EVALUATION AND IMPROVEMENT OF THE NICKEL SULPHIDE FIRE ASSAY METHOD WITH ICP-MS FINISH, FOR ANALYSIS OF ROCKS FOR THE PRECIOUS METALS

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by

AUGUSTINE FRIMPONG, B.Sc (Hons).

A thesis submitted to the School of Graduate studies in partial fulfilment of the requirements for the degree of Master of Science.

Department of Earth Sciences
Memorial University of Newfoundland.
August 1992
St. John's, Newfoundland.

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ISBN 0-315-78123-8

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DEDICATION.

IN MEMORY OF MY BELOVED PARENTS AND

TO THE UNBORN CHILD.

ABSTRACT.

This thesis examines the NiS fire assay, incorporating Te coprecipitation with ICP-MS quantification, procedure for the determination of the Platinum Group Elements (PGE) and gold (Au) in geological materials, with the aim of improving the method. The general analytical methods for the determination of the precious metals are reviewed.

The sensitivity of an analytical procedure is much influenced by the choice of the determinative step. Inductively coupled plasma mass spectroscopy (ICP-MS) offers a precise, accurate method with low limits of detection for quantification of the PGE and Au. However, inherent in the ICP-MS are problems such as ionic interferences, memory, matrix and drift. The matrix effects of HCl, HNO_4 and Te on the sensitivity of the precious metals using ICP-MS were studied. Within the concentration range examined, the sensitivities of the internal standards (Cd and Tl), PGE and Au were found to depend most strongly on the concentration of HCl. The reduction of HCl concentration from 0.6M to 0.2M provides about 20% enhancement in the sensitivities of the internal standards, and the PGE.

The effects of reducing the quantity of Ni and S used in the NiS fire assay method on the recovery of PGE and Au was investigated in a Pt ore grade sample and a low ppb level sample. In the Pt ore grade sample, the recovery of the precious metals was found not to depend on the mass of Ni used as collector. However, the recovery of Ru, Rh, Pd and Pt in the low ppb level sample was found to be a function of the collector mass used, while the recovery of Os, Ir and Au in the low ppb level sample was not. To explain this behaviour of the PGE, a model equation was derived from the mass balance equation of PGE between the sulphide and silicate liquids, and the bulk partitioning coefficient equation. From this equation, the partition coefficients (D) of the PGE were determined. The D values were also independently determined by analysis of the PGE and Au contents of the sulphide and silicate phases. The D values were functions of PGE concentrations. The D values obtained for a Pt ore grade sample were 4 to 103 times higher than those for the low ppb level sample. D values for Ni, Cu and Cr are also reported.

To improve PGE recovery in low ppb samples and to lower reagent blanks, further studies were undertaken. The NiS bead was dissolved in a closed vessel with a smaller amount of HCl, and the quantity of Te (and $SnCl_2$) used for the coprecipitation of PGE was also reduced significantly to lessen the total dissolved solids in the analytical solution.

An improved method has been developed, which offers good precision and acceptable accuracy for the determination of PGE and Au concentration in geological materials. The reagent blank, matrix effect due to HCl, cost of chemicals and sample processing time have been reduced.

ACKNOWLEDGEMENTS.

I thank The Almighty God for upholding me and making this thesis a reality.

My deep heartfelt appreciation and thanks go to my supervisors Drs. Brian J. Fryer and Henry P. Longerich, whose assistance and guidance throughout the various phases of this work are most worthy to be mentioned. I am truly grateful to them.

Sincere thanks go to Dr. S.E. Jackson, whose useful suggestions were always not found wanting. I also salute Dr. Kwame A. Kwakye, former Head, Geochemical and Chemical Lab., Ghana Geologica Survey, Accra; for his encouragement. I will like to record my gratitude to Mr. W. Gosse, Mr. D. Clarke, Mr. Pat Brown, Ms. Beverly Chapman, Mrs. Pamela King, Ms. Pat Horan and Mrs. Lakamali Hewa for their technical assistance.

My special thanks also go to my wife, Augustina, for her encouragement, understanding and companionship. I wish to express my thanks to Messrs. Edward A. Acheampong, Nelson Amoah, Z. Chen (my office mate), George and Clare White of 89 King's Street, St. John's. Finally, I wish to acknowledge the financial supports received from the School of Graduate Studies, and the Department of Earth Sciences, Memorial University of Newfoundland, St. John's.

TABLE OF CONTENTS.

LIST OF TABLES.

LIST OF FIGURES.

CHAPTER 1. SCOPE AND PURPOSE OF THE STUDY.

1.1. INTRODUCTION.

The Platinum-Group Elements (PGE's) consisting of Ruthenium (Ru), Rhodium (Rh), Palladium (Pd), Osmium (Os), Iridium (Ir) and Platinum (Pt), occupy group VIII of the 5th and 6th transition rows of the periodic table, with a characteristic feature of continuous filling of the 4d and 5d electron orbitals (Cotton and Wilkinson, 1980). They have similar outer electron subshell configurations and effective atomic radii which together are responsible for their generally similar chemical properties. They form mainly metallic and covalent compounds.

The distinctive chemical nature of the precious metals (PGE's and Au) makes their geochemistry very interesting. They represent a coherent group of siderophile elements and their distribution reflects the history of rocks containing them, including such aspects as sulphur saturation (Crocket, 1981; Keays, 1982; Barnes *et al.*, 1985). However, the relative behaviour of the platinum-group elements (PGE's), *ie.* their fractionation patterns are not well known, due to analytical difficulties (Barnes *et al.*, 1985); inhibiting the use of the PGE's as a petrogenetic tool.

Studies on the geochemistry of the precious metals have required the determination of each of these metals in a variety of naturally occurring materials at a wide range of concentration levels, *ie.* both at ppm and low to sub ppb levels. The complete analysis of certain PGE's minerals is complicated by their resistance to chemical attack, attributable to the chemical nature of the group and their compounds; and the need to separate the group and their generally associated base metals from one another.

Generally, the classical fire assays, using large sample sizes have been used to analyze PGE's ore grade samples due to the inhomogeneity of the PGE's in these samples (Beamish and Van Loon, 1972, 1977). Analytical work at low concentrations until recently has been limited to neutron activation analysis with and without group separation (Hall and Bonham-Carter, 1988).

Table 1.1 lists the PGE and Au contents of some natural materials. It is clear that literature data for unmineralized mafic and ultramafic rocks are generally restricted to Pd and Ir, due to the poor analytical sensitivity of neutron activation analysis for the remaining elements. New methods having higher sensitivity, and low and controlled reagent blanks are therefore required when dealing with the geochemistry of the PGE's and Au at ultra trace concentrations. The literature on analytical techniques for the determination of the PGE's and Au is reviewed in Chapter 2.

Table 1.1. Platinum-group element concentrations (all concentrations are in ppb) in various natural materials.

	Os	Ir	Ru	Rh	Pt	Pd	Au
Estimate of upper mantle+	-	4.4	5.6	1.6	8.3	4.4	1.2
Basalt, Troodos	-	0.032	-	-	-	2.72	-
Ocean-floor material (MORB estimate)	-	0.01	-	-	-	1.0	-
Komatiites (spinifex) from West Australia	-	1.47	-	-	-	9.0	-
Continental tholeiites (estimate)	-	0.1	-	-	-	12	-
Bushveld complex, Merensky Reef composite	63	74	430	240	3,740	1,530	310
Stillwater, JM Reef	22	19	50	150	5,000	17,300	640
S-bearing komatiite (100% sulphide normalized), Ungava, N. Quebec	305	335	1674	720	3,725	11,120	360
Indian Ocean basalt, Leg 115 (average)*	-	0.11	0.22	0.31	7.3	8.1	3.2

SOURCES: Barnes *et al.*, 1985; + Naldrett, 1981; and * Fryer and Greenough, 1992.

1.2. THE NiS FIRE ASSAY METHOD.

The collection of the noble metals with nickel sulphide (NiS) has been found to be superior or equal to collection by the classical Pb method. The NiS method is applicable to all six PGE's and Au, and can be applied to samples high in Ni and S without the pretreatment that is required in the Pb method (Beamish *et al.* 1977, Robert *et al.*, 1977, 1975, 1971). The NiS procedure offers a precise and accurate method for the concentration and isolation of the PGE's and Au in samples of high PGE's and Au contents such as ores, concentrates and mattes.

With the advent of Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), a NiS fire assay method incorporating Te coprecipitation was developed at the Earth Sciences Department, Memorial University (Jackson *et al.*, 1990), for the analysis of geological materials for the PGE's and Au. This procedure utilises (i) 5 g of Ni and 3 g of S as collector, with a flux of 10 g Na_2CO_3, and 20 g $Na_2B_4O_7$, and a sample size of 15 g, (ii) 600 mL of concentrated HCl for the dissolution of the NiS bead, (iii) 3.5 mL of Te solution (2000 ppm) and 12 mL of saturated $SnCl_2$ to coprecipitate the leached noble metals, (iv) 5 mL of concentrated HNO_3 and 5 mL of concentrated HCl to dissolve the PGE-Te coprecipitate. The final solution for analysis is diluted to 100 g with deionized water, of which only 10 g is used for the analysis of the precious metals.

This NiS procedure incorporating Te coprecipitation, appears to offer a precise and accurate method for the isolation and quantification of the PGE's and Au. Jackson *et al.* (1990) and Longerich *et al.* (1990) have documented calibration strategies to circumvent interferences and matrix effects.

All reagents used in this procedure (and all NiS fire assays) however, contribute to the reagent blank, especially the Ni powder and the HCl used to dissolve the NiS collector. This limits the application of the NiS fire assay procedure for the analysis of background levels of PGE's in rocks.

Generally, instrumental sensitivity is also affected by the composition of the analytical solution. *ie.* acid composition and total dissolved solids. This is the main reason that the final solution of the Jackson *et al.* procedure is diluted to 100 g, of which only 10 g is used for the analysis. This dilution is necessary to reduce total dissolved solids and acid concentrations to acceptable levels, while sacrificing analytical sensitivity. Consequently, to improve sensitivity, and reduce the reagent blank, smaller amounts of reagents should be used at constant sample size.

In spite of the wide usage of the NiS fire assay method, low PGE's values have been reported relative to compiled values. For example, Jackson *et al.* (1990) reported 2% to 28% (PGE's and Au) lower values for the analysis of the reference materials SARM-7 and PTC-1 compared to Steele *et al.* (1975) and Steger (1983) respectively.

1.3. SCOPE AND PURPOSE.

This study systematically examines the NiS fire assay method of Jackson *et al.* (1990) with the aim of improving the method for analysis of the PGE's and Au in ores and in low to sub ppb level geological materials. A well studied Pt ore international reference material, SARM-7 was utilized to monitor precision and accuracy, and the application of this study for low level PGE study was evaluated using a komatiite from the Abetibi Greenstone Belt containing low levels of PGE and Au. Improvement should result in a method having low reagent blank, low limit of detection, increased sensitivity and quantitative recovery for analysis of geological materials.

This study investigates the following: (1) instrumental analysis of the PGE's by ICP-MS, (2) the NiS fire assay method, and (3) the chemical processing involved in the NiS method. In particular, the following areas are investigated:

1. Instrumentation:
   (i). the matrix suppressions of HCl, HNO_3, and Te on the instrumental sensitivity of PGE's and Au.
   (ii). the effectiveness of Cd and Tl as internal standards for the PGE's and Au.
2. The NiS method:

(ii). the effects of reducing the amount of Ni and S used in the NiS procedure on the recovery of PGE's and Au in ores (ppm range) and rocks (low to sub ppb levels).

3. The chemical processing:

(i). an alternative procedure for the dissolution of the NiS bead using reduced quantities of acids.

(ii). the effects of reducing the quantity of Te used to coprecipitate the PGE's and Au.

Using the results of these fundamental studies an improved method for the determination of PGE's and Au in geological materials at both ore grade levels and low to sub ppb levels will be proposed and tested.

CHAPTER 2. LITERATURE REVIEW.

2.1. INTRODUCTION.

Recently, there have been great advances in analytical instrumentation, but the fundamental strategy for the accurate determination of the precious metals continues largely unchanged. The fire assay method still tops the list of pretreatment methods for a variety of samples.

The first comprehensive treatment of the subject of gold and silver assaying was by Lazarus Ercker in his book "Treatise on Ore and Assaying", published in 1574, which detailed the assay procedures used during the Holy Roman Empire. Due to the increased economic interest in the Platinum-Group Elements (PGE's) at the beginning of this century, there was a corresponding increase in PGE research activity. Earlier researchers recorded their frustration which was due to the secretive research practices of the few rival industrial groups engaged in precious metal production (Beamish, 1966), and which to some extent still exists today (Van Loon *et al.*, 1989). The identification of the PGE's can be traced back to 1741, when Charles Wood presented a specimen of native platinum to the Royal Society of London. Wollaston and Tennant identified palladium, rhodium, ruthenium, iridium and osmium soon after the discovery of platinum (Kallmann, 1984).

Fire assay and other methods of isolating and separating the precious metals have been reviewed extensively by Beamish (1966). More recent reviews of the analysis of the precious metals are by Sen Gupta, 1973; Beamish and Van Loon, 1977; Crocket, 1982; Kallmann, 1984; Van Loon and Barefoot, 1988. Many of the procedures are still unsatisfactory as documented by Wilm in 1885, and Lathe in 1940.

A literature survey of the platinum-group elements will be incomplete without mentioning the two books by Beamish and Van Loon, namely; Recent Advances in the Analytical Chemistry of the Noble Metals (1972), and Analysis of Noble Metals:overview and selected methods (1977).

2.2. SAMPLE DECOMPOSITION PROCEDURES.

2.2.1. FIRE ASSAYING.

As stated, the fire assay method predominates in the analysis of PGE's. Without doubt the classical lead assay has proved to be the most important procedure for the concentration and isolation of the noble metals. In 1977, Van Loon noted that 92% of platinum-group element analyses reported by Steele *et al.* (1975) in a 1975 South African Ore Certification program used fire assay usually with lead collection, as the procedure for concentration of the precious metals.

In the Pb fire assay technique for the determination of the PGE's, the sample is fused in a clay crucible with a flux consisting of sodium carbonate, fused borax, litharge (lead oxide), and silica to which a reducing agent, often in the form of maize meal or wheat flour is added. The fusion is carried out in an electric furnace at a temperature of 900° C for 15-20 minutes, then at 1000° C for another 17-20 minutes. During the fusion process, the litharge is reduced to lead, forming lead that collects the PGE's and Au as the Pb falls through the molten mass to the bottom of the crucible. After fusion the slag is removed by hammering off the lead button which is subsequently cupelled and/or scorified to obtain the precious metal bead or prill. Normally silver or gold is added to collect the PGE's.

The following are thought to be the primary reactions occurring during Pb reduction (van Wyk *et al.*, 1983).

(1) $C + PbO = Pb + CO$

(2) $CO + PbO = Pb + CO_2$

(3) $C + 2PbO = 2Pb + CO_2$

Secondary reactions relating to the reaction between the carbon in the reducing agent and the oxygen present in various forms in the mixture of sample and flux can also take place :

(4) $C + O = CO$ (oxygen in flour or molecular O_2 in the furnace).

(5) $2Fe_2O_3 + C = 4FeO + CO_2$

(6) $FeOCr_2O_3 + x\,C = FeCr + FeCr$ carbides $+ x\,CO$ (formed with chromite samples).

The availability of carbon is thought to be important for the primary and secondary reactions. The main reactions in the melt can be represent as follows:

$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$

$Na_2B_4O_7 + Na_2CO_3 = 4NaBO_2 + CO_2$

$(K_2O, MgO, CaO, FeO) + 2SiO_2 = (K_2, Mg, Ca, Fe)SiO_3$

$Na_2CO_3 + Al_2O_3 + 2SiO_2 = 2NaAlSiO_4 + CO_2$

$PbO + SiO_2 = PbSiO_3$

$7PbO + FeS_2 + 2Na_2CO_3 = 7Pb + FeO + 2Na_2SO_4 + 2CO_2$

(in presence of sulphide if ore is not calcined).

Scorification is an oxidizing fusion designed to eliminate base metals from the Pb button and/or to reduce the amount of elemental Pb in the button to a desired weight, which is about 30 g. Scorification is carried out with a mixture of borax and silica as flux in a shallow dish (scorifier). It proceeds at a temperature of 950° C with the furnace door open to admit air for the oxidation of Pb to PbO. The PbO dissolves in the slag along with base metals such as Cu and Ni which may have been in the Pb bead.

Cupellation is the process used since antiquity for the separation of Au and Ag from Pb. This consists of rapidly oxidizing Pb to PbO in a cupel at a temperature of about 850° C in a furnace with the door open to supply air for the oxidation. The PbO formed is absorbed by the cupel and the Ag, Au, and other precious metals are left as a prill at the centre of the cupel.

There are several precautions which must be taken. It has been observed that the presence of significant amounts of Cu, Ni and other transition metals in the Pb bead can result in loss of precious metals to the cupel, and intermediate scorification is necessary. The cupellation temperature also affects the efficiency of the cupellation. Low temperatures result in the formation of a crust over the button which is said to be "frozen", thus maintenance of the correct temperature is very important.

The fusibility and viscosity of the slag, and solubility of carbon dioxide in the slag are very important factors in the fire assay technique. Low fusibility and viscosity, and high CO_2 solubility are highly recommended to prevent boiling of sample and flux.

A number of studies have been done in an attempt to better understand the steps in assays which are susceptible to losses. A good example of such research was reported by Wall and Chow (1974), where effects of fusion temperature, lead button weight, flux composition, cupellation temperature, and use of cover during fusion on losses of gold were monitored. Gold loss of less than 1% was reported. The effect of variable air flow into the fusion furnace has been studied extensively by van Wyk *et al.* (1983). Other parameters such as the ratio of PbO to reducing agent and presence of reducing agent on the surface of the fusion mixture were also investigated by van Wyk *et al.* (1983). They reported that the maintenance of a reducing atmosphere is essential for maximum recovery of

PGE's during assaying.

In general, the PGE's and Au are efficiently collected by lead and appear quantitatively in a silver cupellation bead (Beamish *et al.*, 1973). Ru, Ir, and Os collection is more seriously affected by flux composition and assay conditions. Os and Ru collection are favoured by higher temperature, possibly due to their high melting points. Appreciable losses of Os are encountered with basic fluxes (Van Loon, 1977). Basic slags have been found to cause severe Ir losses (Beamish, 1966). Addition of potassium nitrate to the flux has been employed for ore or rocks containing base metal sulphides, to avoid the need for a preliminary air roasting which invariably influences Os loss, due to volatilization of Os as OsO_4.

Several approaches have been taken to decompose samples containing significant amounts of chromite. A pretreatment procedure in which the sample was roasted with sodium peroxide and silica prior to fusion with a charge that was proportionately reduced in sodium carbonate and silica has been reported by Moloughney (1986). Steele *et al.* (1970) and Robert *et al.* (1977) modified the flux composition and reduced sample weight to obtain effective decomposition of chromites. Addition of calcium fluoride to aluminum-rich samples and chromite ores has been suggested for efficient recovery of the PGE's (Haffty *et al.*, 1968).

For the six PGE's, Au is normally used as a collector (Bugbee, 1948; Haffty, 1968; Grimaldi *et al.*, 1970; Crocket, 1980). Grimaldi *et al.* (1970)

observed no losses of Ir when sufficient gold was added as a collector and the slag ranged from monosilicate (orthosilicate) to bisilicate (metasiilcate) in composition. For Os collection, the cupellation step is not recommended, because Os may volatilized as OsO_4. However, a well-proven procedure exists for the separation and recovery of Os by perchloric acid decomposition of the Pb bead directly (Diamantatos, 1977a, b).

A detailed account of the Pb fire assay method incorporating Au as a collector is reported elsewhere (Haffty, 1980), and a summary derived from Haffty's paper is given below. The Haffty method involves mixing the sample, normally 15 g, with a dry flux component plus 1 mg of pure Au in a fire assay crucible and fusing the mixture at 900° C for 17 minutes and then at 1000° C for 15 minutes. The melt is then cooled and the Pb button is physically separated from the slag. The bead is further cleaned of the slag by digestion in hot 10% HCl and then rinsed and brushed under running water. The Pb is removed by cupellation in a cupel over a temperature range of 840 to 900° C. The resulting Au bead is then used for the quantification of the PGE's.

