at least two minutes for liquid samples, and longer for solids or slurries. Analysis time is further increased if the method of standard additions⁴ is used for calibrations.

Chapter 2 Vaporization of Radium and other Alkaline Earth Elements in Electrothermal Vaporization Inductively Coupled Plasma Mass Spectrometry

2.1 Radium

Radium is the heaviest of the alkaline earth elements. It has 30 reported isotopes, of which only four are found naturally. Radium-226 is the longest living radioactive isotope, with a half-life of approximately 1600 years. It is a noted alpha emitter from the U-238 decay chain (Figure 1). Because of its long half-life, Ra-226 is the most dangerous of the radium isotopes.

Radium acts like the other members of the alkaline earth family with respect to the formation of compounds. Radium exists in solution in the 2+ form. It forms insoluble sulphate, carbonate and chromium salts, whereas the chloride, bromide, nitrate and hydroxide salts are all soluble in water. Existence of an oxide has been reported, but little information is available. It has been assumed that the chemistry of radium is similar to that of barium because of the family characteristics.

Radium was once the primary product of uranium ores because of its importance in medicine.¹³ Radon gas, resulting from the decay of radium, was collected in tubes and was used in the treatment of cancer and other diseases.¹⁴ More recently, isotopes such as ⁶⁰Co have been used for medical treatment instead of radium because they are more powerful or are safer to use. With the decline of radium in clinical medicine and the arrival of uranium in nuclear power, radium is now seen as little more than a waste by-product. The largest amounts of radium are usually found in the mine tailings and waste water from uranium mines.

A review of the routes of intake of radium into the human body has indicated that

Figure 1. Uranium radioactive series (4n+2). $\rightarrow$ represents α -emission, $---\rightarrow$ represents β -emission.

intake occurs mainly through two processes: ingestion and/or inhalation.¹⁵ Radium is transported in the blood and is deposited mainly in the skeleton, with small amounts being deposited in soft tissues. A large fraction is removed through natural body functions (excretion). The reaction of radium within the body is similar to that of calcium. Calcium is incorporated into bones as bone is formed.¹⁵ When a new bone is formed, an increase in the calcium concentration to the area is observed. When present, radium and other alkaline earths can be incorporated into the bone structure in place of calcium.¹⁵ Radium can also enter the bones during calcium ion exchanges.¹⁵ Calcium in the extracellular fluid is constantly exchanging with that in the bones. Radium and other alkaline earths can be transported into the bones through this process.

Radium has been linked to many negative effects in humans and animals.¹⁵ Bone sarcomas, sarcomas in the skull region and deterioration of skeletal tissue are all linked to radium exposure. The reason for this has been linked to the alpha emissions of radium. Radium also produces many radioactive decay products, including ^{222}Rn , that eventually result in the formation of ^{206}Pb . Because of radium's long half-life the radiation dose is accumulated over the lifespan of the affected individual.

2.2 ETV-ICP-MS and Determination of Radium

Electrothermal vaporization has many advantages over other techniques, as noted previously. For radium determination this extends even further. ETV offers a very fast method of analysis in just a few minutes per sample. Other methods, such as alpha spectrometry^{16,17}, thermal ionization mass spectrometry^{18,19}, Cerenkov Counting²⁰ and radon

emanation²¹ can take hours and even days. Preconcentration, which takes a great deal of time, no longer becomes a problem in most cases. Likewise, separation from sample matrices is less of a problem because of the nature of the ETV. Electrothermal vaporization is capable of removing many forms of volatile materials and possible interferences in the drying and pyrolysis steps.

Another set of advantages comes as a result of the operation of the ETV. Electrothermal vaporization is automated by use of an autosampler in the cases of aqueous and slurry samples. Safety is a primary issue when working with radioactive materials. The autosampler reduces the amount of contact that one must have with radioactive materials and offers the ability to isolate the sampling system physically from the rest of the lab. The use of small sample sizes is also an advantage of this technique. Electrothermal vaporization typically uses sample sizes between 10-50 μl . Again, this results in less exposure as only small, representative samples need to be collected for the analysis.

2.3 Introduction

Of the four naturally occurring isotopes of Ra, ^{226}Ra is the most abundant having a half-life of approximately 1600 years. The other isotopes are of lesser importance since they are not as persistent; they have half-lives of 6.7 years for ^{228}Ra , 11.7 days for ^{223}Ra and 3.64 days for ^{224}Ra . No stable isotope of radium exists. Radium found in nature is derived from both natural and anthropogenic sources and is highly toxic. Radium replaces Ca in bone structures and can result in bone degradation and cancer.¹⁵ Radium (^{226}Ra) is also the natural precursor to ^{222}Rn , which is retained in the lungs as ^{206}Pb .

There is a substantial body of literature reporting on the GFAAS studies on the mechanism of atomization of all of the alkaline earth elements with the exception of radium. As will be shown below, much of this information is useful when applied to ETV-ICP-MS studies. Since little published information exists on radium, the vaporization of ^{226}Ra compounds and its determination by ETV-ICP-MS is the focus of this section.

Radium, as ^{226}Ra , is currently determined largely by such techniques as alpha spectrometry^{16,17}, thermal ionization mass spectrometry (TIMS)^{18,19}, Cerenkov Counting²⁰ and radon emanation.²¹ Recently, ^{226}Ra has been successfully determined by inductively coupled plasma mass spectrometry (ICP-MS) using solution nebulization sample introduction²² and electrothermal vaporization (ETV) sample introduction.^{23,24} Whereas these studies have shown promise, no in-depth study on the vaporization of Ra or study of optimal experimental conditions for the ETV determination has been reported.

Alpha spectrometry^{16,17} is the most commonly used technique for the determination of ^{226}Ra . Sample sizes range from 1-50 ml of solution or 1-5 g of solid. The reported limit of detection obtained by alpha spectrometry¹⁶ was 1.8×10^{-4} Bq for a 50 ml sample (0.1 fg ml^{-1}) preconcentrated and counted for 1000 min. If TIMS^{18,19} is used, sample sizes can be as small as 1 g and detection limits of 10 fg ml^{-1} can be obtained. Cerenkov counting²⁰, based on β -particle detection using a liquid scintillator, requires a relatively large sample size and involves a relatively long sample preparation time, yielding a limit of detection of 0.035 Bq l^{-1} (0.95 fg ml^{-1}). Techniques based on radon emanation²¹ involve the collection of ^{222}Rn , a decay product of ^{226}Ra . Large sample sizes (litres) are also required and ingrowth of radon takes from several days to weeks before sufficient quantities of Rn are produced for accurate

determination. Although all of the techniques discussed above generally offer low limits of detection for Ra, this advantage is offset somewhat by long preparation and analysis times. Preparation of liquid samples usually involves an ion-exchange separation of Ra followed by an electrodeposition preconcentration step. Each step necessarily leads to a greater possibility of contamination and/or sample loss.

Studies on the determination of ^{226}Ra by ICP-MS using solution nebulization²² and ETV^{23,24} sample introduction gave limits of detection of 1 fg ml^{-1} for solution nebulization²² and 0.27 fg ml^{-1} for ETV²³ when 50 ml of sample solution was used. These methods used either or both preconcentration of samples by ion exchange and evaporation techniques to improve limits of detection. Determination by ETV-ICP-MS²³ was done by drying successive samples without vaporization (multiple deposition) to increase limits of detection. This approach, however, is not suitable when sample solutions contain large quantities of dissolved salts. Alvarado and Mitchell²⁴ used Freon-23 as a chemical modifier and obtained a limit of detection of 24 fg ml^{-1} for a $25 \mu\text{l}$ sample aliquot. A limit of detection of 40 fg ml^{-1} was obtained without the use of Freon-23. Assuming a $50 \mu\text{l}$ sample, these become 12 and 20 fg ml^{-1} .

The use of ETV sample introduction provides an alternative means of sample introduction for ICP-MS, which serves to extend the range of application of the technique. The main advantages provided by ETV sample introduction include: the use of microlitre or microgram sample sizes; the removal of matrix interferences by thermal pretreatment of the sample prior to vaporization; and the ability to analyse solids, slurries and organic materials directly. Electrothermal vaporization sample introduction provides rapid analysis in minutes,

compared with days or even longer for some counting methods.^{20,21} As an additional advantage, many samples do not require preconcentration, owing to the inherently high sensitivity of ICP-MS. In fact, in a recent paper by Smith *et. al.*²⁵, it was shown that it was advantageous to use ETV-ICP-MS rather than counting techniques for the determination of all radionuclides whose half-lives were greater than 570 years.

The objective of this study is to elucidate the mechanism of vaporization of Ra and the other alkaline earth elements in ETV-ICP-MS and to determine the optimum measurement conditions for these elements. This work is to serve as the basis for the development of methodology for the direct determination of Ra in solids, sampled as slurries, using ETV-ICP-MS.

2.4 Experimental

A Perkin-Elmer SCIEX Elan 5000 ICP mass spectrometer equipped with an HGA-600 MS electrothermal vaporizer and a Model AS-60 autosampler was used. Pyrolytic graphite coated tubes were used throughout the experiment. The experimental conditions for both the Elan 5000 and the HGA-600 MS are given in Table 1.

A PTFE tube of 80 cm and 6-mm i.d. was used to connect the HGA-600 MS to the plasma torch. Optimization of the plasma and mass spectrometer was accomplished using solution nebulization, prior to switching to ETV mode. No further optimization of the ICP mass spectrometer was required with the exception of small ($\pm 50 \text{ ml min}^{-1}$) variations in the carrier Ar flow rate. The operation of the HGA-600 MS was completely computer-controlled. During the drying and pyrolysis steps of the temperature program, opposing flows

Table 1. Instrumental operating conditions and data acquisition parameters

ICP mass spectrometer:		
Rf power, W		1000
Coolant argon gas flow, l min ⁻¹		15.0
Auxiliary argon gas flow, l min ⁻¹		900
Carrier argon gas flow, l min ⁻¹		800
HGA-600MS electrothermal vaporizer:		
Sample volume, μ l		10-20
Dry step		10 s ramp 110°C for 30 s
Pyrolysis step		1 s ramp 400-2650°C for 30 s
Vaporization step		1 s ramp 900-2700°C for 6 s
Data Acquisition:		
Dwell time, ms		20
Scan mode		peak hopping
Points/spectral peak (m/z)		1
Signal measurement		Integrated counts
Resolution		0.7 u at 10% peak-height

of argon (300 ml min^{-1}) originating from both ends of the graphite tube removed water and other vapours through the dosing hole of the graphite tube. During the high-temperature (vaporization) step the dosing hole was sealed by a pneumatically activated graphite probe. Once the graphite tube was sealed, a valve located at one end of the HGA workhead directed the carrier argon gas flow, originating from the far end of the graphite tube, directly to the argon plasma at a flow rate of 800 ml min^{-1} . Signals were measured as integrated intensity (counts).

