DETERMINATION OF PLATINUM GROUP ELEMENTS IN ENVIRONMENTAL SAMPLES USING IN-LINE MINI-COLUMN PRE-CONCENTRATION AND SEPARATION COUPLED TO INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

by

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A thesis submitted to the Department of Chemistry

in conformity with the requirements for

the degree of Master of Science

Queen's University

Kingston, Ontario, Canada

January, 2008

Abstract

A method for the determination of platinum group elements (PGEs) in natural tree samples was developed. An alumina column in-line with inductively coupled plasma mass spectrometry (ICP-MS) achieves the separation of interferents as well as pre-concentration of the analytes.

The application of this proposed method on tree top samples displayed an effective separation of Ru, Rh, Re, Pd, Ir and Pt from the interferents, Ni, Cu and Zn for quantitative analysis of the analytes. The concentration data was compared to ICP-HRMS data and while it was difficult to determine whether the concentrations were in agreement or not, as both methods have a large degree of error. However, both methods displayed elevated concentrations of PGEs in areas over geological conductors in Rock Lake, Manitoba.

This proposed method offers distinct advantages over previous on-line methods, as it is extended to include multiple PGEs as well as reduces sample consumption to a more suitable volume for natural samples. While the detection limit is higher than previous methods due to the lowered sample volume, it is still lower than the detection limits reported in commercial laboratories.

Acknowledgements

I would like to thank Dr. Beauchemin and Dr. Kyser, my supervisors first and foremost for their patience and guidance. To all the members of the Beauchemin lab, who helped figure out ICP-MS problems, and to Kim Wiegand who helped tremendously by assisting me with analysis while I was away on maternity leave. I'd like to thank the members of the Queen's University Facility for Isotope Research, especially Bill MacFarlane, Don Chipley, and April Vuletich. Without all of your constant help and expertise, none of this would have been possible.

I would like to also thank Anglo American for funding for this research, and especially to Chris Oates for keeping me on track with my goals.

My family has been a tremendous source of support through this degree. To my husband, Phil, who has made many sacrifices in order for me to achieve my goals. I appreciate it more than you could ever know. To my daughter, Kaitlyn; the joy you bring to my life far outweighs the challenges of being a mother and a student.

Table of Contents

List of Figures

List of Tables

CHAPTER 1: INTRODUCTION

1.1 Platinum group elements in the environment

The determination of platinum group elements (PGEs) in the environment is of growing importance. In recent years, PGEs have been used for a variety of applications, such as in catalytic converters of automobiles, as a catalyst for the production of pharmaceutical materials and in drugs used for cancer chemotherapy.[1-3] The increased number of these applications have contributed to the increased concentration of PGEs in the environment, especially in the vegetation and soil around heavy traffic areas.[2,4] The concentration of PGEs in these samples is important to determine in order to assess risks to human health and the health of other living organisms.

The determination of low level PGEs is also of growing importance in exploration geochemistry. PGEs are known to be present in vegetation in very low concentrations. However, there is an increased uptake of these elements in vegetation situated in PGE contaminated soils.[5] Therefore, trees that are situated over a possible ore deposit may also have higher concentrations of PGEs than the surrounding trees. A fast and easy method to determine the concentrations of PGEs in tree top samples could greatly reduce the high cost of exploration geochemistry. A helicopter can simply sample a large amount of tree tops over a vast area much quicker than ground teams. The analysis of PGEs in these tree top samples can point to areas that may contain an ore deposit, and thus more localized ground searches can then be conducted. On the other hand, PGEs are extremely difficult to determine in environmental samples because of problems associated with the storage of these elements in solution as well as the limitations of the analytical techniques that are currently available.

PGEs are elements that have some of the lowest abundances in the Earth's crust.[6] At such low concentrations, PGEs are very susceptible to contamination, which may introduce significant error in the analysis. To minimize this error, ultra-pure reagents are required and tedious cleaning procedures must be employed.[6] There are also problems with the longevity of the solutions prepared for analysis of the PGEs. PGEs have a tendency to adsorb to the walls of storage containers as well as the sample introduction tubing used in inductively coupled plasma mass spectrometry (ICP-MS). There can be a significant decrease in the concentration of PGEs in a sample throughout the day.[6] A loss of Pt was observed from solutions stored in polyethylene bottles in the absence of chloride ions in the matrix. In the presence of chloride ions, PGEs may form chlorocomplexes that can stabilize them and minimize adsorption onto the walls of storage bottles.[7] Polystyrene storage containers were found to provide appropriate stability for Pt.[7]

The detection of low level PGEs is difficult to achieve. The detection limits of most instruments are not low enough to properly quantify these elements, which are found in the ng/L concentration range. Furthermore, the complexity of the matrix in geological samples is also a great limitation to the detection of these elements. ICP-MS is the most promising instrumentation for the detection of PGEs, because it has very low detection limits and high sensitivity. It also has the ability to monitor multiple ions in a single run, which is beneficial when the volume of sample is limited.[8]

1.2 Inductively coupled plasma mass spectrometry

ICP-MS was first developed in the early 1980s by Houk *et al.*[9] The first ICP-MS instruments were commercially available in 1984. ICP-MS is the most common technique for elemental analysis. The mass spectrometer can accurately discriminate between ions of different mass-to-charge ratios (m/z), and the extremely high temperatures of the ICP can very efficiently break down molecules and ionize the elements in the sample.[9-11]

1.2.1 Instrumentation and Overview

The plasma of the ICP-MS instrument is generated in a torch that is placed in a radio frequency (RF) coil. The torch, as seen in Figure 1.1, is composed of quartz and consists of three concentric tubes.[12] The outer tube passes the plasma gas, which is responsible for the formation of the plasma, at a rate of approximately 15 L/min.[12] The auxiliary gas is passed through the middle tube at a much lower flow rate (1-2 L/min) and the nebulizer gas is passed through the inner tube of the torch and is the gas that carries the analyte into the plasma (at typically up to 1 L/min). The RF coil is typically made out of copper and is placed close to the end of the torch.

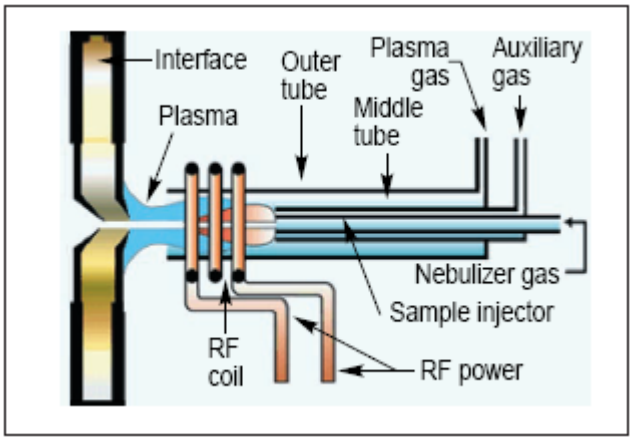

Figure 1.1: Schematic of the ICP torch and RF coil[12]

The plasma is ignited through a complex process that is simplified in Figure 1.2. First the plasma gas is passed through the torch in a tangential trajectory while power is applied to the RF coil. An alternating current oscillates in the RF coil at a frequency of 27 or 40 MHz, creating an intense electromagnetic field around the outside of the torch.[12] A spark is then applied, which causes some of the argon atoms to lose an electron. The electrons are accelerated in the magnetic field, which in turn leads to more collisions with other argon atoms. These argon atoms also then lose electrons and the cycle continues, resulting in a mixture of argon atoms, argon ions and electrons in a discharge known as the inductively coupled plasma.[12] The plasma reaches a temperature of approximately 10,000K and is maintained as long as argon flows through the torch, and the RF power is transferred to the plasma.[13]

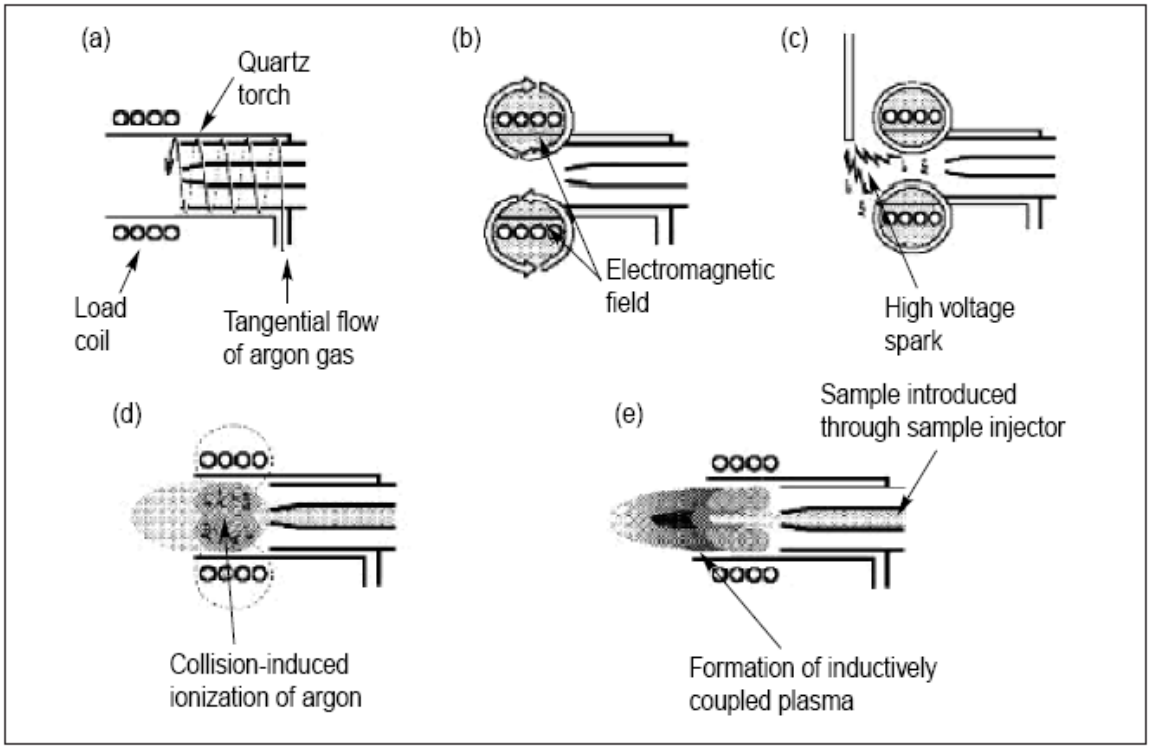

Figure 1.2: Schematic representation of the formation of an inductively coupled plasma[12]

The majority of ICP-MS applications involve the analysis of aqueous samples. Before the sample reaches the plasma, the sample will undergo two processes: aerosol generation and droplet selection. This is essential to the ICP-MS system since the plasma is inefficient at dissociating large droplets of sample. These processes ensure that only the smallest sample droplets are introduced into the plasma.[14] The sample is drawn into the system by a peristaltic pump. It then passes through a nebulizer where aerosol generation occurs, i.e. the liquid sample is hit by the nebulizer gas, which in turn causes an aerosol to be formed.[14] The resulting aerosol is then introduced into the spray chamber where droplet selection takes place. There are many types of commercially available spray chambers that use a variety of methods to discriminate against droplet size. In all cases,

only a small portion, approximately 2% of the original sample actually reaches the plasma, while the rest is drained out.

Once the sample is introduced into the plasma, it undergoes several processes that eventually lead to its analyte ionization. The analyte is first stripped of all water molecules in a process called desolvation, and then vapourized into a gaseous state. Analytes are then atomized into individual atoms and then ionized. The ions then pass through the ICP-MS interface for detection and quantification.[10] There are several mass analyzers that are used in ICP-MS instruments to separate the ions formed in the plasma according to their m/z.

The most widely used is the quadrupole mass spectrometer (QMS). The QMS (Figure 1.3) consists of four cylindrical metal rods of the same shape and size.[15] On one pair of rods, a direct current (DC) field is applied, and the other pair of rods is subjected to an RF current. The potentials are selected such that it will steer only one particular m/z ion through the rods and out the other end. All other ions will collide with the rods and will not reach the detector.[15] The QMS scans across different potentials in order to determine all elements of interest. The most recent ICP-QMS instruments can achieve very low detection limits (i.e. at the ppt or ng/L level) and have very high sensitivity which is ideal for trace analysis.[16]

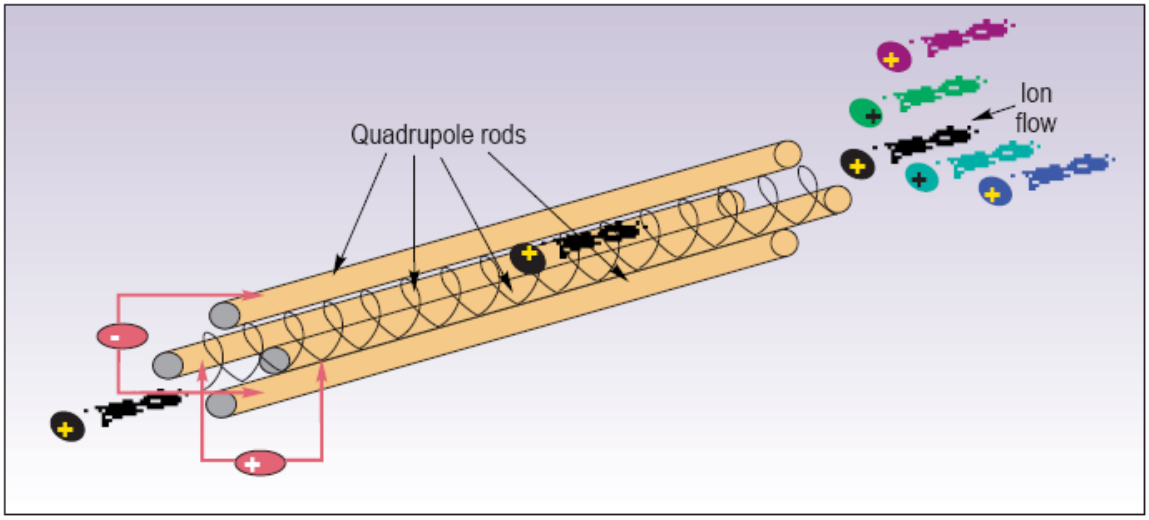

Figure 1.3: Schematic diagram of a quadrupole mass spectrometer[14]

The time-of-flight mass spectrometer (TOFMS) separates ions of different m/z based on the time it takes for each ion to reach the detector.[17] Ions are collected at the entrance of the mass spectrometer. A pulse of positive voltage is then applied to the repeller electrode, sending the ions down the flight tube with the same kinetic energy.[17] Ions then travel down the flight tube at different velocities. Since all ions have the same kinetic energy, the lighter ions will have a higher velocity than the heavier ions, reaching the detector first. A schematic diagram of an ICP-TOFMS instrument is shown in Figure 1.4. An ion mirror is included at the end of most TOFMS instruments. This ion mirror serves to deflect ions into the detector, increasing the length of the flight tube.

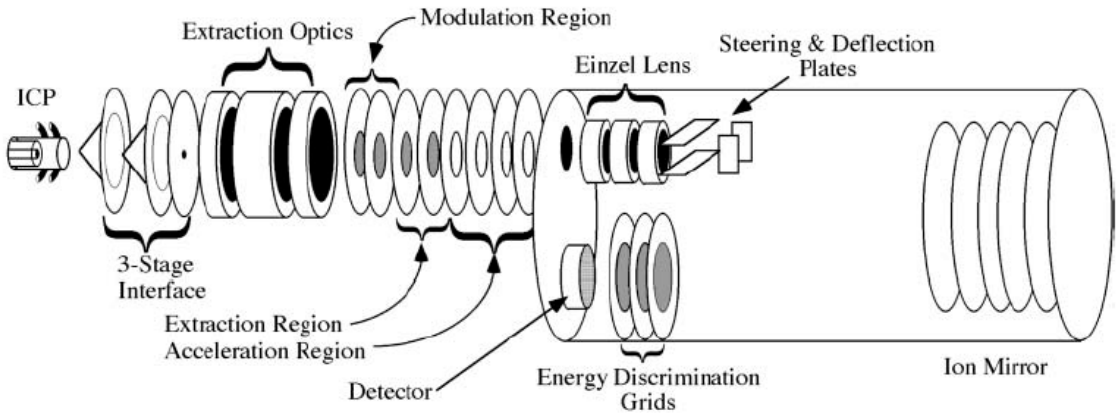

Figure 1.4: Schematic diagram of a time-of-flight mass spectrometer[18]

The main advantage of the ICP-TOFMS instrument is its ability to produce a mass spectrum of all elements in a very short period of time.[19,20] It takes as little as 25 μs to record a full spectrum from mass 1-238 amu[17] whereas a QMS takes about 10 ms to record the same spectrum. This is ideal when recording spectra in transient mode, as more points are used to define peaks. The ICP-TOFMS is also ideal when looking at isotope-ratio measurements. The simultaneous sampling of the TOFMS can greatly reduce uncertainties in these types of measurements.[19] The resolution of the ICP-TOFMS and the ICP-QMS are very similar. However, detection limits of the ICP-TOFMS, are typically an order of magnitude higher than that of the ICP-QMS.[18,21] The sensitivity of the ICP-QMS is also higher than that of the ICP-TOFMS.[16,18,21] The poorer detection limits and sensitivity of the ICP-TOFMS are a consequence of the modulation of the ion beam. Since an ICP is a continuous ion source, its sampling must be modulated into discrete ion packets that are accelerated to the detector. As a result of this modulation, the fraction of ions that are extracted into the mass analyzer is approximately 10% of the

ions that are extracted into the QMS (in single ion monitoring mode), despite the elevated transmission efficiency of the TOFMS.[18,21]

The final mass analyzer that is used with an ICP in a commercially available instrument is the double-focusing high resolution (HR) mass analyzer. This MS consists of both an electromagnet and an electrostatic analyzer (ESA). A charged particle passes through the electromagnet, where it is deflected by the magnetic field at an angle according to its m/z.[22] The ESA then focuses the desired ions onto the exit slit and removes unwanted ions. After detection, the electric field is set to its original value, and the next mass is analyzed. A schematic diagram of an ICP-HRMS is shown in Figure 1.5.

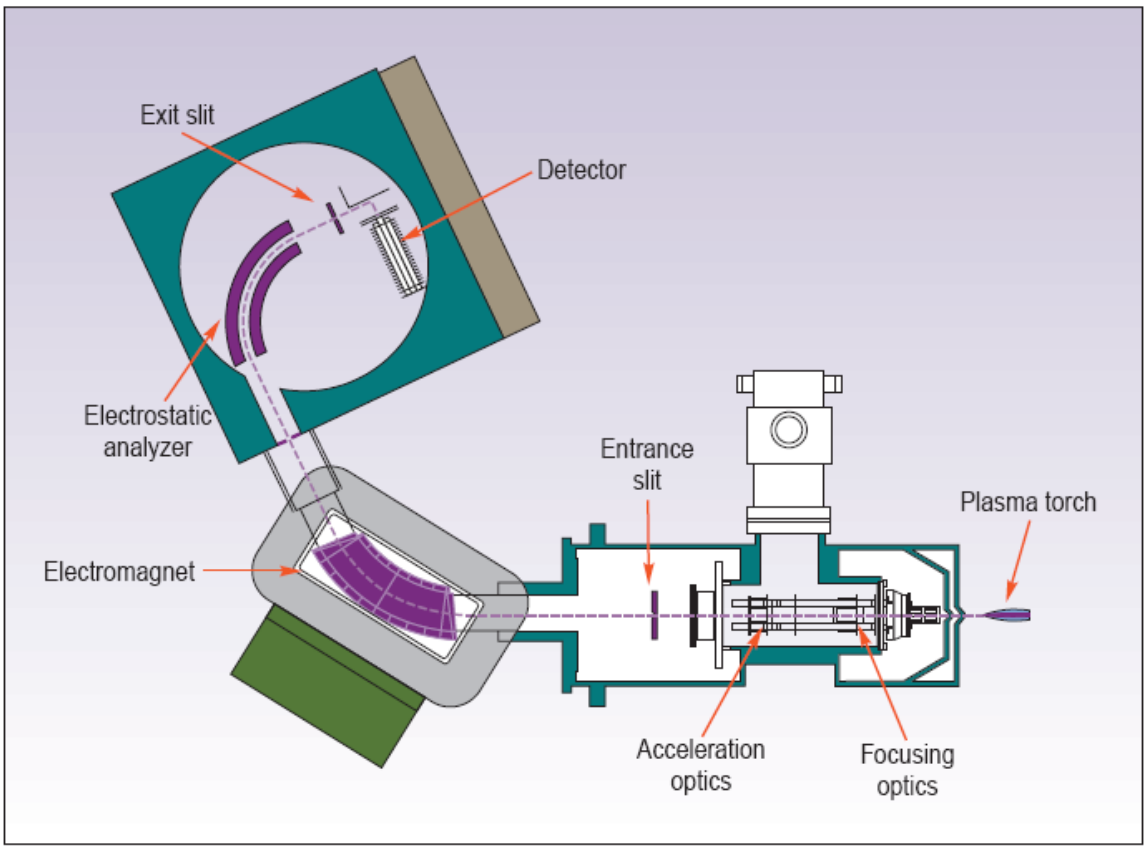

Figure 1.5: Schematic diagram of an ICP-HRMS[22]

An HRMS offers significantly higher resolution than a QMS or a TOFMS. It also has the advantage of very high sensitivity when working in low resolution mode compared to the QMS and the TOFMS.[22] These instruments, however, are expensive as compared to the more conventional mass analyzers.[22]

1.3 Interferences in ICP-MS

When ICP-MS was first introduced in the 1980s, it was hoped that it would be an interference free technique. It was quickly discovered that there are many interferences involved with ICP-MS, which can be divided into two main groups; spectroscopic and non-spectroscopic interferences.[10]

1.3.1 Non-spectroscopic interferences

Non-spectroscopic interferences arise when there are elements in the sample matrix that induce a negative or positive bias in the analyte signal. There are two main causes of these non-spectroscopic interferences.