Platinum has also be used as a collector for the other platinum-group elements, although Ru losses occur (Haffty, 1980; INCO Metal Company procedure noted by Cabri, 1981).

A number of alternative fire assay procedures employing other collectors have been proposed. The main alternative collectors to Pb are Fe, Cu and Ni used together (Plummer *et al..*, 1959a, b), Cu (Ginzberg *et al.*, 1964), Sn (Faye, 1965) and NiS (Robert *et al.*; 1971, 1975, 1977). More recent approaches to quantitative separation of the PGE's involve fusion with powdered Ni-Fe alloy at 1600° C (Rammensee *et al.*, 1982; Brugmann *et al.*, 1990), and fusion with tellurium sulphide (Shazali *et al.*, 1987b).

Plummer's fire assay involves collection of the PGE's by fusion with sodium carbonate, borax and powdered graphite in a carbon crucible at 1450° C to produce an alloy of Fe-Cu-Ni. The "iron" bead is parted in concentrated hydrochloric acid and the precious metals dissolved in a mixture of nitric acid and hydrochloric acid. For reasons unknown to the writer, this method has not often been used in the determination of the precious metals.

In the tin collection procedure proposed by Faye, the PGE's were collected in molten tin when the sample was fused at 1200-1250° C with a flux consisting of stannic oxide, sodium carbonate, silica, borax and coke. The tin button produced is dissolved and the individual PGE's are isolated and determined. The disadvantages of this procedure are contamination and PGE's loss. Stannic oxide typically contains some Au, which increases the reagent blank. Os and Ru loss may occur in the course of roasting of the sulphide ores. Au may also be lost during this process due to volatilization of gold-arsenic/antimony alloys. Strong and Murray-Smith (1974) reported loss of gold during roasting of arsenopyrite ores due to formation of a volatile Au-As alloy.

The nickel sulphide procedure has been found to be particularly useful for the determination of all the six PGE's and Au. It is regarded by Robert *et al.* (1971, 1975) and Hoffman *et al.* (1978) as quantitative for the six PGE's and well suited for Ni-Cu sulphide bearing materials. A concise description of the NiS procedure is given by Robert *et al.* (1971) and Jackson *et al.* (1990). This procedure involves fusion of the sample with Ni, S, $Na_2B_4O_7$, Na_2CO_3 and SiO_2 at a temperature of ≈ 1000° C. The resulting NiS bead formed is separated from the slag, crushed and dissolved with concentrated HCl in an open beaker. The insoluble noble metal sulphides filtered, and dissolved with HNO_3 and HCl, and the PGE and Au concentrations are then measured by a suitable technique. The NiS fire assay traditionally utilized 20 g of NiO or 32 g $NiCO_3$ for a 50 g sample size (Robert *et al.*, 1971, 1975). In the Jackson *et al.* procedure (1990), the PGE's and Au that dissolved on parting of the NiS button were recovered by coprecipitation with tellurium. Date *et al.* (1987) reported the addition of H_2S to precipitate the dissolved PGE's and Au on parting of the NiS bead.

The effects of various matrix elements on the efficiency of NiS collection have been critically examined by Robert *et al.* (1975). Borthick and Naldrett (1984) suggested the use of lithium tetraborate instead of borax for chromite-rich samples for superior fusion. Hall *et al.* (1988) reported that extremely high copper samples promote the formation of insoluble CuS which in turn collects the PGE's and creates dissolution problems. This means that preanalysis of samples, in order to adjust the fusion mixture are important for efficient collection of the PGE's by NiS.

The recently developed NiS fire assay procedure has undergone rapid evolution. Asif *et al.* (1989) reported the non-correlation between the recovery of PGE's and the mass of collector used. They reported that the use of 0.50 g of Ni was as effective for the recovery of the PGE's as 5 g used by Jackson *et al.* (1990) and 10 g by Parry *et al.* (1988).

The PGE's and Au are reported to be extracted into the sulphide bead quantitatively, since it is assumed that the partition coefficients of the precious metals are very large *ie.* $\sim \infty$. The partition coefficient being defined as $[\mathrm{PGE}]_{\mathrm{sulphide}}/[\mathrm{PGE}]_{\mathrm{silicate}}$, as is customary in the geological literature. In theory, the PGE^{+2} ions are of suitable charge to substitute for base metals (here Ni), and bonds in sulphides tend to be more covalent than those in silicate and oxides, because of low sulphur electronegativity. However, the type of reactions occurring during the fusion are uncertain. Possibly, the PGE's form PGE-PGE alloys and PGE sulphides, and the NiS formed from the added Ni and S, nucleates on them and then settles out of the melt to the bottom of the crucible as a bead.

The underlying principle of the NiS collection, is the strongly chalcophilic and siderophilic nature of the precious metals.

The platinum-group elements preferentially enter the metal rather than the sulphide phase when in the presence of both. The literature is encouraging concerning the alloying qualities of iron, nickel, and copper with the precious metals. Invariably, any application of nickel or iron to fire assay collection must deal with the presence of sulphur. Kussman and Nitka (1938, cited in Plummer *et al.*, 1959) believed that the system platinum-nickel comprises a continuous series of solid solution above 600° C. Understanding of the chemistry of the nickel sulphide procedure is important.

The fire assay methods (Pb and NiS) offer precise and accurate isolation and determination of the PGE's and Au in geological materials. The methods are simple and straight forward. For the analysis of all the precious metals in a single solution, the NiS method is preferred, since it affords quantitative isolation of the precious metals from most geological matrices.

2.2.2. WET CHEMICAL DISSOLUTION.

In addition to fire assay procedures, there are acid dissolution methods with subsequent concentration of PGE's by solvent extraction (Rubeska, 1977; Sen Gupta, 1989) and alkali fusion methods which use a mixture of sodium hydroxide, sodium peroxide and potassium nitrate (Van Loon *et al.*, 1989) or sodium peroxide (Schnepfe *et al.*, 1969; Watson *et al.*, 1983).

In standard acid dissolution methods; a mixture of concentrated hydrochloric and nitric acid in the ratio of 3:1 (aqua regia) is typically used. Pretreatment of siliceous and refractory samples with hydrofluoric acid before aqua regia digestion is often recommended (Fryer *et al.*, 1978; Sighinolfi *et al.*, 1984; Sen Gupta, 1989). Sample decomposition by dry chlorination at 700° C in the presence of sodium chloride or bromine-potassium bromide followed by dry chlorination of the insoluble residue has been described by Sen Gupta (1972). Autoclave methods of sample digestion at elevated temperatures using chlorine trifluoride, xenon tetrafluoride, bromine pentafluoride and a mixture of xenon difluoride with potassium hydrogen fluoride have been cited in the literature (Min'kin *et al.*, 1989, and references cited therein). Sample digestion by liquid-phase oxidizing fluorination with bromine trifluoride has been reported by Min'kin *et al.* (1989).

In the peroxide fusion method, the sample (0.2 g) is attacked with 2 g of sodium peroxide at a temperature of 480° C. Os and Ru are normally distilled as the volatile tetroxide and subsequently determined. Distillation of Os and Ru as volatile tetroxide is a well established procedure (Beamish *et al.*, 1972, 1977), and is conducted either by passing chlorine through an alkali solution of ruthenate and osmate or by oxidation with bromate in a weakly acid solution. The latter method has been described in detail by Beamish (1977) and is the preferred technique. Watson *et al.*, (1983) suggested sodium peroxide fusion for high grade sulphide materials and described a dissolution method based on ammonium chloride and HCl leaching of base metals, followed by removal of Si using a mixture of HCl, H_2O and HF, with a final fusion with sodium peroxide.

Complete dissolution of samples by sintering with barium peroxide at a temperature of 900° C for one hour followed by treatment of the sinter with hydrochloric acid, and subsequent fusion of the sample (sinter) with sodium peroxide and sodium fluoride at 800° C for 30 minutes is being practised in the former USSR (Eroshevich *et al.*, 1969). In sintering with barium peroxide, it has been observed that the presence of high concentrations of silver leads to losses of Pt and Rh. These losses are caused by the adsorption of Rh and Pt on the AgCl precipitate formed when the sinter is dissolved in hydrochloric acid. The silver is normally removed from the sample by heating the sample with chloride free nitric acid.

A sodium peroxide and sodium fluoride fusion procedure (Schnepfe *et al.*, 1969; Watson *et al.*, 1983) ensures complete solubility of the sample and removal of silica. The cooled melt is leached with water and the metal hydroxides formed are subsequently dissolved in hydrochloric acid.

Chromatography, especially ion-exchange chromatography has also been reported (Ginzburg *et al.*, 1975; Beamish *et al.*, 1977). The chromatographic separation is based on the work of Rees-Evans *et al.* (1958, cited in Beamish *et al.*, 1977) but has been modified to permit Pt, Pd, Rh, and Ir to be separated on a single column without the need for a second operation to part Ir and Pt (Van Loon and Barefoot, 1989).

The principle of the wet chemical procedure is laudable, but it is time consuming. A week is normally required and accuracy of recovery of microgram amounts of PGE's is not favoured by the multiplicity of extractions, relatively large volumes of liquids used and difficult techniques involved. The wet chemical procedures are therefore not widely used to convert the PGE's to dissolved constituents of familiar composition from geological materials.

2.3. ANALYTICAL METHODS.

The choice of a determinative method is usually governed by the level of precious metals to be handled, nature of the sample matrix, and the availability of equipment.

Before the advent of highly sophisticated instruments, most data published by North American, European and Australian laboratories were obtained by radiochemical neutron activation. Studies from the former USSR used spectrophotometric methods. There is good evidence in data compilations that these two types of methods do not yield entirely consistent results.

Briefly, the main advantages of neutron activation methods are high sensitivity, and freedom from laboratory contamination. The methods are effective for the direct determination of Ru, Pd, Os, Ir, and Pt in ultrabasic rocks in the 0.1 to 1.0 ppb range, 0.01 ppb for Ir and for Pd, Os, and Ir in basic rocks (Hoffman *et al.*, 1978; Crocket, 1979).

A potential interference on ruthenium determinations arises from Ru produced by uranium fission. Other limitations are that the effective sample size for direct determination is limited to 1 g. In general, this leads to erratic values compared to procedures where the analysis of large samples are possible, especially when the sample material is characterized by highly dispersed concentrations of metals (precious metal minerals). Other disadvantages of neutron activation analysis are that the direct determination of Rh is precluded by a short half-life, and fission-product interference effectively inhibits determination of Ru in basic and silicic rocks. Also the necessary high-flux neutron sources are not readily available. Neutron activation analysis continues to be commonly used in PGE determinations (Turkstra *et al.*, 1970; Hoffman *et al.*, 1978; Parry *et al.*, 1980, Flerov *et al.*, 1987; Asif *et al.*, 1989).

The main advantages of spectrophotometric methods are (i) they are comprehensive with respect to PGE's, yielding data for all six elements, (ii) they can be applied to samples of up to 30 g. Their main disadvantages are (i) use of large amounts of reagents which require careful blank control (ii) exacting quantitative chemical separation procedures are required, and (iii) partial loss of Os and Ru.

Palladium in the ppb range was determined by Grimaldi *et al.*, spectrometrically with paranitrosodimethyl aniline. Other colour forming reagents like mepazine hydrochloride for osmium (Gowda *et al.*, 1977), 1-phenyl- 2- tetrazoline-5-thiolone for Pt and Pd, and rhodamine 6G for Pt have been used. Sil'nichenko *et al.* (1973) and Khvostova *et al.* (1971) reported the determination of Ru and Os based upon the volatilisation of their tetraoxides from acid solutions and using the spectrophotometric reagents sulphanilic acid and N,N-dimethylaniline. Diamantatos (1977b, 1977c) detailed the spectrophotometric determination of Ru and Os using thiourea, and Ir using tin (ii) bromide in hydrobromic acid solution.

Determination of PGE's using spectrophotometric methods still continues to be refined and used in Asia (Chen *et al.*, 1989). Chen *et al.*(1989) reported the use of p-hippuric acid chlorophosphonazo as a colour forming reagent to determine Pd in ores without prior separation. They reported that Beer's law was obeyed for 0.12 to 0.8 ug Pd per mL.

Determinative methods such as titrimetry and gravimetry have been used before but are not an important analytical tool in PGE's assaying today. In spite of the substantial number of gravimetric reagents proposed over the years, few have gained wide acceptance. For example, the use of dimethyglyoxime for Pd, thionalide for Os and Ru, hydrogen sulphide for Pt and Rh, dimethylphenylbenzyl ammonium chloride for Pt, and

2-mercaptobenzothiazole for Ir have been reported by Beamish and Van Loon (1977). Gravimetric analysis remains an important standardization method for PGE's solutions.

Titrimetric methods are still being investigated (Xiong *et al.* 1989; Selig, 1990). Xiong *et al.* (1989) reported a complexometric titration of palladium in material containing gold and palladium. The titration is accomplished by using thiourea to displace EDTA with Pb or Zn salt. In the Xiong *et al.* procedure, hydroquinone was initially added to reduce Au^{+3} to Au, and Ir^{+4} to Ir^{+3} both of which interfere in the titration. EDTA was used as masking agent to eliminate these interferences. A relative error of < 1% for the determination of 5-20 mg of Pd was reported. Palaniappan and Revathi (1989) illustrated the complexometric determination of Pt^{+4} using potassium chromate and salicylaldehyde thiosemicarbazone as indicators in EDTA titration.

Other techniques such as electrochemical and catalytic approaches (Pilar Vinas *et al.*, 1987) have important but isolated applications. The electronics revolution has led to new generations of electrochemical equipment which make use of techniques like Differential pulse polarography, twin cell and AC polarography, and anodic stripping voltametry interesting. It is, however, believed that these techniques will make few inroads on PGE analysis, except in the study of precious metal solution chemistry.

Presently, the widely applied determinative steps are X-ray fluorescence (XRF), neutron activation (Asif *et al.*, 1989; Shazali *et al.*, 1987; Hoffman *et al.*, 1978), emission spectrometry, atomic absorption and inductively coupled plasma mass spectrometry (ICP-MS).

The XRF approach is favoured because of the speed with which analyses are accomplished, but its use is limited by relatively poor sensitivity, being limited to samples with higher PGE contents (Chow *et al.* 1966 , cited in Van Loon *et al.*, 1989). But its usage as a preanalyzer for the major constituents of samples in helping to formulate a fusion composition is very important (Jackson *et al.*, 1990).

Arc/spark emission spectroscopy provides a multielement analytical capability with high linear dynamic range, which can be applied to the determination for precious metals in solid samples (Haffty, 1980). However, it has poor sensitivity for the platinum-group elements and requires close matching of sample and standard matrix composition.

Inductively coupled argon plasma source emission spectroscopy is highly recommended for PGE's analysis due to its multielement capability, and low detection limits. It yields results with good precision and freedom from many chemical interferences (Pille *et al.*, 1976; Wemyss *et al.*, 1978, and Chung *et al.*, 1988). It is worth noting that plasma emission spectrometry as applied to PGE analysis, is in its infancy and extensive work is necessary to evaluate its usefulness (Van Loon, 1985).

A resume of the extensive literature on the methods for the determination of the platinum-group metals by atomic absorption spectroscopy (AAS) are given by Beamish *et al.* (1969) and Sen Gupta (1973). Since its invention (Walsh, 1953), atomic absorption spectrometry (AAS) has had a tremendous impact in analytical geochemistry and will certainly continue to be one of the standard tools. Although, it is not a panacea (there simply is none) for analysis of all geological materials , it can provide good quantitative data down to a few ppb, and has low operating and capital costs.

Individually, much work has been done to reduce the interference problems encountered in the atomic absorption spectroscopic determination of the PGE's, although little attention has been paid to the reduction of interferences when the group are determined in the same sample solution. The mechanism for chemical interference in the determination of platinum in air-acetylene flame and its reduction by the addition of a lanthanum buffer has been discussed by Pitts *et al.* (1970).

In AAS, the addition of spectroscopic buffers to reduce interelemental interferences have been suggested (Mallet *et al.*, 1970; Mallet *et al*, 1972; Van Loon, 1969; Pitts *et al.*, 1970, Rowston *et al.*, 1970). In 1972, Sen Gupta reported that in a 0.5% Cu - 0.5% Cd spectroscopic buffer medium, the sensitivity of Ru was the same in air-acetylene and nitrous oxide flames, and that of Os was four times higher in air-acetylene than nitrous oxide-acetylene and iridium's sensitivity was 1.5 times higher in air-acetylene than nitrous oxide-acetylene.

Coprecipitation of the PGE's with tellurium (Fryer and Kerrich, 1978; Sen Gupta, 1989), formic acid (Diamantatos, 1986), and mercury (Tewari *et al.*, 1990) before AAS analysis has also been recommended.

Liquid /liquid extraction with organic solvents, such as methyl isobutyl ketone for Pd (Sen Gupta, 1973), and Pt (Simonsen, 1970), dibutyl sulphide for Au and Pd (Rubeska *et al.* 1977), have been extensively used. However, these organic reagents that are used for chelation and extraction of the PGE's also react with the associated base metals, reducing instrumental sensitivity. For example, the sensitivity of palladium determination was found to be less than 2 ppm when a $Pd(Py)_2(SCN)_2$ complex was extracted with hexone and the extract aspirated into a flame (Ering *et al.*, 1964). No data was given for interelement effects in this technique.

Separation of the PGE's by ion exchange (Sen Gupta, 1989) prior to AAS determination has been reported. However, it is known that separation of nonferrous metals on cation exchangers involves losses of gold and palladium, and the use of anion exchangers leads to loss of Ru.

The use of high temperature flame (Pitts *et al.*, 1970) and flameless techniques have been recommended (Sen Gupta, 1989; Sighinolfi *et al.*, 1984). Improved sensitivity was obtained by Fryer and Kerrich (1978) using graphite furnace atomic absorption spectrometry to determine Pt and Pd. The application of flameless atomic absorption in the determination of PGE's has not been widely applied because of matrix effects with or without prior separation by solvent extraction (Van Loon *et al.*, 1989).

The recently developed inductively coupled plasma mass spectrometer (ICP-MS), 1984; is making inroads in the analytical geochemistry of the PGE's and Au. The first reported work was done by Date, Davis and Cheung in 1987. From that time numerous reports have appeared in the literature.

ICP-MS instrumentation consists of an inductively coupled plasma source, an interface, and a quadrupole mass spectrometer. Akbar Montaser and Golightly (1987), and Date *et al.* (1989) give a detailed discussion of the theoretical aspects of the ICP, such as excitation and the processes taking place within the plasma, the operation of nebulizers and detailed description of the instrumentation.

The important features of the ICP-MS are its multielement analytical capability, linear calibration curves (typically over five orders of magnitude) and low detection limits for most elements (0.01 to 1 ug L^{-1} for conventional nebulization sample introduction), and short times for analysis. It is reported to be a powerful and flexible analytical tool (Thompson *et al.* 1989; Jenner *et al.*, 1990).

ICP-MS sample introduction is not restricted to conventional pneumatic nebulisation. Sample introduction by electrothermal vaporization rather than solution nebulization has been reported (Denoyer *et al.*, 1989; Sen Gupta *et al.*, 1989; Gregoire, 1988). Laser ablation sampling for ICP-MS have also be reported (Gray, 1985; Denoyer *et al.*, 1989, 1990; Jackson *et al.*, 1991).

Inherent in the ICP-MS is the facile measurement of elemental isotope ratio information, thus allowing the routine usage of isotope ratio information and isotope dilution techniques to study and solve analytical problems (Date *et al.*, 1987). Gregoire (1989) used isotope dilution ICP-MS in synthetic solutions approximating the composition of some standard reference materials and obtained reasonable agreement with the certified values. An efficient procedure for application of isotope dilution to ICP-MS has been reported by Longerich (1989).