2.4.1 Standards and Reagents:

High purity argon gas (99.9995%, Matheson Gas products, Ottawa, Ontario, Canada) was used. A solution of mixed alkaline earth elements was prepared by dilution of SPEX standard 1000 or 10 000 $\mu\text{g ml}^{-1}$ stock solutions (SPEX Industries, Edison, N.J., U.S.A.) using de-ionized water (Millipore, Mississauga, Ontario, Canada). Aliquots of all samples and modifier solutions were 10 μl in volume. The ^{226}Ra solution (provided by the Atomic Energy Commission of Canada, Pinawa, Manitoba) contained 5.2 Bq g^{-1} of the element. The concentrated Ra stock solution was calibrated against NIST SRM 4966 (Radium-226) which was certified to contain 268.2 Bq g^{-1} of ^{226}Ra . NASS-3 Open Ocean Seawater reference material was obtained from the National Research Council of Canada and diluted 500-fold with deionized water prior to using it as a chemical modifier or a simulated sample matrix.

2.4.2 Conversion of Units

The unit of radioactive intensity, the Curie (Ci), was once defined as the disintegration

rate equal to that of 1 g of radium. Today it is defined as 3.7×10^{10} Bq and can be applied to any radionuclide.²⁶ In this research, radium concentration was calculated as follows:

$$1 \text{ Ci} = 1 \text{ g Ra}; 0.027 \text{ } \mu\text{Ci} = 1000 \text{ Bq}$$

$$\frac{5.2 \text{ Bq}}{\text{ml}} \times \frac{0.027 \text{ } \mu\text{Ci}}{1000 \text{ Bq}} \times \frac{1 \text{ } \mu\text{g}}{\text{ } \mu\text{Ci}} = \frac{1.4 \times 10^{-4} \text{ } \mu\text{g}}{\text{ml}} = \frac{0.14 \text{ ng}}{\text{ml}} = 0.14 \text{ ppb}$$

2.5 Results and Discussion

2.5.1 Mechanisms of Vaporization of Be, Mg, Ca, Sr and Ba

The mechanisms of atomization for a number of elements have been studied using GFAAS.^{3,27,28} Sturgeon *et al.*³ showed that three processes occur leading to the production of free atoms: (1) carbon reduction of the analyte oxide followed by sublimation of the metal; (2) thermal dissociation of the oxide on the graphite surface or in the gas phase; and (3) thermal dissociation of the metal chloride. Thermogravimetric²⁹ and atomic absorption data^{3,27,28} show that the oxides of the alkaline earth elements (Mg,Ca,Sr,Ba) are common intermediates, resulting from the heating (prior to vaporization) of either the chloride or the nitrate form of the analyte.

In GFAAS, MgO and CaO vaporize from the graphite surface as oxides and dissociate in the vapour phase, giving atoms.³⁰ Hutton *et al.*³¹ showed by molecular emission measurements in a carbon furnace that the gaseous oxide species for Mg, Ca and Sr exist, suggesting dissociation into the elements in the vapour phase. Sturgeon *et al.*³ suggested that the vapour phase composition was dependent upon the sample size; large samples produced gaseous elements directly, with thermal dissociation occurring on the surface, and small

samples produced gaseous oxides before dissociating into gaseous atoms. Kantor *et al.*³² supported this interpretation and Prell *et al.*²⁸ used mass spectrometry, coupled with a graphite furnace, to show that the oxide *directly* precedes production of the analyte atoms.

There is some uncertainty surrounding the vaporization of Sr oxide. It was suggested by Moore *et al.*³³ that $\text{SrO}_{(s)}$ vaporizes to $\text{SrO}_{(g)}$. However, mass spectrometric studies by Porter *et al.*³⁴ suggested direct formation of the gaseous elements from the solid oxide. Nagdaev and Bukreev³⁵ (using a graphite rod atomizer) proposed that the most probable mechanism for free Sr and Ba atom formation is sublimation of the oxide with dissociation in the gas phase. Hutton *et al.*³¹ obtained similar results using molecular emission measurements of SrO and Prell *et al.*²⁸ also showed that the oxide directly preceded the appearance of free Sr.

For Ba, the oxide is thought to exist predominately in the vapour phase as a gas.³⁰ Jasim and Barbooti³⁶ and Nagdaev and Bukreev³⁵ suggested that free Ba is formed from the gas phase thermal dissociation of the oxide. Frech *et al.*³⁷ used thermodynamic calculations to show that the gaseous oxide was a precursor to gaseous Ba atom formation. Byrne *et al.*³⁸ added oxygen to the purge gas to produce signal shifts, providing evidence in support of the gaseous oxide dissociation hypothesis. Prell *et al.*²⁸ showed BaO as the precursor to Ba atom formation. Sufficient vapour pressure (a few Torr) for all oxides³⁰ exists at their appearance temperatures to produce a signal in ETV-ICP-MS.

Beryllium has an atomization mechanism similar to the other alkaline earth elements²⁷ with only one significant difference. For the other alkaline earth elements (Mg, Ca, Sr, Ba), the species preceding the appearance of the free element has been the simple oxide, MO.

Beryllium, on the other hand, forms a polymeric oxide, $(\text{BeO})_n$ and release of the free element proceeds as follows:

There are, however, some differences in the mode of operation of ETV-ICP-MS that may affect the usefulness of data obtained by GFAAS studies. For example, in GFAAS, during the signal measurement step (high-temperature step) no argon flows through the graphite tube. Production of atoms for atomic absorption can proceed by the vaporization of metal from the graphite surface to the gas phase and/or by the thermal dissociation of molecular species in the gas phase. For ETV-ICP-MS, there is a constant flow of Ar of about 0.8 to 1 l min⁻¹ through the graphite tube, which serves to remove any vaporized material (atomic or molecular) and carry it to the argon plasma where atomization and ionization take place. For the alkaline earth elements discussed above and for both GFAAS and ETV-ICP-MS, analyte oxide is vaporized into the gas phase. This does not mean, however, that analyte signal will be observed at the same vaporization temperature for both techniques. As will be shown below, this is because, for GFAAS, the production of the analyte signal is dependent upon a high enough gas phase temperature to produce thermal dissociation of the oxide, whereas, in ETV-ICP-MS, the analyte signal will result at whatever temperature the oxide is vaporized. This means that, in general, the appearance temperatures (defined as the lowest temperature at which the analyte signal can be detected above the baseline noise) for ETV-ICP-MS will always be lower or equal to the appearance temperatures observed in GFAAS.

The appearance temperatures for the alkaline-earth elements observed in ETV-ICP-MS are compared in Table 2 to the literature values for the appearance temperatures observed in GFAAS. Within experimental errors ($\pm 100^\circ\text{C}$), the appearance temperatures agree except for Ba for which the ETV-ICP-MS temperature is significantly lower. This is probably due to the higher sensitivity of ICP-MS compared with GFAAS. There is no reported value for the appearance temperature of radium in GFAAS.

2.5.2 Mechanism of Vaporization for Radium

Radium is the heaviest of the alkaline earth elements and shares many chemical properties with the rest of the group, particularly Ba. When the alkaline-earth elements are discussed as a group, Be and Mg are usually kept separate because they exhibit different chemistries than the rest of the group.³⁹ Calcium, strontium and barium are usually classed together, with radium often grouped separately again with barium.

Radium compounds follow the general solubility trends for the group (sulphate solubility decreases as atomic number increases, hydroxide solubility increases as atomic number increases, *etc.*) except for the nitrate, which is slightly more soluble than the Ba compound. Thermogravimetric analysis of radium nitrate and carbonate⁴⁰ have revealed the existence of several phases of an oxide, believed to be radium oxide (RaO), at temperatures as low as 300°C and as high as 1230°C . Thermochemical properties of the alkaline-earth elements follow well-defined trends⁴¹ and much of the information available on Ra is currently derived from these trends. Few experimental measurements of the thermodynamic properties of RaO have been completed because of its high reactivity.⁴⁰ Radium oxide is a highly

Table 2. Appearance Temperatures for the Alkaline Earth Elements

Element	Appearance Temperature, °C		Reference
	GFAAS	ETV-ICP-MS	
Be	1227	1200	27,28
Mg	1237	1200	3
Ca	1577	1500	3
Sr	1367	1300	28
Ba	1727	1500	36
Ra	-	1600	this work

aggressive substance that readily attacks crucible and calorimeter materials and, to date, no specific material has been conclusively identified for which the formula RaO can be assigned.⁴⁰

In ETV-ICP-MS, it is observed that for many substances there is sufficient vapour pressure (several Torr) at the melting point of the substance to give rise to a signal. Radium oxide was calculated to melt at 1615°C .⁴² This temperature is (within the experimental error) the same as the appearance temperature (1600°C) for Ra obtained from the vaporization of both the nitrate and chloride forms. This supports the probability that the oxide is the most likely form of Ra vaporized at the appearance temperature.

As shown above, all the alkaline-earth elements most probably volatilize as oxides. The chemical and thermodynamic similarities between Ra and the other alkaline-earth elements, the appearance temperature for Ra in ETV-ICP-MS and its similarity to the melting point of Ra oxide suggest a probable mechanism of vaporization. The evidence provided above is incomplete and perhaps circumstantial, but, in the absence of more qualitative data, a reasonable mechanism for the production of the Ra signal at the appearance temperature in the ETV is vaporization of $\text{RaO}_{(\text{s})}$ to $\text{RaO}_{(\text{g})}$ which is then transported to the argon plasma where atomization and ionization take place.

2.5.3 Effects of Ramp and Hold Times on Signal

The ramp time represents the length of time that it takes to rise from one temperature to another. The ramp rate depends on this time. For example, if a program calls for an increase from 100°C to 600°C with a 1 s ramp time then the ramp rate is $500^{\circ}\text{C s}^{-1}$. The maximum rate allowable is $2000^{\circ}\text{C s}^{-1}$ and is known as the maximum power heating. The

length of time that any one temperature is held constant is called the hold time.