The first is physical effects resulting from the dissolved solids in the solution.[10] For example, as the concentration of the total dissolved solids in the sample increases, it is likely that some of the solids will deposit on the sampler cone of the ICP-MS instrument, causing the analyte signal to drift downwards over time. To minimize this type of interference, the amount of total dissolved solids in the sample must be low, typically less than 0.2%.

The second type of non-spectroscopic interferences is suppression and enhancement effects where, in the presence of matrix ions, the analyte signal may either be suppressed or enhanced. There have been many proposed mechanisms for such enhancement and suppression, however they do not account for all observed effects.[23] Matrix effects vary between analytes; lighter ions are more affected by matrix effects than heavier ions, and heavier matrix ions will have a greater effect on the analytes.[10,23] The degree of ionization of the analyte and matrix elements also contributes to the degree of matrix effects. Analytes with a low degree of ionization (i.e. a high first ionization potential) in the plasma are more greatly affected by matrix effects, while matrix elements with a high degree of ionization (or low first ionization potential) in the plasma will have a greater effect on the analytes.[10,23] Ionization energies for the PGEs of interest and common interferents are displayed in Table 1.1.

Table 1.1: First ionization energies[24] of PGEs of interest and common interferents

Element	First Ionization Energy (kJ/mol)
Pd	804
Pt	870
Rh	719
Re	760
Ru	710
Ir	880
Ni	737
Cu	746
Zn	906

PGEs typically have a fairly moderate degree of ionization in the plasma. However, the number of ions formed in the plasma is low, since PGEs are analyzed in ultra-trace concentrations. Should an interferent be present in the plasma that either enhances or suppresses the signal of the PGEs, they can be greatly affected, and the concentration of these elements hard to determine. For this reason, the sample matrix must be separated from the analyte for a more accurate determination of PGEs in environmental samples.

There have been a number of proposed methods to reduce the degree of non-spectroscopic interference effects. Because they depend on the absolute amount of matrix elements, dilution of samples can be employed to bring down the concentration of the matrix elements, if the analyte is at a concentration high enough to allow for dilution.[10] Internal standards have been employed; however, the internal standard must be chosen carefully to ensure that it will behave similarly to the analyte in the presence of the matrix.[25,26] Matrix matching can be a simple solution to non-spectroscopic interferences if the sample matrix is not complex or unknown. Indeed, the concentration of acid and matrix elements must be the same in all samples. There have also been studies involving mixed gas plasmas to eliminate non-spectroscopic interferences, where a mixture of nitrogen and argon in different ratios can be used to eliminate interferences, with, however, a concurrent decrease in sensitivity.[27,28]

1.3.2 Spectroscopic interferences

Spectroscopic interferences are caused by ions that have the same m/z as the analyte. These interferences are very common with quadrupole mass analyzers. The mass resolution of a QMS, defined as $R = m/\Delta m$, where the height at the valley between peaks

is 10% of the mean of these peak heights, is R = 300.[29] There are three main causes of spectroscopic interferences: isobaric overlap, doubly charged ions and polyatomic ions.[10] In many cases a double-focusing high resolution ICP-MS instrument can be used to resolve spectroscopic interferences, as the mass resolution can reach as high as R = 10,000[10,11,30]. However, due to the cost of these instruments, other means have also been employed to compensate for spectroscopic interferences.

Isobaric overlap is the most common and easiest interference to correct. It exists when two elements have isotopes of the same mass. Although their masses may differ very slightly, the unit mass resolution of the ICP-QMS is insufficient to resolve them.[10] Since the abundance of all isotopes can be approximated, the interference can be subtracted from the analyte signal using the signal measured at an interference-free m/z of the interfering element. There is now software available on modern ICP-MS instruments that will perform these corrections automatically.

Most of the ions produced in the plasma are singly-charged ions. However, there are some elements that will undergo a second ionization and produce doubly charged ions. This occurs when the second ionization energy of the element is lower than the first ionization energy of argon.[10] Although this is the case of only a few elements, a correction is required if the m/z of the analyte is overlapped by that of doubly-charged ions. Separation of the analyte from the matrix will alleviate spectroscopic interferences arising from the latter. However, this is not always possible. There have been some attempts to mathematically subtract the signal of interferent elements[31], but this is a very long and time-consuming process.

The main concern with spectroscopic interferences arises with polyatomic ions. This occurs when two or more atoms combine to make a larger ion. Nitrogen, hydrogen and argon are the most abundant elements in the plasma, and they can easily bind together, or with other atoms from the solution.[10] In the analysis of PGEs, there are a significant number of polyatomic ions originating from the sample matrix that interfere with the determination of these elements. Table 1.2 gives some examples of potential interfering polyatomic ions for Pd, Pt and Rh. In natural tree samples, where there is a significant amount of Ni, Cu and Zn, these interferences can be expected to inhibit the determination of PGEs in these samples. The best way to eliminate them is to separate the analyte from the matrix. Other methods such as collision and reaction cells can also be used to reduce spectroscopic interferences.[32]

Table 1.2: Potential interferents for Pd, Rh and Pt[2]

Analyte	Abundance (%)	Interferent
^{105}Pd	22.33	$^{40}Ar^{65}Cu$ $^{88}Sr^{17}O$ $^{89}Y^{16}O$ $^{87}Sr^{18}O$ $^{87}Rb^{18}O$
^{106}Pd	27.33	$^{40}Ar^{66}Zn$ $^{38}Ar^{68}Zn$ $^{90}Zr^{16}O$ $^{88}Sr^{18}O$ ^{106}Cd
^{103}Rh	100.00	$^{38}Ar^{65}Cu$ $^{40}Ar^{63}Cu$ $^{36}Ar^{67}Zn$ $^{87}Sr^{16}O$ $^{85}Rb^{18}O$ $^{206}Pb^{2+}$
^{194}Pt	32.90	$^{178}Hf^{16}O$
^{195}Pt	33.80	$^{179}Hf^{16}O$, $^{178}Hf^{17}OH$

1.4 Separation and pre-concentration methods for platinum group elements

Although laser ablation can directly ablate PGEs from solid environmental samples,[33] calibration is not straightforward due to a lack of matrix-matched solid materials whose PGEs concentrations are certified and because of the non-spectroscopic interferences arising from the concurrently ablated matrix. For accurate determination of PGEs in environmental samples, the sample must undergo a pre-concentration and separation step. The pre-concentration step will assist analytical instrumentation to more accurately determine the concentration of PGEs in the sample, while the separation step will remove the sample matrix and thus reduce spectroscopic and non-spectroscopic interferences.

Earlier separation/pre-concentration methods were performed off-line. These methods provide accurate determination of PGEs, but are very time-consuming and, in many cases, a large sample volume is required for such analyses.

On-line flow injection (FI) methods are currently being developed in order to minimize the amount of sample required for analyses as well as to provide rapid analysis of PGEs. FI is described as the insertion of a discrete plug into unsegmented continuously flowing carrier with subsequent detection of the analyte.[34] It was first introduced in 1975, and has many advantages over conventional batch analyses.[35] FI methods are fast and precise and minimize human error as it is easily automated. They also reduce sample consumption, which is of concern in many environmental analyses.[36]

Many of these on-line methods for the determination of PGEs are still in the development stage and the procedures are being optimized and extended to different environmental samples and analytes. In many cases, these procedures are limited to the determination of Pt and Pd.[6] In general, all available procedures can be divided into four groups: precipitation/co-precipitation, liquid-liquid extraction, solid phase extraction and ion-exchange methods.[6]

1.4.1 Precipitation/co-precipitation

Precipitation is one of the earliest methods of separation. PGEs are precipitated out of a solution by forming sparingly soluble complexes.[6] Pt can be precipitated from a solution as diammonium hexachloroplatinate, potassium hexachloroplatinate or platonic sulfide. Pd can also be precipitated as a sulfide or as a complex of dimethylglyoxime.[6] Co-

precipitation is useful in the determination of multiple elements, as more than one element is precipitated at the same time. This will provide faster sample analysis for all PGEs. In the case of PGEs, co-precipitation has been most successful using tellurium, although, elements such as selenium, arsenic, mercury and copper have also been used.[37-40] While precipitation is highly effective at the removal of most interferents, about 5% of yttrium and copper will precipitate and will still interfere with the determination of Pd.[40] In this case, a mathematical correction must also be made.

Recently, Te co-precipitation experiments have utilized ultrasonication for the acceleration of the precipitation process.[41] This addition to the procedure allows the co-precipitation to occur at lower temperatures than previously required. This is beneficial for the determination of Os, as it is typically lost in the co-precipitation process at temperatures above 55 °C.[42,43] Though the ultrasonication decreases the precipitation time, this off-line method is still quite time consuming and involves expensive reagents. The mass of solid sample required for this analysis is 20 g, which is quite high when sample is limited.

1.4.2 Liquid-liquid extraction

Liquid-liquid extraction has also proved to be a successful method for the separation of PGEs from the sample matrix. In this procedure, analytes from the solution are extracted into an organic liquid according to their partition coefficient.[6] PGEs have a high tendency to form complexes. Thus, organic complexing agents have been used along with liquid-liquid extraction for their successful separation. Examples of such organic reagents include dithiocarbonate, dimethylglyoxime, benzoylthiourea and

triphenylphosphine.[44-47] The main problems that arise with the liquid-liquid separation are the long reaction times and the need for multiple extractions. However, it does provide accurate results with detection limits of 0.02 μg/L for Pd and 0.07 μg/L for Pt using graphite furnace atomic absorption spectrometry (GFAAS).[47] Liquid-liquid extractions of PGEs have not been used for on-line methods.

1.4.3 Solid phase extraction

Solid phase extraction (SPE) is very similar to liquid-liquid extraction, as the analytes are distributed between two phases according to their partition coefficients. SPE, however, involves both a solid phase and a liquid phase. The sample is passed through a column packed with the solid sorbent onto the surface of which the analytes will adsorb. The analyte can then be released from the column using a suitable eluent. There are a large number of sorbents that have been used for the pre-concentration and separation of PGEs, but the most commonly used packing materials are chemically-bonded silica or polymeric resins.[1, 48-56]

While SPE can be performed both on-line and off-line, many recent procedures are moving toward the on-line approach. A recent FI method for the determination of palladium uses a column packed with 1,5-bis(di-2-pyridyl)methylene thiocarbohydrazide immobilized on silica gel.[50] The Pd sample was maintained at pH 7.6 (buffered with phosphate ions) and passed through the column. Pd ions were adsorbed onto the column while interferent ions were sent to waste. The palladium was then eluted with 40 μL of 14M HCl and sent to analysis by GFAAS. Detection limits were reported as 0.4 μg/L using this method.[50]

A knotted reactor (KR) has been used with an FI manifold for the on-line determination of PGEs. [2,57,58] A chelating agent is first introduced into the knotted reactor, where it adsorbs onto the surface of the KR. The sample solution is then passed through the reactor where the analytes form complexes with the chelating agent and are thus immobilized on the surface of the reactor. The analytes are then recovered using a suitable eluent. Chelating agents such as ammonium pyrrolidinedithiocarbamate have been succesfully used for the determination of Pt, with detection limits of 0.1 μg/L using GFAAS.[58]

This method has also been successfully used for the determination of Pt, Pd and Rh in human urine and dust using ICP-TOFMS.[2] Diethylthiourea was used as a chelating reagent in this case and detection limits of 0.54, 0.36 and 2.12 ng/L for Pt, Pd and Rh, respectively, were obtained.[2] A schematic diagram of the procedure is shown in Figure 1.6.

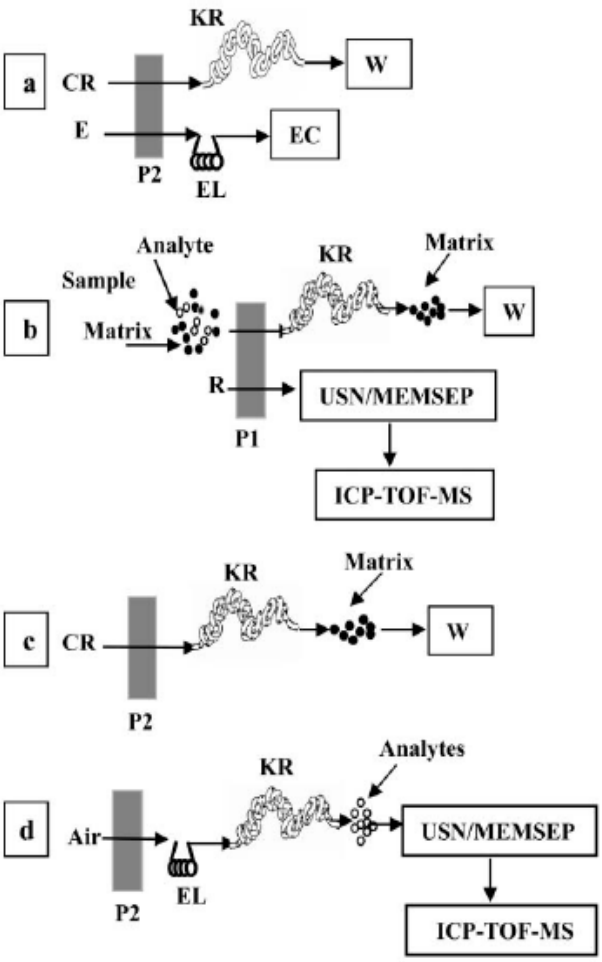

Figure 1.6: Schematic diagram of the FI– knotted reactor pre-concentration procedure.[2] CR: chelating reagent, E: eluent, W: waste, EC: eluent container, KR: knotted reactor, P1, P2: peristaltic pumps, EL: eluent loop, R: rinse.[2]

The chelating reagent is first loaded into the KR off line (Figure 1.6(a)), while excess solution goes to waste. The sample is then passed through the KR, where the PGEs react with the chelating reagent and adsorb to the walls of the reactor as the matrix is sent to waste (Figure 1.6(b)). The KR is then washed using the chelating reagent to remove any residual sample matrix from the KR as shown in (Figure 1.6(c)) and then finally the sample is eluted (Figure 1.6(d)), using 500 µL of the eluent. In this case, the only eluent

suitable for complete elution of the elements was methanol. Thus, an ultrasonic nebulizer with membrane desolvation (USN/MEMSEP) was required for analysis by ICP-MS.

On-line displacement SPE methods have recently been employed for the determination of Pd in rock samples.[59] This method employs a complexing agent, ammonium pyrrolidine dithiocarbamate (APDC) to a common sorbent (cigarette filter). Ag^+ ions are sorbed onto the APDC and then loaded onto the filter. The sample solution containing the Pd^{2+} analyte and interferents (Zn, Pb, Cu, and Cd) is passed though the column.[59] Since the dithiocarbamate stability of Ag^+ is less than that of Pd^{2+}, but greater than those of the interferents,[60] the Pd^{2+} displaces the Ag^+, while the interferents remain in solution and are passed through the filter. The Pd^{2+} is then eluted with 2% v/v HNO_3.[58] Detection limits as low as 3.0 ng/L have been achieved.[59] In order to extend this work to encompass all PGEs, further studies into the dithiocarbamate stability is required to determine if there is a suitable displacement ion.

1.4.4 Ion-exchange methods

Ion-exchange methods have been very successful for the determination of PGEs in geological samples. These methods utilize the tendency of PGEs to form anionic chloro or oxy-complexes, which are highly stable in solution.[6] Both anion-exchange and cation-exchange resins have been used.[61-73] When PGEs form chlorocomplexes with Cl ions, they have a strong affinity for strong base anion-exchange resins. The sample solution is passed through the resin and the PGEs will adsorb onto the resin while the interferents pass through. The PGEs are subsequently eluted from the column.[61] One disadvantage of anion-exchange resins is that there may be incomplete elution of the analyte from the

column.[66] Corrections arising from this effect include isotope dilution techniques and direct analysis of the resin for PGEs. Isotope dilution occurs when a known concentration of an isotope of the element of interest is added to the sample before separation. The efficiency of the separation and elution procedure can then be accurately determined.[63,68,73] Detection limits using in-line isotope dilution have been reported as 0.075 μg/L for Pd and 0.15 μg/L for Pt.[71] Direct analysis of the resin overcomes the incomplete recovery of the PGEs, but does pose some challenges with the analysis using ICP-MS.[61] Direct analysis methods also require that analysis is performed off-line, increasing analysis time. Detection limits have been reported as 4.2 μg/L using this method with GFAAS.[70]

Cation-exchange resins have also been used for the determination of PGEs. Since PGEs do not have a strong affinity for cation-exchange resins, when the sample solution is passed through, the interferents are retained on the column, while the PGEs are passed through for analysis.[61,69] Cation-exchange methods are typically performed off-line since large amounts of cation-exchange resin is required to completely adsorb all interferents.[6] In other cases, PGEs are converted into stable cationic complexes and are separated from the interferents using gradient elution. However, complete separation of the interferents from the analytes is not achieved.[61]

Activated alumina has been used for the determination of platinum and palladium.[7, 74-75] Activated alumina can function as either a cation or an anion pre-concentrator, depending on the pH.[7] In acidic conditions, the alumina column is positively charged, attracting negative ions. In basic conditions, the alumina column is negatively charged, attracting

positively charged ions. This simple chemistry provides a fast and simple in-line means for separating and pre-concentrating PGEs. A schematic diagram for the flow injection manifold is shown in Figure 1.7.

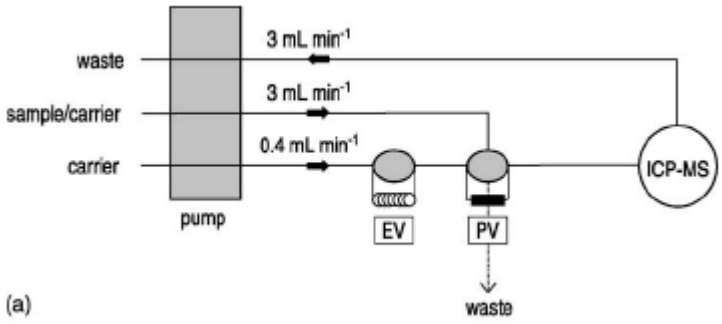

Figure 1.7: Flow injection manifold used for the pre-concentration and separation of palladium and platinum.[74]

The alumina column is situated inside the pre-concentration valve (PV). The column was packed with 150 mg of activated alumina and had a turn end at each end to prevent loss of alumina during analysis. The sample solution is loaded onto the column at 3 mL/min in an off-line position. The interferents and sample matrix are sent to waste. Once loading is complete, the column is switched to an on-line position and the Pt or Pd is eluted using the elution valve (EV).[74] All samples were stored in 2% HCl, but the pH of the samples was different for the determination of Pt and Pd. The pre-concentration and elution parameters were also different for the two elements and are displayed in Table 1.3.

Table 1.3: Operating parameters for the determination of Pt and Pd with the use of an alumina column[7, 74-75]

Analyte	Pt	Pd
pH of sample	2.5	1.0
Carrier acid	0.01 M HNO_3	0.01 M HNO_3
Volume of sample	15 – 30 mL	15 mL
Flow rate of sample	3 mL/min	3 mL/min
Eluent	2 M NH_4OH	0.3 M KCN
Volume of eluent	50 µL	300 µL
Flow rate of eluent	1 mL/min	0.4 mL/min
Pre-concentration factor	300 – 600	50
Detection limit	0.001 µg/L	0.004 µg/L

While detection limits are excellent using this method, there are several disadvantages. The sample volume used in each run is high, which poses a definite disadvantage when sample volume is limited. One method for the determination of both Pt and Pd was not achieved. While the parameters were optimized for the retention and elution of each element, it does not provide a universal method that can be used for all PGEs.

While many methods have been developed for the determination of platinum and palladium, most methods are very costly and time consuming. SPE methods utilize solid phases that are typically not commercially available and must be fabricated in a laboratory prior to analysis. Precipitation methods also use expensive reagents and require modification to the ICP-MS sample introduction system. Due to these

limitations, a standard method for accurate determination of PGEs in commercial laboratories has not been established. A fast, cost effective, simple method for the determination of PGEs in geological samples is needed.

1.5 Thesis Objectives

The objective of this research is to develop a new in-line method for the simultaneous determination of all PGEs in geological samples, primarily tree samples. This method was based on the previous work that utilized activated alumina columns for the determination of platinum and palladium.[7, 74-75] Research focused on reducing the sample consumption for each run, as only 1 g of tree sample was digested, and 5 mL of sample solution was provided. The method was also modified to include the determination of Pt, Pd, Ir, Re, Rh and Ru. While Re falls outside the platinum group elements, it behaves similarly to the PGEs and is an element of interest in exploration geochemistry. Os was not analyzed as it is lost in the sample preparation step by evaporation.