The advantages of ICP-MS are offset with problems such as mass spectral interferences, matrix effects, instrumental drift and memory effects. While not as prevalent as in atomic emission spectrometry, spectral overlaps do exist in ICP-MS. When they occur, they may be quite serious. In addition, a number of interfering molecular species are observed in ICP-MS from analyte, background and matrix induced species. The solutions to these interferences have been documented by Jackson *et al.* (1990).

Longerich *et al.* (1986, 1987, 1990) and Jackson *et al.* (1990) have illustrated a judicious application of calibration strategies; namely; external calibration,internal standardization and standard addition, to solve matrix, drift and memory problems associated with ICP-MS. For example, Jackson *et al.* (1990) reported the use of Re as a surrogate standard for memory prone Os and long periods of flushing between samples with a mixed acid solution to minimize Au memory effects. Hirata *et al.* (1989) discussed the determination of osmium and osmium isotope ratios by microelectrothermal vaporization inductively coupled plasma mass spectrometry. This method reduces memory effect.

Hall and Bonham-Carter (1988) mentioned the role played by inductively coupled plasma optical emission (ICP-OES) in the analytical geochemistry of the precious metals but there are virtually no citations in the literature. However, mention was made of Wemyss *et al.* (1978) and Watson *et al.* (1983) who used ICP-OES to determine simultaneously the precious metals in a wide variety of samples from a plant for extraction and refining of platinum.

Application of inductively coupled plasma atomic fluorescence ICP-AFS is also reported by Hall *et al.* (1988) and was used by Caughlin in 1989. Blum *et al.* (1990) report the determination of Os using resonance ionization of sputtered atoms.

Though, a detailed discussion of field sampling is beyond the scope of this work. It is important to mention that proper sampling practices are needed to produce representative samples for analysis due to the inhomogeneous nature of the precious metals in rocks, ores and even alloys.

CHAPTER 3. MATRIX EFFECTS OF HYDROCHLORIC ACID, NITRIC ACID AND TELLURIUM ON THE SENSITIVITY OF THE PRECIOUS METALS USING ICP-MS.

3.1. INTRODUCTION.

ICP-MS, with its inherent wide linear dynamic range and low detection limits, is an extremely useful analytical instrument for the determination of the PGE's for geochemical applications (Date *et al.*, 1989; Longerich *et al.*, 1987, 1990; Jackson *et al.*, 1990). However, matrix and interference effects inherent in ICP-MS can limit the precision, accuracy and detection limit of PGE's determinations by ICP-MS. There are two main mechanisms which affect signals in ICP-MS, namely; polyatomic ion spectral overlaps and matrix induced signal intensity changes. Spectral overlap effects are associated with the production of polyatomic ions in the ICP-MS when samples are analyzed in solutions of some common acid matrices, *eg*. $^{63}Cu^{40}Ar^{+}$, $^{65}Cu^{40}Ar^{+}$, $^{41}Ni^{40}Ar^{+}$, $^{64}Ni^{37}Cl^{+}$, and $^{181}Ta^{16}O^{+}$. Matrix effects are the poorly understood variations in analyte signal intensity caused by concomitant elements which are not due to a recognisable spectral overlap.

Jackson *et al.* (1990) and Longerich *et al.* (1990) have documented calibration strategies to circumvent drift, memory and matrix effects. They involve the utilization of internal, external and surrogate standardization. In spite of these stratagem, Jackson *et al.* (1990) reported low values for the analysis of the three international reference materials SARM-7, PTC-1 and SU-1A. It has been established that the concomitant matrix elements can alter the sensitivity of the ICP-MS (Gillson *et al.*, 1988; Thompson *et al.*, 1989). This may partially account for the low values reported by Jackson *et al.* It is therefore, the objective of this study to examine (i) the accuracy of the internal standards as matrix correctors for the PGE's, and (ii) if a significant increase in sensitivity can be achieved by reduction of concomitant (matrix) element concentrations.

To elucidate acid induced matrix effects, and to determine whether significantly enhanced sensitivity could be achieved by changing the Jackson *et al.* (1990) procedure, synthetic solutions of PGE's and Au were prepared with different HCl and HNO_3 acid concentrations. Te and Sn were added to these solutions at concentrations similar to those normally resulting from the Te coprecipitation step in the sample preparation. Te concentrations ranged from 25 to 75 ppm (75 ppm being the mean concentration of normal sample solutions). The ability of the two internal standards (Cd and Tl) to accurately correct for instrumental drift and matrix effects was also evaluated using these solutions.

Although, variation of ICP-MS matrix effects in relation to plasma operating parameters is important (Tan *et al.*, 1987), it was felt that the standard operation conditions described by Jackson *et al.*(1990) were appropriate for this study.

3.2. REAGENTS.

All reagents were certified American Chemical Society (ACS) grade except where indicated.

Concentrated Hydrochloric Acid (12M). (E.M. SCIENCE).

Hydrochloric Acid Solution (6M). To 500 mL of distilled water was added 500 mL of concentrated hydrochloric acid and the solution was allowed to cool to room temperature.

Concentrated Nitric Acid (16M). (B.D.H. ACS 579-43).

Nitric Acid solution (8M). 500 mL of concentrated nitric acid was cautiously diluted to 1 litre with distilled water.

A mixed Precious Metals Standard Stock Solution (PM*). - (SPEX INDUSTRIES INC) was prepared with concentrations of 20 ppm of Ru and Pt, 10 ppm of Rh, Re and Ir, 15 ppm of Pd and 6.5 ppm of Au.

Precious Metals (PM) Working solution. An aliquot of PM* stock solution was diluted to give a solution containing 200 ppb of Ru and Pt, 100 ppb of Rh, Re and Ir, 15 ppb of Pd, and 65 ppb of Au.

Aqua regia. A mixture of 3 volumes of concentrated HCl with 1 volume of concentrated HNO_3.

Aqua regia 10%. 10 mL of a mixture of 3 volumes concentrated HCl and 1 volume concentrated HNO_3 was diluted to 100 mL.

Te solution - 2000 ppm in 1.2M HCl. Prepared by dissolving 2 g Te metal (99.999%,SPEX industries, Metuchen,N.J) in 15 mL aqua regia followed by two evaporations to dryness with concentrated HCl, then redissolved and diluted to final volume with 1.2M HCl.

Sn solution - 200 ppm. 0.38 g of $SnCl_2.2H_2O$ (Fisher) was dissolved in concentrated HCl, and diluted to volume with 1.2M HCl.

Internal Standards (Cd and Tl) solution. 5 ppm Cd and 3.6 ppm Tl solution was prepared by diluting a 50 ppm Cd and 36 ppm Tl stock solution with 10% aqua regia.

3.3. INSTRUMENTATION.

The ICP-MS instrument used was an upgraded ELAN Model 250 (SCIEX, Thornhill, Ontario, Canada). The initial installation and modification to the instrument have been reported by Longerich *et al.* (1936, 1987). The instrument now uses new Perkin-Elmer supplied hardware for the model 250 and 500 instruments which upgrades the computer system to that of the current 5000 system. The new ELAN 5000 software, from Perkin-Elmer, version 1.04-ICPS (a modified version of 1.04 which incorporates an ICP shut off enhancement) was used. The old printed circuit boards in the computer rack have been replaced with two new ones. Utilizing IEEE-488 interface hardware, one of the new boards is connected to an IBM PS/2

Model 70, 386/387.

Count rates of individual analytes were collected using the ELAN software and "report" files which contain the count rate data in an ASCII format were created. The files were then translated into a Lotus formatted spread sheet file using a compiled, in-house written, Microsoft Basic program and saved on a floppy disc. This program is executed under the SCIEX recommended DOS shell, vpix.

The operation conditions were those given by Jackson *et al.* (1990) {Tables 3.1 and 3.2}. The samples were run in the following order: reference blank solution (10% aqua regia), sample, reference blank solution, sample ...., to monitor the matrix effects, instrumental drift and memory effects. The sample delay time (time to allow for the sample to equilibrate before analysis) was 100 seconds.

Table 3.1. ICP-MS operating conditions.

Inductively coupled plasma:	Forward power	1200W
	Reflected power	<5 W
Argon gas flows:	Plasma (outer)	13L min^{-1}
	Auxiliary(intermediate)	1L min^{-1}
	Nebulizer (inner)	~1L min^{-1}
Sampling distance (load coil to sampler aperture)		13 mm
Sample uptake rate		0.64mL/min
Internal standard uptake rate		0.36mL/min
Data acquisition parameters		
	Measurement mode	Multichannel
	Dwell time	50 ms
	Integration time	15 s/mass
	Wash delay time	240 s
	Sample delay time	100 s
Typical ion lens settings		digipot
	B lens (barrel)	95
	P lens (plate)	4
	E-1 lens (Einzel)	70
	S-2 lens	0

Table 3.2. Analytical ions and corrected polyatomic ion interferences used for the calculation of PGE and Au concentration.

Determined ion	Isotopic abundance	Corrected interferences	Ionization potential (eV)
$^{61}Ni^+$	1.16%		
$^{65}Cu^+$	30.90%		
$^{101}Ru^+$	17.10%	$^{61}Ni^{40}Ar^+$, $^{64}Ni^{37}Cl^+$	7.4
$^{103}Rh^+$	100.00%	$^{63}Cu^{40}Ar^+$	7.5
$^{105}Pd^+$	22.20%	$^{65}Cu^{40}Ar^+$	8.3
$^{111}Cd^+$	12.80%		9.0
$^{115}Sn^+$	0.35%		
$^{123}Te^+$	0.87%		
$^{185}Re^+$ *	37.40%		7.9
$^{189}Os^+$	16.10%		8.7
$^{193}Ir^+$	62.60%		9.1
$^{195}Pt^+$	33.80%		9.0
$^{197}Au^+$	100.00%		9.2
$^{203}Tl^+$	29.50%	$^{181}Ta^{16}O^+$	6.1

* Re was used as a surrogate for Os calibration in the standard solution (see Jackson *et al*, 1990).

3.4. EXPERIMENTAL METHODS.

The experiment was designed to monitor both the matrix effects and the effectiveness of the internal standardization as function of matrix component (HCl, HNO_3 and Te) concentrations. Synthetic solutions of the precious metals having different concentrations of the main matrix components were prepared and analyzed. The procedure was as follows:

(1). 10 g aliquots of the working PM solution were diluted to 100 g with 0.6M HCl / 0.8M HNO_3, 0.4M HCl / 0.8M HNO_3 and 0.2M HCl /0.8M HNO_3.

(2). Serial dilutions of the working solution were prepared using 0.6M HCl with 0.6M, 0.4M or 0.2M HNO_3.

(3). 10 g aliquots of the working PM solution were spiked to give final solutions with 25, 50 and 75 ppm of Te respectively, and 2 ppm Sn. thess solutions were diluted to 100 g with 0.6M HCl / 0.8M HNO_3, 0.4M HCl / 0.8M HNO_3 and 0.2M HCl / 0.8M HNO_3.

(4). The reference blank solution (10% Aqua regia) was prepared by diluting 600 mL of concentrated HCl (12M) and 400 mL of 8M HNO_3 to 4 L with nanopure water.

3.5. RESULTS AND DISCUSSION.

The matrix effects of HCl, HNO_3 and Te on the sensitivity of Cd, Tl, PGE's and Au were systematically monitored by analyzing synthetic solutions of the precious metals having different concentrations of the main matrix components. The results from the ICP-MS analysis of the samples are listed in Table 3.3. The concentrations of the hydrochloric and nitric acid listed are those of the final solutions. The data given are the mean count rates (cps) and acid concentrations. The mean count rates (cps) of Cd and Tl in the reference blank (10% aqua regia) solution are 1.811×10^5 cps with a relative standard deviation (RSD) of 2.83% and 8.808×10^5 cps with a RSD of 3.64%, respectively. The analytical ions of the PGE's, Au and the internal standards monitored are listed in Table 3.2.

Instrumental drift, *i.e.* variation of analyte sensitivity with time, for this experiment was very small as shown by Figure 3.1 for the two internal standards; Cd and Tl. The internal standard (Cd and Tl) signals show precision better than 3% and 4% RSD respectively for the reference blanks over the course of the experiment. Memory effects, which are signal enhancements in a sample due to deposition and erosion of elements along the sample path during nebulization of previous solution, were also not significant in this study. This is exhibited by Au count rates,

Table 3.3. The count rates of the PGE's, Au, and the internal standards, and the final concentrations of the matrix elements. Number of determinations = 2.

HCl (M)	HNO3 (M)	Te (ppm)	Ru	Rh	Pd	Cd	Re	Ir	Pt	Au	Tl
0.2	0.8	50	598	506	4791	229691	478	361	223	106	72514
0.2	0.8	75	605	582	4774	227378	481	365	225	105	71553
0.2	0.8	0	554	535	4502	210306	432	338	207	96	64714
0.4	0.8	50	568	537	4472	211541	452	353	212	101	67728
0.4	0.8	25	534	522	4392	204787	443	337	208	96	65244
0.4	0.8	75	520	506	4222	198798	419	323	198	94	63331
0.6	0.8	25	532	512	4347	202867	443	332	206	96	65149
0.4	0.8	0	489	477	4012	191915	396	304	187	88	60229
0.6	0.8	50	505	485	4101	188954	413	317	193	92	60000
0.6	0.8	0	493	476	3987	187586	409	309	190	91	60011
0.6	0.6	0	459	446	3769	177176	372	293	181	86	55670
0.6	0.8	75	484	468	3976	184314	397	308	189	91	59748
0.6	0.4	0	441	427	3655	176740	360	286	178	84	54433
0.6	0.2	0	428	414	3519	174767	351	277	174	84	53499

Sensitivity = count rate/ppb/abundance.

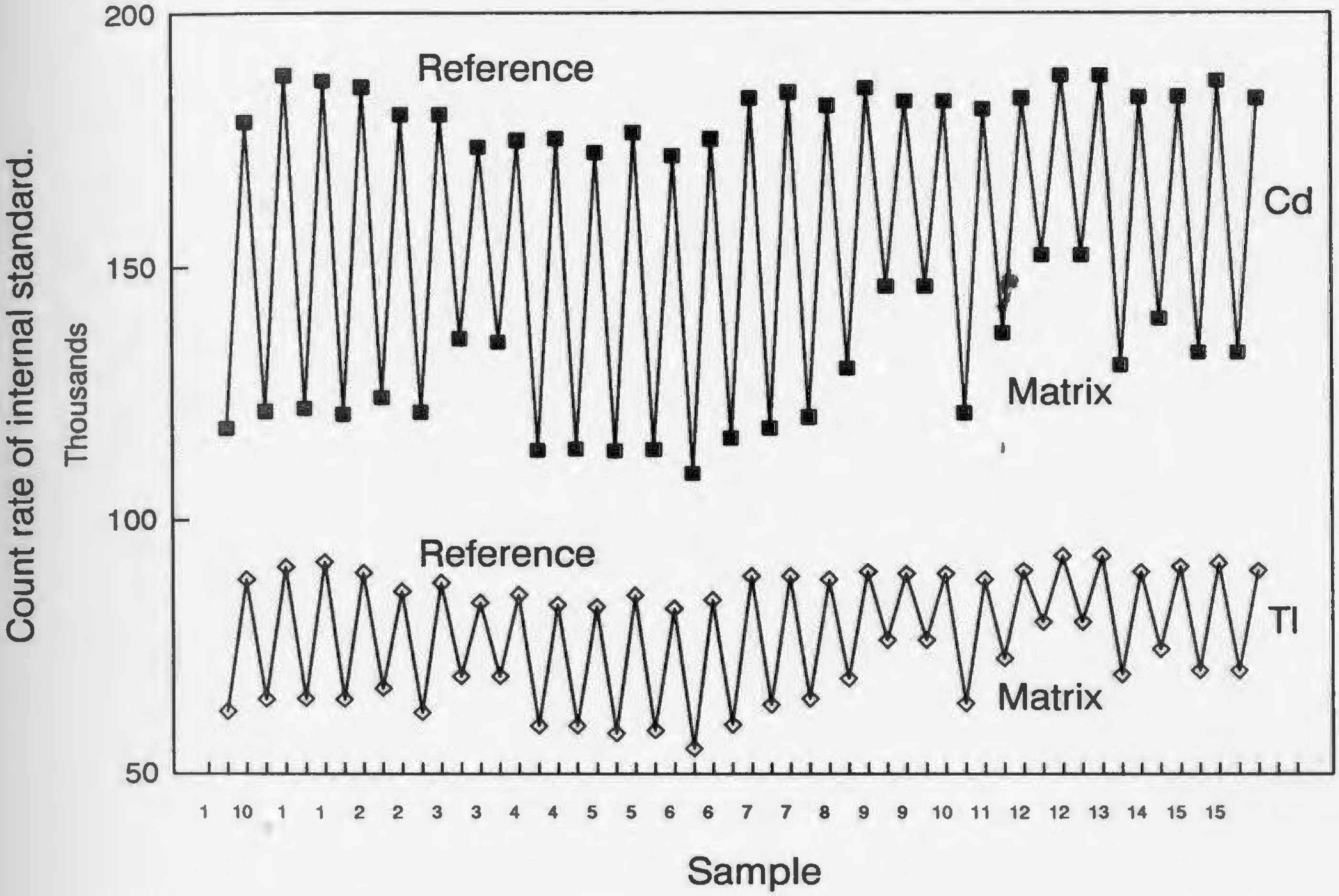


Figure 3.1. Variation of analyte sensitivity with time, of the two internal standards Cd and Tl. Instrumental drift during this experiment was very small. Reference is 10% aqua regia solution, the Cd and Tl concentrations were the same in all solutions.

an element especially prone to memory problems (Figure 3.2). The reference blank solution count rate is insignificant and constant, demonstrating low memory effects.

Cd and Tl have been selected as internal standards for the PGE's (Jackson *et al.*, 1990) because of the close proximities of their masses to the light (Ru, Rh, and Pd), and heavy (Re, Os, Ir, Pt and Au) noble metals, respectively and their negligible concentration in the analytical solution.

The sensitivity of Cd, Tl, PGE's and Au normalized to 100% isotopic abundance are listed in Table 3.4a. The sensitivity (counts per second per unit concentration of analyte) of an analyte can be enhanced or suppressed by the presence in the solution of other dissolved solids and acids (Date *et al.*, 1989). The matrix composition of a sample can thus have an effect on the analyte ion signal intensities (Beauchemin *et al.*, 1987). Matrix effects are matrix element(s), and concentration dependent (Gillson *et al.*, 1988; Longerich *et al.*, 1990). The more dilute the solution, the less the matrix effect.

Changes in the count rates (cps) of the internal standards, PGE's and Au are attributable to the matrix effects of HCl, HNO_3 and Te collectively or individually, and instrumental drift. As demonstrated later, the matrix effects are similar for both the internal standards and the PGE's.