The effects of the ramp rate and the hold time of the pyrolysis step on the signal were studied by changes in the rate and time, making the program longer or shorter. Times tested were picked arbitrarily and were as follows, in order of ramp and hold times: 1.0 s and 10 s; 10 s and 30 s; 10 s and 100 s. Figure 2 shows the effects of ramp and hold times on the Mg signal. This trend is similar for the rest of the alkaline earth elements. It was observed that as the time was increased, the pyrolysis curve was shifted to the left, *i.e.*, a decrease in the signal intensity was observed at a lower temperature. As the pyrolysis step was shortened, the observed onset of signal decrease occurred at higher temperatures. This could be due to the longer times freeing up more analyte by allowing it to heat longer. The analyte would be removed from the dosing hole during this stage. Conversely, as times are shorter, higher temperatures are required to free up analyte in such a short time before losses through the dosing hole would occur. This effect would be comparable to the effects observed when heating water. For the same heating time (under a given pressure) more water is lost at 100°C than at 70°C. Both temperatures will result in loss of water, although longer times are required to achieve the same loss at lower temperatures. The optimal time was decided upon as the one which provided pyrolysis temperatures that were the same as or lower than the results of Slavin.⁴³ It was determined that the best times for analysis were a 10 s ramp and a 30 s hold. This is in agreement with most other ETV work.

2.5.4 Optimization of Experimental Conditions

A typical ETV heating program consists of at least three steps: drying, pyrolysis and

Figure 2. Effects of pyrolysis ramp and hold times on the Mg signal. (◆) 1 and 10 s; (△) 10 and 30 s; (□) 10 and 100 s.

vaporization. A low temperature step ranging from 80°C to 110°C is used to remove solvent and volatile matter not containing the analyte. A second step, generally called the pyrolysis step, is used to remove selected matrix components and/or to activate chemical modifiers. The third step is the high temperature or vaporization step which is used to vaporize the analyte. It is during this step that ICP-MS data are collected. The temperature and rate of heating of the drying step are normally determined experimentally and are usually dependent on the nature of the sample matrix. The upper limit for the pyrolysis temperature is governed by the volatility of the analyte. This limit, the maximum pyrolysis temperature, is usually defined as the highest temperature prior to significant loss of the analyte. In order to determine the maximum allowable pyrolysis temperature for the alkaline earth elements, a curve was constructed of analyte signal obtained at different temperatures for a 30 s hold and 1 s ramp pyrolysis step. The same vaporization temperature (2500°C) was used throughout. The pyrolysis and vaporization curves for Ra are shown in Figure 3. These results show that losses begin to occur at a pyrolysis temperature of around 1400°C for Ra. Figure 4 shows the normalized pyrolysis curves for the other alkaline earth elements. All results in this graph have been calculated as the ratio of the intensity at temperature T to the intensity at the lowest pyrolysis temperature (usually 500°C) for a given element. This gives a value of 1 for all elements at the lowest pyrolysis temperature. The pyrolysis temperatures obtained for these elements (Table 3) are generally lower, by several hundred degrees, than those reported in the GFAAS studies. This may be due to the much smaller quantities of analyte vaporized in ETV-ICP-MS (fg-pg) compared with the GFAAS (ng-μg) studies.⁴⁷ As shown in Figure 4, Be losses occurred at relatively low temperatures. This may result from the low temperature

Figure 3. Pyrolysis (■) and vaporization (Δ) curves for radium.

Figure 4. Pyrolysis curves for the alkaline earth elements vaporized at 2500°C. Be (■), Mg (◇), Ca (□), Sr (▲), and Ba (○).

Table 3. Maximum pyrolysis temperatures for the alkaline earth elements in GFAAS and ETV-ICP-MS.

Element	Pyrolysis Temperature, °C		Reference
	GFAAS	ETV-ICP-MS	
Be	900	500	44
Mg	900	900	43
Ca	1200	700	45
Sr	1500	800	46
Ba	1500	1500	45
Ra	-	1400	this work

vaporization of Be compounds such as $\text{Be}(\text{NO}_3)_2$ (b.p. 142°C) or BeCl_2 (b.p. 520°C) depending on the acid used in preparing the solutions. Maessen *et al.*⁴⁴ reported that approximately 10% of the Be is lost from the furnace due to diffusional losses before the free atom signal is observed in GFASS. Vanhoe *et al.*⁴⁸ reported loss of Be around 900°C when no chemical modifier was used. Meah⁴⁹ also recorded Be losses at very low temperatures when the Be was vaporized in the presence of acids and salt matrices. Thus, if all alkaline earth elements are to be determined as a group by ETV-ICP-MS, a pyrolysis temperature of 700°C or less should be used to prevent losses of the more volatile Be. However, with the use of magnesium nitrate as a chemical modifier, Be can be made thermally stable up to a temperature of 1500°C .⁴⁸

A second set of experiments exploring the relationship between the vaporization temperature and the integrated signal for the alkaline-earth elements showed that the maximum signal was obtained at a vaporization temperature of 2500°C or more when a 500°C pyrolysis step was used. As an example, the vaporization curve for Ra is given in Figure 3. Use of these vaporization conditions completely removes the analyte from the surface of the graphite tube with no memory effects observed.

2.5.5 Analytical Figures of Merit

Analytical figures of merit for the determination of ^{226}Ra by ETV-ICP-MS are given in Table 4. The limit of detection for Ra was calculated as the mass of Ra equivalent to a signal equal to three times the standard deviation of the blank. An absolute limit of detection of 1.7 fg was obtained which corresponds to a relative limit of detection of 34 fg ml^{-1} in a 50

Table 4. Analytical figures of merit for radium in aqueous solutions.

<u>Blank</u>	Integrated Signal	Peak-Height
^{226}Ra	53	94
σ , n=10	8	16
RSD, %	15	17
3σ	24	49
 <u>Radium</u>		
^{226}Ra (1.4 pg)	19 600	36 737
σ , n=5	760	1 959
RSD, %	3.9	5.3
L.O.D. _{abs} , fg	1.7	1.7
L.O.D. _{rel} (50 μl), fg ml ⁻¹	34	34
L.O.D., Bq g ⁻¹	1.3×10^{-3}	1.3×10^{-3}

μl sample. The analyte signal can be measured with a precision of 3.9% and 5.3% for integrated and peak-height signal measurements, respectively.

2.5.6 Effects of Physical Carrier and Signal Suppression due to Matrix Components

The effects of using physical carriers to improve analyte transport from the graphite tube to the argon plasma were reported by Hughes *et al.*⁵⁰ In this study,⁵⁰ the use of NASS-3 (Reference water diluted 500 times) was shown to be an effective carrier for many elements, resulting in signal enhancements of up to a factor of ten. The effects of adding NASS-3 on the Ra (Table 5) were studied by adding 10 μl of solutions containing increasing NASS-3 concentrations to 10 μl samples of 0.1 ng ml^{-1} Ra. Pyrolysis and vaporization temperatures of 700°C and 2500°C, respectively, were used. A seawater matrix can also be used to determine the effect of added matrix components on possible signal enhancements.

When small quantities of NASS-3 were added, the Ra signal was enhanced by up to 30%. Upon adding greater quantities of NASS-3 (NASS-3 contains approximately 36% w/v of salt), the signal was suppressed by as much as 75% when 360 μg of salt was added. Radium is present in seawater at $8.9 \times 10^{-11} \mu\text{g ml}^{-1}$ ¹⁴ corresponding to 8.9×10^{-4} fg in a standard 10 μl sample. This quantity of ^{226}Ra is well below the observed ETV-ICP-MS limit of detection for Ra (1.7 fg) and will not affect the observed signal in experiments using seawater as a chemical modifier.

As was reported by Hughes *et al.*⁵⁰ the initial enhancement effect is probably due to an increased transport efficiency, whereas, at higher added salt masses, signal suppression occurs. The modest enhancement observed for Ra when small quantities of salt were added

Table 5. Effects of added NASS-3 on radium signal

Amount of NASS-3 salt, μg	Enhancement*
0	1.0
0.0014	1.32
0.0072	1.29
0.014	1.12
0.072	0.78
0.14	0.61
0.72	0.25

* Defined as the ratio of the signal obtained when Ra is vaporized with NASS-3 divided by the Ra signal obtained when vaporized alone.

may be due to the presence of Ba in solution with Ra, which itself acts as a physical carrier. The Ra standard used, as well as the NIST material, contained Ba which served as a carrier during the Ra purification step. Both Ra and Ba are co-volatilized during the vaporization step as shown in Figure 5.

2.6 Summary

It has been suggested that the mechanism of radium is the same as the other alkaline earth elements, in that it volatilizes as an oxide before being dissociated and ionized by the argon plasma. The optimum parameters for the determination of radium have been found to consist of a maximum pyrolysis temperature of 1400°C and a vaporization temperature of 2500°C. The addition of small amounts of NASS-3 as a chemical modifier or a physical carrier were shown to enhance the radium signal. This is thought to be a mass transport effect as radium co-vaporizes with other members (especially barium) of the alkaline earth elements.

Figure 5. Co-volatilization of radium and barium in an AECL sample vaporized at 2500°C with a 1400°C pyrolysis temperature.

Chapter 3 Slurry Sampling Techniques

3.1 Introduction

The analysis of slurries and solids in graphite furnaces has been well documented in a wide variety of samples.⁵¹ The use of graphite furnace AAS for solid sampling was first introduced by Kerber⁵² when he determined Au in polyester fibres by direct insertion of the sample. Many problems were encountered that have since been surmounted to make the graphite furnace a valid source of atomization for solid samples. Electrothermal vaporization (ETV), coupled with an inductively coupled plasma, has also been shown to be capable of handling slurries and solids for various types of samples.⁵³⁻⁵⁶ By analysing solid samples as slurries one can combine the advantages of both solid and liquid sampling.⁵⁷ These advantages include: 1) easy and reproducible introduction into the graphite tube; 2) reduced preparation time; 3) reduced possibility of contamination; 4) decreased possibility of analyte loss through volatilization prior to analysis; and 5) reduced loss of analyte through retention by insoluble residues. However, as with all techniques, there are disadvantages to the use of slurries: 1) difficulties in obtaining representative samples; 2) difficulties in maintaining sample homogeneity; 3) particle size; and 4) dilution of the solid sample. The advantages of slurry sampling coupled with the advantages of ETV-ICP-MS make for a very effective and sensitive technique.