The experimental design involved a simple FI manifold for in-line determination of PGEs similar to that previously reported.[74] In order to allow the determination of multiple elements, several factors were considered. The carrier acid and the eluent had to be selected to ensure complete retention of the PGEs onto the column and their complete subsequent elution. Thus, the concentration of both the carrier acid and eluent were of concern as well as the content and concentration of acid in the sample solutions. The size of the alumina column and flow rate of sample solution through the column was also investigated.

This method was then compared to results obtained using ICP-HRMS. Tree samples from Rock Lake, Manitoba were analyzed using both techniques and the results compared.

CHAPTER 2: EXPERIMENTAL

2.1 Instrumentation

A LECO Renaissance ICP-TOFMS (LECO, St. Joseph, Michigan) was used primarily for the development of the method for the separation and pre-concentration of Pt and Pd. This system consisted of a Meinhard concentric pneumatic nebulizer and a Smith-Hieftje cyclonic spray chamber. Before analysis, the ICP was optimized using a 5 µg/L mass calibration solution containing Li, Mg, Sc, Co, Y, In, Ce, Ba, Pb and Bi. The X, Y and Z position of the torch and the carrier gas flow rate were adjusted to maximize the signal intensity of $^{115}In^{+}$. Deflections of masses that contain background elements of very high concentrations were also made in order to preserve the longevity of the detector. These deflections occurred at m/z at 40, 56, 76 and 80. Typical operating conditions are listed in Table 2.1. Data acquisition was done in transient mode with a 981.75 ms integration time. Only data collected in the ion counting detection mode were used (the analog mode being reserved for higher concentrations).

A Varian UltraMass 700 ICP-QMS (Mulgrave, Victoria, Australia) was used for the method development for the determination of PGEs, the analysis of the Rock Lake tree samples as well as for the determination of detection limits and sensitivity. This instrument used a Meinhard concentric pneumatic nebulizer and a Sturman-Masters spray chamber for sample introduction into the plasma. Prior to analyses, optimization of the ICP-QMS was performed using 100 µg/L multi-elemental solution of Ba, Be, Ce, Co, In, Pb, Mg, Tl and Th. This sample was continuously nebulized while the X and Y torch positions were optimized. The torch position that yielded the highest sensitivity was selected for analyses. Typical operating conditions are listed in Table 2.2. Data

acquisition was done in time-resolved peak-hopping mode with 1 point/peak, 1 scan/replicate, 10-s measurement time and 0.025-amu spacing.

Table 2.1: Typical operating conditions for Leco Renaissance ICP-TOFMS

Operating Condition	**Setting**
ICP Conditions	
Ar plasma gas flow rate (L/min)	15
Ar auxiliary gas flow rate (L/min)	0.90
Ar aerosol carrier gas flow rate (L/min)	0.99
R.F. power (kW)	1.32
R.F. frequency (MHz)	40.7
Sample uptake rate (mL/min)	0.90
Mass spectrometer settings	
Flight Tube (V)	-1500
Reflectron low (V)	200
Reflectron high (V)	1537
X Steering (V)	-1505
Y Steering (V)	-1570
Einzel lens 1 (V)	-1350
Einzel lens 2 (V)	-980
Detector (V)	-2400

Table 2.2: Typical operating conditions for Varian UltraMass 700 ICP-QMS

Operating Condition	Setting
ICP Conditions	
Ar plasma gas flow rate (L/min)	15
Ar auxiliary gas flow rate (L/min)	1.05
Ar aerosol carrier gas flow rate (L/min)	0.89
R.F. power (kW)	1.20
R.F. frequency (MHz)	40
Sampling depth (mm)	6.5
Sample uptake rate (mL/min)	0.90
Mass spectrometer settings	
Extraction lens (V)	-600
First Lens (V)	-237
Second Lens (V)	-12.0
Third Lens (V)	0
Fourth Lens (V)	-67
Photon Stop (V)	-11.0
Dwell time (ms)	100

A Thermo Finnigan Element magnetic sector ICP-HRMS (Mulgrave, Victoria, Australia) was used by the department of geology for the analysis of the Rock Lake tree samples for comparison of results obtained using the method developed in this thesis. This instrument used a Meinhard concentric nebulizer and a Scott double-pass spray chamber

for sample introduction into the plasma. Data acquisition was done in batch mode with 20 point/peak, 2 scans/replicate. Operating conditions are summarized in Table 2.3.

Table 2.3: Typical operating conditions for the Thermo Finnigan Element ICP-HRMS

Operating Condition	**Setting**
Ar plasma gas flow rate (L/min)	16
Ar auxiliary gas flow rate (L/min)	0.8
Ar aerosol carrier gas flow rate (L/min)	0.5
Additional gas (L/min)	0.180-0.220
R.F. power (kW)	1.25
R.F. frequency (MHz)	40
Sampling depth (mm)	6.5
Sample uptake rate (mL/min)	0.10
Extraction lens (V)	-2000
Guard Electrode	Engaged
Resolution	High
Mass Window	80%
Samples per peak	20
Detector mode	Both
Integration Window	60%

2.2 Data analysis

For the calculation of peak areas, raw data files were treated with in-house QBASIC® software for peak smoothing and peak area calculation. Data files were imported into a

Microsoft Excel® (Microsoft Office 2007, Microsoft, Redmond, WA) spreadsheet for the construction of elution profiles.

The percent retention; defined as the percentage of the peak area that was retained on the mini-column over the total peak area of both retained and unretained portions, and all other calculations were made using Microsoft Excel®.

2.3 Reagents

All volumetric flasks and polypropylene bottles used in the preparation and storage of solutions, were soaked in 10% (v/v) HCl overnight and rinsed with reverse osmosis doubly deionized water (DDW, Milli-Q Plus System, Millipore, Mississauga, Canada) before use.

High purity concentrated HCl, HNO_3 (Fisher Scientific, Nepean, Ontario, Canada) and ammonium hydroxide (EM Science, Darmstadt, Germany) were diluted to their appropriate concentrations using DDW. The PGE and interferent solutions were prepared from the dilution of 1000 mg/L mono-elemental standard solutions (SCP Science, Baie D'Urfé, Quebec, Canada) with the previously diluted HCl solution.

2.4 Alumina mini-column preparation

The alumina mini-column was prepared by packing the desired amount of alumina (Fluka, Switzerland) into a 4-cm long, 3/16-in. o.d., and 1/8-in. i.d. polytetrafluoroethylene (PTFE) tube between two quartz wool plugs of approximately 15 mg each. A blank mini-column was prepared by inserting 30 mg of quartz wool into an

empty tube. Since no detectable analyte was observed for the blank, there was no need to perform blank subtraction.

2.5 On-line pre-concentration and separation

2.5.1 Single-line manifold

A simple single line FI manifold (Figure 2.1) was used for the pre-concentration and separation of PGEs. The sample was introduced using an injection loop into the carrier acid (0.01 M HNO_3) for retention on the mini-column. The sample injection valve (model 5020, Rheodyne Inc., Cotati, CA, USA) was manually actuated. Elution was then obtained by passing the eluent base (2 M NH_4OH) through the mini-column.

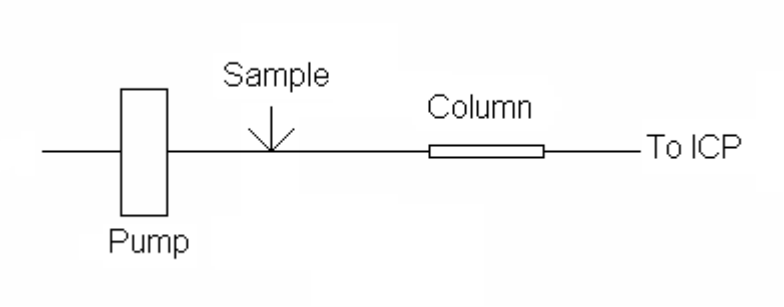

Figure 2.1: Single line flow injection experimental setup

2.5.2 Dual-line manifold

A dual-line FI manifold (Figure 2.2) (with a second valve identical to that described above) was used for experiments when different flow rates were desired for the retention and elution of the PGEs. The sample was introduced using an injection loop into the carrier acid (0.01 M HNO_3) for retention on the mini-column. This was performed off-line so the interferents that pass through the mini-column are sent to waste. Elution was

obtained by changing the position of the mini-column in-line with the ICP-MS and injecting the eluent base (2 M NH_4OH) using an injection loop into the carrier acid.

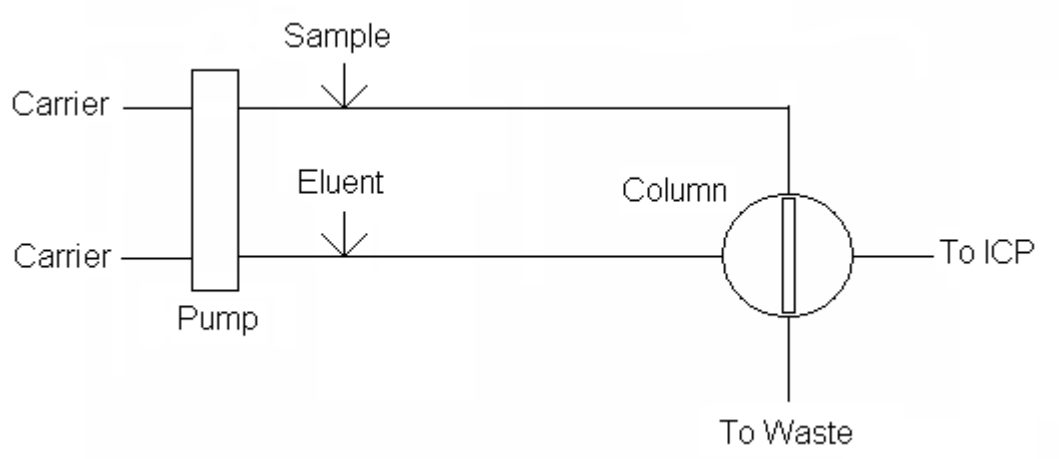

Figure 2.2: Dual valve flow injection experimental setup

2.5.3 Selection of conditions for the separation/pre-concentration method

Selection of the operational parameters for the method was done using the single-line manifold setup. Experiments were first performed with Pt and Pd, and then extended to Re, Rh, Ru and Ir. The conditions that were found using the single-line FI manifold were also used by the dual-line FI manifold. Each experiment followed the same general procedure, while individual variables were tested. The initial procedure took 10 minutes to complete and was as follows:

The sample solution was injected into the carrier acid using a single-line FI manifold, followed by the pumping of carrier acid for 3 minutes to ensure that the unretained sample matrix passed through the mini-column. The eluent was then pumped for 5 minutes to release Pt and Pd as well as to clean the mini-column. Finally, the carrier acid

was passed for 2 minutes to re-acidify the mini-column for the next analysis. The mini-column was then immediately ready for the next analysis. Basic operating parameters for the selection of the conditions of the separation/pre-concentration method are shown in Table 2.4.

Table 2.4: Basic operating parameters used for method development for the determination of PGEs by ICP-TOFMS.

Parameter	**Setting**
Mass of alumina mini-column (mg)	160
Flow rate (mL/min)	0.5
Carrier acid	0.01 M HNO_3
Sample	50 μg/L Pt, Pd
Volume of sample injection loop (μL)	50
Eluent	2.0 M NH_4OH
Volume of Eluent (mL)	2.5
Sample matrix	0.1 M HCl
Procedure	**Time (min)**
Carrier acid passed after sample injection	3
Elution with 2 M NH_4OH	5
Reacidify mini-column with 0.01 M HNO_3	2
Total time	10

2.5.3.1 Selection of the carrier acid

HCl and HNO_3 were tested as potential carrier acids. These experiments utilized the 10 minute procedure as described in Section 2.5.3. 1 mM and 1.2 M HCl were tested as well as 0.01 M HNO_3. The experiments were repeated 3 times for each concentration of carrier acid.

2.5.3.2 Selection of the eluent

The eluent was 2 M NH_4OH, which was selected based on previous work that utilized an alumina mini-column for the determination of PGEs.[7,75] Several concentrations were tested, 2 M, 4 M and 6 M following the same procedure as described above. All experiments were repeated three times.

2.5.3.3 Adjustment of the flow rate and alumina mini-column

The flow rate was optimized by determining the mini-column efficiency at various flow rates, from 0.5 mL/min to 1.5 mL/min, with a 160-mg alumina mini-column. The effect of the mass of the alumina mini-column on mini-column efficiency was also assessed by varying the mass of alumina from 22 mg to 300 mg. These experiments were performed at a flow rate of 0.5 mL/min. All experiments were performed using the 10 minute procedure as described above and repeated three times each.

2.5.3.4 Adjustment of the sample matrix

To ensure that the PGEs would be in the form of chlorocomplexes, the concentration of HCl was varied over the range of 1 mM to 0.1 M (0.01 to 1% v/v). Several concentrations, over the range of 8 mM to 0.3 M (0.05% to 2.0% v/v) HNO_3 were also

tested as it is used in the digestion procedures of tree top samples. The effect of interferents (Zn, Cu and Ni) on the effectiveness of the separation was also studied in the concentration range of 200 μg/L to 10 mg/L for Ni and Cu and 40 mg/L for Zn. The higher concentrations were selected based on previously determined concentrations of interferent elements naturally found in the tree samples at Rock Lake, Manitoba.[76]

During these experiments, the procedure was modified to accommodate several factors. The concentration of the analytes were reduced to 5.0 μg/L to more closely resemble the actual concentration of PGEs in the tree samples.[76] A larger sample injection loop was used to increase the volume of sample to 1 mL to increase the pre-concentration of PGEs. The experiments were also performed on the ICP-QMS, which required longer sample introduction tubing to reach the ICP. Since the total length of the sample introduction tubing was increased, the re-acidification wash step was increased by 4 minutes to ensure that all the tubing contained nitric acid prior to the experiment. The volume of the eluent was also reduced to 1 mL, so that the time required for the eluent to pass through the mini-column was reduced to 2 minutes from 5 minutes. It was also noted that the interferents moved slowly through the mini-column and required more time to pass through. The sample was given an extra 5 minutes to pass through the mini-column before elution. The experiments were now increased to 16 minutes in length and were as follows:

The sample solution was injected into the carrier acid using a single-line FI manifold, followed by the pumping of carrier acid for 8 minutes to ensure that the unretained portion passed through the mini-column. The eluent was then pumped for 2 minutes to

release Pt and Pd as well as to clean the mini-column. Finally, the carrier acid was passed for 6 minutes to re-acidify the mini-column for the next analysis. Basic operating parameters for the selection of the conditions of the separation/pre-concentration method are shown in Table 2.5.

Table 2.5: Basic operating parameters used for method development for the determination of PGEs by ICP-QMS.

Parameter	**Setting**
Mass of alumina mini-column (mg)	160, 300
Flow rate (mL/min)	0.5
Carrier acid	0.01 M HNO_3
Sample	5 µg/L Pt, Pd
Volume of sample injection loop (mL)	1
Eluent	2.0 M NH_4OH
Volume of Eluent (mL)	1.0
Sample matrix	0.1 M HCl
Procedure	**Time (min)**
Carrier acid passed after sample injection	8
Elution with 2 M NH_4OH	2
Reacidify mini-column with 0.01 M HNO_3	6
Total time	16

When the experiments were extended to include all the PGEs of interest, the mass of alumina was increased to 300 mg to accommodate the increased number of analyte to be adsorbed onto the column.

2.5.4 Calibration

Quantification of the PGEs (Pt, Pd, Ir, Ru, Rh and Re) was obtained using an external 5 point calibration curve. The calibration standards ranged from 0 μg/L to 5 μg/L in 1 mM HCl and contained the major interferents (Ni, Cu, Zn) at a concentration of 200 μg/L. Each calibration standard was analyzed 5 times and treated in the same manner as the sample solutions. The calibration standards were prepared daily from a 10 mg/L stock solution.

2.6 Rock Lake tree top samples

2.6.1 Collection of tree top samples

The tree samples were collected by helicopter, which flew over the Rock Lake area in Manitoba that contains known geological conductors. The top 30 centimeters of black spruce trees were snapped off selected trees along specific lines over the conductors.[76] The exact location of the tree samples were documented using a GPS system. The tree tops were bagged and brought to Acme Labs for grinding and analysis.[76] Ground samples from various locations were sent to Queen's University for analysis by ICP-HRMS and the new method that was developed in this thesis.

2.6.2 Digestion of tree top samples

Digestion of the tree top samples was carried out by the Queen's Department of Geological Science and Engineering in a clean lab.[77] Approximately 1 gram of sample was placed in a Teflon vial with DDW and placed in an ultrasonic bath for 10 minutes to clean the sample. After removal of the water, samples were placed in an 80°C oven overnight to dry. They were then placed in a Savillex Teflon container with screw cap. Concentrated nitric acid was added to each sample, which was placed on a 200°C hot plate for 24 hours. The samples, which were not fully dissolved were removed to cool and then dried on a 70°C hotplate. Nitric acid was again added to the samples which were again placed on the 200°C hotplate for 24 hours. This procedure was repeated until all solids were dissolved. Then 30% hydrogen peroxide was added to the samples, which were on a hotplate for 12 hours. Finally, the samples were dried on a 70°C hot plate and dissolved in approximately 15 g of 0.3 M nitric acid.

Approximately 3g of sample was used for elemental analysis by ICP-HRMS. The remaining 12 g were placed in Savillex Teflon containers and placed on a 70°C hot plate until all of the nitric acid had evaporated. Approximately 5 mL of 1 mM HCl was then added to the samples, which were transferred into 50 mL polypropylene bottles for analysis. A total of 38 tree top samples and 2 blank samples, prepared similarly to the sample but without sample, were then analyzed.

2.6.3 Analysis of tree top samples

The tree top samples were analyzed on the Varian UltraMass 700 ICP-QMS. A single valve flow-injection set-up was used with a 300 mg alumina packed mini-column. The

samples were analyzed using the 16 minute procedure as described in Section 2.5.3.4. To ensure that the interferents were not retained on the mini-column and that all the PGEs were retained, both the interferents and the analytes were monitored continuously throughout the whole procedure. Each tree top sample was analyzed 3 times and compared against a 3-point calibration curve that was performed daily. All tree samples were blank-subtracted using the signal obtained for the blank samples.

CHAPTER 3: METHOD DEVELOPMENT

3.1 Method development for the separation and pre-concentration of Pt and Pd

Initially, the method was developed for the separation and pre-concentration of Pt and Pd. Once this method was optimized, it was tested for the inclusion of Ir, Re, Ru and Rh. Interferents were then added to test the effectiveness of their separation from the analytes.

3.1.1 Selection of the carrier

The carrier solution must be acidic in order to ensure that the alumina mini-column remains positively charged for retention of the negatively charged PGE chloro or oxy-complexes. Since HCl contains Cl^- ions that could assist in the formation of the chlorocomplexes of PGEs, a 0.1 M solution of HCl was first tested. An elution profile is shown in Figure 3.1.

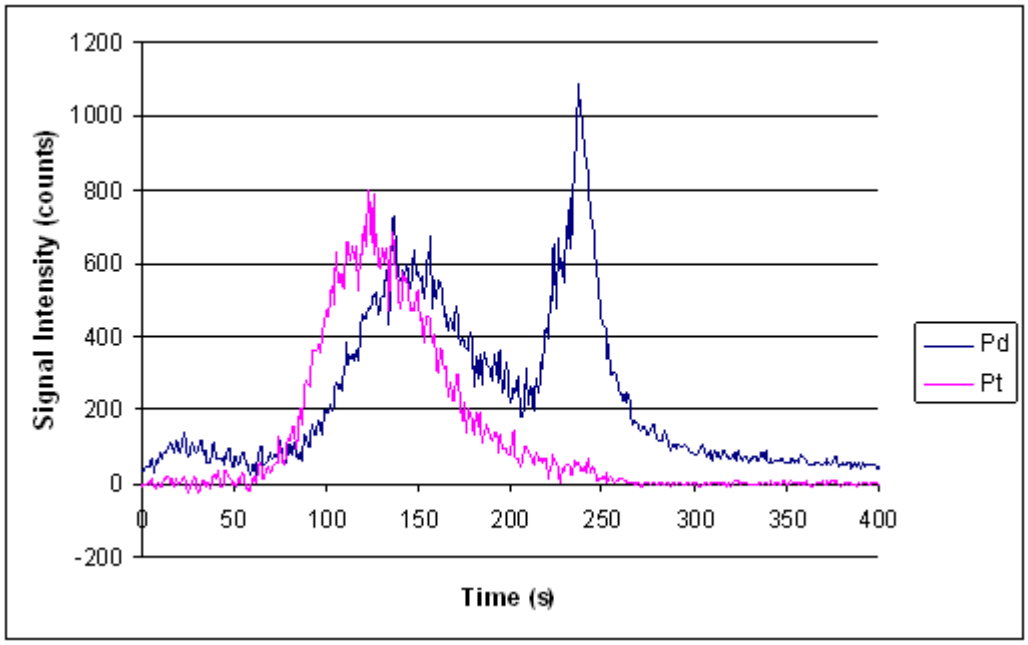

Figure 3.1: Elution profile for a 50-µL sample of 50 µg/L Pt and Pd in 0.1 M HCl using a 0.1 M HCl carrier and 2 M NH_4OH eluent (see Table 2.4 for detailed conditions)

The broad peak at around 140 seconds indicates that the analyte was not retained on the mini-column (and was in fact dispersed by it), whereas the narrower and taller peak at approximately 240 seconds resulted from elution of retained analyte off the mini-column. This profile clearly shows that Pt was not retained while Pd was only partially retained on the mini-column. An increase in the concentration of carrier acid to 1 M HCl only decreased the partial retention of Pd, as can be seen in Figure 3.2.