Multiple linear regression fits were made for HCl, HNO_3 and Te (Table 3.5), using the relationship between Beta (matrix effect) and solution

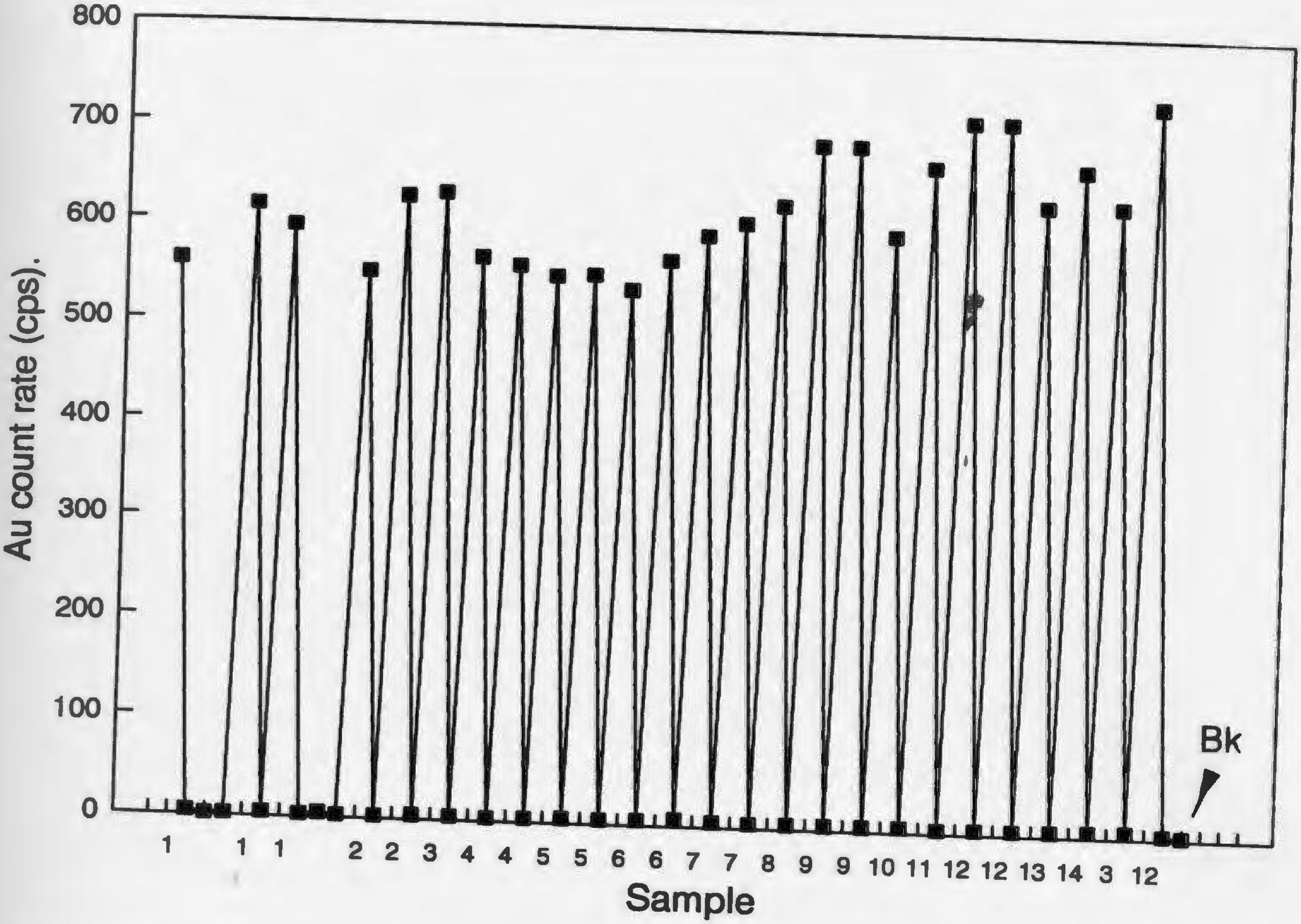


Figure 3.2. Illustration of the low memory effect on Au, an element prone to memory problems. The reference blank (BK) solution count rate is constant and near zero, suggesting low memory effects.

Table 3.4a. The sensitivity of PGE, Au, Cd and Tl,for various concentrations of the matrix elements.

MATRIX			SENSITIVITY OF ANALYTE IONS (cps/ppb/abundance).								
HCl M	HNO3 M	Te ppm	Ru	Rh	Pd	Cd	Re	Ir	Pt	Au	Tl
0.2	0.8	50	598	506	4791	229691	478	361	223	106	72514
0.2	0.8	75	605	582	4774	227378	481	365	225	105	71553
0.2	0.8	0	554	535	4502	210306	432	338	207	96	64714
0.4	0.8	50	568	537	4472	211541	452	353	212	101	67728
0.4	0.8	25	534	522	4392	204787	443	337	208	96	65244
0.4	0.8	75	520	506	4222	198798	419	323	198	94	63331
0.6	0.8	25	532	512	4347	202867	443	332	206	96	65149
0.4	0.8	0	489	477	4012	191915	396	304	187	88	60229
0.6	0.8	50	505	485	4101	188954	413	317	193	92	60000
0.6	0.8	0	493	476	3987	187586	409	309	190	91	60011
0.6	0.6	0	459	446	3769	177176	372	293	181	86	55670
0.6	0.8	75	484	468	3976	184314	397	308	189	91	59748
0.6	0.4	0	441	427	3655	176740	360	286	178	84	54433
0.6	0.2	0	428	414	3519	174767	351	277	174	84	53499

Table 3.4b. The ratio of PGE and internal standards count rate.

Sample Numbe	MATRIX			The ratio of PGE and internal standard.						
	HCl	HNO3	Te	Ru/Cd	Rh/Cd	Pd/Cd	Re/Tl	Ir/Tl	PT/Tl	Au/Tl
12	0.2	0.8	50	0.0139	0.0394	0.0109	0.0232	0.0293	0.0196	0.0089
9	0.2	0.8	75	0.0142	0.0400	0.0109	0.0237	0.0301	0.0200	0.0090
3	0.2	0.8	0	0.0141	0.0397	0.0111	0.0235	0.0308	0.0204	0.0091
14	0.4	0.8	25	0.0139	0.0395	0.0110	0.0235	0.0295	0.0195	0.0089
11	0.4	0.8	50	0.0144	0.0397	0.0110	0.0235	0.0307	0.0199	0.0092
15	0.2	0.8	25	0.0139	0.0399	0.0112	0.0239	0.0304	0.0203	0.0090
8	0.4	0.8	75	0.0140	0.0398	0.0110	0.0233	0.0301	0.0199	0.0091
13	0.6	0.8	25	0.0140	0.0394	0.0112	0.0239	0.0300	0.0202	0.0091
2	0.4	0.8	0	0.0136	0.0389	0.0109	0.0231	0.0298	0.0198	0.0089
10	0.6	0.8	50	0.0143	0.0401	0.0113	0.0242	0.0312	0.0204	0.0094
1	0.6	0.8	0	0.0140	0.0396	0.0111	0.0240	0.0304	0.0202	0.0092
4	0.6	0.6	0	0.0139	0.0394	0.0111	0.0235	0.0310	0.0207	0.0095
7	0.6	0.8	75	0.0140	0.0397	0.0112	0.0234	0.0304	0.0202	0.0093
5	0.6	0.4	0	0.0133	0.0377	0.0108	0.0233	0.0309	0.0208	0.0094
6	0.6	0.2	0	0.0131	0.0370	0.0105	0.0231	0.0305	0.0207	0.0096
			Average	0.0139	0.0393	0.0110	0.0235	0.0303	0.0202	0.0092
			Std	0.0003	0.0008	0.0002	0.0003	0.0005	0.0004	0.0002
			RSD	2.33%	2.10%	1.80%	1.41%	1.73%	1.96%	2.38%
	Slope relative to HCl			−0.001	−0.002	−0.000	0.0003	0.0014	0.0012	0.0010
			std	0.0005	0.0013	0.0003	0.0005	0.0008	0.0006	0.0004

composition as given by :

$$\text{Beta} = a_1[\text{HCl}] + a_2[\text{HNO}_3] + a_3[\text{Te}] + b$$

Beta is the ratio of the cps of the internal standard in the interpolated blank (to correct for drift) and the sample, which is a measure of matrix suppression (or enhancement) of an analyte in the sample solution relative to the blank solution. The constants a_1, a_2 and a_3 are the regression coefficients, [ ] denotes concentration of HCl, HNO_3 and Te, and b is the intercept of the regression line.

The coefficient of HCl (a_1) was 0.41 with relative standard deviation of 35%, HNO_3 (a_2) was -0.09 with RSD of 179%, and that of Te (a_3) was -0.00157 with a RSD of 52% for the Beta_{Cd} regression fit (Table 3.5, Equation 1). With the [HNO_3] and [Te] terms in the above equation set to zero (as a_2 and $a_3 \approx 0$, Equation 2), a_1 was determined to be 0.44, with a RSD of 34%. For the Beta_{Tl} regression fit, the HCl coefficient (a_1) was 0.31 (RSD = 39%), a_2 was -0.15 with RSD of 87%, and that of Te (a_3) was near zero (-0.001) with RSD of 46% (Table 3.5). With the [HNO_3] and [Te] terms set to zero (equation 2), a_1 value of 0.37 with RSD of 40% was obtained. Thus, there is no clear statistical relationship between HNO_3 and Te concentrations and sensitivities of the internal standards the over concentration range (HNO_3: 0.2M to 0.8M, and Te: 25 ppm to 75ppm) studied.

Table 3.5. Regression coefficients of HCl, HNO_3 and Te with their relative standard deviation (RSD).

β of Cd	HCl coefficient	HCl RSD	HNO_3 coefficient	HNO_3 RSD	Te coefficient	Te RSD
1	0.41	35%	-0.09	179%	-0.0016	52%
2	0.44	34%	0.0		0.0	
β of Tl						
1	0.31	39%	-0.15	87%	-0.0015	46%
2	0.37	40%	0.0		0.0	

1. Beta = $a_1[HCl] + a_2[HNO_3] + a_3[Te] + b$.
2. Beta = $a_1[HCl] + b$.

Within the range of concentrations of HCl, HNO_3 and Te studied; the counts rates of the internal standards, PGE's and Au were found to depend most strongly on the concentration of HCl used (Figures 3.3 and 3.4).

Since Te concentrations have very little effect on matrix suppression or enhancement, it will not be useful to look into other coprecipitation agents, such as Se, for improvement in sensitivity for the Jackson *et al.* (1990) technique. Similarly, little can be gained by manipulating the HNO_3 concentration of the sample solution. However, it might be useful to reduce the quantity of Te (and Sn) as a means of lessening the total dissolved solids in the analytical solution and reagent blank.

The major matrix effect is related to HCl concentration. While, theoretically an increase of 50% in sensitivity could be attained by reducing HCl to 0M, this is not practical, as Cl^{-1} ions are required to complex the PGE's and Au ions in solution.

The ratio of the noble metal and the internal standard(s) count rates (Table 3.4b and Figure 3.5) in the different medium are approximately constant. The relative standard deviations of the ratios are less than 3% (Table 3.4b). Figure 3.5 shows that the internal standards do not exhibit appreciable differential matrix effects compared to the PGE's and Au. As shown in Figure 3.5, the slope of the individual PGE and the internal standard ratio as a function of HCl are not statistically different from zero. However as seen in Table 3.4b, all light PGE/Cd slopes were negative, and

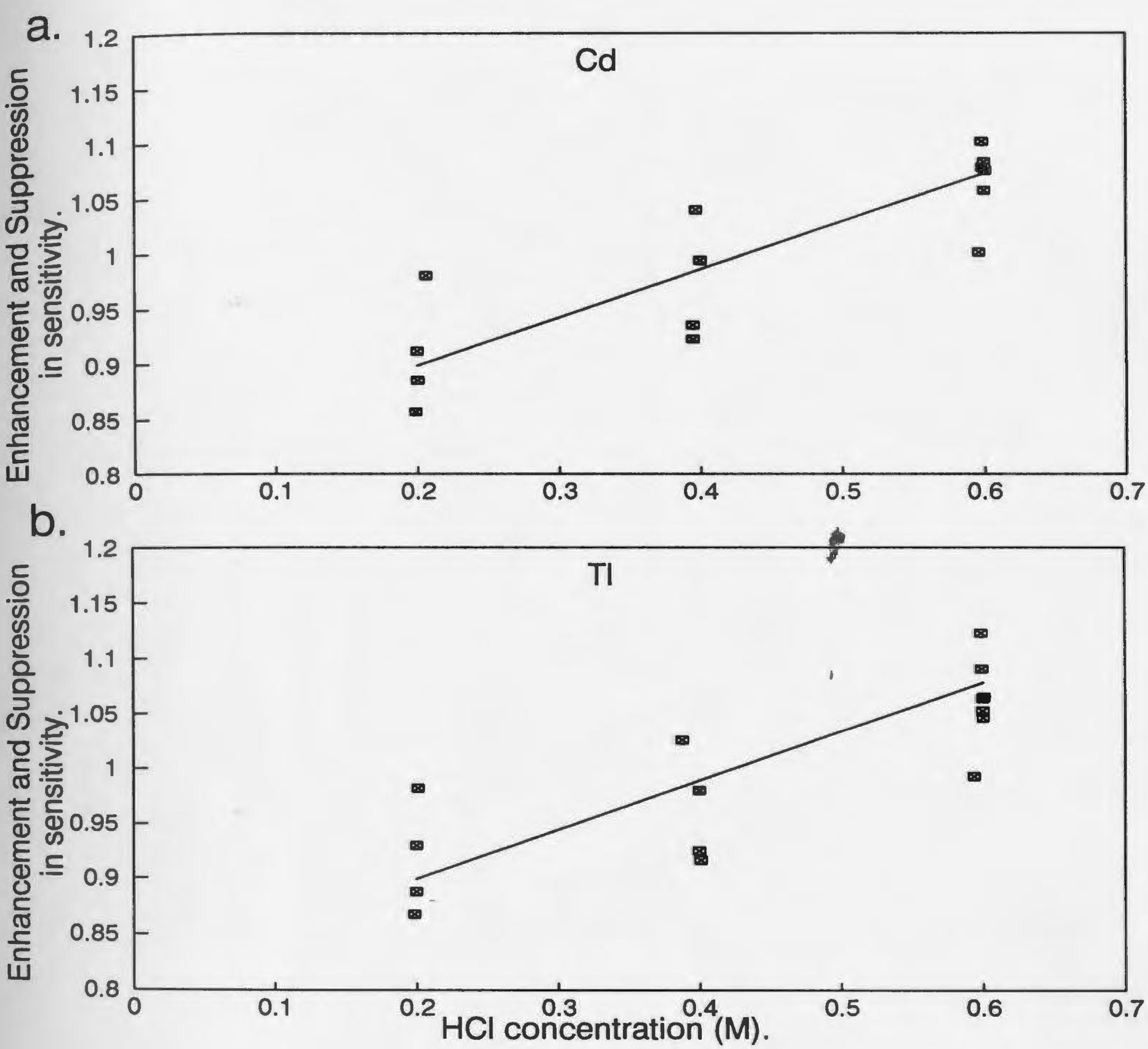


Figure 3.3. Matrix effect of HCl on the count rate of the internal standards, (a) Cd and (b) Tl, relative to the reference solution. B < 1 indicates enhancement, B > 1 indicates suppression and B = 1 indicates No effect.

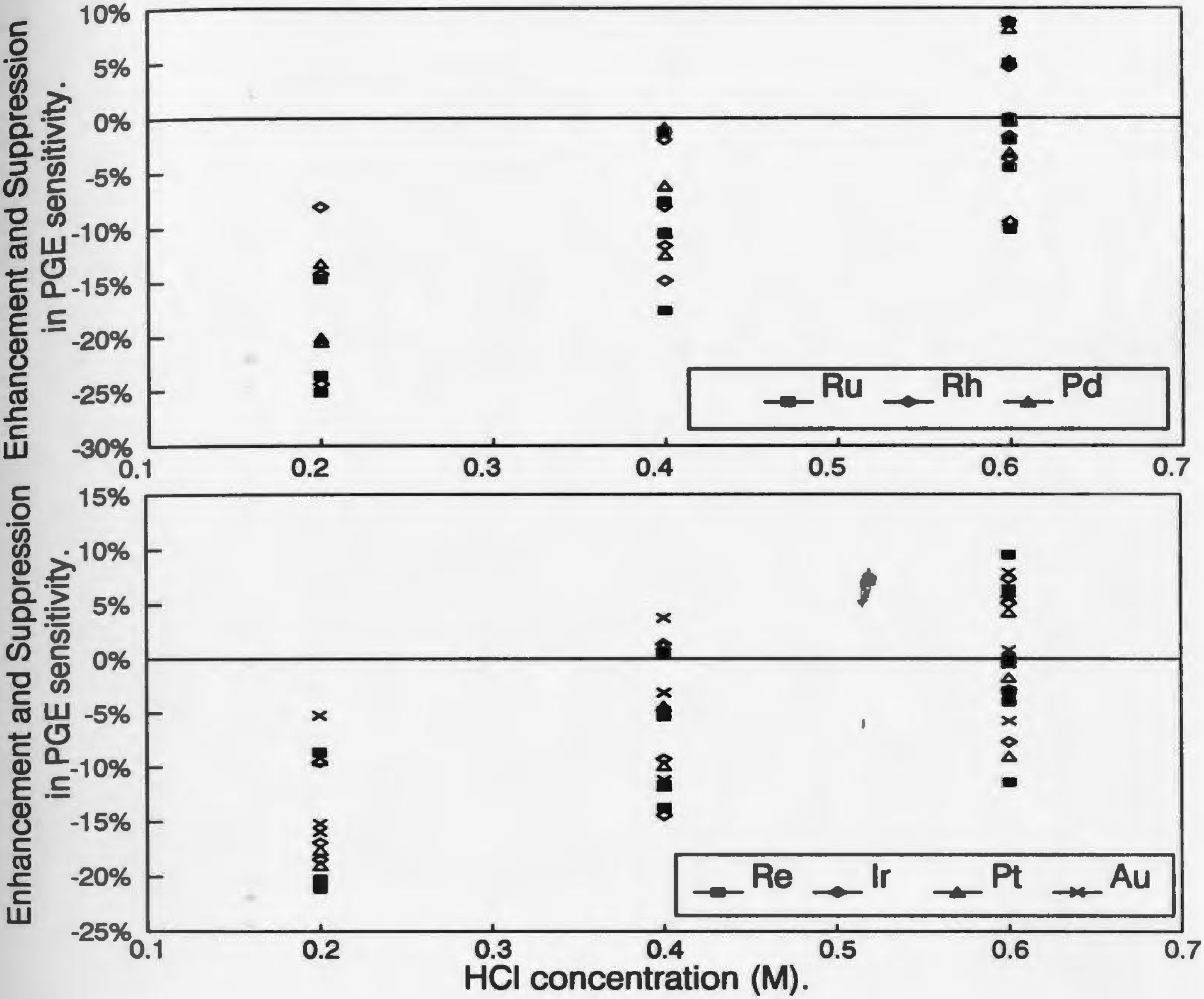


Figure 3.4. Matrix effect of HCl on the PGE's and Au count rates. Percentage count rates of PGE's in different HCl solutions relative to that of 0.6M HCl (75 ppm Te and 0.8M HNO_3). The reduction of HCl concentration in the final solution from 0.60 M to 0.20 M provides up to approximately 20% enhancement in the sensitivities of the internal standards.