3.2 Slurry and Solid Sampling for ETV-ICP-MS

Analysis of solids by slurry sampling involves the analysis of a suspension of a finely divided sample. The slurry sampling technique offers the same advantages as direct solid

sampling and liquid sampling plus the ability to use conventional liquid sample handling devices such as autosamplers. Other advantages are offered for samples that occur naturally as slurries, such as milk and blood, and for the completion of surveys where the analysis of large numbers of samples, such as contaminated soils, is required. Reviews of the literature on slurries by Bendicho and de Loos-Vollebregt⁵¹, Miller-Ihli⁵⁸ and Arruda *et al.*⁵⁹ show the considerable amount of work done in this area, especially in graphite furnace atomic absorption spectrometry (GFAAS). A wide range of elements have been determined in slurries of varying matrices, ranging from food to glass to soils.^{51,58,59} More recently, Grégoire *et al.*⁵³ have shown the feasibility of slurries analysis by ETV-ICP-MS.

The technique of slurry analysis was introduced by Brady *et al.*^{60, 61} to determine the concentration of Zn in marine sediments and Pb in leaves, by GFAAS. The method of standard additions was successfully applied in these determinations. As well, the use of liquid calibration standards was successful. Analytical calibration curves constructed from aqueous and slurry standards were exactly superimposable, verifying the validity of using liquid standards for the analytical calibration of slurries. This provides another advantage over direct analysis of solids, in that solid standards of similar matrices to the sample are often difficult to find. However, for very complex matrices the use of liquid standards may prove to be difficult. The presence of a matrix can result in non-spectroscopic (matrix) interferences, which can enhance or suppress analyte ion signals in ETV-ICP-MS, resulting in higher or lower results when compared with the true values.

Slurry analysis involves many limiting factors that can greatly affect accuracy and precision. These factors include: (1) sample homogeneity, (2) grinding and sieving, (3) slurry

preparation, (4) mixing and slurry homogeneity, (5) extraction of analyte into the slurry medium, (6) influence of the size of the slurry sub-sample, and (7) the influence of particle size on atomization efficiency. These factors will be discussed in the following paragraphs.

Sample heterogeneity is a major problem in the analysis of solids. The degree of homogeneity of a sample can be determined by performing multiple analysis on samples. Miller-Ihli^{62,63} found that 3-5 replicate readings of 3-5 slurry preparations provides sufficient information to determine homogeneity. Homogeneity is usually determined by the relative standard deviation (RSD) values. As homogeneity increases, the RSD value decreases. If the sample appears not to be homogeneous more readings may be required, a larger mass of sample (or less diluent) may be needed or a conventional acid digestion may be preferred over ultrasonic mixing.⁶³ It is suggested that the amount of solid used to make each slurry be varied in order to rule out a dependence upon the sample mass.

If required, the solid sample may undergo some type of grinding and/or sieving to improve homogeneity and reduce particle size. Since not all samples are received in a form that can be readily made into a slurry and introduced into the ETV or a graphite furnace, grinding can become a very important, if not the only, preparation step required. Techniques for grinding samples may vary depending on the sample matrix. For biological samples of all types, Teflon beads are often used in a polyethylene bottle for grinding.⁶² Often the sample may have to be freeze-dried before grinding to ensure for a proper breakup. For other samples grinding techniques, such as mortar grinding or the use of centrifugal mills, may be used.⁶² Care must be taken not to introduce any contaminants into the sample. The use of silicon nitride and boron carbide parts have been shown to cause significantly fewer problems

than zirconium oxide beads⁶⁴ and stainless steel parts.⁶²

Slurry preparation consists of adding a liquid diluent to a measured amount of a solid sample. The diluent may be water, a liquid acid, a liquid stabilizing agent, or any combination of these. Stabilizing agents such as Viscalex⁵⁸ and glycerol⁶⁵ have been used to reduce problems with sedimentation. The use of these highly viscous liquids allows particle distribution to remain constant throughout the slurry and not accumulate at the lower portions of the container. Stabilization by these agents is dependent upon sample characteristics and particle size. Surface tension effects are seen with particles that are light enough or have low enough density to float on top of the medium. Triton X-100⁶⁵ has been shown to be useful in dispersing these particles. With the addition of any of these agents problems can arise. For viscous solutions the efficiency of the autosampler can be inconsistent because of particles sticking on or inside the autosampler capillary. Samples may also stick to the outside of the graphite tube and not be analysed. A pyrolysis step will enable the stabilizing agent to be removed and thereby made incapable of interfering with vaporization and/or detection. A simple cleaning step should also be inserted between each successive determination in case any stabilizing agent remains after the vaporization step.

Introduction of the sample into the graphite tube may be made either by an autosampler or by manual input, after some sort of mixing. Many types of agitation have been used to mix and create a homogeneous slurry. Magnetic agitators and vortex mixing were used at the initial stage of investigations into slurry analysis.⁵¹ However, these require the use of manual pipetting. With slurries, the opening of the pipet tip may not be large enough to pick up large particles, which creates the problem that the sample is no longer

representative of the original sample. Gas mixing from the bottom of the sample container using argon has been reported⁶⁶, but is dependent upon particle size and characteristics of the sample. Ultrasonic agitation, automated by Miller-Ihli^{65,67}, appears to be the choice method of agitation today. Other techniques only provide homogenous slurries for sampling whereas ultrasonic agitation offers the advantage of extracting the analyte of interest into the liquid phase by ultrasonic action.

Besides the use of ultrasonic agitation, the use of acids as diluent has been shown to be effective in extracting the analyte of interest into the liquid phase. Extraction of the analyte into the liquid phase is important since large solid particles may cause problems with the autosampler operation. Miller-Ihli⁶³ showed that the use of 5% HNO₃ was useful in extracting some analyte into the liquid phase. This was shown for samples of small particle sizes (<250 μm i.d.). Bendicho and de Loos-Vollebregt⁶⁶ showed that HF was useful in extracting Cu from glass slurries. Both examples are a result of either analyte dissolution or matrix dissolution resulting in analyte dissolution.

The amount of solid sample required is dependent upon the concentration of the analyte in the sample and the final volume of the slurry. The lower the concentration of the analyte in the sample, the more solid that is needed for measurement. With some knowledge of the concentration of the analyte, one can optimize the slurry to the instrument being used. The recommended level for determinations is at least five times the detection limit of the analyte. The greater the mass of the sample used to make the slurry, the more representative the determined concentration will be of the original material. However, when working with ICP-MS, care must be taken not to overload the plasma with material, as this will cause

suppression of the analyte signal.

The amount of sample injected into the graphite tube is an important factor in the analysis of solids as slurries. The mass of the sample injected into the tube may be calculated as follows⁶²:

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

where M_F is the total mass of the sample injected into the graphite tube, V_F is the volume injected into the graphite tube, M_S is the mass of the sample added to make the slurry, and V_S is the volume of the suspension (slurry). Both the mass and volume of the slurry are important factors that determine the mass of the sample placed in the graphite tube. The larger the mass of the slurry, the larger the mass of the sample that is injected into the graphite tube for a fixed volume of diluent. The larger the volume of diluent added to the slurry, the lower the mass of the sample that is introduced into the graphite tube for a fixed mass of solid. Miller-Ihli⁶³ found that, when determining the concentration of Pb in Buffalo River Sediment (SRM 2704), the larger the mass of the sample in the slurry, the better were the results. This is reasonable because a larger amount of analyte and a more representative sample of the original material is analysed. It was found that slurry preparations of 2.0 mg/ml and above (minimum of 40 μ g in a 20 μ l drop) provided results that were sufficiently close to the certified value (<5%).⁶³ Larger sample masses provided better overall results and higher precision, with 1.5 mg/ml slurries being suggested as the minimum concentration of slurry required to yield results with reasonable accuracy ($\pm 15\%$).⁶³

The density of the material is another important factor in slurry sampling. It has been suggested that at least 50 particles for any type of material are required to be injected into the graphite tube to yield representative and reproducible results.⁶⁸ The number of particles, N_p , is given by⁶⁸:

$$N_p = \frac{M_s}{(D \times V_p)}$$

where D is the density of the solid and V_p is the volume of the particle (given by $\frac{4}{3} \pi r^3$). Directly related to this is particle size, which will also have a large influence on the results. Fuller *et al.*⁶⁹ showed that particle size was a factor for particles with a diameter greater than 25 μm . Jackson and Newman⁷⁰ confirmed that particle sizes of 30 μm and less were necessary for successful determinations of soil slurries using GFAAS. Miller-Ihli⁶⁴ found that precision was better for larger particle sizes (250-600 μm) than for smaller particle sizes for seven of eight different elements in a mixed diet reference. This effect was the result of all particles falling into a narrow range and not necessarily because of the larger particle sizes. However, this leaves open the possibility that samples may not need to be finely ground to provide reproducible results. The problem associated with large particles is that whereas they often contain larger portions of the analyte, they may exhibit inhomogeneity. Large particle sizes also require that greater masses of the sample be used in the slurry to ensure that enough particles are available for the instrument-analyser to produce a representative sample. Some particles may be too large and may not be picked up by the autosampler or result in clogging of the capillary tube.

Chapter 4 Matrix effects arising from slurry samples

4.1 Matrix Effects: Slurry Sampling of Geological and Environmental Materials

Many geological samples contain large quantities of silicon (Si) as SiO_2 and silicates, along with many other elements, their oxides, and organic materials. The content of geological and soil samples can differ greatly depending upon the region from where they are obtained. Many of these compounds are difficult to vaporize and they often contain or form refractory oxides or carbides in the ETV. As well, many geological samples may contain high levels of organic materials. High levels of organic materials add carbon to the plasma and can result in the formation of argon carbides (ArC^+), which interfere with the determination of ^{52}Cr . When geological materials are vaporized as slurries, large quantities of solids are vaporized, possibly causing suppression of the analyte signal and plasma overloading. Problems may also occur with the formation of argides (compounds of argon with other atoms), which may interfere with the determination of other elements.

Separation of the matrix from the analyte is very important when analysing complex matrices by ICP-MS. This is where the ability of ETV-ICP-MS to perform an *in situ* separation becomes important. Grégoire⁵ reported the effects of concomitant elements on the signal of the analyte. He found that the greater the mass of the concomitant element, the greater was the suppression of the analyte signal. He also observed that the greater the mass of the analyte, the less it was affected by the presence of concomitant elements.