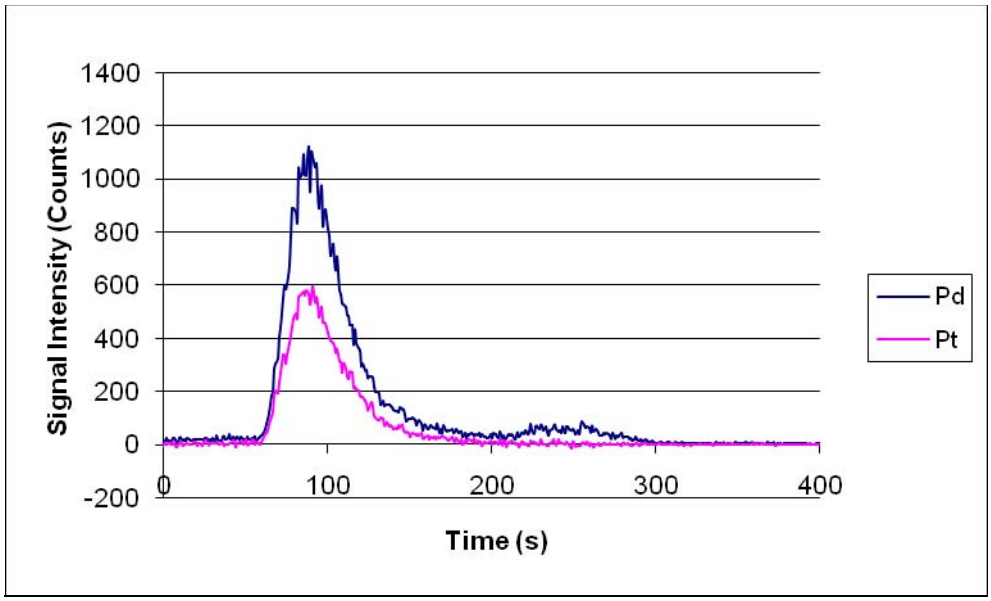

Figure 3.2: Elution profile for a 50-µL sample of 50 µg/L Pt and Pd in 1 M HCl using a 0.1 M HCl carrier and 2 M NH_4OH eluent (see Table 2.4 for detailed conditions)

Thus, the excess Cl^- ions are competing with the Pt and Pd chloro or oxy-complexes for adsorption onto the alumina mini-column. A carrier that does not contain chloride ions may thus be more suited. Indeed, previous studies used a solution of 0.01 M nitric acid as the carrier acid for similar experiments. [7, 74-75] This acid was tested and, as shown in Figure 3.3 did enhance retention of the Pt and Pd onto the alumina mini-column.

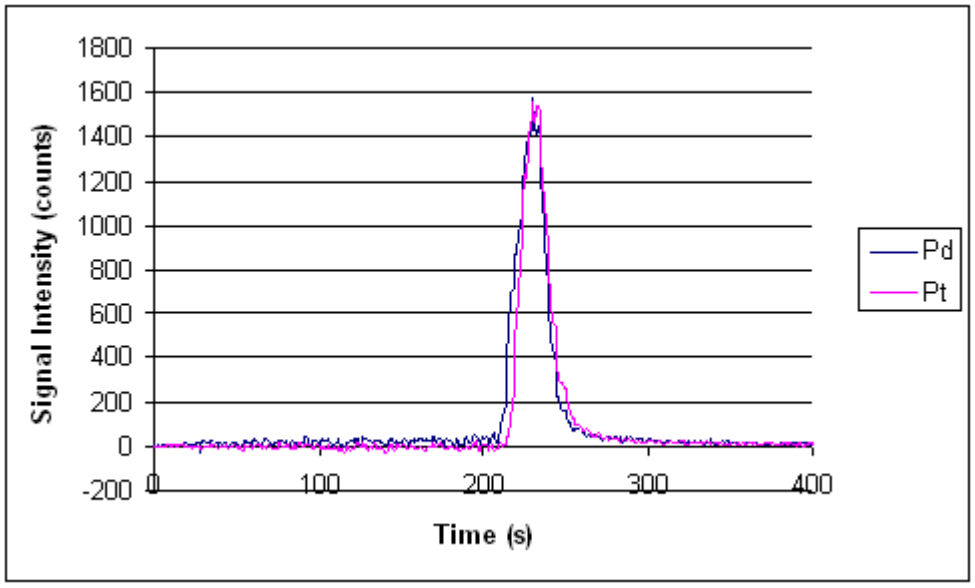

Figure 3.3: Elution profile for a 50-µL sample of 50 µg/L Pt and Pd in 0.1 M HCl using a 0.01 M HNO_3 carrier and 2 M NH_4OH eluent (see Table 2.4 for detailed conditions)

This confirms the hypothesis that the Cl^- ions were in competition with the PGE chloro or oxy-complexes to bind onto the mini-column. Since the Cl^- ions provide significant competition with the PGE complexes, the number of free Cl^- ions must be kept to a minimum to prevent competition with the PGEs. The NO_3^- ions do not compete as strongly with the Pt and Pd complexes, thus they allow all of the Pt and Pd complexes to be retained onto the mini-column. Thus, 0.01M HNO_3 was selected as the carrier acid for the remainder of this work.

3.1.2 Selection of the eluent

For efficient elution of the PGE complexes from the alumina mini-column, the eluent must be basic to ensure that the alumina mini-column becomes negatively charged to release the PGE complexes. Previous studies[7] indicate 2 M NH_4OH was suitable for the

determination of Pt whereas 0.5 M KCN[75] was recommended for Pd. 2 M NH_4OH was first tested and, as already shown in Figure 3.3, it appears to be a suitable eluent for both Pt and Pd.

3.1.3 Optimization of flow rate

The fastest possible flow rate is desired to maximize sample throughput. If the flow rate is too fast, however, the residence time may be too short to allow sufficient time for analyte retention on the mini-column.

Various flow rates were tested in triplicate using the method as described in Table 2.4. The results are summarized in Figure 3.4.

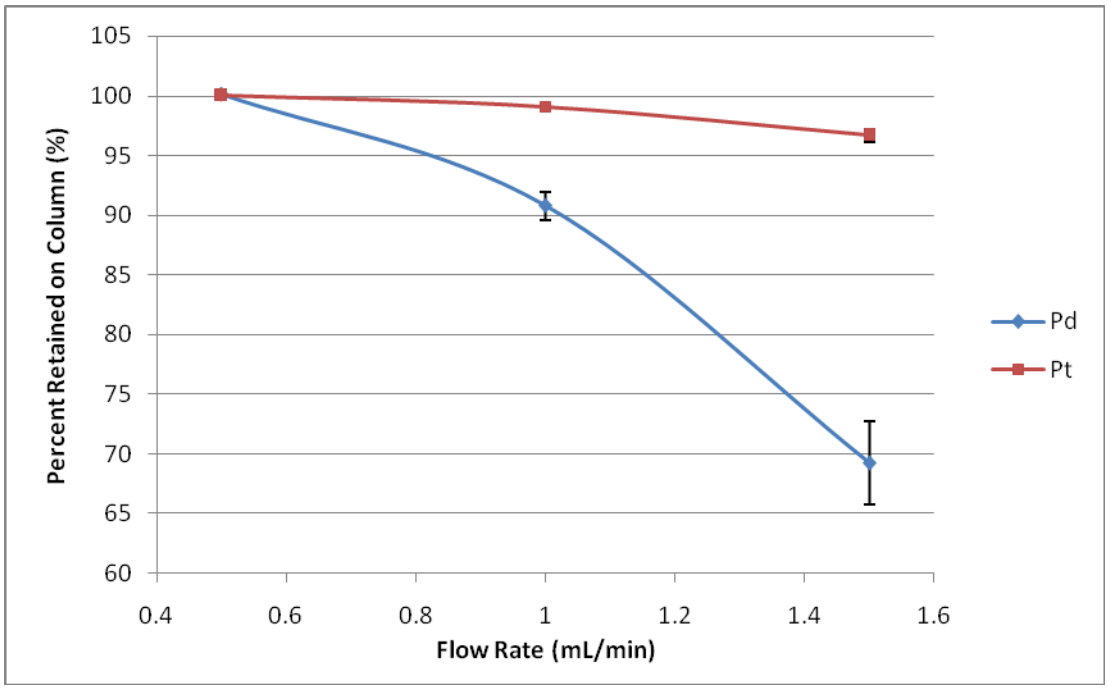

Figure 3.4: Effect of carrier flow rate on the percent retention of Pt and Pd (error bars correspond to 1 standard deviation; n=3)

The general trend, as expected is a decrease in the efficiency of the mini-column with an increase in flow rate of the carrier acid. The retention of Pt is mimimally affected in contrast to that of Pd. An increase in the amount of activated alumina in the mini-column may increase the efficiency of the mini-column at higher flow rates, but back-pressure problems then become an issue. Elution profiles for both Pt and Pd at 0.5 and 1.5 mL/min are shown in Figures 3.5 and 3.6, respectively.

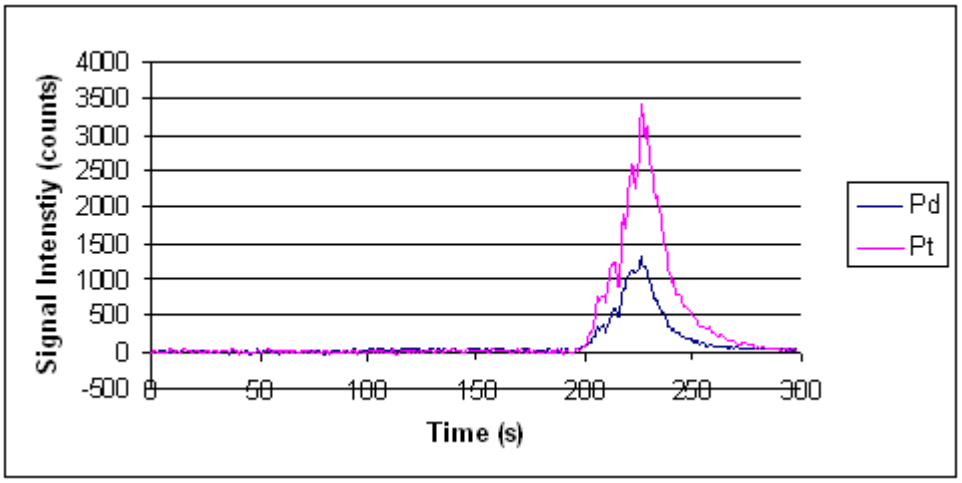

Figure 3.5: Elution profile for 50 µg/L Pt and Pd carried at 0.5 mL/min (see Table 2.4 for detailed conditions)

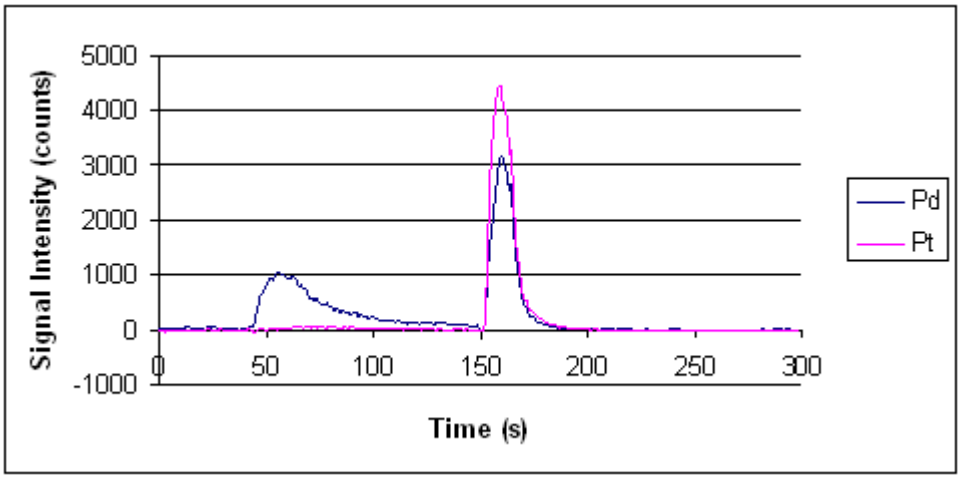

Figure 3.6: Elution profile for 50 µg/L Pt and Pd carried at 1.5 mL/min (see Table 2.4 for detailed conditions)

Examination of these elution profiles indicate that, at 1.5 mL/min, the elution peaks are smoother and more reproducible than those at a flow rate of 0.5 mL/min. The relative standard deviation of the elution peak areas at 0.5 mL/min and 1.5 mL/min are 9% and 3% respectively. However, Pd breaks through the mini-column at 1.5 mL/min. Although the higher flow rate is not favourable for the retention of Pt and Pd onto the mini-column, it is favourable for their elution. A dual-line FI manifold was thus examined to accommodate a lower flow rate for retention and a higher flow rate for elution.

3.1.3.1 Dual-line flow injection manifold

Calibration curves for Pt and Pd using the single-line and dual valve manifold are displayed in Figure 3.7 and 3.8 respectively.

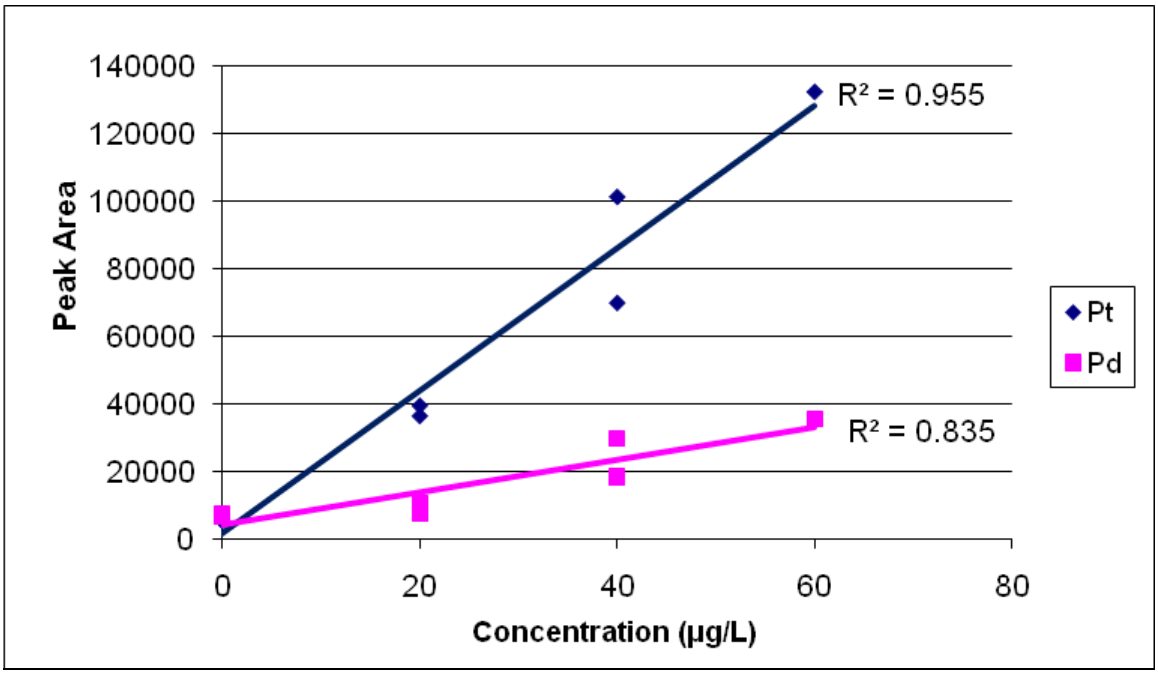

Figure 3.7: Calibration curve for Pt and Pd using a single-line FI manifold

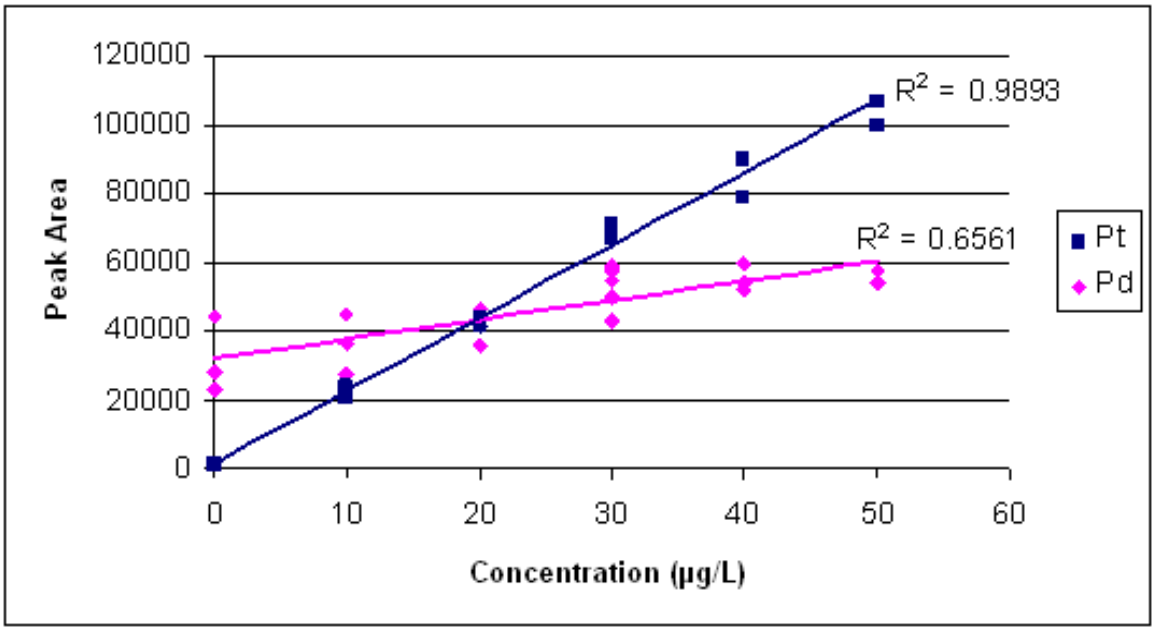

Figure 3.8: Calibration curve for Pt and Pd using a dual-line FI manifold

The calibration curve for Pt is more reproducible using the dual-line FI manifold, however the calibration curve for Pd does not show any improvement. The non-zero intercept in the calibration curve indicates that there is contamination present in one of the valves used. The contamination was isolated to one particular valve in the dual-line FI manifold set-up and despite numerous attempts at removing this contamination, there was no improvement in the reproducibility of the Pd results as the contamination was still present.

The dual-line FI manifold offers a number of advantages over the single-line one. The increased flow rate for the elution of PGEs increases not only the reproducibility of results, but also the sample through put as the elution and re-acidification steps can be performed at a faster rate. The interferents are also sent to waste using the dual-line system, whereas they go to the ICP-MS with the single-line manifold. This is particularly an advantage for analysis on the ICP-TOFMS, as the detector is bombarded by all ions produced in the ICP. While the dual-line FI manifold may be optimal for the retention and elution of Pt and Pd, the Pd contamination of the second valve of this system prevented valid results for Pd. For this reason the single-line manifold was used for the remainder of the experiments. The single-line FI system is also an advantage during method development, as the elements that pass unretained through the mini-column need to be monitored.

3.1.4 Optimization of the alumina mini-column

The mass of alumina in the mini-column was considered, as it should be large enough to fully retain the PGEs, but should also be minimized to prevent backflow problems in the

FI system. Alumina mini-columns ranging from 22 mg to 300 mg were tested at a flow rate of 0.5 mL/min. The results are shown in Figure 3.9.

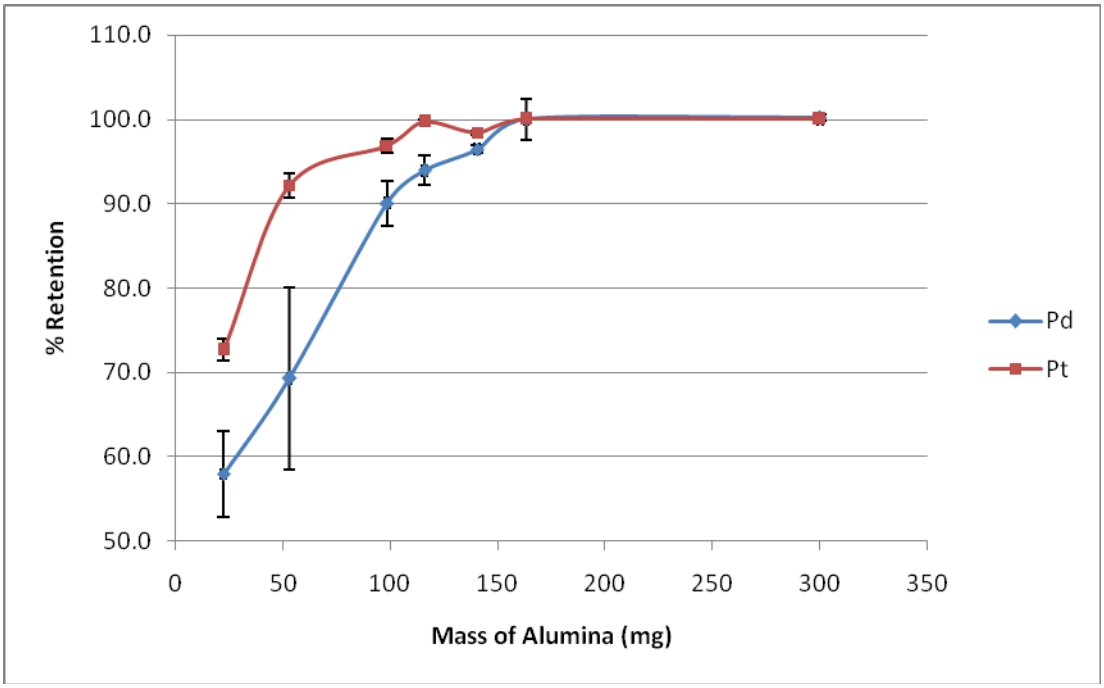

Figure 3.9: Percent retention of 5 µg/L Pt and Pd with various amounts of alumina (error bars correspond to 1 standard deviation, n=3)

Alumina mini-columns ranging from 150 mg to 300 mg can effectively retain all Pt and Pd with no indication of backflow problems. For the determination of Pt and Pd, a mini-column of 150 mg is sufficient. Further studies to incorporate other PGEs may require a larger alumina mini-column, as the number of complexes that are required to adsorb on the surface of the alumina will increase.