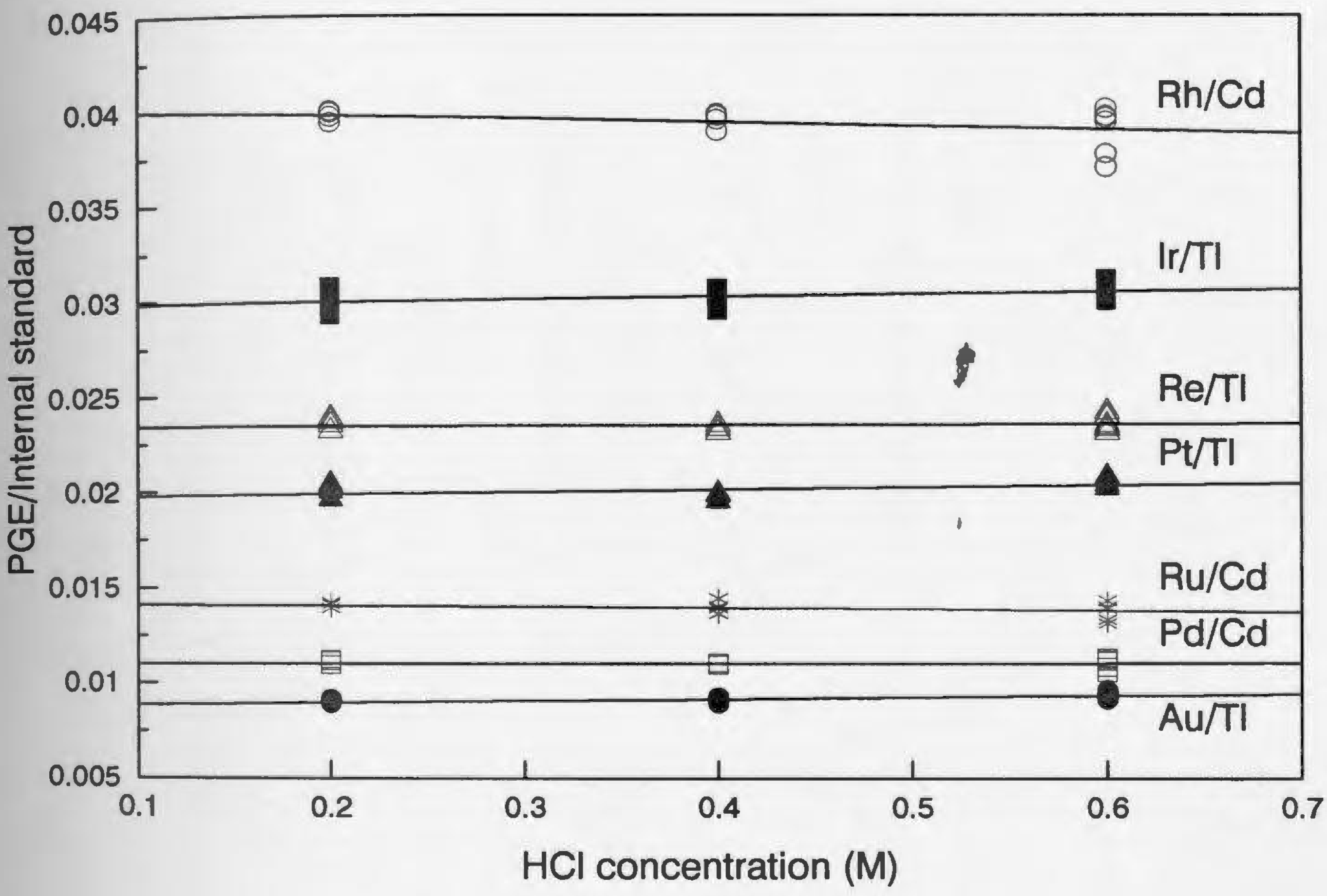


Figure 3.5. Variation of the ratio of PGE's and internal standards count rates in the different medium. The horizontal slope of the plots suggest that Cd and Tl provide sufficiently accurate correction for the matrix effects.

all heavy PGE/Tl slopes were positive. The ratio decreases (with increased HCl) for the high ionization potential (IP) internal standard (Cd), and increases for the low IP internal standard (Tl) (Table 3.2). The magnitude of this effect is < 2%, and although small, it is nonetheless real. However, this matrix effect can not be responsible for 2% to 28% bias in SARM-7, PTC-1 and SU-1 values reported by Jackson *et al.* (1990). In the context of other much larger analytical errors associated with PGE analysis, Cd and Tl are suitable for correcting the matrix variations.

In summary, the 15 - 25% increased sensitivity achievable by realistic changes in the sample matrix is not sufficient to provide a useful increase in the method sensitivity relative to geological concentration levels. The internal standards (Cd and Tl) do provide an accurate measure and correction for the normal variations in sample and standard, *i.e.* matrix effect, sensitivities.

CHAPTER 4. INVESTIGATIONS INTO THE NiS FIRE ASSAY PROCEDURE.

GENERAL INTRODUCTION.

The purpose of this section is to systematically examine the NiS fire assay, and the chemical procedures involved, with the aim of improving the method for determination of the PGE's in ores, and especially, in low to sub ppb level natural materials.

This work seeks to:

1. study the relationships between the amount of Ni employed as collector and PGE recovery in both ore grade samples and low to sub ppb level samples.
2. minimize the reagent blank associated with the NiS fire assay.
3. make the chemical procedures involved simpler, use smaller quantities of reagents, shorten the processing time and develop a less complicated procedure.
4. lower the total dissolved solids in the analytical solution to decrease instrumental drift and matrix effects.

The individual experiments and their results are reported.

4.1. THE EFFECTS OF REDUCTION OF THE QUANTITY OF NICKEL AND SULPHUR ON THE RECOVERY OF THE PRECIOUS METALS USING NiS FIRE ASSAY COLLECTION.

4.1.1. INTRODUCTION.

Fire assay using NiS as the collector is a well established preconcentration method used in PGE and Au analysis (Robert *et al.*, 1971, 1975; Davydova *et al.*, 1979). It is regarded by Robert *et al.*(1975), and Hoffman *et al.* (1978) as quantitative for the six PGE's and well suited, with suitable modification, for most sample types.

The standard nickel sulphide fire assay procedure (Robert *et al.*, 1971, 1975) has undergone rapid evolution. Parry *et al.*(1988) and Jackson *et al.* (1990) reported the use of 10 g and 5 g of Ni as the collector, respectively, rather than the 16 g Ni (20 g NiO or 32 g $NiCO_3$) of Robert *et al.* Asif *et al.* (1989) further decreased the amount of Ni and reported that 0.5 g Ni was as effective for the recovery of the PGE's as 5.0 g and 10 g. Parry *et al.* (1988) reported that approximately 20% of each of the PGE's and Au is lost during the dissolution of the bead to the parting acid. Shazali *et al.* (1987) and Jackson *et al.* (1990) added a Te coprecipitation step and demonstrated significant improvement in precious metal recoveries.

All reagents used in the NiS procedure contribute to the reagent blank. Especially important, are PGE's contained in the Ni powder and in the HCl used to dissolve the NiS bead. These can both be reduced by using smaller amounts of nickel and other reagents.

In this section, the effect of a reduced amount of nickel (and sulphur) on the recovery of PGE's and Au in both PGE's ores and low to sub ppb samples was investigated. The main objectives were (i) to minimize the reagent blank associated with the NiS fire assay, (ii) to determine if PGE's recoveries are independent of sample types (PGE's concentrations) and collector mass, and (iii) to utilize the results of (i) and (ii) to develop a better method for analysis of the PGE's and Au in geological materials at both ppm and low to sub ppb levels.

4.1.2. MATERIALS AND EXPERIMENTAL PROCEDURE.

4.1.2.1. REAGENTS.

All reagents were certified American Chemical Society (ACS) grade except where indicated.

Nickel - carbonyl nickel powder, 99.8% Ni (INCO powder T-123)

Sulphur - precipitated sulphur powder (United States Pharmicopia (U.S.P.) B.D.H. B30317)

Sodium carbonate - anhydrous granular (B.D.H. ACS 777)

Borax - disodium tetraborate (B.D.H. ACS 861)

Concentrated HCl (12M) - (E.M. SCIENCES)

Concentrated HNO_3 (16M) - (B.D.H. ACS 579-43)

Silica - silicon dioxide floated powder, 240 mesh (Anachemia AC-8130)

Aqua Regia - A mixture of 75% concentrated hydrochloric acid and 25% concentrated nitric acid by volume.

Te solution - 2000 ppm in 10% HCl. Prepared by dissolving 2 g of Te metal (99.999%, SPEX Industries, Metuchen, New Jersey, U.S.A) in 15 mL aqua regia, followed by two evaporations to dryness with concentrated HCl. Dissolved in 15 mL 1.2M HCl and diluted to volume with 1.2M HCl.

$SnCl_2$ solution. 110 g of stannous chloride ($SnCl_2.2H_2O$) (Fisher) dissolved in 150 mL concentrated HCl and diluted to 500 mL with water.

SARM-7 : The South African National Institute of Metallurgy (NIM) Pt ore reference material. This standard is a composite of 7 tonnes of rocks from five sites in the Meresky Reef of the Bushveld igneous complex (Steele *et al.*, 1975).

BF-4 : A komatiite rock containing low to sub ppb concentrations of PGE's and Au from Munro Township, Ontario.

The major and trace element contents of both SARM-7 and BF-4 were determined, and are listed in Table 4.1 and Appendix 1.

4.1.2.2. EXPERIMENTAL PROCEDURE.

The effect of the amount of Ni (and S) used in the NiS fire assay procedure on PGE and Au recovery was examined. The weight of Ni was varied from 0.25 g to 5g.

As recommended by Jackson *et al.* (1990), the major constituents of the samples were determined using XRF (Table 4.1) to formulate an optimum flux composition prior to fusion. The XRF procedure for the determination of major and trace elements of the sample is described in Section 4.2. In the samples analyzed, the potential problematic constituents (Ni, S, Cu and Zn) have low concentrations so that they are unlikely to cause fusion, dissolution, or interference difficulties. The experimental procedure follows that of the Jackson *et al.* (1990). A brief description of the procedure is given below.

(1). 10 g of sample, 6.7 g of Na_2CO_3, 13.3 g $Na_2B_4O_7$, 5 g silica, and different Ni and S masses in the ratio of 1 part of Ni to 0.66 parts of S were weighed into clay crucibles and mixed thoroughly with a spatula.

(2). The mixture was fused in a preheated oven at 1050° C for 1.25 hours. The crucible was removed and allowed to cool.

(3). The crucible was broken open and the NiS bead retrieved, weighed, crushed to small chips and transferred to a tall 1000 mL pyrex beaker.

The NiS transferred was weighed to correct for loss on crushing. Beads resulting from 1 g or less of Ni (0.25 and 0.5 g) were not crushed.

(4). 400 mL of concentrated HCl was added. The beaker was covered with a watch glass, transferred to a hot plate at ~150° C, and the bead dissolved.

(5). The solution was allowed to cool until warm, 2.5 mL of Te solution (2000 ppm) was added. The solution was diluted with 400 mL of water and 10 mL of saturated $SnCl_2$ solution was added to precipitate the Te. The solution was brought slowly to boiling over a period of 30 minutes to coagulate the black Te precipitate formed.

(6). The solution was cooled until warm and then filtered through a Millipore filter system (Whatman 0.45 μm cellulose nitrate membrane filter paper) and washed with deionized water.

(7). The filter paper and its contents was placed in a 30 mL refluxing pyrex test tube, 5 mL of concentrated HNO_3 were added, a reflux condenser attached, and the filter paper allowed to dissolve. 5 mL of concentrated HCl was then added through the top of the condenser and the solution warmed ($\leq$100° C).

(8). The solution was cooled. The inside of the condenser was washed with deionized water, the solution quantitatively transferred to a 125 mL polypropylene bottle and diluted to 100 g with deionized water.

Table 4.1. Concentration of the major and trace elements of BF-4 and SARM-7 measured in this study (N = 4) using XRF. Major elements are reported in %, and trace elements are in ppm. Uncertainty (1σ) = reproducibility of the measured value.

	BF-4	SARM-7
SiO_2	44.94 ± 0.06	46.25 ± 0.15
Na_2O	0.39 ± 0.00	0.84 ± 0.00
MgO	34.13 ± 0.09	23.53 ± 0.08
Al_2O_3	5.33 ± 0.01	8.77 ± 0.03
P_2O_5	0.02 ± 0.00	< 0.01
K_2O	0.06 ± 0.00	0.21 ± 0.00
CaO	4.87 ± 0.02	6.12 ± 0.01
TiO_2	0.25 ± 0.00	0.23 ± 0.00
MnO	0.16 ± 0.00	0.20 ± 0.00
Fe_2O_3	10.89 ± 0.02	12.59 ± 0.01
S	358 ± 11	5455 ± 64
Cr	2886 ± 31	6039 ± 64
Ni	2010 ± 5	2211 ± 7
Cu	34 ± 1	876 ± 5
Zn	43.0 ± 0.5	81.0 ± 0.6
As	< 2	14.0 ± 1.6
Sr	12.6 ± 0.3	109.0 ± 0.3

Data reduction was done on a personal computer using commercial spread sheet software. The Jackson *et al.* (1990) algorithm for external calibration and drift/matrix corrections; using Cd and Tl as internal standards for the light and heavy PGE's respectively, was used to calculate sample concentrations. The isotopic abundances of the PGE's and other elements are listed in Table 3.2. The Os sensitivity was calculated by using Re as a surrogate standard due to the severe instrumental memory effect of Os and the difficulty of maintaining an Os standard solution. The Os intensity normalized to 100% isotopic abundance was 96.35% of that of 100% Re abundance normalized intensity (Jackson *et al.*, 1990). Sensitivity (counts per second of analyte per its unit concentration in solution) for Os is: ^{189}Os sensitivity = ^{191}Re sensitivity * 0.9635 * 16.1% / 37.4%). This corrects for isotopic abundance, mass discrimination and ionization potential effects on sensitivity.

4.1.3. RESULTS AND DISCUSSION.

Pt ORE GRADE SAMPLE (SARM-7).

When the South African National Institute of Metallurgy (NIM) Pt ore reference material (SARM-7) was analyzed, the PGE recovery was found to be independent of the weight of collector (Table 4.2), for experiments using 1, 3.3, and 5 g Ni with corresponding amounts of S as seen in Figure 4.1.

Table 4.2. The mean concentration of PGE's and Au (ppb) recovered from a Pt ore grade sample (SARM-7) using various masses of Ni as collector. 3 separate NiS beads were prepared for each weight of collector considered.

SARM-7.

	1.0 g Ni	3.3 g Ni	5.0 g Ni	Literature value.
Ru	376	335	462	430
Rh	237	214	319	240
Pd	1671	1365	1892	1530
Re	0.2	0.1	0.2	
Os	41	44	42	63
Ir	70	69	75	74
Pt	4460	3249	3815	3740
Au	219	225	254	310

	1.0 g Ni	3.3 g Ni	5 g Ni
NiS bead recovered (g)	1.32	4.42	6.74
Theoretical wt. (g)	1.55	5.12	7.76
% recovery	84.84%	86.33%	86.86%

Source of the literature values: Steele *et al.*, 1975.

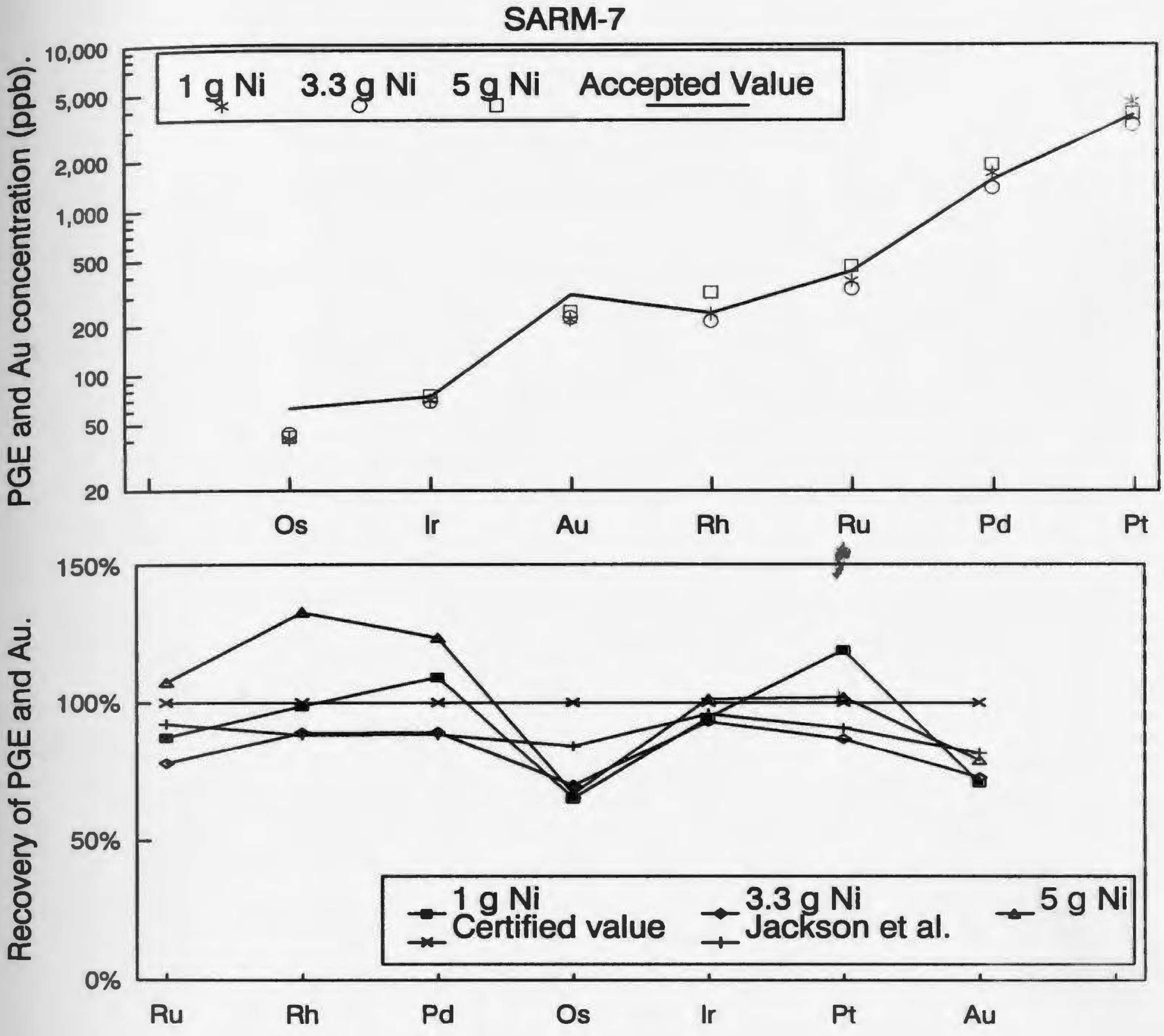


Figure 4.1. Variation of PGE and Au contents in SARM-7 with collector (Ni) mass added relative to the certified values. The PGE and Au content in the Pt ore grade sample (SARM-7) recovered by different masses are independent of the mass of Ni added as collector.

These findings agree with the results of Asif and Parry (1989).

BACKGROUND LEVEL SAMPLES.

To test the above experimental procedure for low level PGE samples, the komatiite sample, RF-4, was used. Table 4.3 lists the concentrations (N = 2) and standard deviations of PGE's and Au recovered by each mass of Ni used. The collector mass of 0.25 g Ni/0.17 g S did not form a recoverable bead, thus no data is recorded. Figure 4.2 is an illustration of the percentage recovery of PGE's and Au by the various masses of Ni used relative to the recovery for 5 g Ni. The inescapable conclusion from Figure 4.2 is that the recoveries of Ru, Rh, Pd and Pt are functions of collector mass. Iridium is quantitatively recovered for all collector weights. Although Au and Os show high variability, there is no apparent relationship with the weight of the collector.

The mass of NiS bead formed from the individual collector masses relative to the theoretical mass (sample component + mass added), follows a similar trend to that of Ru, Rh, Pd, and Pt recoveries (Table 4.3 and Figure 4.3). The bead in each case was assumed to be pure NiS. The percentage (relative to the theoretical yield) of NiS bead formed from the Pt grade ore (SARM-7) fusion was ≈ 85% for the different masses of the collector (Ni) added (Table 4.2). As shown later (Section 4.2) the missing Ni (and S) were found "dissolved" in the glass.

Table 4.3. The mean concentration of PGE's and Au (ppb) in the low ppb sample (BF-4) recovered using various masses of Ni as collector. 2 separate NiS beads were prepared for each collector weight, ± = 1 standard deviation.