In order to avoid interferences from the sample matrix, it would be ideal to separate the analyte from the matrix elements completely. The efficiency of the separation will depend on the relative volatilities of the analyte element and the matrix components. If the analyte

can be vaporized separately from the matrix (either earlier or later), problems from signal suppression will be greatly reduced. Figure 6a displays two signals (one corresponding to analyte and the other to the matrix) that do not overlap and, therefore, do not suffer from interference problems. As the volatilities of the analyte and matrix become more alike, *i.e.*, as they volatilize closer together (Figure 6b), then matrix interferences are more likely to occur. More ions would be present in the ion beam and, therefore, the analyte signal would be more likely to be affected by space charge effects. This would lead to a suppression of the analyte signal, since fewer analyte ions would be on a stable path through the mass spectrometer. Suppression of the analyte signal degrades the limit of detection and causes problems with analytical calibrations.

4.2 Experimental

A Perkin-Elmer SCIEX Elan 5000 ICP mass spectrometer was equipped with an HGA-600 MS electrothermal vaporizer. The electrothermal vaporizer system was fitted with a Model AS-60 autosampler equipped with an ultrasonic mixing probe (USS-100). The ultrasonic mixing probe was constructed of high-purity titanium. Pyrolytic graphite coated tubes were used throughout the experiment. The experimental conditions for both the Elan 5000 and the HGA-600 MS are given in Table 6.

A PTFE tube of 80 cm and 6-mm i.d. was used to connect the HGA-600 MS to the plasma torch. Optimization of the plasma and mass spectrometer was accomplished using solution nebulization, prior to switching to ETV mode. No further optimization of the ICP mass spectrometer was required except for small ($\pm 50 \text{ ml min}^{-1}$) variations in the carrier Ar

Figure 6. Depiction of ideal (a) and non-ideal (b) separation of analyte from matrix components.

Table 6. Instrumental operating conditions and data acquisition parameters

ICP mass spectrometer:

Rf power, W	1100
Coolant argon gas flow, l min ⁻¹	15.0
Auxiliary argon gas flow, l min ⁻¹	900
Carrier argon gas flow, l min ⁻¹	850

HGA-600MS electrothermal vaporizer:

Sample volume, μ l	20
Modifier volume, μ l	40
Reaction step	1-10 s ramp 20-60°C for 30-180 s
Dry step	5-10 s ramp 100-120°C for 30-600 s
Pyrolysis step	1-10 s ramp 200-1600°C for 30 s
Vaporization step	0 s ramp 2500°C for 6 s

Data Acquisition:

Dwell time, ms	10-20
Scan mode	peak hopping
Points/spectral peak (m/z)	1
Signal measurement	Integrated counts
Resolution	0.7 u at 10% peak-height

flow rate. The operation of the HGA-600 MS was completely-computer controlled. During the drying and pyrolysis steps of the temperature program, opposing flows of argon (300 ml min^{-1}) originating from both ends of the graphite tube removed water and other vapours through the dosing hole of the graphite tube. During the high-temperature (vaporization) step, the dosing hole was sealed by a pneumatically activated graphite probe. Once the graphite tube was sealed, a valve located at one end of the HGA workhead directed the carrier argon gas flow, originating from the far end of the graphite tube, directly to the argon plasma at a flow rate of 800 ml min^{-1} .

4.2.1 Standards and Reagents

High purity argon gas (99.9995%, Matheson Gas products, Ottawa, Ontario, Canada) was used. De-ionized water (Millipore, Mississauga, Ontario, Canada) was used throughout for all slurries and dilutions. Concentrated hydrofluoric acid (49-51%, Anachemia, New York, USA) and subsequent dilutions were used as chemical modifiers and are represented as % (w/w). Solutions of NH_4F and $\text{NH}_4\text{F-HF}$ were prepared from the solid (Aldrich Chemical Company, Inc., Milwaukee, WI, USA). Pure SiO_2 (Geological Survey of Canada, Ottawa, Ontario) was obtained and used for study of the effects of HF on silicate matrices. Standard Reference Material 4353 (Rocky Flats Soil-1) was used to monitor the organic matrix of samples.

4.2.2 Preparation of slurries

A portion of the sample (SiO_2 or SRM 4353) was weighed out into a 10 ml plastic test

tube. Deionized water was used as a diluent to prepare the slurry and the slurry was mixed using a vortex mixer. An aliquot of slurry was withdrawn immediately following the mixing, placed in another test tube and diluted with water again. This procedure was continued until the 1 ml aliquot contained the desired mass to volume ratio of solid to diluent for the determinations, *e.g.* 25 mg ml⁻¹.

4.2.3 Ultrasonic mixer (USS-100)

The system was equipped with a Perkin-Elmer USS-100 ultrasonic mixing probe constructed of high-purity titanium. The system was automated directly from the HGA-600MS and AS-60 autosampler systems. Ultrasonic mixing has been shown to be very effective in the mixing of slurry samples.^{53,63-65} The action of the ultrasonic mixing should be such that the slurry is vigorously mixed in a rolling manner, while avoiding spillage and loss of slurry due to spattering.⁶⁴ It was found that a mixing time of 30 s coupled with a power level of 30 (12 W) provided adequate mixing for slurries. Miller-Ihli⁶² has reported that the power levels are not consistent from unit to unit, therefore making a standard set of settings difficult to find.

The USS-100 consists of two parts: the mixer, consisting of a shaft of high-purity titanium (approx. 26 cm in height and 3 cm max. diameter), and an argon gas driven piston (approx. 23 cm in height and 2 cm max. diameter), which are both attached by a plastic casing (Figure 7). The total unit occupies a space of approximately 30 cm in height, 5 cm in width and 20 cm in length. The gas piston controls the vertical movement of the instrument into and out of the slurry being mixed. When the mixing probe is down, *i.e.*, in the sample cup,

Figure 7. Diagram of the Perkin-Elmer Ultrasonic Mixer (USS-100).

the probe produces its ultrasonic action with the aid of an external power source. When the mixing probe is up, *i.e.*, not in the sample cup, there is no power to the probe. The portion of the probe that does the mixing is approximately 2 mm i.d. and 25 mm in length. A power supply is provided to control the length of time for mixing and the amount of power that controls the mixing; the higher the power, the more vigorous is the mixing.

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

The purpose of high powered ultrasonic application is to cause some permanent change in the material being treated.⁷¹ For slurries, equal distribution of solid particles throughout the liquid portion of the slurry is required for reproducible sampling. The ultrasonic probe aids the particles in becoming more flocculent and keeps them in suspension longer.⁶⁹ The action of ultrasonics, which uses high frequencies, is effective at dislodging mechanically interlocked particles, *i.e.*, particles trapped or entrained within the matrix.⁷¹ This promotes dissolution by freeing analyte from the matrix and by breaking the sample into smaller particles.^{72,73}

Ultrasonics have also been reported to break down macromolecules such as cellulose, gelatin, proteins and others.^{74,75} This is especially useful for environmental samples that may contain large quantities of organic materials. The breaking down of these large, and often

difficult to vaporize, molecules aids in the removal of organic material from the graphite tube during the pyrolysis step of the temperature program. Organic material is broken down into smaller molecules that may be more easily volatilized.

4.3 Pre-vaporization of Carbon

Samples having high organic material content can cause a build up of carbonaceous residues in graphite tubes during analysis by electrothermal techniques. In GFAAS, this build up results in the blocking of light from the hollow cathode lamp(s) and degrades the signal of the analyte. In ETV-ICP-MS, the introduction of large amounts of carbon into the plasma can result in matrix effects which will have varying effects on the signal of the analyte. The removal of organic material from SRM 4353 (Rocky Flats Soil-1) in this study was examined by monitoring the ^{13}C signal from the sample at various pyrolysis temperatures. The removal of carbon at this stage reduces the amount of material entering the plasma. The introduction of large amounts of materials into the plasma could result in poor reproducibility of results and higher detection limits because of suppression of the signal due to the matrix.

The removal of carbon from slurry samples was monitored by measuring the ^{13}C signal. Since so much carbon is produced by the graphite tube, in addition to the carbon coming from the organic matrix, ^{13}C (1% abundance) was monitored instead of ^{12}C (99%) to reduce wear on the detector. To study the removal of ^{13}C from a soil sample a 20 μl aliquot of a slurry containing SRM 4353 was added to the graphite tube and the loss of ^{13}C was monitored as the pyrolysis temperature was increased with a 50 s hold time. All samples were vaporized at 2500°C. A blank of 20 μl of water was used to determine how much ^{13}C was

produced as a result of the vaporization of carbon from the graphite tube. Figure 8 shows the signals corresponding to the ^{13}C signal of the slurry, blank and the blank-subtracted slurry. Between 200°C and 1100°C the blank value is stable with the signal steadily increasing as the pyrolysis temperature is increased above this point. This steady increase is the result of greater and greater amounts of carbon vaporizing from the surface of the graphite tube caused by the deterioration of the tube from exposure to higher temperatures. The blank-subtracted signal shows a general increase in the amount of carbon vaporized up to 1000°C and then a decrease at higher temperatures. As the pyrolysis temperature increases, greater amounts of carbon-containing compounds will be either volatilized or decomposed into compounds of varying volatility. As well, the chemical state of carbon volatilized at a 400°C pyrolysis temperature may be different from the form of carbon volatilized at 1000°C. If this is true, then more carbon may condense on the cooler ends of the graphite tube and in the PTFE tubing connecting the ETV unit to the ICP. This would result in a less efficient transport at lower pyrolysis temperatures and consequently lower ^{13}C signals when using lower pyrolysis temperatures. Fonseca and Miller-Ihli⁷⁶ suggested that large carbon particles may become trapped within the ETV cell and transfer line, not reach the plasma and decrease sample transport efficiency. If this is the case, then the ^{13}C signal below 1000°C may not be rising, but may actually be stable up to 1000°C. At temperatures greater than 1000°C, the ^{13}C signal begins to decrease, as a result of the loss of volatile material through the dosing hole during the pyrolysis stage. Examination of the ^{13}C signal from the slurry before blank subtraction shows that the optimum temperature for the removal of organic material is 1200°C. This point represents the lowest ^{13}C signal in the temperature range where organic material is

Figure 8. Monitoring of ^{13}C signal for the study of the loss of organic material from SRM 4353 as a function of pyrolysis temperature. a) actual signal; b) blank signal; c) blank-subtracted signal

removed from the graphite tube prior to vaporization. Temperatures greater than 1200°C yield higher total ^{13}C signals because of the increasing blank value from the graphite tube. Whereas not all of the organic material is removed from the graphite tube, the remaining carbon may act as a physical carrier for the analyte.⁷⁶ The optimum pyrolysis temperature of 1200°C for removal of carbon is low enough to be used for this purpose without loss of radium, which is lost from the graphite tube at a temperature of 1400°C and above.⁷⁷

The use of oxygen or air ashing has also been reported to be effective in reducing the effects of organic materials on the signal. Oxygen ashing allows for the complete removal of the organic-based matrix by converting the pyrolysis process into a combustion process. Salmon *et al.*⁷⁸ showed that oxygen ashing also resulted in a shift in the appearance temperature of lead to a higher temperature in GFAAS. Fonseca and Miller-Ihli⁷⁶ applied oxygen ashing to ETV-ICP-MS and concluded that the organic material present in the slurry acts as a physical carrier between the ETV and the ICP-MS. Oxygen ashing improved their results by providing a more complete combustion of the slurry matrix, making the analyte transport more like the transport of aqueous calibration standards. However, the slurries used by Fonseca and Miller-Ihli⁷⁶ were of a highly organic nature (SRM 1548 Total Diet, SRM 1628a Coal, SRM 1566a Oyster Tissue and LUTS-1 Lobster Hepatopancreas) compared to the samples analyzed in this research. Time restraints have prevented investigation of oxygen ashing as an alternative to high temperature pyrolysis steps and future investigations should be conducted in this area.