3.1.5 Selection of the sample matrix

The PGE solution must contain Cl^- ions to form appropriate chlorocomplexes for retention onto the mini-column. Previous research utilized approximately 2 M HCl solution to form stable chlorocomplexes of Pt and Pd.[7, 74-75] For these experiments, an initial concentration of 1 M HCl was chosen to see if it would allow effective retention of Pt and Pd onto the alumina mini-column while minimizing the competition of the Cl^- ions for the alumina mini-column. As shown in Figure 3.3, the 0.3 M HCl seems to be an appropriate concentration for the retention of Pt and Pd onto the alumina mini-column.

The procedure that is used to digest the tree samples requires that the sample solution be diluted with 15 g of 0.3 M nitric acid. This is necessary for analysis on the ICP-HRMS. In order to determine if the 0.3 M nitric acid was suitable for the proposed method, experiments were performed using the conditions in Table 2.5, where the concentrations of ranged from 8 mM to 0.3 M. Figure 3.10 displays the elution profiles for 8 mM and 0.3 M nitric acid, while Figure 3.11 plots the percent retention of Pt and Pd against the concentration of HNO_3 in the sample matrix.

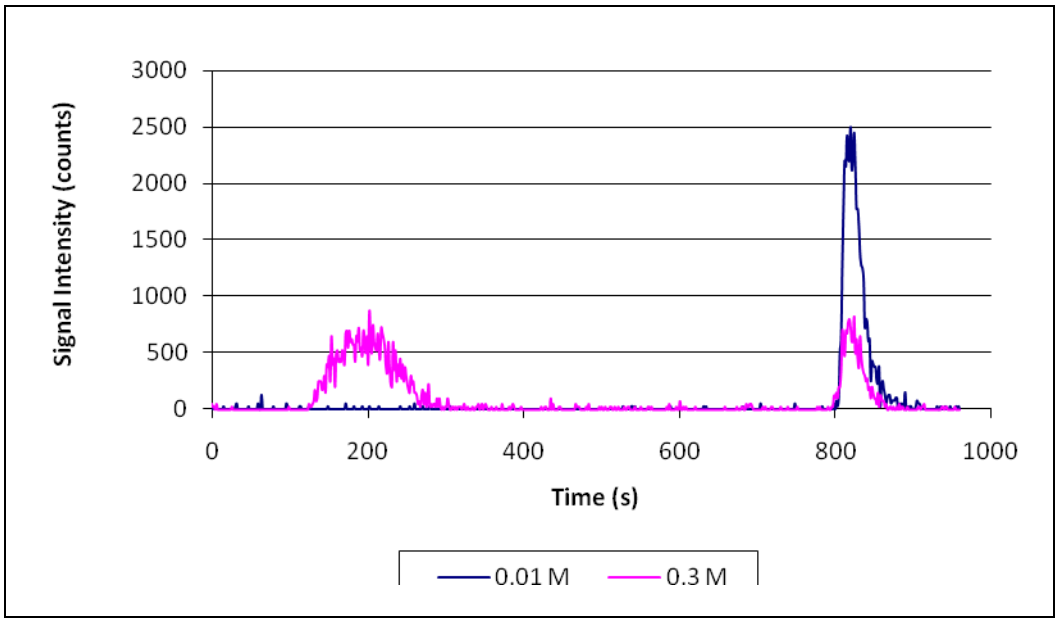

Figure 3.10: Elution profile for 5 µg/L Pt with 8 mM and 0.3 M HNO_3 in the sample matrix (other conditions are summarized in Table 2.5)

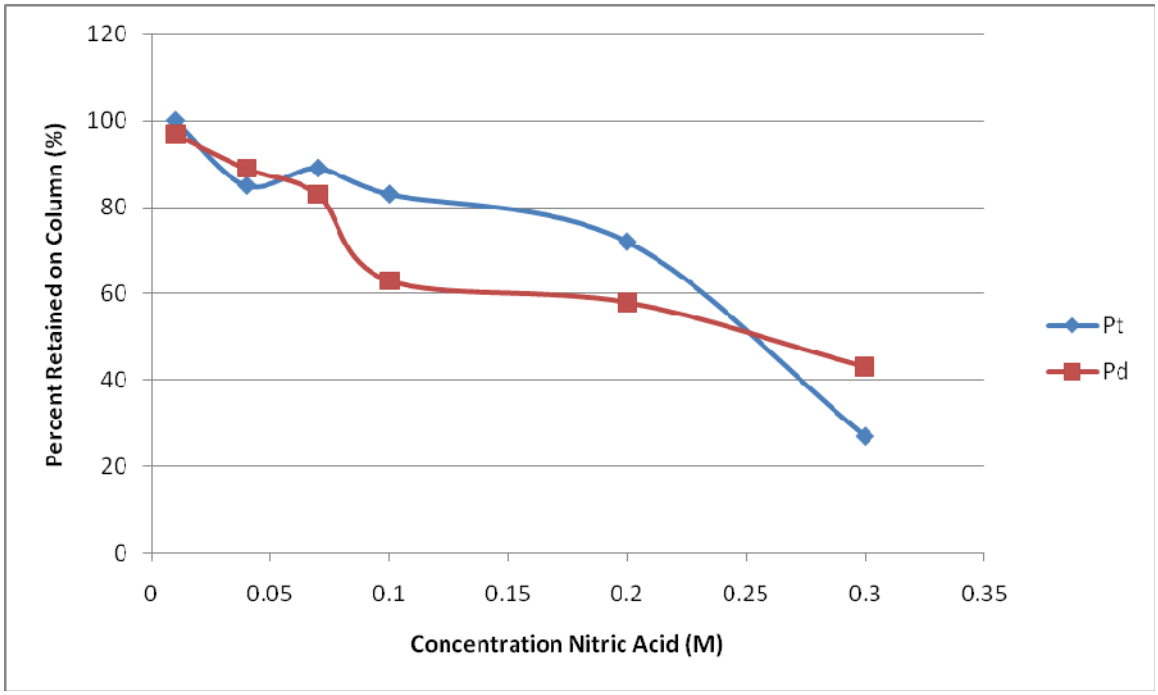

Figure 3.11: Results displaying the percentage of Pt and Pd that was retained on the alumina mini-column with varying concentrations of HNO_3 in the sample matrix

These data indicate that small concentrations of nitric acid in the sample matrix do not affect the retention of the PGEs onto the mini-column. However, as the concentration of nitric acid increases, the retention of the PGEs onto the mini-column decreases. Thus the 0.3 M nitric acid matrix of the digested tree samples samples is unsuitable for this procedure. That is why a sample pretreatement step was added as described in Section 2.6.2, which involves evaporation of HNO_3 and re-dissolution of the residue in 1 mM HCl.

The effects of potential interferents were assessed. The most common interferents with the PGEs, which are in large quantities in tree samples, are Cu and Zn. Ni was also considered as it can also be found in large quantities in natural tree samples.

The interferents were initially added to the Pt, Pd solution at a concentration of 200 μg/L. These experiments used the 16 minute procedure as summarized in Table 2.5. The results shown in Figure 3.12 indicate that Zn and Ni pass through the alumina mini-column completely, while Cu has minimal retention on the mini-column under these conditions.

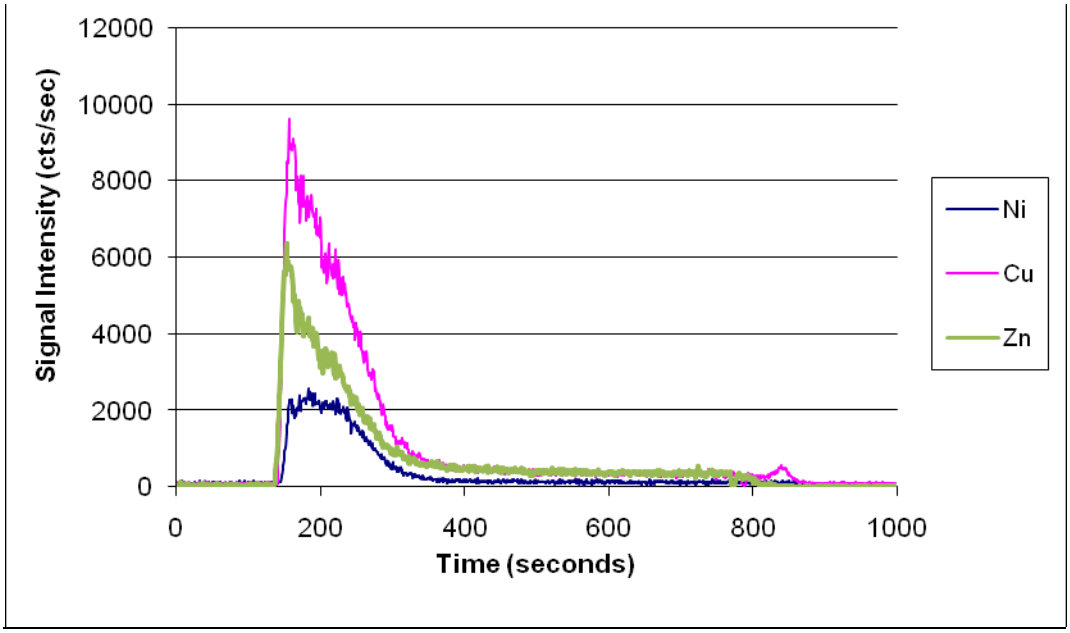

Figure 3.12: Elution profiles of 200 µg/L Ni, Cu and Zn (experimental conditions are summarized in Table 2.5)

Experiments were performed in triplicates to determine if the partial retention of Cu would affect the signal intensity of the Pt or Pd by using 5 µg/L solutions of Pt and Pd that also contained 200 µg/L of the interferents. Results are summarized in Table 3.1. These data indicate that there is no statistical difference between the peak area of Pt or Pd while in the presence of the interferents under these conditions.

Table 3.1: Peak areas and their corresponding relative standard deviation (n=3) for Pt and Pd with and without 200 µg/L interferents

	5µg/L Pt, Pd solution with 0 µg/L Ni, Cu, Zn	5µg/L Pt, Pd solution with 200 µg/L Ni, Cu, Zn
Average peak area Pt	32600	31300
Standard deviation Pt	4%	5%
Average peak area Pd	28600	29500
Standard deviation Pd	5%	3%

Interferents were then added to the sample matrix at concentrations that resemble the concentrations that are expected to be present in natural tree samples in Rock Lake, Manitoba as seen in Table 3.2[76]. 10 mg/L of Ni and Cu were tested along with 40 mg/L of Zn. The results shown in Figure 3.13 demonstrate that the interferents are not retained on the mini-column at the concentration naturally found in tree samples. A comparison of Pt and Pd with and without the interferents under these conditions showed no statistical difference between the peak areas (Table 3.3).

Table 3.2: Concentrations of interferents reported in vegetation in Rock Lake[76]

	Minimum concentration (mg/L)	Maximum concentration (mg/L)	Average Concentration (mg/L)
Ni	3	9	5
Cu	2	10	3
Zn	18	60	40

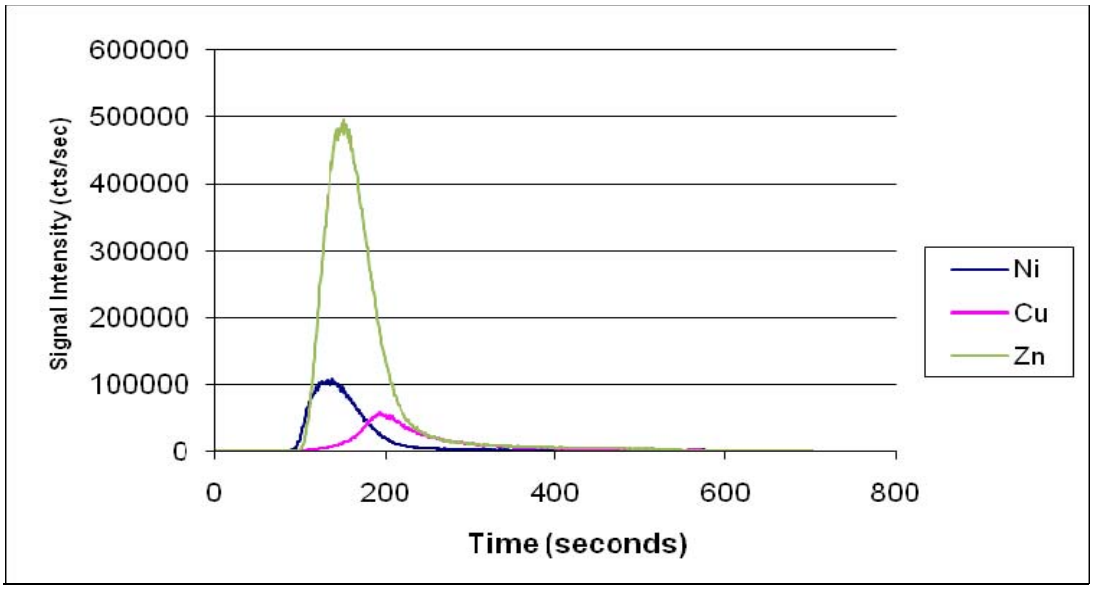

Figure 3.13: Elution profiles of 10 mg/L Ni, Cu and 40 mg/L Zn (experimental condidtions are summarized in Table 2.5)

Table 3.3: Peak areas and their corresponding relative standard deviation (n=3) for Pt and Pd with and without 10 mg/L Ni and Cu and 40 mg/L Zn

	5µg/L Pt, Pd solution with 0 µg/L Ni, Cu, Zn	**5µg/L Pt, Pd solution with 10 mg/L Ni and Cu and 40 mg/L Zn**
Average peak area Pt	48600	44600
Standard deviation Pt	3%	6%
Average peak area Pd	28500	32500
Standard deviation Pd	7%	3%

3.1.6 Method selected for the determination of Pt and Pd

The conditions that were selected for the determination of Pt and Pd are summarised in Table 3.4. The 16 minute procedure is listed in the bottom portion of Table 2.5.

Table 3.4: Operating parameters for the determination of Pt and Pd

Parameter	Setting
Mass of alumina mini-column (mg)	150
Flow rate of carrier acid (mL/min)	0.5
Flow rate of eluent (mL/min)	0.5
Carrier acid	0.01 M HNO_3
Volume of sample injection loop (mL)	1.0
Eluent	2.0 M NH_4OH
Volume of Eluent (mL)	1.0
Sample matrix	0.1 M HCl with 200 µg/L Ni, Cu, Zn
Analysis time/sample (min)	16

3.2 Optimization of method to include Ir, Re, Rh and Ru

The above method was tested for other PGEs of interest, Ir, Re, Rh and Ru using 5 µg/L sample solution. Results for Ru and Rh are displayed in Figure 3.14 and for Ir and Re in Figure 3.15.

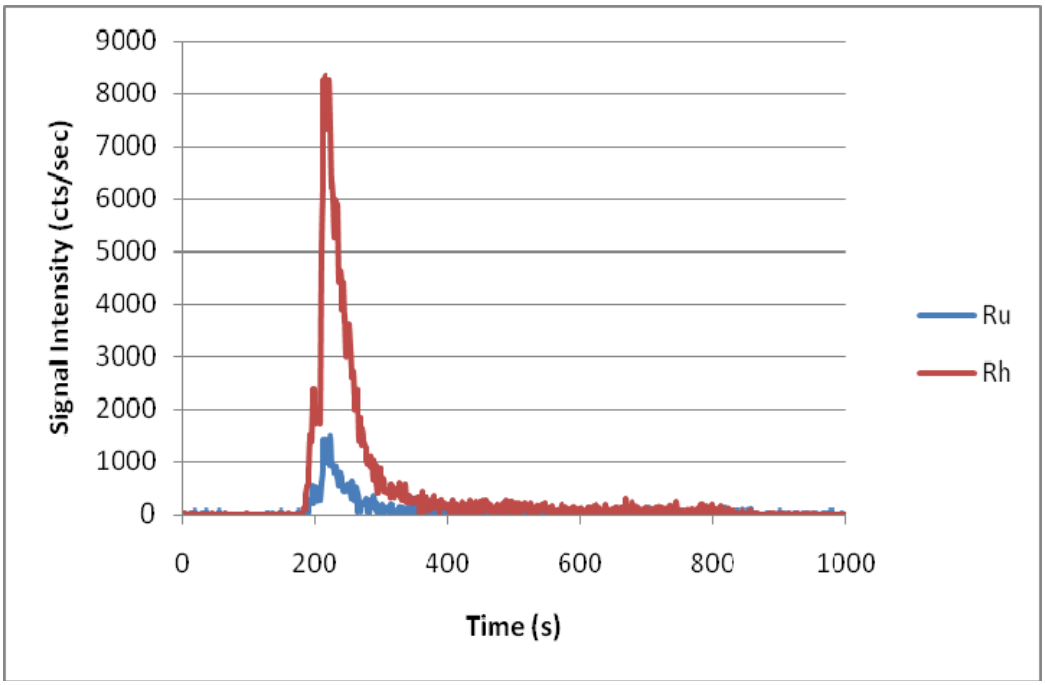

Figure 3.14: Elution profile for 5 µg/L Ru and Rh using the method as described in Section 3.1.6

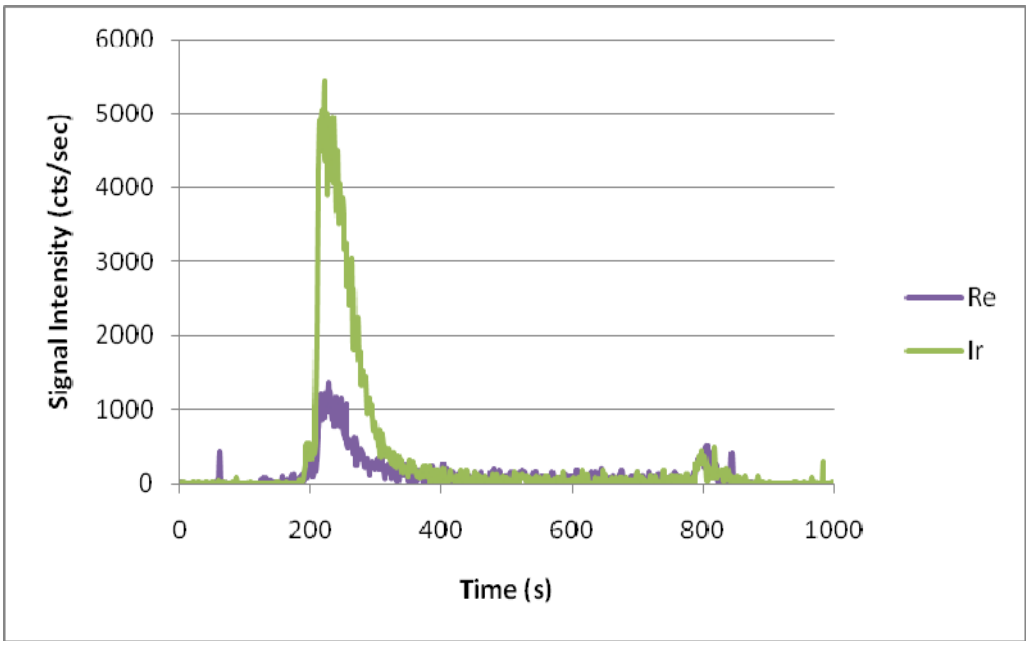

Figure 3.15: Elution profile for 5 µg/L Re and Ir using the method as described in Section 3.1.6

There is very little retention of Re, Ir, Rh and Ru onto the mini-column. This is likely a result from competition of the PGE chlorocomplexes with Cl^- ions in solution.

The effect of HCl concentration in the sample matrix was thus examined in the range from 1 mM to 0.1 M HCl. The mass of the alumina mini-column was increased as well to 300 mg to accommodate for the extra PGEs in the solution. Figure 3.16 plots the percentage of the PGE that was retained on the mini-column against the concentration of HCl in the sample matrix.