BF-4

	0.5 g of Ni	1.0 g of Ni	2.0 g of Ni	3.3 g of Ni	5.0 g of Ni
Ru	1.34 ±0.24	2.19 ±0.17	2.42 ±0.12	2.98 ±0.31	3.15 ±0.32
Rh	0.31 ±0.11	0.52 ±0.02	0.62 ±0.01	0.71 ±0.13	0.76 ±0.05
Pd	3.03 ±0.93	3.71 ±0.67	4.79 ±0.01	5.85 ±1.25	6.24 ±0.21
Re	0.00	0.01	0.03	0.00	0.01
Os	1.04 ±0.13	0.92 ±0.43	1.35 ±0.42	1.19 ±0.23	1.05 ±0.07
Ir	1.25 ±0.21	1.28 ±0.11	1.20 ±0.05	1.17 ±0.19	1.31 ±0.26
Pt	2.53 ±0.67	3.07 ±0.25	3.31 ±0.05	3.64 ±0.67	4.68 ±0.55
Au	1.52 ±0.12	1.43 ±0.10	3.11 ±0.26	1.88 ±0.32	1.31 ±0.28

	0.5 g Ni	1 g Ni	2 g Ni	3.3 g Ni	5 g Ni
NiS bead recovered (g)	0.37	1.07	2.36	4.19	6.67
Theoretical wt. (g)	0.78	1.55	3.10	5.12	7.76
% recovery	47.04%	68.63%	75.88%	81.73%	86.97%

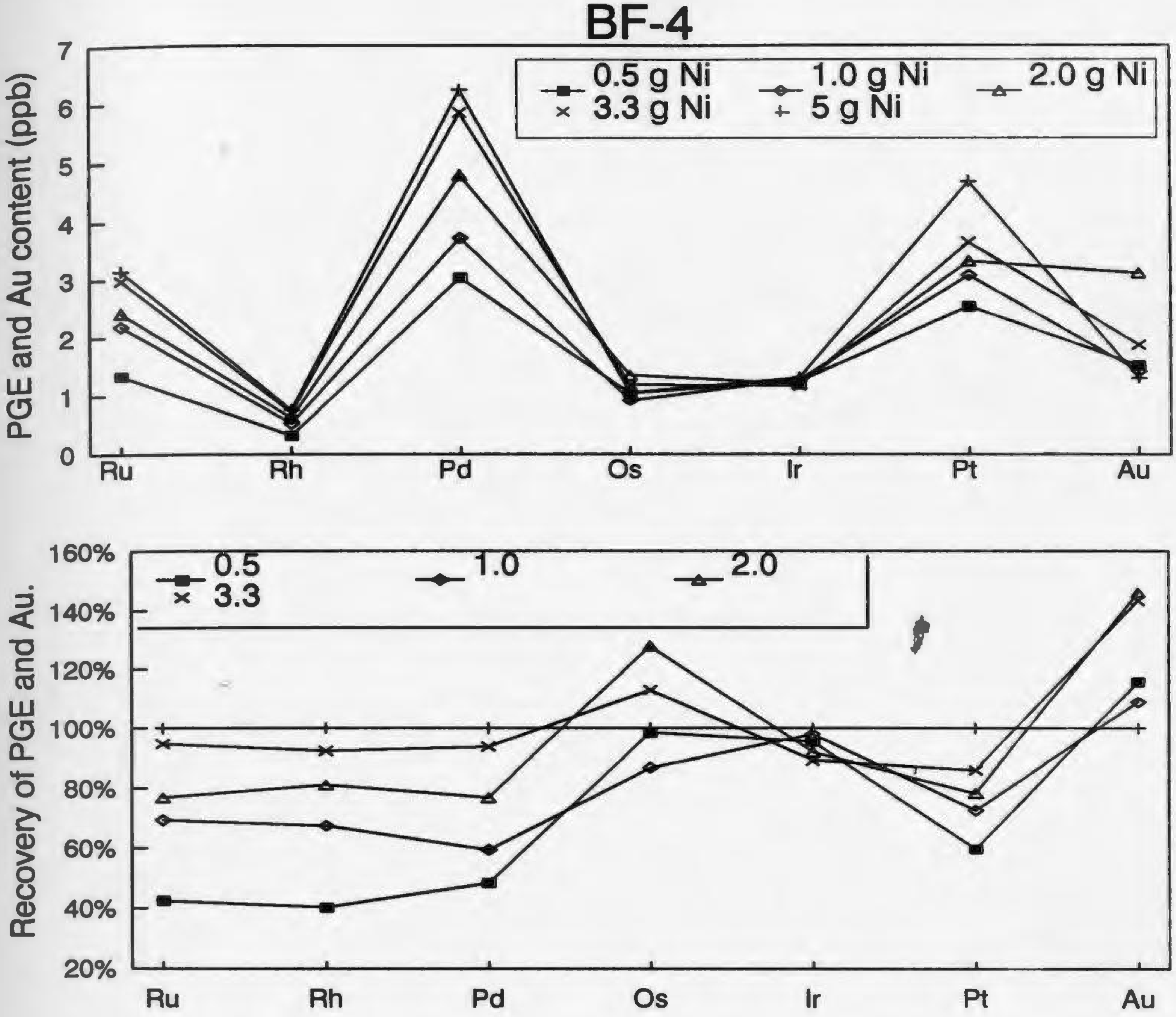


Figure 4.2. Relationship between PGE's and Au in BF-4 recovered by collector mass, relative to a 5 g bead. The percentage recovery of Ru, Rh, Pd, and Pt varies with the weight of Ni added as collector. There are no significant differences in the recoveries of Ir, Os, and Au as a function of Ni mass used.

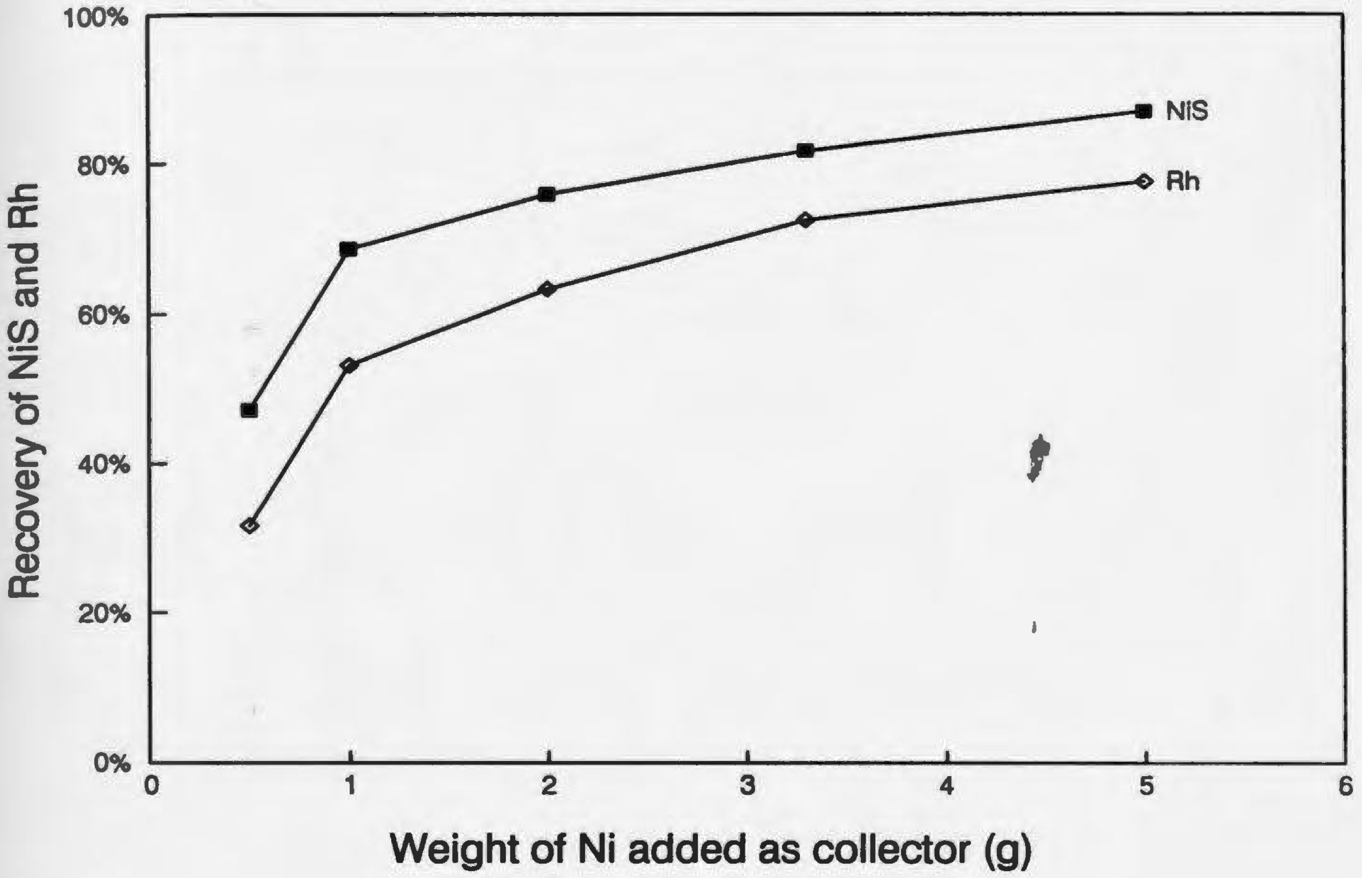


Figure 4.3. Variation of mass of NiS formed relative to the theoretical collector mass for BF-4 experiments. The weight percentage of NiS bead formed follows a similar trend to that of Rh, Pd, Pt and Ru recoveries.

As part of this study, the efficiency of Re collection by the NiS method was investigated. Reference materials NIST 330 and 331 were analyzed. Determined Re in NIST 330 and 331 were 1.51 ppb (± 0.88) and 0.33 ppb (± 0.10) respectively compared to the certified values of 303 ppb and 43 ppb, clearly indicating that only traces of Re are recovered in the NiS bead. Consequently, Re data is not reported further in this thesis.

In conclusion, the NiS collection for PGE's and Au in the ore grade sample, SARM-7, is quantitative, for the different collector masses, and the recovery is not a function of the mass of collector. The recovery of Ir, Os and Au in the low ppb sample, BF-4, is also quantitative and not collector mass dependent. The recovery of Ru, Rh, Pd and Pt in the low ppb sample was found to depend on the mass of the collector. The recovery of Re by NiS fire assay is very poor.

4.1.3.1. MODELLING THE RECOVERY RATES OF PGE's AND GOLD IN BF-4 AS A FUNCTION OF VARIABLE PARTITION COEFFICIENTS (D).

The low recoveries of Ru, Rh, Pd and Pt were found to be dependent on the mass of the collector. To ascertain this effect on the recovery of PGE's, a model was derived from the mass balance equation for the PGE's between the silicate and sulphide phase, and the bulk partition coefficient equation.

A mass balance equation of the PGE's for the silicate (borax glass) and the sulphide phases can be written as:

$$(W_{PGE})_{rock} = (W_{PGE})_s + (W_{PGE})_g \qquad \text{.......} (1)$$

where s and g represent the sulphide and glass phases respectively, (W_{PGE}) represents the amounts of individual PGE's in the phases.

Rearranging,

$$(W_{PGE})_s = (W_{PGE})_{rock} - (W_{PGE})_g \qquad \text{..........} (2)$$

Defining the Partition Coefficient,

$$D = [metal_s]/[metal_g]$$

where [ ] indicates concentration.

$$D = \frac{(W_{PGE})_s / W_s}{(W_{PGE})_g / W_g} \qquad \text{...........} (3)$$

W_g and W_s are the masses of the glass (silicate) and NiS respectively. The term W_g refers to the total amount of sample, additional silica, sodium tetraborate and sodium (from the sodium carbonate) used. W_g was calculated from the weight of reagents used, assuming all the H_2O (from $Na_2B_4O_7.10H_2O$), and CO_2 (from Na_2CO_3) were volatilized during fusion. W_{rock} is the mass of rock used.

Rearranging,

$$D = \frac{(W_{PGE})_s * W_g}{(W_{PGE})_g * W_s} \qquad \text{..........} (4)$$

Defining R, the ratio of mass of silicate to mass of sulphide,

$$R = W_g / W_s. \qquad \text{.................} (5)$$

Substituting 5 into 4 gives,

$$D = \frac{(W_{PGE})_s * R}{(W_{PGE})_g} \qquad \text{............} \ (6)$$

But $\qquad [PGE,s]_{found} = (W_{PGE})/W_{rock}$

Hence, $\qquad (W_{PGE})_s = [PGE]_{found} * W_{rock}$

Hence, the Bulk Partition Coefficient equation can be written as,

$$D = \frac{[PGE]_{found} * W_{rock} * R}{(W_{PGE})_g} \qquad \text{...........} \ (7)$$

Rearranging,

$$(W_{PGE})_g = [PGE]_{found} * W_{rock} * R/D \qquad \text{........} \ (8)$$

Substituting equation (8) into equation (2),

$$[PGE]_{found} * W_{rock} = (W_{PGE})_{rock} - [PGE]_{found} * W_{rock} * R/D \qquad \text{.....} \ (9)$$

The above equation is the equation of a straight line.

$$y = a_1 - a_2 x$$

where $y = [PGE]_{found} * W_{rock}$, $x = [PGE]_{found} * W_{rock} * R$,

$a_1 = (W_{pge})_{rock}$,and slope, $a_2 = D^{-1}$

The PGE concentrations in the sulphide melt are a function of D and the silicate to sulphide mass ratio (R). A large D value indicates strong partitioning of the noble metal into the sulphide. Table 4.4 compares the silicate (glass) to sulphide ratios used in this work. Figures 4.4a,b and 4.5a,b show the relations between PGE's content and D, and were obtained from $y = a_1 - a_2x$ (a linear regression was sought for y and x). The data used is given in Appendix 2.

The slope of the line equals the negative reciprocal of D. The individual slopes were -0.0162 ± 0.0034 (Ru), -0.0150 ± 0.0051 (Rh), -0.01157 ± 0.0055 (Pd), -0.0064 ± 0.0031 (Pt), 0.0006 ± 0.0041 (Os), 0.0009 ± 0.0019 (Ir) and -0.0009 ± 0.0065 (Au). The calculated D values calculated from the slope (± 1 standard deviation, S) are presented in Table 4.4b, with infinite values corresponding to zero or positve slopes. For Os and Ir, the (mean - S) slopes set the D values at the 82% confidence level. These results support the previous observations (Fig. 1) that the collector weight used did not affect the recoveries of Ir, Os and Au but did affect the recoveries of Ru, Rh, Pd, and Pt. A detailed comparison of the D's derived from the model and that from direct analysis of the 2 phases is given in Section 4.2.

Table 4.4a. The ratio of mass of silicate (glass) and sulphide (R) used for the SARM-7 and BF-4 experiments.

Amount of Ni added (g).	Glass/Sulphide (R)	Standard deviation of R	RSD of R
0.5	83.3	3.4	4.0%
1.0	28.5	0.4	1.4%
2.0	12.89	0.14	1.1%
3.3	7.23	0.10	1.4%
5.0	4.53	0.003	0.07%

RSD = relative standard deviation of R.

Table 4.4b. The slopes of the PGE and Au plots with their calculated partition coefficients.

	Slope ± S	K_d		
		Mean + S	Mean	Mean - S
Ru	-0.016 ± 0.003	78	62	51
Rh	-0.015 ± 0.005	102	67	50
Pd	-0.012 ± 0.006	164	86	59
Os	0.0006 ± 0.004	∞	∞	283
Ir	0.0009 ± 0.0019	∞	∞	999
Pt	-0.006 ± 0.003	304	156	105
Au	-0.0009 ± 0.0065	∞	1150	136

S is 1 standard deviation of an individual determination.

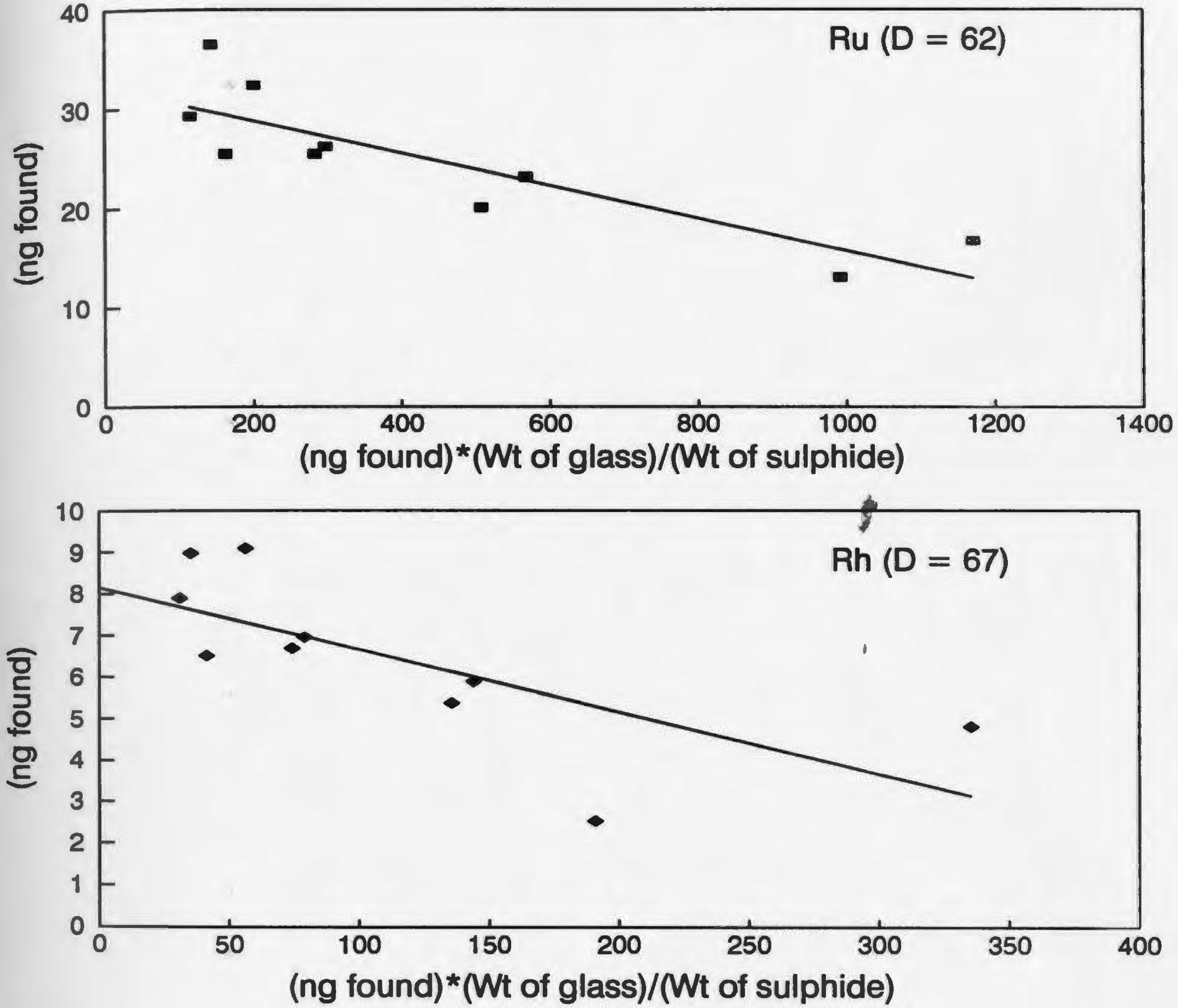


Figure 4.4a. Illustration of the model plot for Ru and Rh recovery for sample BF-4. The slopes equal the reciprocals of the mean D's (62 for Ru, and 67 for Rh). The Ru and Rh recovery is a function of collector mass used.