4.4 Pre-vaporization of Silicon

The major component in many geological samples is silicon (Si) in the form of SiO_2 and silicates. One problem in working with these samples is the effect that SiO_2 has on graphite tubes. Bendicho and de Loos-Vollebregt⁷⁹, working with glass slurries in GFAAS, noted that after 50-100 firings the absorbance signals decreased whereas the relative standard deviation (RSD) values increased. Eames and Matousek⁸⁰ and Müller-Vogt and Wendl⁸¹ surmised that this was due to the reaction of silicon oxide with the graphite tube surface at high temperatures (1650°C) to yield silicon carbide:

The addition of HF to the samples reduced this problem considerably. Bendicho and de Loos-Vollebregt⁶⁶ were the first to use HF to remove Si from a glass matrix. They monitored the release of Cu, a contaminant in fibre optic glass, from the glass matrix. As the percentage of HF in each slurry sample increased, the absorbance of Cu increased, suggesting that more Cu was being released from the matrix. This was thought to be due to the conversion of SiO_2 (b.p. 2230°C) to volatile SiF_4 (b.p. -85.7°C). Hydrofluoric acid is highly reactive and attacks SiO_2 in the following manner:

The increase in the absorbance of Cu was also caused by the extraction of the analyte into the liquid phase of the slurry. As the concentration of HF is increased more analyte should be

released into solution because of the dissolution of the sample. The mixing time of the slurries also had an influence on how much analyte was extracted into the liquid phase. An optimum time of three minutes of mixing by Ar gas bubbling gave close to 100% extraction of Cu in glass slurries containing 3% HF.⁶⁶ This may be the best method for mixing slurries containing HF in view of its strong reaction with various materials, *e.g.*, HF attacks titanium probes used for ultrasonic agitation. The use of HF was also shown to prolong the life of the graphite tubes, resulting from the removal of SiO₂ before high temperatures were attained.

López-García *et al.*⁸² added HF to soil samples for the determination of selenium by GFAAS. They found that the silica (SiO₂) content in the soil samples appeared to cause the greatest signal suppression when compared with Fe₂O₃ and Al₂O₃. They found that the selenium signal increased for the samples as the concentration of HF was increased.

For the geological samples analysed in this research, the SiO₂ content was between 45% and 80%. The effects of various chemical modifiers containing fluoride (NH₄F, NH₄F-HF, HF) were studied on a Si matrix (pure SiO₂) to determine which would be most effective in removing Si from the graphite tube. Silica forms volatile silicon fluoride in the presence of fluorinating compounds. It was found that without removal of SiO₂, the analysis of materials with low concentrations of Ra was likely not possible because of signal suppression caused by matrix effects, since slurries containing greater than 1 mg ml⁻¹ of solid material caused these effects. The analysis of slurries has been shown to be most successful in samples with a minimum slurry content of 1.5 mg ml⁻¹ in the graphite furnace.⁶² At this concentration and above, RSD values decreased and the accuracy of the determination of analyte in standard reference materials increased.⁶² Therefore, modification of the matrix to remove SiO₂ was

considered for the quantitative analysis of radium in soils.

The choice of NH_4F , $\text{NH}_4\text{F-HF}$ and HF as chemical modifiers was based on their potential to fluorinate the SiO_2 . Wanner *et al.*⁸³ used NH_4F and HF as chemical modifiers for the determination of B, U and La by ETV-ICP-MS. They found that the release of HF from NH_4F was beneficial at low temperatures for the formation of BF_3 . The dissociation of NH_4F into NH_3 and HF is complete at 350°C ¹⁴ and would therefore be useful for moderate vaporization and drying steps without loss of the chemical modifier in large quantities.⁸³ The choice of $\text{NH}_4\text{F-HF}$ was based on its similarity to NH_4F and the potential for fluorination due to both the NH_4F dissociation and the initial dissociation of HF . Hydrofluoric acid was chosen as a chemical modifier based on the work on Bendicho and de Loos-Vollbrecht⁶⁶ on glass slurries. Glass contains high amounts of silica and the effectiveness of this work and the work of Lopez-García *et al.*⁸² on soils support the use of HF for these types of samples.

A study was conducted to determine which isotope of Si ($m/z = 28, 29$, or 30) should be monitored since carbon-based spectral interferences occur with all three isotopes. The isotopes are all subject to interference by the various isotopic combinations of C, O and N (^{12}C , ^{13}C , ^{16}O , ^{18}O , ^{14}N , ^{15}N). Contributions of the chemical modifiers to the total C, N and O content, through carbon stripping of the graphite tube and direct addition of N, may produce high levels of interferents with the three isotopes. Table 7 shows the isotopic ratios for the background-subtracted Si signals determined from the experimental data. A ratio for $^{28}\text{Si}:^{29}\text{Si}:^{30}\text{Si}$ of 92:5:3 was found, which is fairly close to the natural abundance ratio of 92.2:4.67:3.10. The ratio was found to hold for samples vaporized with each chemical modifier.

Table 7. Isotopic ratios for Si determined from the experimental studies using fluorinating chemical modifiers.

Sample		Counts			Ratio	Found	
NH ₄ F, %	²⁸ Si	²⁹ Si	³⁰ Si	Total Si	²⁸ Si	²⁹ Si	³⁰ Si
0.0	972000	51360	40690	1064050	91.3	4.8	3.8
0.5	1742000	98915	67230	1908145	91.3	5.2	3.5
1.0	1925000	109200	74650	2108850	91.3	5.2	3.5
2.0	1112000	60530	40690	1213220	91.6	5.0	3.4

Actual ratio: 92.2 : 4.67 : 3.10

Note: All values have an RSD of $\leq 10\%$.

Of the three chemical modifiers chosen, only HF provided a sufficient decrease of Si signal to proceed with further experiments. The effects of 0-2.0% (w/v) NH_4F and NH_4F -HF provided little to no decrease in Si signal intensity. Modifiers were added as 20 μl aliquots with 20 μl aliquots of SiO_2 slurry. At concentrations of 2.0% (w/v) for these chemical modifiers, a significant decrease in the Ar dimer intensity suggested possible matrix effects arising from the use of these modifiers. At this concentration of NH_4F and NH_4F -HF a slight decrease in Si signal over the signal for Si without modifier addition was observed. However, it is felt that the addition of higher concentrations of these modifiers would result in severe matrix effects that would outweigh the benefits of their use.

Hydrofluoric acid was found to be the most effective of the three chemical modifiers. This was expected based on the research of Bendicho and de Loos-Vollebregt⁶⁶ on glass slurries. When reaction times for the SiO_2 and HF were short (drying time 30 s) the 40% HF was more effective than the 50% HF in decreasing the Si signal. This was a little unexpected, since it was assumed that the concentrated acid would provide the best removal of Si because of the larger amounts of fluoride present. This may be explained simply by experimental variance of the results due to the violent nature of the reaction. The reaction generally resulted in a plume of vapour being expelled from the dosing hole of the graphite tube along with violent spattering of the SiO_2 and HF (observed through the quartz window) throughout the graphite tube during the ramp to the pyrolysis temperature. When the length of time of interaction between HF and SiO_2 (the digestion time) was increased between 30 s and 120 s, there was little difference among the three acid strengths, although the 50% acid did provide a slightly lower Si signal than the 25% and 40% HF. Therefore, 50% HF was used for later

experiments. A study of hold (digestion) times ranging between 30 s and 120 s (Figure 9) for 50% HF showed a decreasing trend in Si signals between 30 s and 90 s, with similar signals between 90 s and 120 s for a 125 μg sample. A pyrolysis temperature of 1200°C and a vaporization temperature of 2500°C were used to maintain continuity with the optimum carbon matrix removal temperature from earlier studies. Whereas the signal did stabilize for the samples with a 90 s reaction time, the reaction still produced some spattering of the solid and the HF in the graphite tube and expulsion of vapour.

The next step was to reduce the rate of the exothermic reaction between SiO_2 and HF before continuing on to the analysis of real samples. The violent nature of the reaction was always observed during the ramp to the pyrolysis step. The temperature program was analyzed and a stop watch was used to decide an approximate time and temperature at which the reaction occurred. A varying temperature intermediate step was added between the drying step and the pyrolysis step to narrow down the temperature of this event further. It was

found that the reaction was occurring at a temperature close to 120°C (the boiling point of HF). Therefore, the intermediate step was changed to 120°C to see if this would further reduce the problem. A drying time of 30 s was maintained and a hold of 30 s for the intermediate step at 120°C was used to eliminate the problem. No spattering of the SiO_2 and the HF and only minimal vapour losses were observed.

Once the violence of the reaction was reduced, the optimum conditions for the removal of silica from the graphite tube were examined. One factor was to determine the optimum reaction time and the optimum amount of HF required for complete dissolution and

Figure 9. Effects of reaction times of concentrated hydrofluoric acid (50% HF) on the Si signal from 125 μg SiO_2 vaporized at 2500°C.

conversion of SiO_2 into SiF_4 . Calculations show that for a 1 mg sample, the minimum amount of 50% HF (28.9 M) required to convert all of the SiO_2 into SiF_4 would be 2.3 μl . Samples of SiO_2 of various masses were weighed into a plastic container and the time for dissolution by 50% HF at room temperature was monitored. When adding HF directly to dry SiO_2 , a white vapour, which was likely SiF_4 , was observed. A complete dissolution of the samples was achieved at an average time of 10 minutes using mild, manual shaking and a volume of HF of 40-60 μl per mg of SiO_2 .