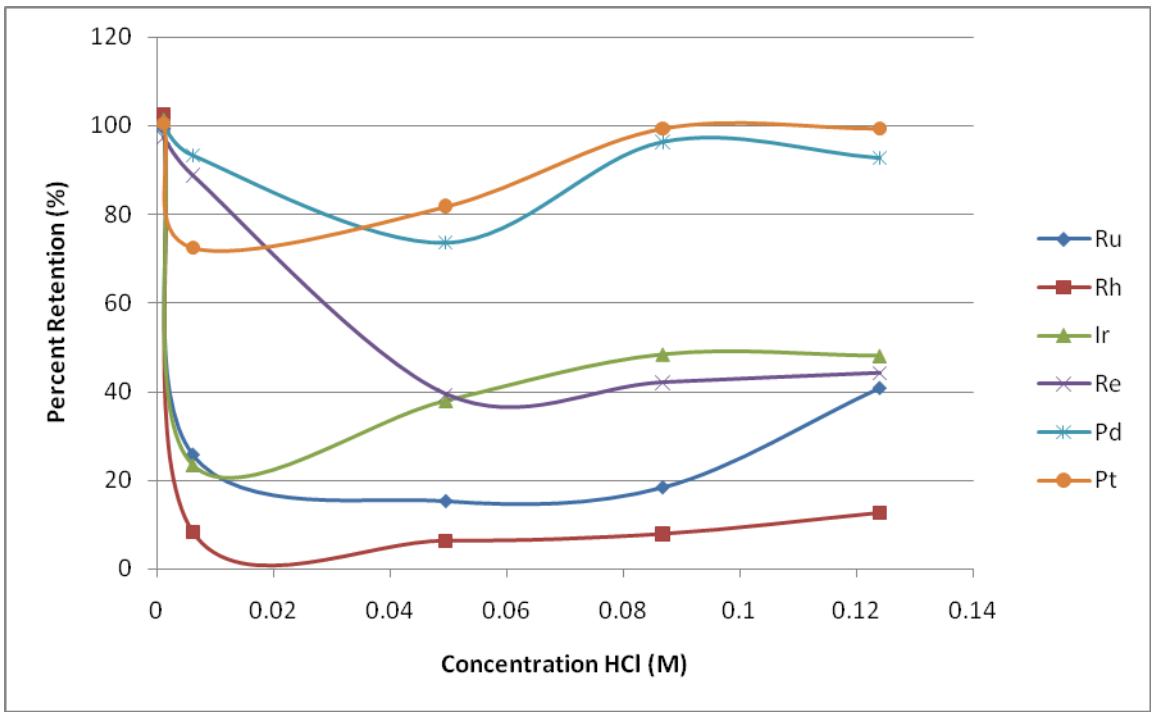

Figure 3.16: Percent retention of each PGE on 300 mg alumina at varying concentrations of HCl in the sample matrix

At 1 mM HCl, in the sample, all elements are 100% retained on the mini-column. However when the concentration of HCl increased to 0.01%, there is then a drastic decrease in the retention of Ru, Rh and Ir. In order to ensure complete retention of all PGEs, the concentration of HCl was thus decreased to 1 mM HCl and the amount of alumina increased to 300 mg, compared to the method developed for Pt and Pd.

The revised method for the determination of PGEs is displayed in Table 3.5.

Table 3.5: Operating parameters for the determination of Ru, Rh, Pd, Re, Ir and Pt

Parameter	**Setting**
Mass of alumina mini-column (mg)	300
Flow rate of carrier acid (mL/min)	0.5
Flow rate of eluent (mL/min)	0.5
Carrier acid	0.01 M HNO_3
Volume of sample (mL)	1.0
Eluent	2.0 M NH_4OH
Volume of eluent (mL)	1.0
Sample matrix	1 mM HCl with 200 µg/L Ni, Cu, Zn
Sample run time (min)	16

3.2.1 Pre-concentration Factor.

The concentration of PGEs in environmental samples are typically at or below the detection limits of modern analytical instrumentation. To obtain accurate concentration results, pre-concentration of the PGEs is desired. Previous studies involving the pre-

concentration of Pt using an alumina mini-column preconcentrated 15 and 30 mL of Pt solution down to 50 μL eluent, i.e. a pre-concentration factor of 300 and 600.[7]

For the analysis of tree-top samples, it would be very time-consuming and inefficient to digest enough tree product to allow for 15 mL of sample per replicate. 1 mL of sample is a more aproppriate volume for this type of analysis. Since a dual-line FI manifold was not used for these analyses, low volumes of eluent were also not used. In this case, 1 mL sample was eluted with 1 mL of eluent, however all of the analyte is eluted within 53 seconds, which corresponds to a pre-concentration factor of 2.3. While there was little pre-concentration of PGEs with this method, there is a definite separation of the analytes from the interferents, which should allow for a more accurate determinaton of PGEs in natural samples. Further studies into a possible dual-line or a dual-valve, single-line FI manifold will be able to increase the preconcentation factor to 20 if 50 μL of eluent is used.

3.2.2 Calibration and detection limits

Calibration curves were constructed using the Ultramass 700 ICP-QMS for Ru, Rh, Re, Ir, Pd and Pt. Each calibration point was repeated 5 times and concentrations ranged from 0 μg/L to 5 μg/L using the method for the determination of PGEs as described. Calibration data, including errors on the slope and intercept of the calibration curves obtained by performing a least squares analysis on Microsoft Excel® are listed in Table 3.6.

Table 3.6: Slope and intercept data for calibration curves with concentrations of 0 µg/L, 0.05 µg/L, 0.5 µg/L, 1.0 µg/L, and 5.0 µg/L

Element	Ru	Rh	Pd	Re	Ir	Pt
Slope value	2720	2353	22600	114500	31307	38490
Standard Deviation on slope	240	84	2000	1200	400	910
Intercept value	2270	1600	17500	-200	1739	1300
Standard Deviation on intercept	550	200	3800	2700	917	2100
R^2	0.917	0.986	0.917	0.998	0.997	0.992

The calibration curve for Pd has the lowest linearity and reproducibility. It is suspected that there may be some contamination of Pd in the introduction system or solutions given the large, nonreproducible blank signal. This will greatly deteriorate the detection limit for Pd. Re is the element for which the highest sensitivity was achieved, while the sensitivity for Pt, Pd and Ir are similar. The sensitivities for Ru and Rh however are low compared to the other PGEs.

The poor reproducibility of Pd can be further seen in Figure 3.17. The large variation between each sample profile could be a result of accumulation of contamination in the valve system or uneven elution of the element. In contrast, the excellent reproducibility of Pt (Figure 3.18) shows overlapping elution profiles with peak areas that are statistically the same.

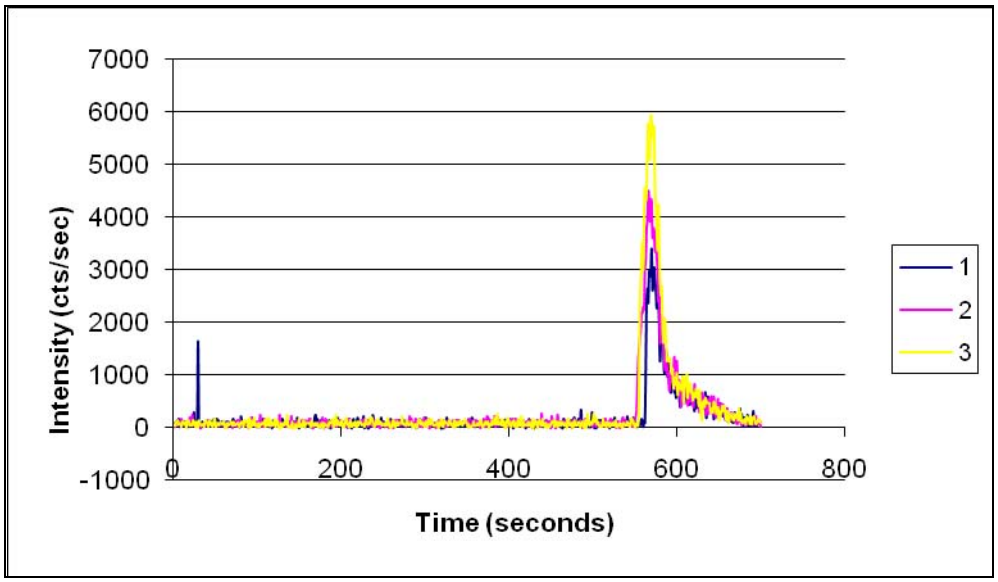

Figure 3.17: Elution profiles of 3 replicates of 5.0 µg/L of Pd using the method as described in Table 3.5

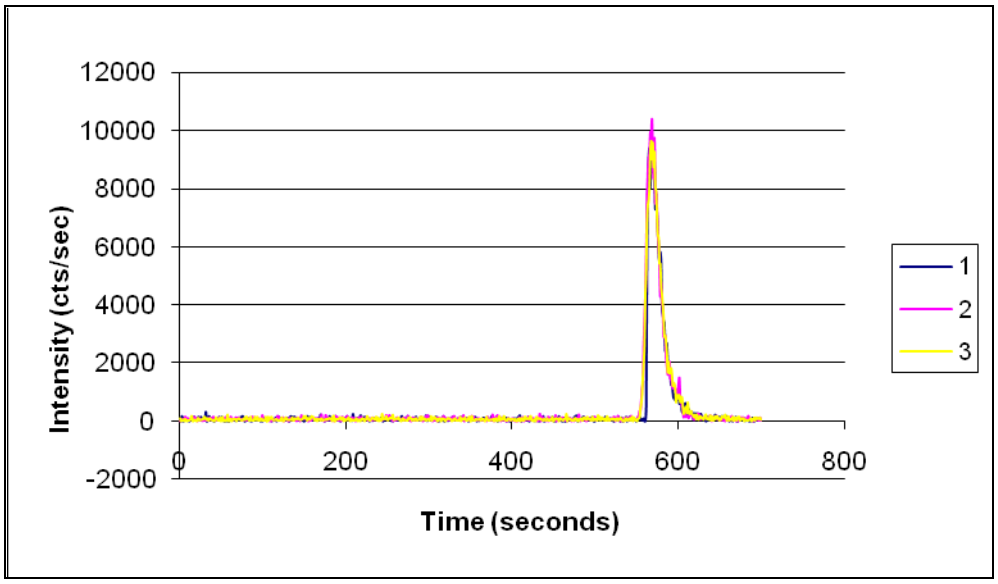

Figure 3.18: Elution profiles of 3 replicates of 5.0 µg/L of Pt using the method as described in Table 3.5

The detecton limits (DL) for the PGEs were calculated using the equation $DL = 3\sigma_B / b$, where σ_B = standard deviation of the blank and b = slope of calibration curve. The detection limits were multiplied by the dilution factor of 6.25 involved in the preparation of tree samples to express them in terms of tree sample. They are compiled in Table 3.7, where they are compared to those obtained using ICP-HRMS.

Table 3.7: Average detection limits of Ru, Rh, Pd, Re, Ir and Pt in solution, the estimated detection limit of the PGEs in tree samples and detection limits using ICP-HRMS

Element	DL in solution (µg/L)	DL in tree (µg/kg)	DL in tree using HR-ICP-MS (µg/kg)
Ru	0.6	20	5
Rh	0.4	10	2
Pd	2	50	2
Re	0.01	0.3	3
Ir	0.01	0.5	2
Pt	0.5	20	3

As expected, the detection limits for Pd is significantly higher than the other PGEs due to suspected contamination of the introduction system and solutions. While all the detection limits varied from day to day (with the average detection limit reported in Table 3.5), the detection limit of Pd had the greatest degree of variation. Detection limits for Re and Ir are better than those with ICP-HRMS by up to an order of magnitude, whereas the detection limits of Ru, Rh and Pt are approximately 4-6 times higher than those with ICP-

HRMS. The detection limits for PGEs in solution at Acme Labs, a commercial analytical laboratory, have been reported to be 1-2 μg/L.[76] The detection limits using this separation method are lower than or comparable to the methods that are available commercially. Commercial laboratories also do not attempt to remove the sample matrix from the analytes, thus are subjected to more spectroscopic interferents.

The detection limit for Pt using this method is 200 times higher than the detection limit of 0.001 μg/L obtained in previous studies, whereas the detection limit of Pd is 500 times higher than 0.004 μg/L obtained in previous studies.[7, 74-75] While the detection limits for Pt and Pd using this method are substantially higher than those obtained in previous works, our method has been appropriately modified to accommodate the low sample volumes required for the analysis of tree top samples.

The blank samples of all the PGEs, with the exception of Pd, do not show detectable levels of analyte. This is an indication that our method for most of the PGEs is not blank-limited. Removal of contamination of Pd as well as a greater pre-concentration factor would greatly reduce the detection limits for these PGEs. For a greater pre-concentration factor, a dual-line FI manifold is recommended.

CHAPTER 4: ASSESSMENT OF PLATINUM GROUP ELEMENTS IN TREE TOP SAMPLES OVER ROCK LAKE, MANITOBA

Tree samples were taken from the area of Rock Lake, north of Thompson, Manitoba. This area is of interest for exploration geochemistry as it includes several known geophysical conductors. There is also Ni mineralization in the area; however, the extent of mineralization must be assessed to determine if its exploitation could be profitable.

The purpose of analyzing tree top samples is to determine whether or not there is a significant increase in the concentration of PGEs in tree tops over areas of Ni mineralization compared to the background concentration of PGEs. If elevated levels of PGEs in tree samples do indicate mineralization in the area, then this method can be used as a low cost screening process to refine exploration strategies. It only requires 3 people and approximately 20 hours of helicopter time to cover an area such as Rock Lake.[76] It is far more costly in money and time to send ground crews in the area to test for possible mineralization.

4.1 Map of tree sampling area

A map of the whole Rock Lake area is shown in Figure 4.1. This map displays the many lines along which samples were collected. Maps of Zone 19 and 24 are shown in Figure 4.2 and 4.3, respectively. These maps show the exact location of the samples taken over the conductor, which is indicated as a red line.

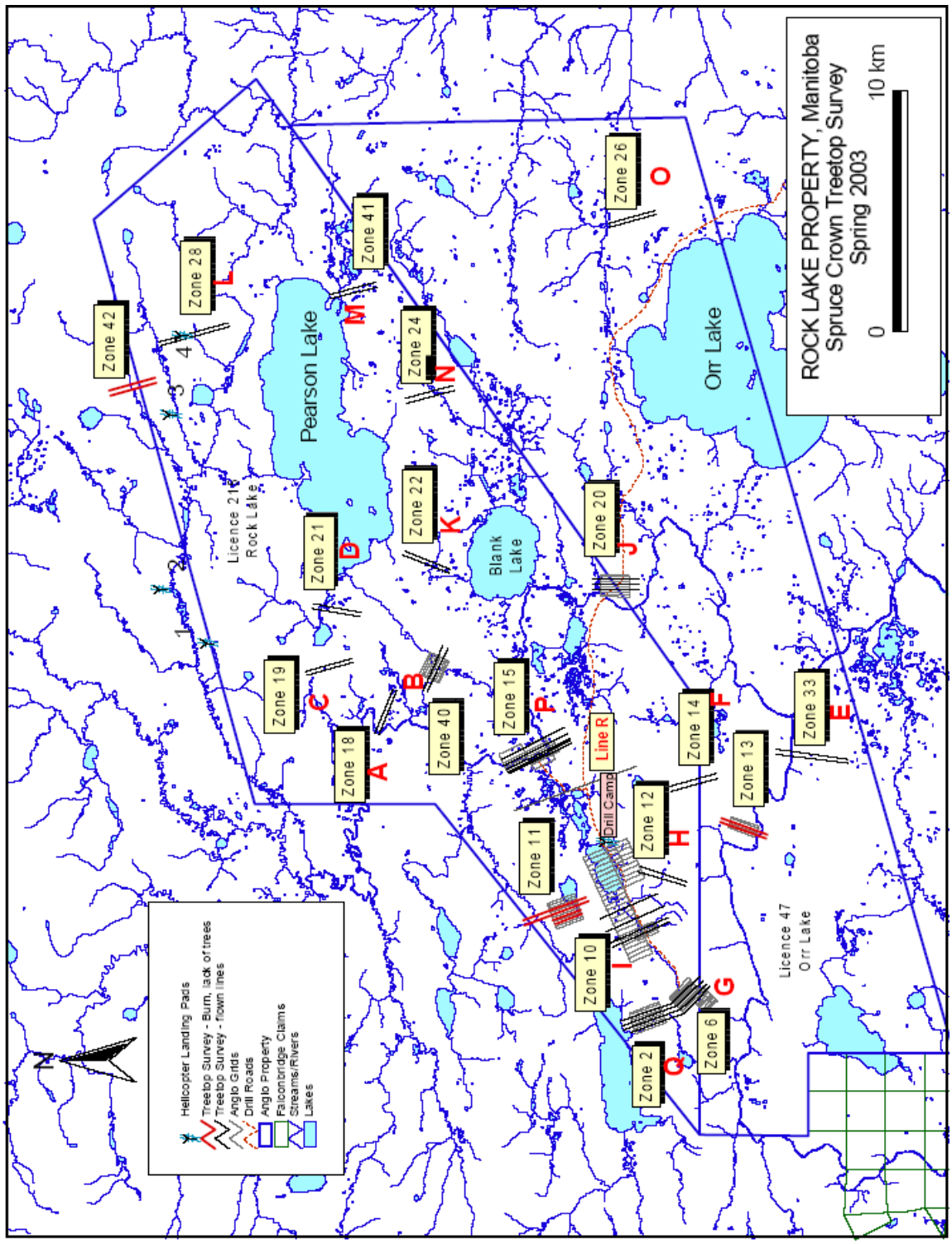

Figure 4.1: Survey area showing the locations of the zones in which tree top samples were taken[76]

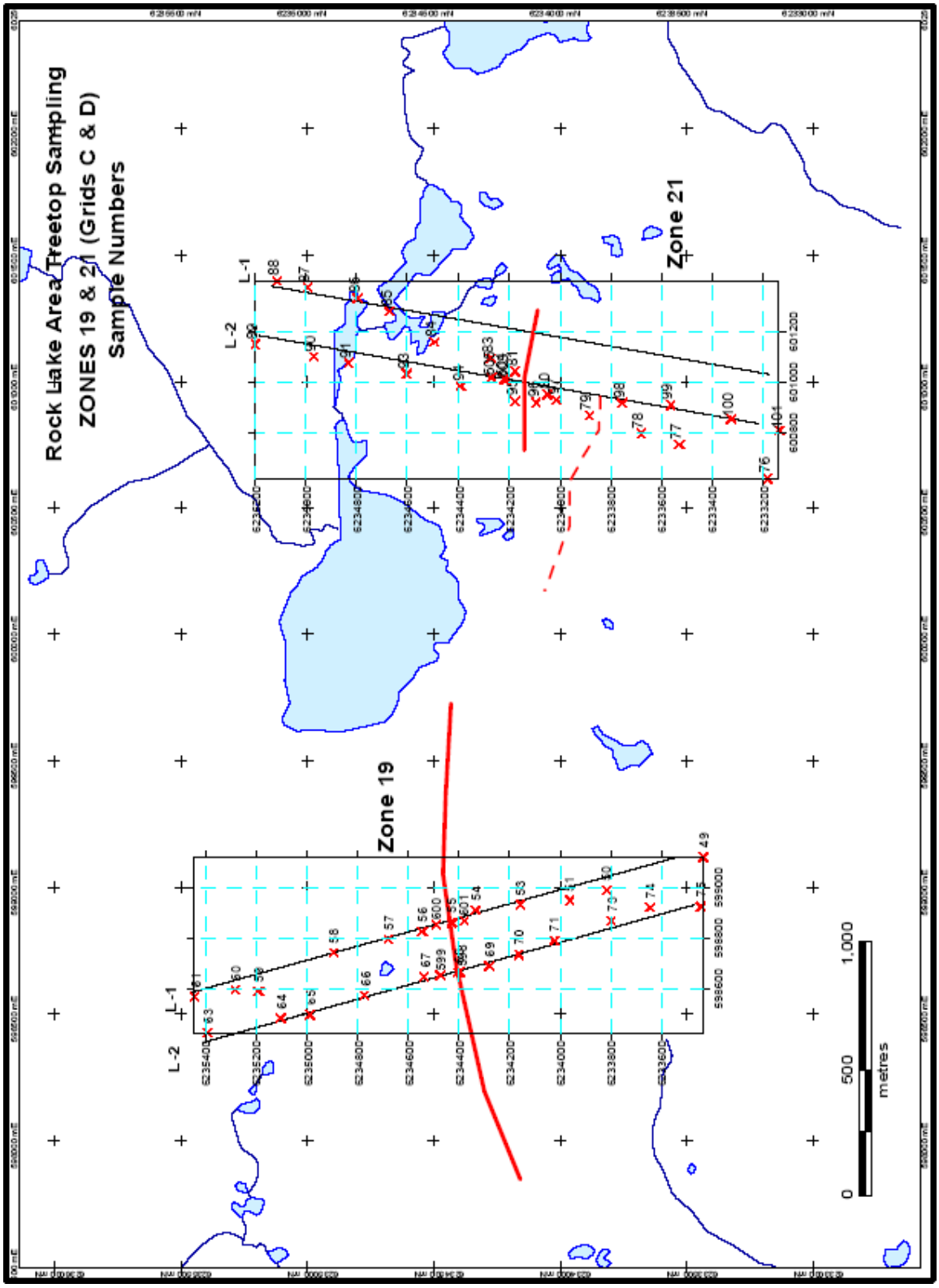

Figure 4.2: Map displaying the Zone 19 conductor and the tree sample numbers[76]