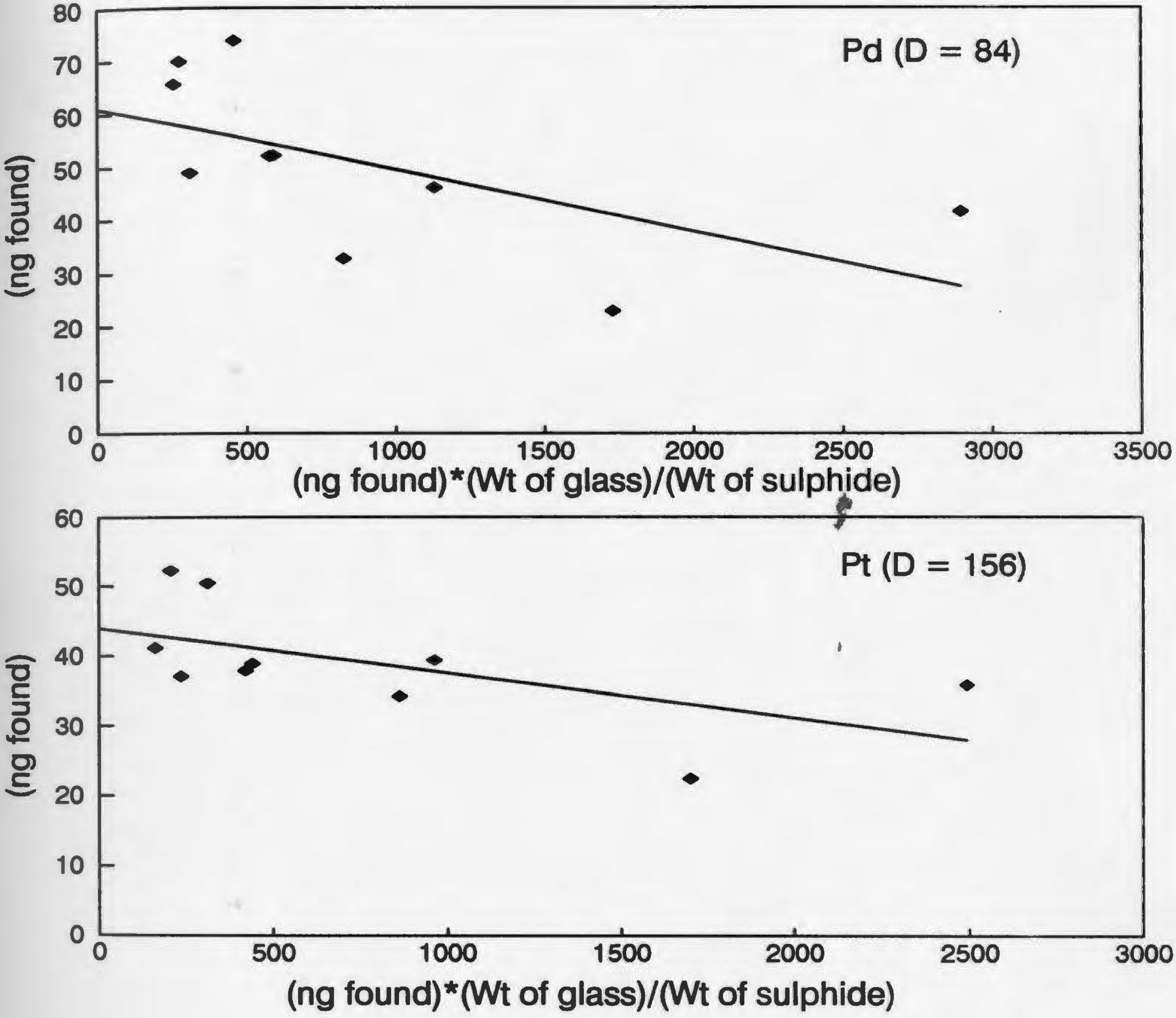
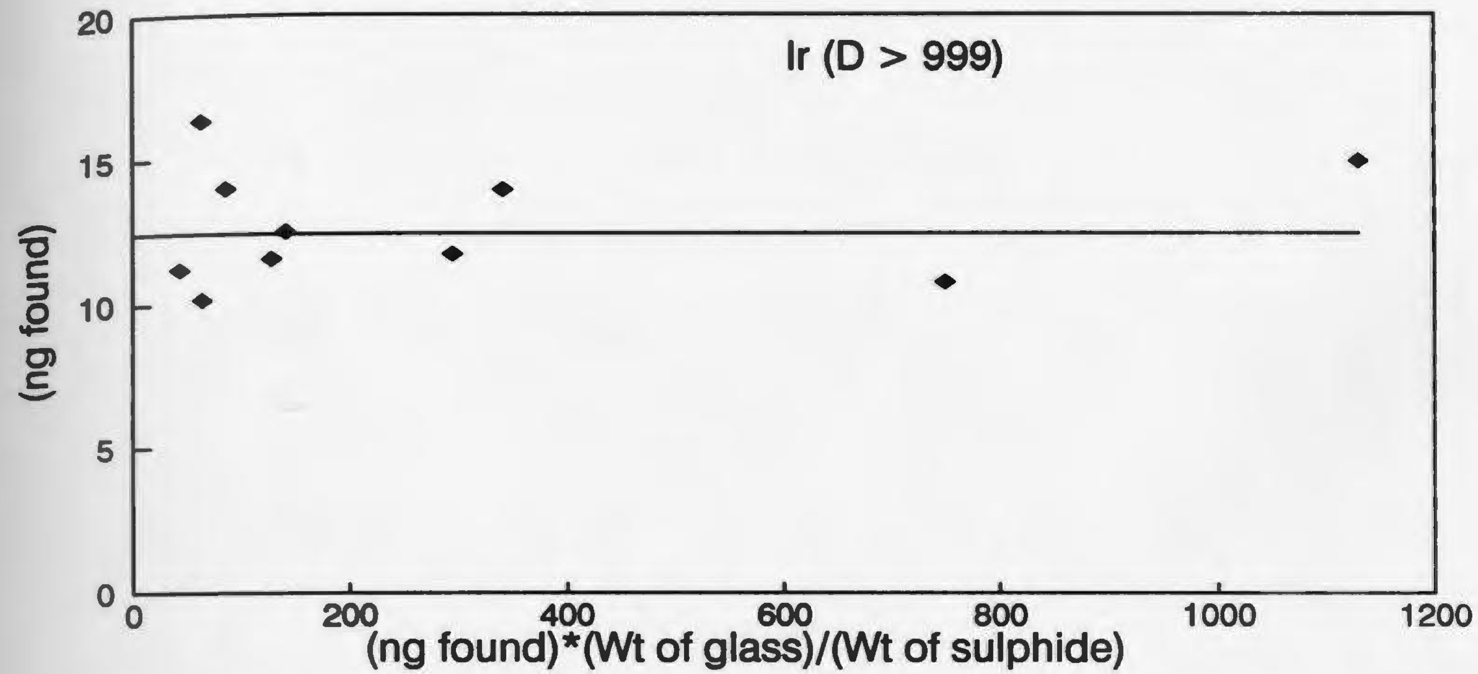


Figure 4.4b. Illustration of the model plot for Pd and Pt for sample BF-4. The slopes equal the reciprocals of the mean D's (86 for Pd, and 156 for Pt). The Pd and Pt recovery is a function of collector mass used.



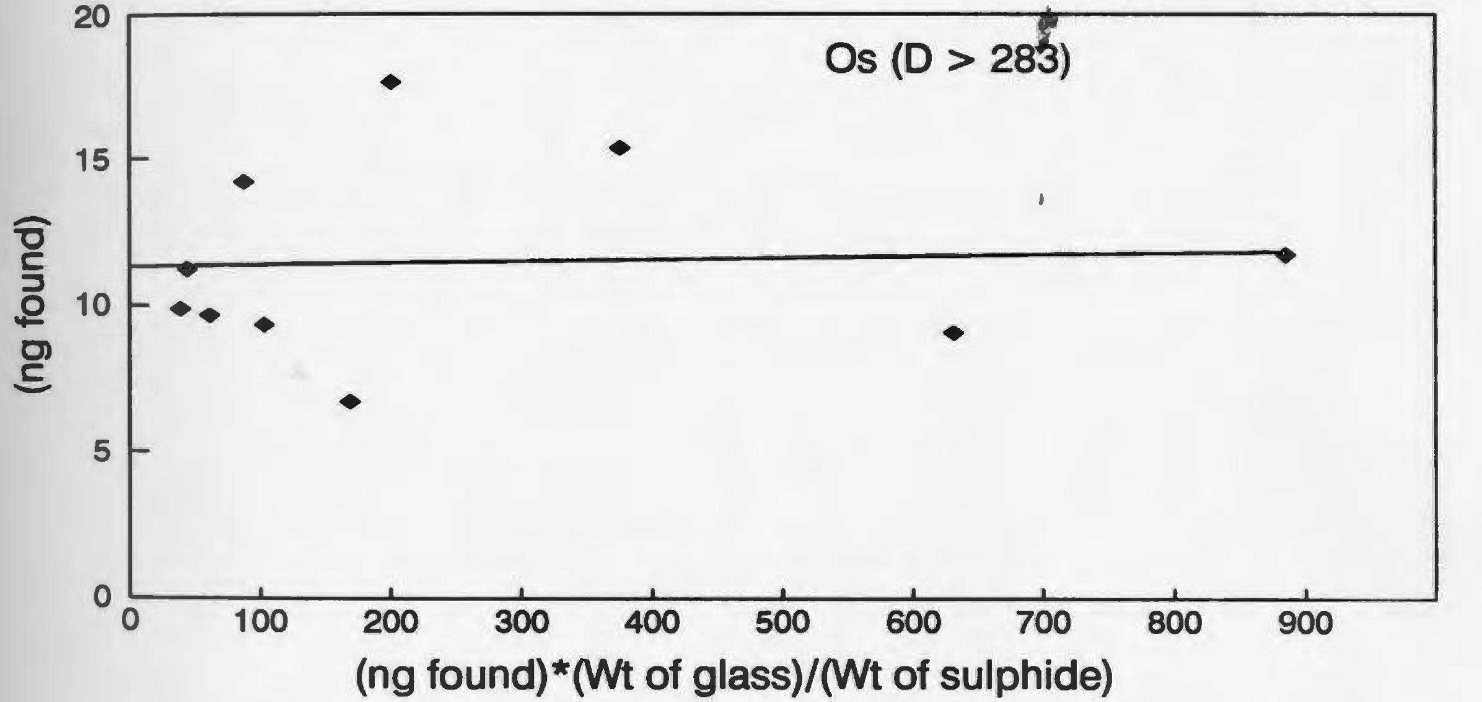


Figure 4.5a. Illustration of the model plot for Ir and Os for sample BF-4. Note the slopes ≈ 0; which indicate the independence of Ir and Os recoveries on collector mass. Calculated D's are > 999 for Ir, and > 283 for Os.

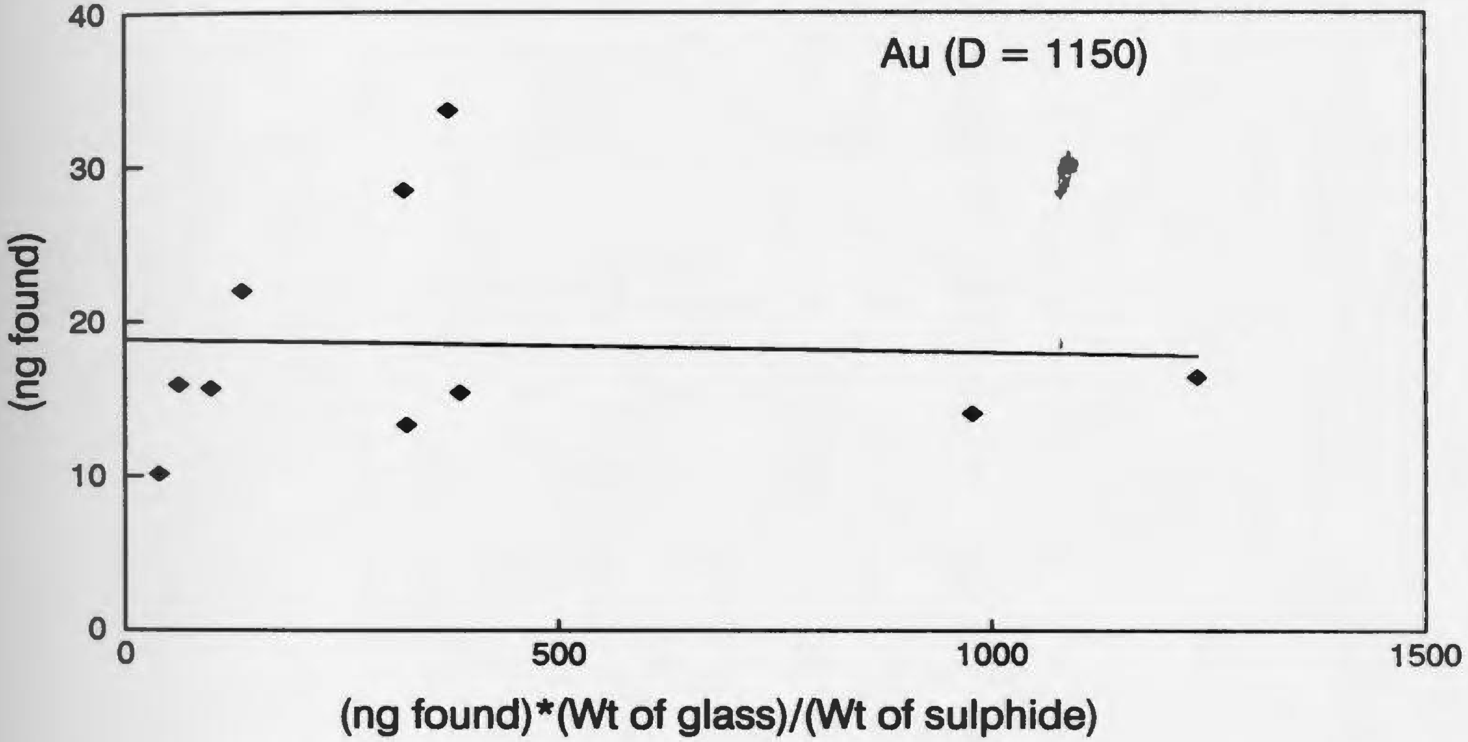


Figure 4.5b. Illustration of the model plot for Au for sample BF-4. Note the slopes ≈ 0, D = 1150. The Au recovery follows the same trend as Ir recovery, thus the independence of Au recovery on collector mass.

The physio-chemical cause for the partitioning of PGE's is a subject of much debate (Barnes *et al.*, 1985; Crocket, 1979). Possible explanations for the variable PGE's recovery (and D) in the low ppb level sample are:

i. Ir, being one of the least soluble of the PGE's in a silicate melt (Amossè *et al.*, 1987), attains saturation in the melt and then scavenges Os, as Ir-Os form extensive binary solid solutions. Even though, the PGE's are thought to be entirely included in the NiS formed, as PGE sulphides; the insolubility of Ir and Os in the silicate melt helps to concentrate Ir and Os in the NiS phase. Hence, the recovery of Ir and Os is not a function of the amount of Ni (/S) used.

ii. At low levels; Pd, Ru and Rh are able to find suitable silicate melt sites. This mechanism has been used to explain high Pd concentrations in spinel (Capobranco *et al.*, 1990). Also, Pt is thought to aid the nucleation of alkali oxides in glasses (Rindone, 1962).

4.1.4.2. REDUCTION OF THE QUANTITY OF THE GLASS (FLUX) AND ITS EFFECT.

From equation (9) and Figures 4.4 to 4.5, the total PGE content in the sulphide phase is maximized by reducing the $W_{glass}/W_{sulphide}$ ratio. This can be achieved by either decreasing the W_{glass} or increasing the $W_{sulphide}$. To improve recovery, a study to investigate the possibility of reducing the glass mass (sample, SiO_2 and flux) relative to the Ni mass was undertaken. The same sample size (10 g) was maintained, as the noble metals are not homogeneously distributed in their host rocks and ores (Hoffman *et al.*, 1978; Barnes *et al.*, 1985), and large sample sizes are required to obtain representative analyses without increasing the detection limits.

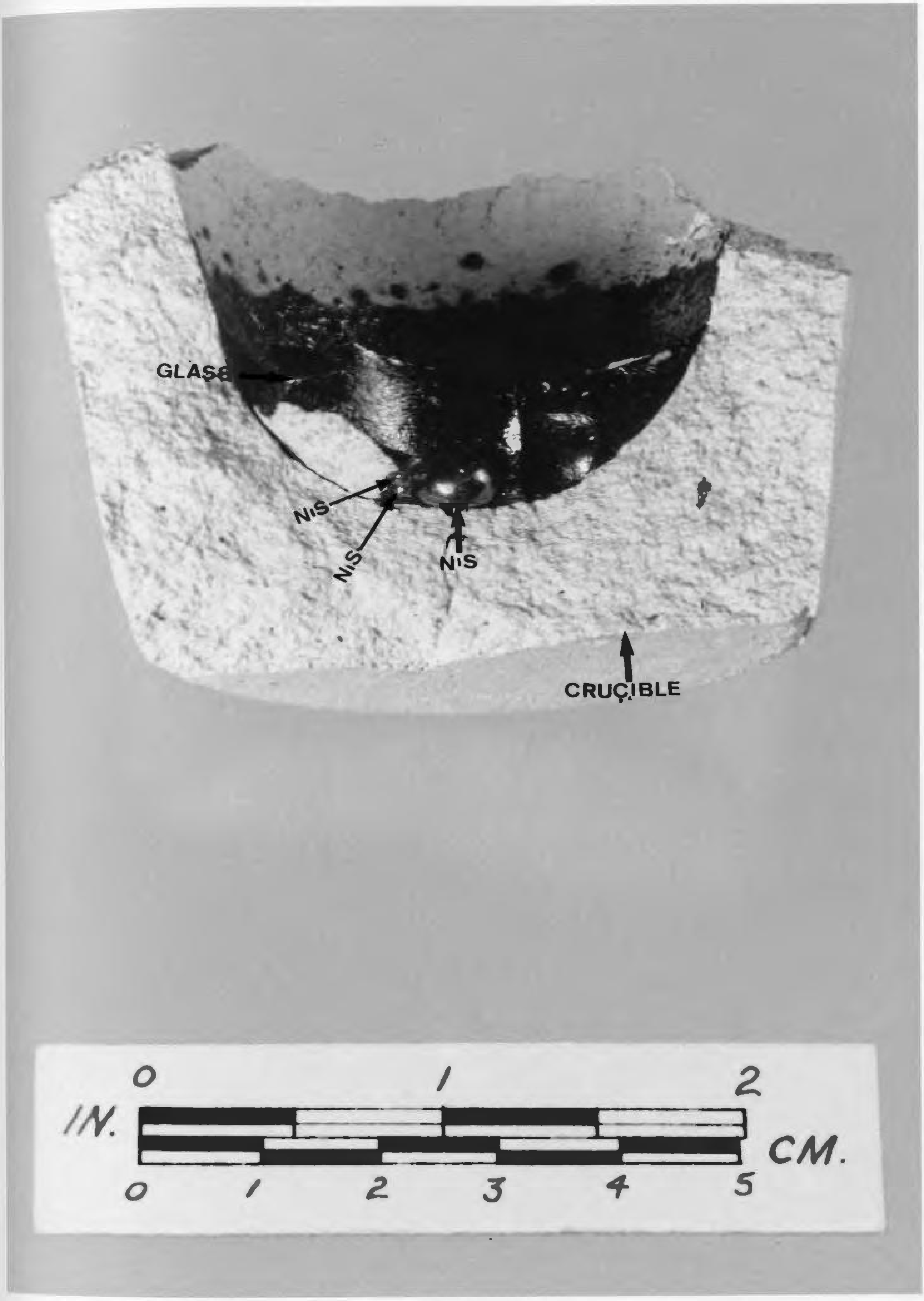
Based on a 5 g collector mass recipe, the amounts of Na_2CO_3 and $Na_2B_4O_7$ corresponding to the individual collector masses were calculated (Table 4.5). The calculated flux compositions relative to Ni masses of 2.0 g, 1.0 g and 0.5 g are lower than the flux-to-sample ratio of 1 to 1, which is the optimum ratio for a fluid slag formation (Robert *et al.*, 1971). To test these limits of flux to sample ratios, the calculated flux composition for a Ni mass of 3.3 g was used in the following experiment. To a 10 g sample was added 4.42 g Na_2CO_3, 8.91 g $Na_2B_4O_7$, 1 g Ni, 0.66 g S and 5 g SiO_2. The NiS formed was found dispersed in the silicate phase and very difficult to retrieve (Figure 4.6). This can be attributed to the slag's viscosity, which was higher, most likely due to the smaller amount of Na_2CO_3 used.

The reduction of the glass mass relative to Ni mass, to enhance recovery is not practicable, due to poor separation of the sulphide and silicate phases.

Table 4.5. Flux weight proposed for increased recovery of the PGE's. All masses are in grams.

Ni	S	Na_2CO_3	$Na_2B_4O_7$	SiO_2	Sample size
5.0	3.00	6.70	13.50	5	10
3.3	2.00	4.42	8.91	5	10
2.0	1.22	2.68	5.40	5	10
1.0	0.66	1.34	2.70	5	10
0.5	0.33	0.67	1.35	5	10

Figure 4.6. Cross section of a broken crucible showing dispersed NiS beads in the glass. This is attributed to the reduction in the fusibility and viscosity of the glass, and solubility of CO_2 in the glass. Low fusibility and viscosity, and high CO_2 solubility are recommended for better phase separation. The significant reduction of the glass mass to enhance recovery is not practicable, due to poor NiS bead recovery.