The previous two studies suggest that a longer time of interaction between the two reagents would probably increase the amount of volatile SiF_4 formed prior to the ramp to higher temperatures. Bendicho and De Loos-Vollebregt⁶⁶ examined various mixing times and found that three minutes of mixing the glass slurries in HF produced the maximum amount of Cu extraction into solution for 15 μm particle sizes. This was determined by GFAAS from the maximum Cu absorbance observed from a study of various mixing times. Mixing times of greater than three minutes showed virtually no change in the Cu absorbance. For particles of 25 μm in size the length of time for the Cu extraction was nearly 15 minutes. To determine the length of time required for optimal removal of SiO_2 from the graphite tube an experiment was conducted using the reaction between the SiO_2 and HF. Using sample sizes of 500 μg SiO_2 and 40 μl of HF, the SiO_2 and HF were allowed to react at a temperature of 60°C for 2-10 minutes, prior to the drying, pyrolysis and vaporization steps. A temperature of 60°C was chosen to enhance the reaction between SiO_2 and HF since physically mixing the samples inside the ETV was not possible. Tertykh *et al.*⁸⁴ observed that the rate of reaction between anhydrous HF and SiO_2 was slow at 20°C, but was much faster at 150°C and instantaneous

at 250°C. The reaction was also observed to be accelerated by the presence of water in the system. It was found that the minimum time required to observe a decrease in the Si signal for a 500 μ g sample was 5 minutes.

Based on the above finding for the 500 μ g sample (5-10 minutes to reduce Si signal) and the findings of the 125 μ g sample (approximately 90 s for optimal removal of SiO₂), a time of three minutes was chosen for the digestion time for future studies. This intermediate time should be effective for the analysis of real samples. The geological samples that will be analyzed below have a SiO₂ content between 45% (w/w) and 80% (w/w). For a 500 μ g sample this corresponds to 225-400 μ g of SiO₂ per sample. For smaller sample sizes, the total quantity of SiO₂ would be even lower. The composition of geological samples is much more complex than pure SiO₂, often containing silicates that are difficult to dissolve. However, it is reasonable to assume that a three-minute reaction time, along with a further one minute of interaction during the two drying stages, should provide sufficient removal of the silica/silicate matrix.

4.5 Summary

Geological and environmental samples may contain high amounts of silica, silicates and/or organic material. Removal of these components from a sample prior to vaporization should allow the analyte in a sample to be more easily vaporized and to be less prone to matrix effects. The removal of the organic and silica matrices of these types of samples prior to vaporization has been addressed through selective vaporization and chemical modification.

Chapter 5 THE DETERMINATION OF RADIUM IN SLURRIED GEOLOGICAL SAMPLES BY ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

5.1 Introduction

Graphite furnace atomic absorption spectrometry (GFAAS) has been successfully applied to the analysis of slurries. Reviews by Bendicho and de Loos-Vollebregt⁵¹, Miller-Ihli⁵⁸ and Arruda *et al.*⁵⁹ have shown the wide variety of sample types analyzed by GFAAS. A wide range of elements have been determined in soils^{85,86}, sediments^{87,88} and rocks.⁸⁹ However, the determination of radium by atomic absorption spectrometry has been hindered by the unavailability of radium hollow cathode lamps and an analytical sensitivity too poor to be of use.

Inductively coupled plasma mass spectrometry (ICP-MS) can analyze most of the elements present in the periodic table. The coupling of ICP-MS with electrothermal vaporizers (ETVs) has improved detection limits by 10-100 times over those achieved using solution nebulization (SN) sample introduction and eliminates some background spectral interferences. As well, detection limits are improved over those found using GFAAS.⁶ ETV-ICP-MS has also been shown to be able to handle a wide range of sample matrices existing as slurries^{53,75,90} or solids.^{56,91,92}

Recent research has been conducted into the determination of radium (²²⁶Ra) by ICP-MS using SN²² and ETV^{23,24,77} sample introduction. A detection limit of 1 ng ml⁻¹ was obtained for SN²² while detection limits of 12-34 fg ml⁻¹ were obtained using ETV sample introduction.^{23,24,77} These studies were performed using aqueous solutions.

Electrothermal vaporization sample introduction into an ICP-MS offers similar

detection limits for radium to those found in alpha spectrometry^{16,17}, thermal ionization mass spectrometry^{18,19} and radon emanation.²¹ As well, ETV-ICP-MS offers advantages over other methods of radium determination such as: (1) faster analysis time, (2) ability to handle small sample sizes (μl , μg -mg) and (3) little to no pre-lab work-up required.

The objective of this study was to determine ^{226}Ra in samples of geological and environmental origin, introduced as slurries in ETV-ICP-MS. Previous studies using slurries with ETV-ICP-MS have been performed on samples containing less difficult matrices such as coal⁵³ and biological⁵³ and plant⁵⁶ samples. Geological and environmental samples are often more difficult to vaporize because of the presence of large quantities of silica, silicates and oxides of other elements.

5.2 EXPERIMENTAL

A Perkin-Elmer SCIEX Elan 5000 ICP mass spectrometer was equipped with an HGA-600 MS electrothermal vaporizer. The electrothermal vaporizer system was fitted with a Model AS-60 autosampler equipped with an ultrasonic mixing probe (USS-100). The ultrasonic mixing probe was constructed of high-purity titanium. Pyrolytic graphite coated tubes were used throughout the experiment. The experimental conditions for both the Elan 5000 and the HGA-600 MS are given in Table 8.

A PTE tube of 80 cm and 6-mm i.d. was used to connect the HGA-600 MS to the plasma torch. Optimization of the plasma and mass spectrometer was accomplished using solution nebulization, before switching to ETV mode. No further optimization of the ICP mass spectrometer was required with the exception of small ($\pm 50 \text{ ml min}^{-1}$) variations in

Table 8. Instrumental operating conditions and data acquisition parameters

ICP mass spectrometer:

Rf power, W	1100
Coolant argon gas flow, l min ⁻¹	15.0
Auxiliary argon gas flow, l min ⁻¹	900
Carrier argon gas flow, l min ⁻¹	850

HGA-600MS electrothermal vaporizer:

Sample volume, μ l	20
Modifier volume, μ l	40
Digestion step	10 s ramp 60°C for 180 s
Dry step	5 s ramp, 100°C for 30 s 10 s ramp, 120°C for 30 s
Pyrolysis step	10 s ramp 500-1200°C for 30 s
Vaporization step	0-2 s ramp 2500°C for 6 s

Data Acquisition:

Dwell time, ms	10-20
Scan mode	peak hopping
Points/spectral peak (m/z)	1
Signal measurement	Integrated counts
Resolution	0.7 u at 10% peak-height

the carrier Ar flow rate. The operation of the HGA-600 MS was completely computer-controlled. During the drying and pyrolysis steps of the temperature program, opposing flows of argon (300 ml min^{-1}) originating from both ends of the graphite tube removed water and other vapours through the dosing hole of the graphite tube. During the high-temperature (vaporization) step, the dosing hole was sealed by a pneumatically-activated graphite probe. Once the graphite tube was sealed, a valve located at one end of the HGA workhead directed the carrier argon gas flow, originating from the far end of the graphite tube, directly to the argon plasma at a flow rate of 800 ml min^{-1} .

5.2.1 Standards and Reagents

High purity argon gas (99.9995%, Matheson Gas products, Ottawa, Ontario, Canada) was used. De-ionized water (Millipore, Mississauga, Ontario, Canada) was used throughout. Concentrated hydrofluoric acid (49-51% Anachemia, New York, USA) was used as a chemical modifier. Nitric acid (Anachemia, New York, USA) was used as a diluent for slurries. Four standard reference materials were used: BL-5 (low-grade concentrate), DH-1a (ore grade pebble conglomerate), EJB 5-81 (sub-volcanic rock) and SRM 4353 (Rocky Flats Soil-1). Granite (GS-N) was used as the blank when determining the limits of detection. Dilutions of a stock solution of radium-226 (NIST SRM 4966), which was certified to contain 268.2 Bq g^{-1} of ^{226}Ra , were used for the standard additions experiments.

5.2.2 Preparation of slurries

Slurries were prepared by placing 12.5 - 75 mg of sample material into a 1.5 ml cup

and diluted with 1 ml of 5% (v/v) nitric acid. One sample of 0.00625 mg was prepared by removing 1 ml of a 4 ml dilution of 0.0250 g in a plastic test tube mixed by a vortex mixer. All slurries were prepared from powdered standard reference materials. Samples were measured by the addition of 40 μ l HF, 20 μ l H₂O and 20 μ l of slurry to the graphite tube. For the standard addition calibration the 20 μ l H₂O was replaced by 20 μ l of diluted radium standard. The addition of 20 μ l of H₂O was required to maintain a consistent drop size before and after the standard additions. Slurries were mixed using the Perkin-Elmer USS-100 for 30 s with a power setting of 30 W.

5.3 RESULTS AND DISCUSSION

5.3.1 Radium Fluoride, RaF₂

The addition of fluorinating compounds in ETV-ICP-MS was first attempted by Kirkbright and Snook⁹³ when they added Freon to the argon gas stream as a chemical modifier. The idea was to convert elements that formed refractory compounds into their more volatile fluorides. They observed improvements of 1-2 orders of magnitude in the limits of detection for five elements.⁹³ Wanner *et al.*⁸³ successfully used NH₄F as a chemical modifier for determining boron using ETV-ICP-MS. As well, Bendicho and de Loos-Vollbregt⁶⁶ have shown the effectiveness of HF as a fluorinating agent.

In these experiments HF was used as a chemical modifier to convert SiO₂ into the more volatile compound SiF₄. It was hoped that this would improve the determination of radium in geological and environmental samples by removing a portion of the sample matrix prior to vaporization and avoiding the matrix effects caused by adding large amounts of

materials to the plasma. The addition of HF to the samples also leads to the possibility of the formation of radium fluoride. Radium fluoride, RaF_2 has been obtained by dissolving radium carbonate in HF ^{94,95} and by the conversion of the chloride into the fluoride.⁹⁶ Since fluorides are often more volatile than other compounds, a study was conducted to determine the effects of HF addition on the parameters for radium determination in geological and environmental samples.