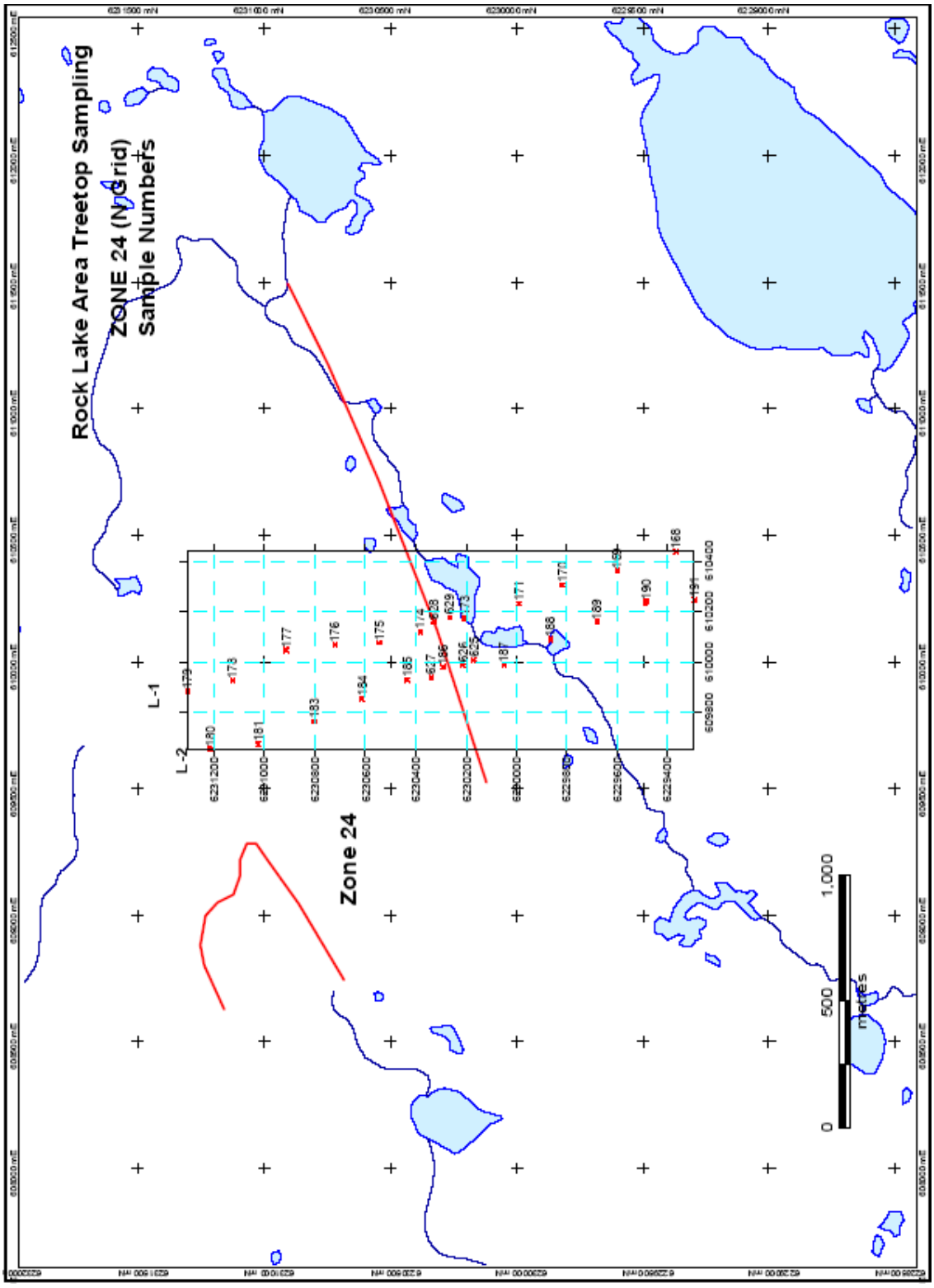

Figure 4.3: Map displaying the Zone 24 conductor and the tree sample numbers[76]

4.2 Results for the determination of PGEs in tree top samples

Tree top samples were analyzed using the method described in Section 2.5.3.4. Results were analyzed individually as well as compared to results obtained by ICP-HRMS. An elution profile of Pd for a tree sample is shown in Figure 4.4.

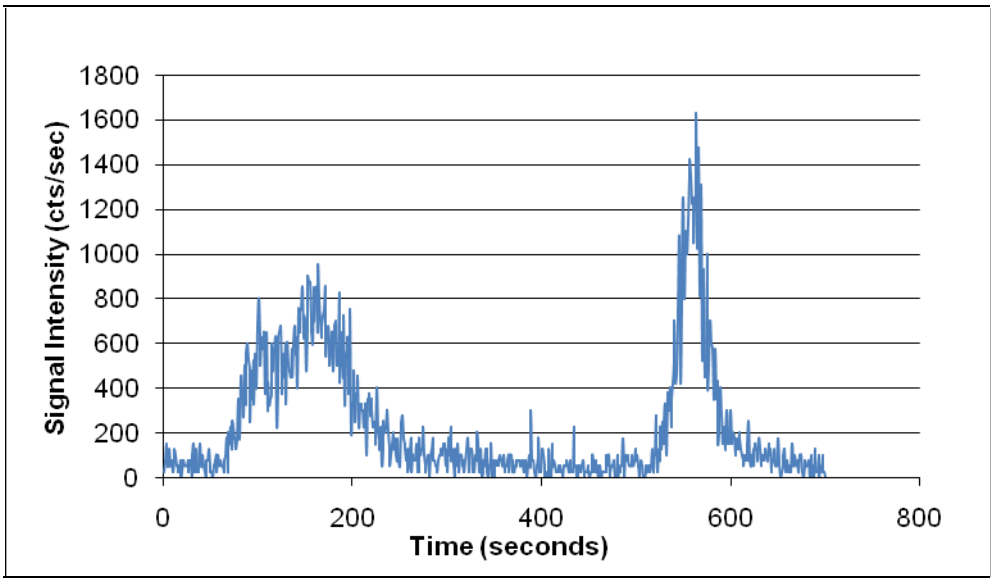

Figure 4.4: Elution profile for Pd from Sample RLTT-470

The broad peak at around 150 seconds is indicative of the interferents, primarily ArCu and ArZn that are formed in the plasma from the Zn and Cu in the tree samples. There does not appear to be any indication of matrix effects from the sample matrix on the elution peak at approximately 545 seconds. The separation of the interferents from the analytes will provide a more accurate determination of the concentrations in the samples. Elution profiles for the other PGEs were similar in shape to that of Pd.

Results of the tree sample analysis and their relative standard deviation (RSD) by the separation method and by ICP-HRMS are listed in Table 4.1 and 4.2, respectively. Results of the tree sample analysis using the separation method was obtained as an average of three separate measurements with carrier passed through the column after each injection. Results of the tree sample analysis by ICP-HRMS were obtained with one measurement in a batch mode. Each measured value is the mean of ten runs and each run is the average of two passes. Results that are below the detection limit are indicated with BD, and results that are above the limit of quantitation (LOQ) are highlighted in red.

Table 4.1: Tree sample results using the proposed separation method

Acme #	Ru (µg/kg)	RSD (%)	Rh (µg/kg)	RSD (%)	Pd (µg/kg)	RSD (%)	Re (µg/kg)	RSD (%)	Ir (µg/kg)	RSD (%)	Pt (µg/kg)	RSD (%)
RLTT - 58	12	51	11	114	4	120	0.01	93	BD		BD	
RLTT - 59	6	41	0.7	83	8	110	BD		BD		BD	
RLTT - 64	10	65	12	45	5	100	BD		BD		BD	
RLTT - 74	3	93	0.3	50	BD		BD		BD		BD	
RLTT - 75	5	94	BD		BD		BD		BD		BD	
RLTT - 79	2	26	BD		BD		0.004	200	BD		BD	
RLTT - 187	4	120	0.1	119	BD		BD		BD		BD	
RLTT - 200	2	51	BD		BD		BD		BD		BD	
RLTT - 204	1	110	BD		BD		BD		BD		BD	
RLTT - 333	9	30	0.5	40	10	44	0.02	190	BD		BD	
RLTT - 356	1	140	BD		BD		BD		BD		BD	
RLTT - 439	8	38	BD		BD		0.2	66	BD		BD	
RLTT - 443	5	120	20	186	0.3	260	0.1	130	BD		BD	
RLTT - 448	3	94	8	64	BD		0.1	59	BD		BD	
RLTT - 450	3	37	5	70	BD		0.06	120	BD		BD	
RLTT - 452	4	290	33	387	49	310	0.1	80	7	394	0.4	240
RLTT - 456	7	96	BD		1	69	BD		BD		BD	
RLTT - 466	7	260	BD		BD		BD		BD		BD	
RLTT - 470	6	95	BD		6.0	140	BD		BD		BD	
RLTT - 473	1	81	BD		BD		BD		BD		BD	
RLTT - 488	0.5	78	BD		BD		BD		BD		BD	
RLTT - 489	6	41	2	32	6	120	0.04	23	BD		BD	
RLTT - 492	3	56	0.2	39	BD		0.04	30	BD		BD	
RLTT - 505	2	18	BD		BD		0.01	320	BD		BD	
RLTT - 606	0.5	68	BD		BD		0.01	110	BD		BD	
RLTT - 612	3	90	BD		2	100	BD		BD		BD	
RLTT - 620	0.5	160	BD		BD		BD		BD		BD	
RLTT - 622	BD		3	22	BD		BD		BD		BD	
RLTT - 628	11	55	0.6	51	9	120	0.03	52	BD		BD	
RLTT - 629	4	75	BD		BD		0.02	92	BD		BD	
RLTT - 630	4	24	BD		BD		BD		BD		BD	
RLTT - 635	5	88	BD		0.7	130	BD		BD		BD	
RLTT - 644	2	34	BD		BD		BD		BD		BD	
RLTT - 646	0.04	110	BD		BD		BD		BD		BD	
RLTT - 673	7	14	BD		14	130	BD		BD		BD	
RLTT - 674	3	120	BD		6	130	BD		BD		BD	
RLTT - 676	4	31	BD		13	60	BD		BD		1	48
RLTT - 677	2	45	BD		3	26	BD		BD		0.1	54

Table 4.2: Tree sample results by ICP-HRMS

Acme #	Ru (µg/kg)	RSD (%)	Rh (µg/kg)	RSD (%)	Pd (µg/kg)	RSD (%)	Re (µg/kg)	RSD (%)	Ir (µg/kg)	RSD (%)	Pt (µg/kg)	RSD (%)
RLTT - 58	BD		BD		1	28	BD		BD		BD	
RLTT - 59	BD		0.07	72	2	14	BD		BD		0.04	330
RLTT - 64	BD		0.6	18	4	10	BD		1	58	0.3	69
RLTT - 74	BD		BD		1	14	BD		BD		BD	
RLTT - 75	BD		BD		2	16	BD		BD		BD	
RLTT - 79	BD		0.1	43	1	14	BD		BD		BD	
RLTT - 187	BD		0.07	43	2	11	BD		BD		BD	
RLTT - 200	BD		BD		1	21	BD		BD		BD	
RLTT - 204	BD		BD		1	16	BD		BD		BD	
RLTT - 333	BD		BD		14	8	BD		BD		BD	
RLTT - 356	BD		BD		0.5	49	BD		BD		0.01	390
RLTT - 439	BD		BD		3	10	BD		BD		BD	
RLTT - 443	BD		0.08	50	3	10	BD		BD		BD	
RLTT - 448	BD		BD		0.7	23	BD		BD		BD	
RLTT - 450	0.03	410	BD		1	27	BD		BD		BD	
RLTT - 452	BD		BD		1	17	BD		BD		BD	
RLTT - 456	BD		BD		2	8	BD		BD		BD	
RLTT - 466	BD		0.1	21	2	23	BD		0.1	50	0.01	220
RLTT - 470	0.04	160	0.01	110	2	18	BD		0.07	55	0.05	110
RLTT - 473	BD		BD		2	15	BD		0.01	330	0.06	69
RLTT - 488	0.5	24	0.08	31	1	17	BD		BD		0.01	240
RLTT - 489	0.04	160	0.09	49	2	20	0.01	1200	0.01	320	0.07	140
RLTT - 492	BD		0.2	19	3	12	BD		BD		0.01	220
RLTT - 505	BD		0.08	51	2	15	BD		BD		BD	
RLTT - 606	0.01	380	0.03	53	1	20	BD		BD		BD	
RLTT - 612	BD		0.09	47	5	13	BD		BD		0.1	69
RLTT - 620	0.02	300	0.2	31	1	22	BD		BD		0.02	180
RLTT - 622	0.03	250	0.4	23	5	11	BD		BD		0.1	45
RLTT - 628	0.04	250	0.05	71	3	14	BD		BD		BD	
RLTT - 629	BD		BD		1	17	BD		BD		BD	
RLTT - 630	0.02	320	0.06	33	3	17	BD		BD		0.07	90
RLTT - 635	0.03	390	0.3	24	1	19	BD		BD		0.03	220
RLTT - 644	0.06	190	0.4	27	1	21	BD		BD		0.04	190
RLTT - 646	BD		0.3	20	1	22	BD		BD		0.01	280
RLTT - 673	0.01	340	0.1	34	1	18	BD		BD		0.03	190
RLTT - 674	BD		0.05	93	1	17	BD		BD		0.06	100
RLTT - 676	BD		0.03	56	1	24	BD		BD		BD	
RLTT - 677	BD		BD		2	17	BD		BD		0.06	120

The detection limit for the PGEs varied greatly from day to day during the analysis of these samples using the separation method with ICP-QMS. All reported results are above the detection limit that was obtained and calculated daily. Very few results using the

separation method with ICP-QMS were above the LOQ, with most results just above the detection limit for the instrument. This is also seen in the ICP-HRMS data, where there are only few results above the LOQ, with the exception of Pd.

Calibration curves were obtained daily from 3 standard solutions that ranged from 0 μg/L to 5.0 μg/L. This range was chosen based on previous results for these tree samples.[76] Many of the concentrations that were obtained using the separation method with ICP-QMS are outside the range of the calibration curves. Concentrations for these samples were found by extrapolating the equation of the calibration curve beyond the concentration range. Previous calibration curves that tested up to 50 μg/L of the elements indicate that the calibration curves are linear at these concentrations, however without a calibration curve that encompassed the reported concentrations, the results may not be accurate.

Results from the tree top samples using the separation method by ICP-QMS display a much higher RSD of the replicates compared to the standard samples using the same method. Moreover, the RSDs are not consistent from sample to sample. This may reflect differences in the matrix of the standard solutions relative to the sample matrix because non-interferent elements in the tree samples may have also been retained on the alumina mini-column, providing competition with the PGEs. In addition, there may have not been full retention of the analytes onto the mini-column that cannot be seen in the elution profiles due to the high peak that is attributed to the interferents. If this is indeed the case, the percent retention of the sample analytes will vary according to the sample

matrix, so that the RSD will be higher than the standard samples that show complete retention of the analytes.

4.2.1 Comparison of results to ICP-HRMS

While the comparison of results should be limited to those above the LOQ, there is too few data in both the separation method with ICP-QMS and ICP-HRMS to do so. In this case, results above the detection limit were compared.

Only 1 sample of the 38 tested samples yielded a result that was above the detection limit of ICP-HRMS for Re. In contrast, Re was detected in 34% of the samples using the separation method in combination with ICP-QMS, which is consistent with the lower detection limit achieved (see Table 3.7). On the other hand, while 50% of the Pt data were above the detection limit by ICP-HRMS, there were only 3 results above the detection limit for Pt using the separation method with ICP-QMS. This again is consistent with the lower detection limit by ICP-HRMS. In the case of Ir, very few results were above the detection limit by ICP-HRMS and the separation method with ICP-QMS.

Figure 4.5 shows a comparison of the concentrations of Ru obtained using both methods. An example of a typical error bar for these scatter points is shown in the top right corner of the figure.

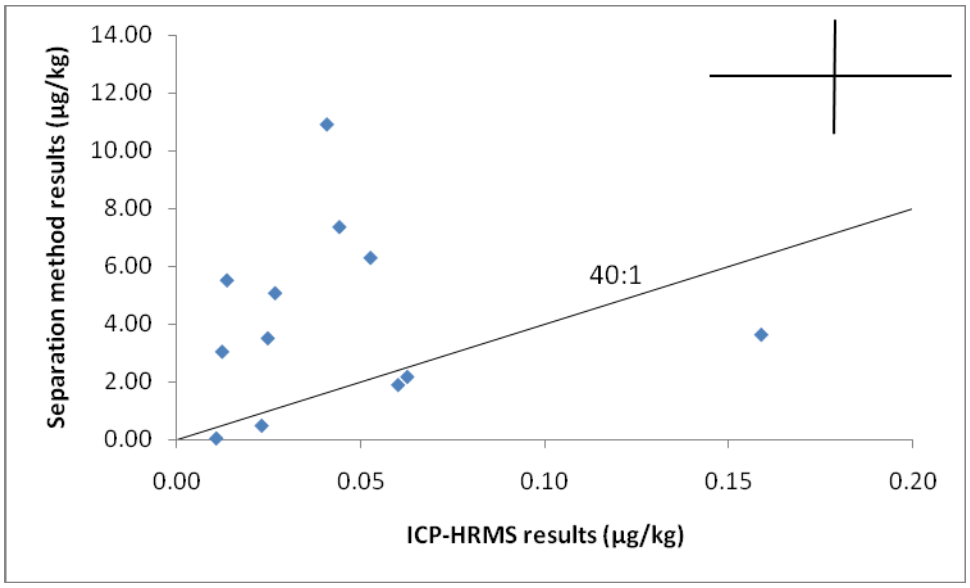

Figure 4.5: Comparison plot of the separation/ICP-QMS data with ICP-HRMS data for Ru

The results obtained using the separation method are 40-100 times higher than the results obtained using ICP-HRMS. Since the concentration of Ru in natural samples is typically at ultra trace levels, it can be assumed that the data using the ICP-HRMS is likely more accurate. With concentrations so close to the detection limit of the method, there is a great amount of error associated with the readings, and cannot be considered a very precise concentration reading.

The results for Rh were also compared to the results obtained using ICP-HRMS. The comparison plot is shown in Figure 4.6, with a typical error bar displayed in the top right corner of the plot.

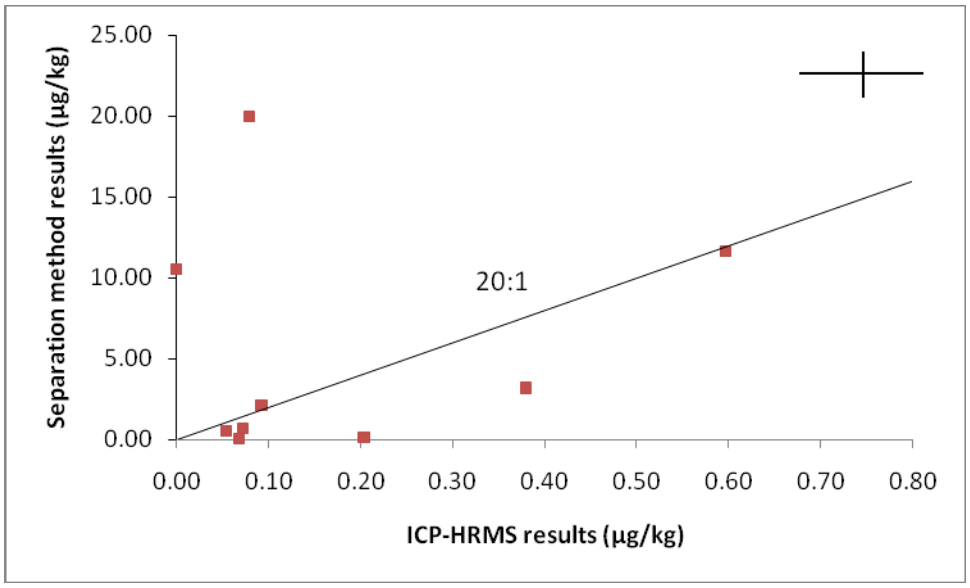

Figure 4.6: Comparison plot of the separation/ICP-QMS data with ICP-HRMS data for Rh

These results are again significantly higher than those results obtained on the ICP-HRMS. In these cases, the concentrations of some of the samples are significantly higher than the detection limit of this method for Rh and indicate that these data are outliers and have possibly become contaminated in the digestion and solvent exchange processes or during analysis. Removal of the outliers (above 10 µg/L), shown in Figure 4.7 yields a closer relationship between results.