A 20 μl aliquot of aqueous radium standard and 40 μl of HF were added to the graphite tube and a pyrolysis curve was constructed between 500°C and 1100°C to determine the effects of HF addition on the radium signal. Figure 10 shows that the optimum pyrolysis temperature occurs at 800°C, whereas the optimum pyrolysis temperature without HF addition was found at 1400°C.⁷⁷ The results of an examination of the appearance times for radium with and without HF addition, using a 2 s ramp, are shown in Figure 11. The difference in the appearance time of the signals (0.3 s) suggests that a different mechanism of vaporization is occurring in the sample containing HF. If the signals had appeared at the same time then one could assume that the mechanism of vaporization, with and without the addition of HF, is the same. McIntyre *et al.*⁷⁷ determined that the chloride and nitrate forms of radium (taken as the oxide) appear at approximately 1600°C. However, it is observed that a difference in the appearance temperature of between 133°C (4.5 s to maximum signal) and 300°C (1000°C s⁻¹) occurs between the sample containing HF and the sample without HF during the 0.3 s time difference. This places the appearance temperature of the sample containing HF somewhere between 1300°C and 1470°C. The melting point of RaF_2 was determined by Kolowrat⁹⁶ to be 1212°C. If the actual appearance temperature is closer to

Figure 10. Pyrolysis curve for 20 μl ^{226}Ra with the addition of 40 μl of concentrated HF vaporized at 2500°C.

Figure 11. Shift in the appearance time of radium signal due to addition of HF for a 2 s ramp to 2500°C; a) without HF and b) with HF.

1300°C then the radium may be volatilizing directly as the fluoride. If the actual appearance temperature is closer to 1467°C, the radium may be volatilized as a different compound, most probably not the oxide, because the difference between the appearance temperature of this sample and that of the oxide does not support this hypothesis. More research needs to be conducted in this area in order to determine the actual mechanism. The most important thing to extract from this experiment is the fact that the sample containing HF does vaporize earlier and therefore a lower pyrolysis temperature, determined to be 800°C, is required to obtain the maximum radium signal.

5.3.2 Method of Standard Additions

Analytical calibration curves constructed from aqueous solutions cannot always be used for determination of analyte in solid samples. In many cases, the sample matrix may cause enough interference to enhance or suppress the analyte signal, whereas the aqueous solution would not be affected, resulting in either high or low results. As well, solid samples with similar matrices to the sample are not always available for use. When this situation occurs, the method of standard additions is useful for analytical calibrations. The method of standard additions is usually exempt from these problems since standards are added directly to the sample, thus leaving the matrix unchanged. The suggested range for standard additions is the concentration that produces a rise in the analytical signal of between 1.5 and 3 times the signal of the unspiked sample.⁹⁷ Often, the larger the standard addition, the greater is the error of the result. Therefore, in these studies additions producing signals less than 1.5 times the original signal in the unspiked sample were made occasionally.

The method of standard additions was applied to determine the concentration of ^{226}Ra in four geological samples. The performance of both single and multiple addition was studied. The single addition method is valid only when exactly the same amount of radium is added to the sample as the sample contains, *i.e.*, the concentration of radium in the slurry is equal to the concentration of radium in the addition. Vanhaecke *et al.*⁵⁶ successfully used the single standard addition method for the determination of As in solid standard materials. Their results were within 10% of the certified values for 3 of 4 standards.⁵⁶

This research suggested that the method of standard additions could give results with a $\pm 10\%$ difference from the certified value for 3 of 4 standards (Table 9). Relative standard deviation values ($\sim 10\%$) indicated sample homogeneity within even small (0.0125 g ml^{-1}) samples for some of the standards analyzed. Sample homogeneity generally improved (RSD values were lower) as the mass of solid in the slurry was increased (Table 9). The use of external calibration was shown to be unfavourable since the samples were prone to matrix effects and could yield much lower results for radium than the actual sample contained. Figure 14 shows the signals for radium and the argon dimer for uranium ore EJB 5-81 for slurry concentrations of 0.0125 , 0.0250 and 0.0500 g ml^{-1} . If a linear relationship occurred that was not subject to matrix effects, then an increase in the signal would be expected for higher masses of solid. However, as the sample mass was increased, the radium signal decreased. It was also observed that the signal for the argon dimer, monitored to indicate matrix effects, reached near zero intensities for most of the radium signal. This suggests that most of the matrix material that causes suppression is vaporizing during this time. The major components in most of these samples (Table 10) gave signals that overlapped, to some extent,

Table 9. Results of the determination of ^{226}Ra in three* geological reference materials.

Sample	Slurry	^{226}Ra in slurry	Std. Add.	Result	RSD	Error
	mg ml ⁻¹	pg 20 μl^{-1}	pg 20 μl^{-1}	ng g ⁻¹	%	%
DH-1a	25	0.43	0.43	0.017	31	-98.0
0.85 ng g ⁻¹	50	0.85	0.09	0.080	16	-90.6
	75	1.3	0.26	0.79	6.76	-7.43
BL-5	6.3	2.9	2.9	2.67	-	-88.4
23.1 ng g ⁻¹	12.5	5.8	5.8	21.6	16.84	-6.49
	25	12	23	24.6	7.84	+6.49
EJB 5-81	12.5	0.59	0.62	2.01	3.59	-14.8
2.4 ng g ⁻¹	25	1.2	2.5	2.6	2.4	+10.6

* SRM 4353 contained quantities of ^{226}Ra below the limit of detection.

Figure 12. Suppression of ^{226}Ra signal in standard reference material EJB 5-81 uranium ore matrix vaporized at 2500°C . — ^{226}Ra , --- Ar dimer.
a) 12.5 mg ml^{-1} , b) 25 mg ml^{-1} , c) 50 mg ml^{-1}

Table 10. Major components of the four standard reference geological materials, as percent composition.

Component, %	BL-5	DH-1a	EJB 5-81	SRM 4353
Al ₂ O ₃	11.3	6.50	11.41	12
CaO	5.6	0.06	7.74	0.92
Fe ₂ O ₃	-	-	-	5.7
K ₂ O	0.5	1.72	3.12	1.8
MgO	2.5	0.12	0.31	0.49
MnO ₂	0.06	-	0.09	0.072
Na ₂ O	4.9	0.05	1.40	1.1
SiO ₂	47.1	79.75	65.17	73
Th (ppm)	40	910	2310	22
U (ppm)	7.09%	2629	7030	320
Ra (ng g ⁻¹)	23.1	0.851	2.36	0.001

with the radium signal (Figure 15). The suppression of the signal here is most probably caused by the massive amounts of material being vaporized into the plasma causing severe space charge effects. This results in less energy being available to dissociate and then ionize compounds of radium.

5.3.3 Analytical Figures of Merit

Analytical figures of merit for the determination of ^{226}Ra in solid samples by ETV-ICP-MS are given in Table 11. The limit of detection for Ra was calculated as the mass of Ra equivalent to a signal equal to three times the standard deviation of the blank. Standard reference material GS-N (granite), which contains no radium, was used for the blank. An absolute limit of detection of 9.3 fg was obtained for a 0.0250 g ml⁻¹ slurry which corresponds to a relative limit of detection of 186 fg ml⁻¹ in a 50 µl sample. An absolute limit of detection of 20 fg was obtained for a 0.0125 g ml⁻¹ slurry which corresponds to a relative limit of detection of 401 fg ml⁻¹ in a 50 µl sample. The analyte signal could be measured with a precision of 1.6% for the 0.0250 g ml⁻¹ slurry and 2.2% for the 0.0125 g ml⁻¹ slurry.

5.4 Summary

It was found that radium, as the isotope ^{226}Ra , can be successfully determined in solid samples of geological and environmental origin using slurry sampling with ETV-ICP-MS. Radium has been successfully determined in three reference materials with good accuracy and precision. A limit of detection of 9.3 fg was obtained for samples containing 500 µg of sample in a 20 µl aliquot. Matrix interferences caused by organic matter have been reduced,

Figure 13. Major elemental components found in standard reference material EJB 5-81 vaporized at 2500°C. (A) ^{27}Al , (B) ^{56}Fe , (C) ^{44}Ca , (D) ^{30}Si , and (E) ^{226}Ra . (F) represents the argon dimer.

Table 11. Analytical figures of merit for the determination of radium in slurries of geological materials.

	0.0125 g ml ⁻¹	0.0250 g ml ⁻¹
<u>Blank</u>		
	Integrated Signal	Integrated Signal
²²⁶ Ra	243	75
σ , n=10	49	20
RSD, %	20	26
3 σ	148	59
 <u>Radium</u>		
²²⁶ Ra, 14.7 pg	108 500	92 544
σ , n=5	2 334	1 507
RSD, %	2.2	1.6
L.O.D. _{abs} , fg	20	9.3
L.O.D. _{rel} , ppq	401	186
L.O.D., Bq l ⁻¹	15	6.9

using high pyrolysis temperatures, and by silica, using HF addition, with only partial success.

Chapter 6 SUMMARY AND FUTURE WORK

The determination of radium by ETV-ICP-MS has been shown to be successful in both aqueous and solid samples. The optimum conditions for determinations in aqueous samples include a pyrolysis temperature of 1400°C and a vaporization temperature of 2500°C. The optimum conditions for direct analysis of solid samples as slurries require a more complex temperature program and a more complex analytical method to be used. The addition of concentrated HF as a chemical modifier decreases the pyrolysis temperature of radium to 800°C. This is probably due to the formation of radium fluoride, which probably vaporizes *via* a different mechanism than the chloride and nitrate forms of radium. The chloride and nitrate forms of radium vaporize as an oxide from the graphite tube surface, similar to the other alkaline earth elements (Be, Mg, Ca, Sr and Ba). Detection limits for both aqueous and solid sampling are 1.7 fg and 9.3 fg, respectively.

Future research should be conducted for the determination of radium and other elements in solid samples. Samples of geological and environmental origin contain many more components than those researched in this thesis. Since most elements volatilize more easily as halides, the introduction of various Freon compounds to the argon gas during the pyrolysis step could significantly reduce even further the interferences caused by the sample matrix. As well, removal of organic materials using oxygen ashing should be investigated. This could help lower the pyrolysis temperature and provide a more complete removal of organic material from the graphite tube prior to determination of the analyte, resulting in better accuracy and precision.

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IMAGE EVALUATION TEST TARGET (QA-3)

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