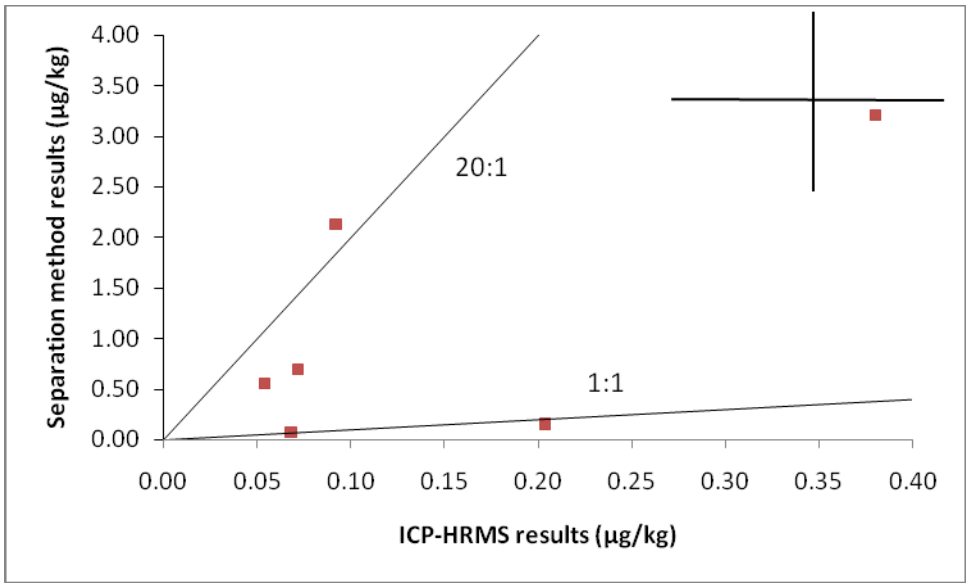

Figure 4.7: Comparison plot of the separation/ICP-QMS data with ICP-HRMS data for Rh with outliers removed

Two of the concentration results plot exactly on the 1:1 line where two of the others are within the associated error of the results. Because there are very few data points to compare, it is difficult to determine the relationship between these two data sets, however this indicates that results are in agreement with each other. There are still many samples below the detection limit for the proposed method with ICP-QMS, if the detection limit for Rh was lowered, there would be more data to compare and thus a more accurate comparison can be made.

Pd results using the separation method were compared to the ICP-HRMS results. Comparison results are found in Figure 4.8 with a typical error bar displayed in the top right corner of the plot.

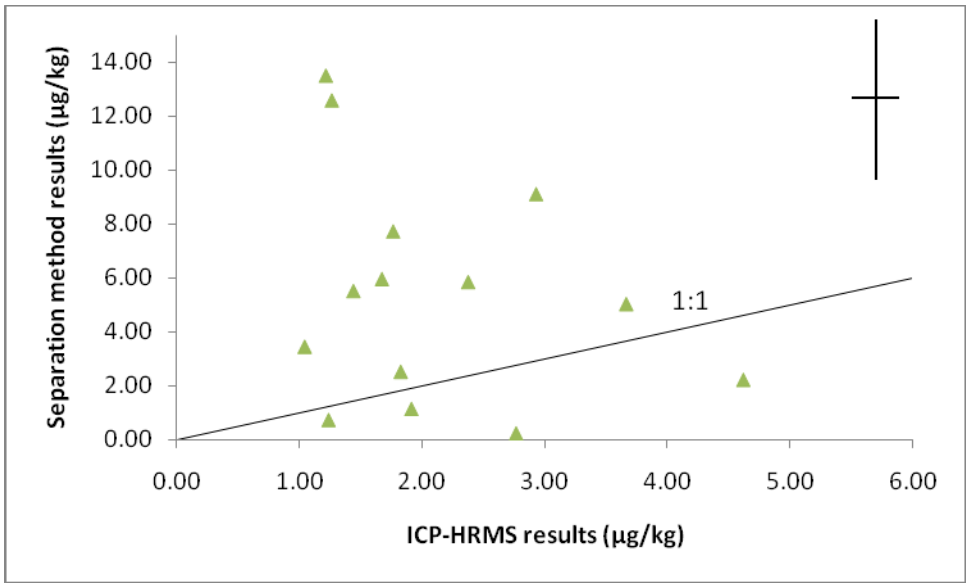

Figure 4.8: Comparison plot of the separation data with ICP-HRMS data for Pd

Results for Pd are in much better agreement with ICP-HRMS results. Although many values are still slightly higher than those obtained in using ICP-HRMS, the error on the data points can bring most points right on the 1:1 line.

There is also a great amount of error in the ICP-HRMS results. Like the separation method, the concentrations in the tree samples are very near to the detection limits of the ICP-HRMS and thus do not yield precise results. There are no certified reference materials for these PGEs available, so it is not possible to make a comparison to a known natural sample.

The detection limit of this separation method can be improved. The use of a dual valve FI manifold system would allow for the introduction of smaller amounts of eluent, thus higher pre-concentration. If a pre-concentration factor of 20 is achieved, it should bring

the detection limits of the PGEs down significantly, since most of the PGEs are not blank-limited. This should provide more accurate determination of the analytes. A new-generation ICP-MS have also reported significantly lower detection limits than the Ultramass 700 ICP-QMS. The use of this newer machine may also prove to lower the detection limits of this method.

4.2.2 Zones 19 and 24

The concentrations of the tree samples along Zone 19 were investigated. The concentrations of Ru, Rh and Pd were plotted against the distance along the sampled line in Figure 4.9. The area of the known conductor was at 1100 km from the beginning of the line and is also marked in the figure. The shape of this concentration profile was compared to the results obtained on the ICP-HRMS shown in Figure 4.10.

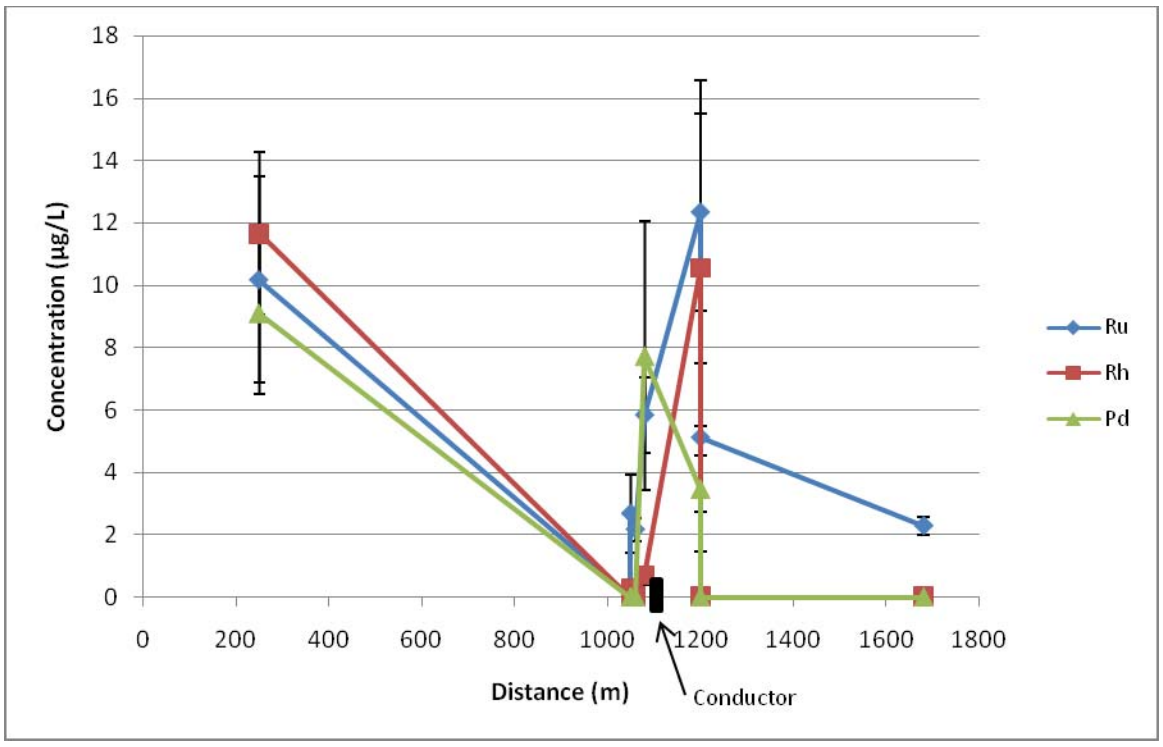

Figure 4.9: Concentrations of Ru, Rh and Pd along Zone 19 using the separation method (error bars correspond to 1 standard deviation, n=3)

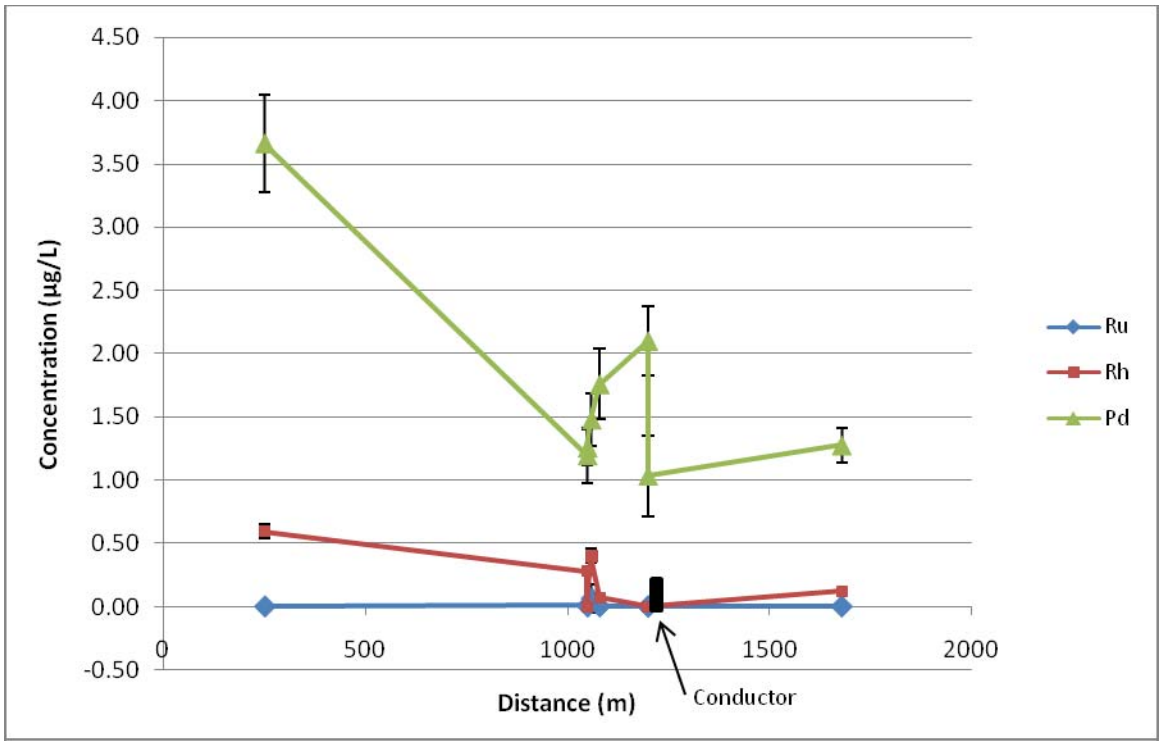

Figure 4.10: Concentrations of Ru, Rh and Pd along Zone 19 using ICP-HRMS (error bars correspond to 1 standard deviation, n=20)

Results clearly show an increase in the concentration of Ru, Rh and Pd in the immediate area of the conductor compared to the background results for data from both ICP-HRMS and the separation method using ICP-QMS. While the error on the elevated concentration readings is tyically high for the separation method, they are still above the detection limits and point to true elevated concentrations of PGEs. There is an anomalous point at 250 km where there is no known mineralization, however since it appears as elevated concentrations in both methods, as well as in analyses outside of this study, it is either a representation of true elevated concentration of PGEs in that tree sample or the original tree sample has been contaminated.

Profiles for Zone 24 were also compared in Figures 4.11 and 4.12. In this zone, the area of the known conductor was 1000 m from the beginning of the line and is marked in the figures. In the case of Zone 24, the background tree samples from the beginning of the line were not properly digested, and thus were not analyzed.

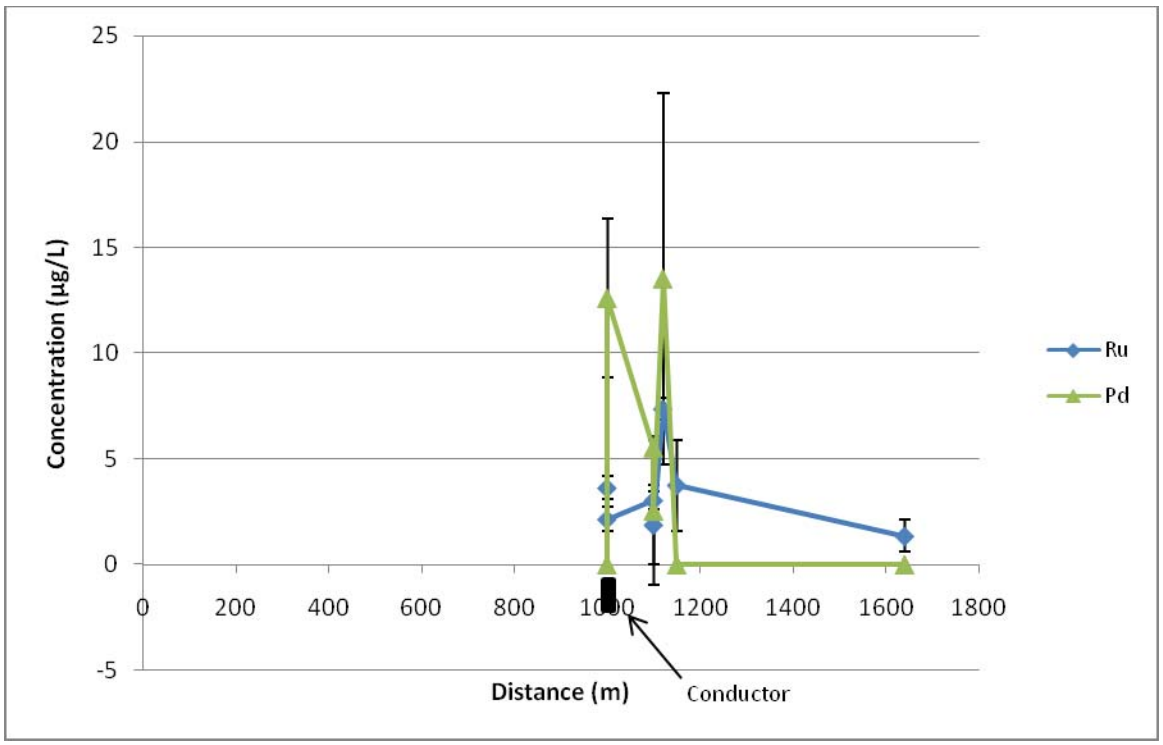

Figure 4.11: Concentrations of Ru and Pd along Zone 24 using the separation method (error bars correspond to 1 standard deviation, n=3)

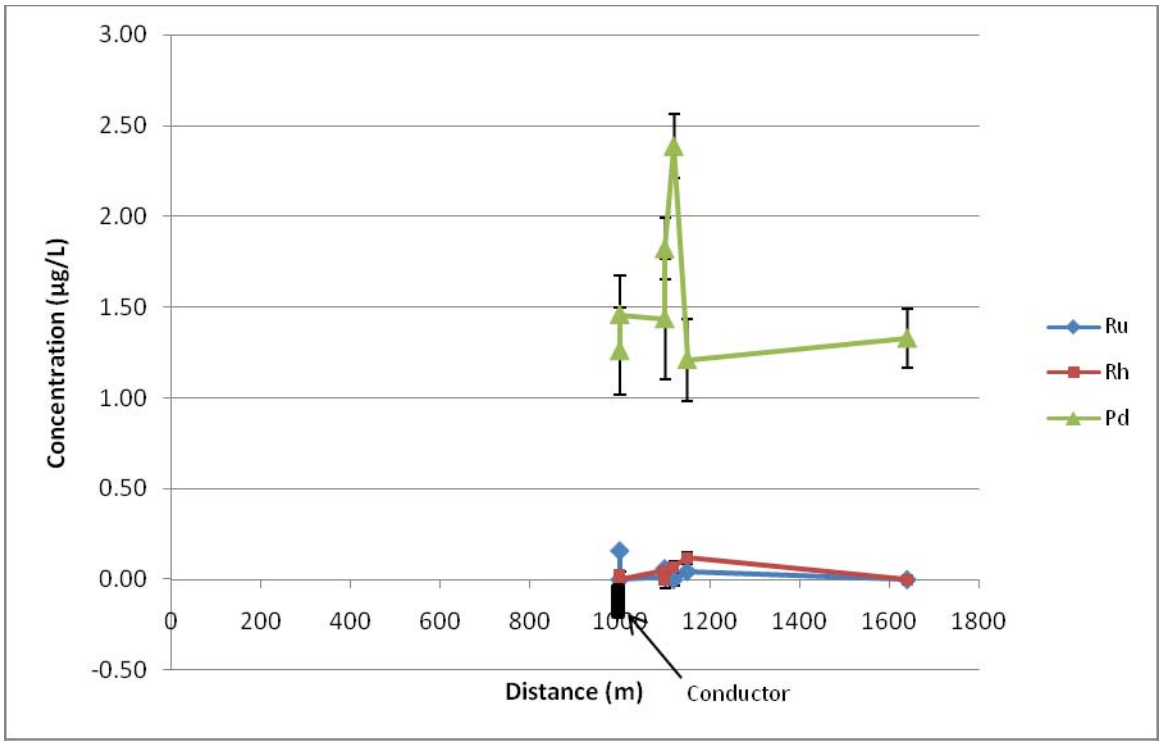

Figure 4.12: Concentrations of Ru, Rh and Pd along Zone 24 using ICP-HRMS (error bars correspond to 1 standard deviation, n=20)

Similar to the results of Zone 19, both separation/ICP-QMS method and ICP-HRMS results show elevated concentration levels in the region of the conductor compared to the background signal despite the large standard deviation of the readings. Although the concentrations of the elements using the separation method with ICP-QMS are elevated compared to the concentrations using ICP-HRMS, the shapes of the peaks over the area are very similar.

The true concentration of the PGEs is not known in these tree samples since both methods are not in agreement. There are a number of possible sources of error for both the proposed method and analysis by ICP-HRMS. Since the matrix is not separated from the analyte for analysis by ICP-HRMS, it is susceptible to matrix effects. The low concentrations reported by ICP-HRMS is possibly the result of a matrix induced supression. The high RSD of the results of the proposed method indicate that there may not have been complete retention or elution of the analytes. While incomplete elution is unlikely, as the elution profiles always returned to baseline, it cannot accurately be determined whether a small portion of analyte is passed through the colum due to competition of other elements in the sample matrix. Nonetheless the proposed method is still able to show areas of elevated concentrations of PGEs over areas of mineralization, which is the main purpose of this investigation.

The major advantage of the proposed separation method coupled to ICP-QMS is the reduced cost of analysis as compared to ICP-HRMS. The availability of analysis by ICP-HRMS is often limited and is quite expensive. This proposed method allows for

inexpensive analysis of PGEs which could be eventually applied in commercial laboratories. This method, however, has several drawbacks. The experimental setup is very susceptible to contamination, especially from Pd. Extra care must be taken to ensure that all contaminants are removed prior to analysis. Analysis is time consuming and tedious. The 16 minute procedure contains many steps that require supervision. A calibration curve must be constructed daily due to the variable sensitivity of the ICP-QMS which takes away from analysis time as well. If a sample is run in triplicate, it takes nearly an hour to analyze one sample. It can take weeks for large quantities of sample to be analyzed, which is not ideal for PGEs as they are very susceptible to degradation. Further research to minimize contaminants and the experimental time is needed before this method can be recommended for commercial use.

CHAPTER 5: CONCLUSIONS AND FUTURE WORK

A single-line flow injection method for the determination of PGEs in tree top samples was developed using an alumina mini-column, for the selective separation of the PGEs combined with ICP-MS. The main purpose of this method is to pin point areas of elevated concentrations of PGEs that are indicative of underground mineralization. The method was tested with real tree top samples and compared to results by ICP-HRMS. While concentration data was not in great agreement with those by ICP-HRMS, this method did reveal elevated concentrations of PGEs in areas over geological conductors in Rock Lake, Manitoba.

This new method offers several advantages over conventional off-line methods as well as newer in-line methods. While most off-line methods for the determination of PGEs are time-consuming, this method only requires 16 minutes total analysis time, where off-line methods can take hours for sample preparation and analysis.[6,40,47,64] Reagents are easily available and relatively inexpensive as compared to in-line SPE and precipitation methods that have been developed.[2,50,58]

This method has improved and expanded on previous work using an in-line alumina mini-column method for the determination of Pt and Pd.[7, 74-75] Sample consumption has been reduced from 15-30 mL to 1 mL, and the method was adjusted to include Ir, Re, Ru and Rh. However, the pre-concentration of 300 and 600 were not achieved, and the detection limits of Pt and Pd were substantially higher.[74]

While the method was successful in separating interferents from the PGEs, and was able to detect elevated levels of PGEs in several tree top samples, the detection limits of this method could be greatly improved. While the detection limits are comparable to those from commercial laboratories, they are still not sufficient to accurately determine the concentration of all PGEs in many natural samples. In future work, the method should be modified to lower these detection limits. This may be achieved with the use of a dual-line FI system, which should greatly increase the pre-concentration of the PGEs. A dual line FI system should also decrease the sample analysis time as it allows an increase in the flow rate during the elution of the PGEs. The current method could also be used in combination with newer generation ICP-MS instruments, which have reportedly lower detection limits by several orders of magnitude.

As there is no standard reference material (SRM) with certified PGEs concentrations, a vegetation SRM could be spiked with known quantities of PGEs to check for complete recoveries. The method of standard addition could also be used and the results compared to those obtained by external calibration to verify the absence of significant matrix effects. Although these effects should be negligible with the proposed approach, which separates the matrix from the analytes, they may be significant during the direct analysis of the digested tree samples by ICP-HRMS. Hence, the lower concentration obtained by the latter technique are likely the result of matrix-induced suppression, as it is very unlikely that contamination would preserve the concentration profiles indicative of a geophysical conductor that were repeatedly observed with the proposed method.

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