GLASS
NiS
NiS
NiS
CRUCIBLE
0
1
2
IN.
CM.
0
1
2
3
4
5

4.2. THE PARTITIONING OF THE PRECIOUS METALS AND NICKEL BETWEEN SULPHIDE AND SILICATE (BORAX GLASS) MELTS.

4.2.1. INTRODUCTION.

The values of partition coefficient (D) for PGE's between sulphide liquids and silicate melts are poorly known, although they are considered to be relatively high (Cambell *et al.*,1984 ; Stone *et al.*, 1990; Peach *et al.*, 1990; Fleet *et al.*, 1991). Experimental determination of D values by analysis of the PGE contents of sulphide and the silicate melt has proved difficult, due to the difficulty in separating the two phases and most importantly the analytical difficulty of determining the very low PGE's contents, in the silicate glass phase.

D values for PGE's have been inferred from PGE and Au contents of magmatic sulphides and coexisting silicates (Naldrett *et al.*, 1980; Sharpe, 1982; Barnes *et al.*, 1985). These values are uncertain because of the assumptions inherent in the modelling.

The following study was intended to directly measure D, by analyzing both the glass and NiS phases, compare these values to the modelled values, and to investigate relationships between mass of collector, PGE recovery, D, and PGE's concentrations in the sample. The D values were determined by the analysis of the PGE and Au contents of the sulphide and silicate (borax glass) melts produced by fusing a rock powder and a flux at

1050° C for 1.25 hours. Note that the NiS fire assay method is based on the assumption that D's are very large.

The partition coefficients of Ni, Cu, and Cr were also determined by XRF analysis of the silicate glass and the NiS bead. The NiS bead was not analyzed directly, but the concentrations were calculated by difference between the quantities used and that found in the glass.

4.2.2. EXPERIMENTAL PROCEDURES.

4.2.2.1. REAGENTS.

The materials used were described previously in Section 4.1.2.

The Pt ore grade (SARM-7) and the low ppb level (BF-4) samples were again used.

4.2.2.2. INSTRUMENTATION AND DATA REDUCTION.

The major and trace element compositions were obtained using an ARL 8400$^+$ X-ray fluorescence sequential spectrometer with a 75 KV generator. To maximize performance of the instrument all determinations were carried out at 3 KvA (KW). The instrument routinely analyses a suite of elements using no matrix, Lachance-Traill matrix and Compton matrix corrections (Longerich, unpubl.) for the light, intermediate and heavy elements.

No corrections were applied for the light elements Na to Cl, and thus they are semi-quantitative. The data acquisition time for these light analytes varied from a low of 6 seconds for Al, Si, P, S, and Cl, to a high of 10 seconds for the two light, less sensitive major elements Na and Mg.

The Lachance-Traill matrix correction was applied to the set K to Fe; including Ba and Ce, with data acquisition time of 4 seconds. The compton matrix correction was used for Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Pb, Th and U. A data acquisition time of 100 seconds is used for Rb, Y, and Nb, and 20 seconds for most of the other elements (Ni, Cu, Zn, Th, Pb and U).

4.2.2.3. ANALYSIS OF THE GLASS AND IT'S COEXITING SULPHIDE FOR THE PGE AND Au.

The Pt ore grade SARM-7 and the komatiite BF-4 were fused using 1 g Ni as collector weight for the direct determination of partition coefficient of PGE. To analyze the silicate for the PGE and Au, the HF-aqua regia dissolution procedure of Fryer and Kerrich (1978) was followed. Following conversion to chlorides, by successive evaporations with HCl. The major and trace elements of the glass were also determined using XRF/pressed pellet method.

(1). An empty clay crucible was weighed and placed in a preheated furnace (1050° C). The crucible was ignited for 1 hour, cooled and weighed.

(2). The ignition was repeated until a constant weight was obtained.

(3). 10 g of sample, 1 g Ni, 0.66 g S, 13.5 g $Na_2B_4O_7$, 6.7 g Na_2CO_3 and 5 g SiO_2 were weighed into the ignited crucible and mixed thoroughly with a spatula. The weight of the crucible and contents were recorded.

(4). The mixture was fused in a preheated furnace at 1050° C for 1.25 hours. The crucible was removed and allowed to cool. The weight of the crucible and its contents was again recorded.

(5). The crucible was carefully broken, the NiS bead and the borax glass were separated and both weighed.

(6). The Jackson *et al.*(1990) method was then followed to determine the PGE and Au concentrations in the NiS bead.

(7). The glass was optically checked for sulphide inclusions, and hand ground to -100 mesh using a porcelain mortar and pestle. The mortar and pestle were thoroughly cleaned with methanol between samples.

(8). The major and trace element composition of the silicate glass was determined using XRF. (Described in section 4.2.2.3).

(9). Determination of the PGE's and Au in the glass was performed using a modification of the procedure of Fryer and Kerrich (1978) as follows.

i. 5 g of glass powder was weighed into a 150 mL Teflon beaker and 15 ml of concentrated HF was added, thoroughly stirred and covered with Teflon lid.

ii. The next day, 40 mL aqua regia (3 volumes of HCL and 1 volume of HNO_3) was added to the mixture, the Teflon beaker was covered with a Teflon cover and slowly digested on a hot plate ($\leq 100°$ C). The solution was slowly evaporated to dryness with occasional agitation.

iii. An additional 40 mL aqua regia was added, and evaporation to dryness was repeated.

iv. 15 mL concentrated HCl was added, and the solution was evaporated to dryness. The addition of HCl and evaporation to dryness was repeated three times.

v. The residue was dissolved with 20 mL HCl, 30 mL nanopure H_2O was added, and the solution heated on a hot plate.

vi. The solution was then transferred into a 1000 mL pyrex beaker, and the Jackson *et al.* (1990) procedure for the Te coprecipitation of the PGE's was followed to concentrate and isolate the PGE's and allow the PGE and Au concentrations in the glass to be subsequently measured by ICP-MS.

4.2.2.4. PREPARATION OF XRF PRESSED PELLETS FOR MAJOR AND TRACE ELEMENTS DETERMINATION.

1. 5 g of sample powder was weighed into a clean bottle and 0.7 g of sieved phenolic resin (as a binder) was added.
2. Two ball bearings were added and the bottle was closed. The bottle was swirled gently to initially mix the powder.
3. The mixture in the bottle was rolled for 5 minutes. The ball bearings were removed, and the powder was stirred with a spatula.
4. The mixed powder was transferred into a pellet press and pressed for 5 seconds at 20 ton/in^2.
5. The pressed pellet was then baked in an oven at 200° C for 15 minutes. The baked pellet was allowed to cool and then labelled on the bottom side.

4.2.3. RESULTS AND DISCUSSION.

In each run, data from a set of 10 reference materials (AGV-1, BCR-1, BHVO-1, DNC-1, GSP-1, MP-1, PACS-1, SiO_2, SY-2, and SY-3) were used for the calibration and to serve as quality control (Table 4.6). The reference material, SY-3 was used as a calibration standard for Ce and Nb, PACS-1 for

S, Cl and As, BHVO-1 for MgO, Sc, TiO_2, V, Cr, Ni, Cu, and Zn; and SY-2 for the other elements. There is good agreement between the values obtained in this work and the accepted values for the reference materials. The precision of the reference materials measurements is reasonably good (Table 4.7).

The major and trace element compositions of the experimental glasses are shown in Table 4.8. The sample numbers G1, G2, G3, G4, and G5 correspond to the individual glasses formed from the BF-4 experiments, and SG1, SG2, SG3 and SG4 those from the SARM-7 experiments. The sample labelled G10 is a reagent blank using SiO_2 in place of the sample. Note the clay crucible was weighed before and after fusion, in order to calculate the glass mass. Quantitative separation of the glass from the crucible is not practicable as some of the glass invariably adheres to the crucible after fusion.

Table 4.6. Accuracy of XRF analysis as shown by the measured values of the reference materials by this work compared to Govindaraju (1989). Major elements are in %, and the trace elements are in ppm.

	BCR-1	BCR-1	BHVO-1	BHVO-1	MP-1	MP-1	SY-2	SY-2	SY-3	SY-3	AGV-1	AGV-1
Element	This work	Govin.	This work	Govin.	This work	Govin.	This work	Govin.	This work	Govin.	This work	Govin.
SiO2	55.77%	54.06%	47.94%	49.94%	41.94%	41.50%	60.05%	60.05%	61.63%	59.62%	58.95%	58.79%
Na2O	3.46%	3.27%	2.50%	2.26%	3.91%	1.00%	4.31%	4.31%	5.20%	4.31%	3.97%	4.26%
MgO	2.74%	3.48%	6.75%	7.23%	1.69%	7.00%	2.69%	2.69%	2.98%	2.67%	1.31%	1.53%
Al2O3	13.84%	13.64%	13.80%	13.80%	8.92%	6.35%	12.04%	12.04%	12.49%	11.75%	16.03%	17.14%
K2O	1.80%	1.69%	0.52%	0.52%	0.86%	0.12%	4.44%	4.44%	4.51%	4.23%	2.85%	2.91%
CaO	6.95%	6.95%	11.39%	11.40%	3.96%	4.70%	7.96%	7.96%	8.35%	8.26%	4.98%	4.94%
P2O5	0.37%	0.36%	0.22%	0.27%	0.12%	0.00%	0.43%	0.43%	0.51%	0.54%	0.44%	0.49%
TiO2	2.21%	2.24%	2.71%	2.71%	0.42%	0.12%	0.12%	0.14%	0.15%	0.15%	0.98%	1.05%
MnO	0.18%	0.18%	0.18%	0.17%	0.06%	0.06%	0.32%	0.32%	0.32%	0.32%	0.10%	0.09%
Fe2O3	13.10%	13.41%	12.31%	12.23%	7.41%	8.12%	6.31%	6.31%	6.31%	6.49%	6.76%	6.76%
S	815	410	527	102	48745	118000	562	160	1680	510	479	26
Cl	35	59	76	92	12203	155	898	140	4876	150	638	119
Sc	33	33	32	32	10	0	8	7	4	7	16	12
V	408	407	317	317	82	0	50	50	19	50	118	121
Cr	13	16	289	289	62	0	5	11	13	11	7	10
Ni	12	13	121	121	29	0	7	9.9	16	11	18	16
Cu	22	19	136	136	18411	21500	3	5.2	ND	17	61	60
Zn	160	129.5	105	105	159261	163000	251	248	296	248	87	88
Ga	23	22	21	21	209	0	29	27	29	27	ND	20
As	3	0.7	ND	0.4	7898	7900	16	17.3	9	18.8		0.9
Rb	50.0	47	9.1	11	33.7	0	222.0	217	222.2	206	69.4	67.3
Sr	333.2	330	390.3	403	136.1	0	2[illegible]5.0	271	310.3	302	662	662
Y	35.2	38	25.3	27	155.8	0	125.0	128	777.2	718	18.3	20
Zr	190.4	190	170.4	179	128.1	0	268.0	280	318.9	320	235	227
Nb	12.7	14	18.7	19	31.4	0	30.3	29	140.0	148	14.7	15
Ba	707	681	132	139	327	0	447	460	428	450	1196	1226
Ce	64	54	46	39	302	0	187	175	2230	2230	103	67
Pb	17	14	3	3	18931	19300	94	85	150	133	42	36
Th	8	6	1	1	84	0	390	379	1003	1003	9	7
U	3	2	1	0	6	0	294	284	668	650	2	2

Number of determination = 4.

Table 4.7. Precision of XRF analysis of the reference materials by this work.

	BCR-1		BHVO-1		PACS-1		SY-2		SY-3	
	STD	RSD	STD	RSD	STD	RSD	STD	RSD	STD	RSD
Na2O	0.00%	0.12%	0.01%	0.4%	0.01%	0.2%	0.01%	0.2%	0.01%	0.3%
MgO	0.01%	0.45%	0.02%	0.3%	0.01%	0.2%	0.00%	0.2%	0.00%	0.1%
Al2O3	0.00%	0.02%	0.02%	0.2%	0.00%	0.0%	0.02%	0.2%	0.01%	0.1%
SiO2	0.10%	0.18%	0.06%	0.1%	0.08%	0.1%	0.08%	0.1%	0.12%	0.2%
P2O5	0.00%	0.76%	0.00%	0.9%	0.00%	1.6%	0.00%	0.9%	0.00%	0.5%
S	16.2	2.0%	13.1	2.5%	46.1	0.3%	10.2	1.8%	34.3	2.0%
Cl	13.7	4.1%	14.8	2.5%	82.1	0.3%	12.1	1.3%	49.3	1.0%
K2O	0.00%	0.28%	0.00%	0.5%	0.00%	0.2%	0.01%	0.1%	0.01%	0.3%
CaO	0.01%	0.18%	0.02%	0.2%	0.01%	0.2%	0.01%	0.1%	0.02%	0.2%
Sc	2.66	8.02%	4.03	12.6%	1.84	10.9%	0.98	12.5%	0.43	11.6%
TiO2	0.01%	0.26%	0.01%	0.4%	0.01%	0.8%	0.00%	1.4%	0.00%	1.6%
V	4.08	1.00%	3.30	1.0%	3.19	2.1%	1.97	3.9%	1.02	5.5%
Cr	1.97	14.63%	4.56	1.6%	2.36	2.0%	1.74	33.8%	4.64	35.8%
MnO	0.00%	0.49%	0.00%	1.3%	0.00%	0.3%	0.00%	0.5%	0.00%	0.4%
Fe2O3	0.02%	0.18%	0.02%	0.1%	0.02%	0.2%	0.01%	0.1%	0.02%	0.4%
Ni	2.00	6.72%	1.34	1.1%	0.34	0.8%	3.10	44.6%	1.83	11.3%
Cu	0.84	3.84%	0.70	0.5%	0.83	0.2%	0.95	33.7%	0.81	-23.4%
Zn	1.37	0.86%	2.17	2.1%	1.49	0.2%	0.74	0.3%	2.32	0.8%
Ga	0.55	2.40%	0.46	2.1%	0.15	1.0%	0.80	2.7%	1.12	3.9%
As	1.99	58%	3.33		4.20	2.0%	4.28	25.9%	0.96	10.5%
Rb	1.11	2.22%	0.16	1.7%	0.41	0.9%	0.41	0.2%	0.21	0.1%
Sr	0.97	0.29%	0.84	0.2%	0.67	0.3%	0.52	0.2%	1.00	0.3%
Y	0.24	0.68%	0.13	0.5%	0.13	0.8%	0.47	0.4%	0.83	0.1%
Zr	0.53	0.28%	0.51	0.3%	0.66	0.5%	0.91	0.3%	0.61	0.2%
Nb	0.04	0.32%	0.15	0.8%	0.09	1.1%	0.05	0.2%	0.18	0.1%
Ba	10.1	1.4%	8.1	6.1%	21.8	3.3%	6.45	1.4%	10.12	2.4%
Ce	13.7	21.3%	15.3	33.0%	4.11	5.5%	17.9	9.6%	37.2	1.7%
Pb	1.60	9.2%	0.42	12.9%	2.37	0.6%	0.89	0.9%	0.80	0.5%
Th	1.45	18.3%	0.94	75.5%	1.54		2.01	0.5%	1.86	0.2%
U	1.26	42.5%	0.61	63.8%	0.09		1.11	0.4%	0.71	0.1%

Table 4.8. Major and trace element compositions of the glasses formed from BF-4 and SARM-7. 1 g of Ni and 0.66 g S were added as collector. G1-G5 are the glasses formed from BF-4, and SG1 - SG4 from SARM-7. B_4O_6 was calculated by difference. * excess Na_2CO_3 added.

	G1	G2	G3	G4*	G5	SG1	SG2	SG3	SG4	G10
SiO_2	34.58%	32.47%	31.46%	28.77%	33.91%	37.86%	37.86%	37.33%	36.64%	48.42%
Na_2O	23.65%	21.67%	21.17%	31.94%	24.09%	23.51%	23.09%	22.82%	22.46%	28.66%
MgO	11.71%	10.79%	10.53%	8.63%	11.39%	7.00%	7.02%	6.87%	6.72%	<0.01%
Al_2O_3	2.02%	1.75%	1.65%	1.88%	1.94%	2.89%	2.91%	2.84%	2.79%	1.11%
P_2O_5	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%
K_2O	0.12%	0.10%	0.10%	0.12%	0.11%	0.13%	0.14%	0.14%	0.13%	0.12%
CaO	2.07%	2.02%	2.01%	1.72%	2.07%	2.43%	2.42%	2.44%	2.40%	0.12%
TiO_2	0.15%	0.14%	0.14%	0.16%	0.15%	0.14%	0.14%	0.14%	0.14%	0.07%
MnO	0.08%	0.08%	0.08%	0.07%	0.08%	0.11%	0.11%	0.10%	0.11%	0.00%
Fe_2O_3	5.52%	5.66%	5.72%	4.77%	5.55%	6.44%	6.41%	6.44%	6.43%	0.15%
B_4O_6	17.54%	23.38%	25.14%	20.06%	18.73%	17.40%	17.98%	19.04%	20.07%	
S	1.41%	1.31%	1.42%	1.20%	1.28%	1.47%	1.33%	1.33%	1.53%	1.42%
V	59	63	62	59	60	82	80	82	78	9
Cr	1092	1113	1083	898	1061	2874	2836	2816	2839	96
Sc	11	13	9	8	8	11	19	15	12	< 7

Ni	10079	4844	4407	5545	5661	2438	2676	2025	2600	8800
Cu	25	14	13	13	13	30	29	24	27	11
Zn	25	20	21	19	20	34	32	33	32	2
Ga	4	3	3	4	3	3	3	3	5	< 2
As	< 13	< 13	< 13	< 13	< 13	< 13	< 13	< 13	< 13	< 13
Rb	2.1	1.6	1.7	2.5	1.7	3.2	3.6	3.1	3.2	2.2
Sr	23	23	22	33	23	54	56	56	55	22
Y	3.8	3.2	3.2	3.8	3.6	2.8	2.8	3.2	3.2	2.1
Zr	31	31	30	33	31	34	35	34	35	6
Nb	1.0	0.5	0.8	1.3	1.1	1.0	1.3	1.0	1.1	1.0
Ba	15	6	9	14	8	32	35	46	35	2
Ce	12	14	16	< 13	0	23	11	21	18	< 13
Pb	3	2	0	3	3	4	5	5	6	2
Th	1	< 3	2	< 3	1	1	0	1	0	2
U	2	1	< 4	1	2	1	1	3	2	2

The results indicate similar major and trace compositions for both silicate glasses. However, the Ni concentration found in the BF-4 glasses was two fold higher than that found in the SARM-7 glasses. Table 4.9 lists the Ni and S content of the glasses and their corresponding contents in the sulphide; found by difference and the masses of the phases.

The Ni concentration in the BF-4 glass was 0.51% (± 0.05%) with a relative standard deviation (RSD) of 10% compared to 0.24% (± 0.03%) with a RSD of 10% in SARM-7 glass and 0.88% in the blank. The Ni concentration in the NiS beads was calculated by difference, assuming no loss of Ni (Table 4.10). The partition coefficient of Ni was 149 ± 15 for BF-4 and 301 ± 34 for SARM-7, with RSD of 9.79 % and 11% respectively (Table 4.10). For comparison the D found for the blank was 84. The D is defined as $[Ni]_{sulphide}/[Ni]_{silicate}$ as is customary in the geological literature. The partitioning of Cu followed a similar trend as Ni, while the distribution of Cr was approximately the same in both samples (Table 4.11).

The glass was found to consistently contain 1.4% (± 0.09%) by weight of sulphur, which is independent of the Ni content.

The analyses of the sulphide and glass for the PGE's and Au are reported in Tables 4.12. The variability in PGE contents of the silicate reflects analytical uncertainty arising from the low concentrations in the glass; some of which were close to the detection limit.

Table 4.9. Product compositions, and weight of sulphide and silicate. 1 g of Ni and 0.66 g S were added as collector. G1 - G5 are the glasses formed from BF-4, and SG1 - SG4 from SARM-7. G10 is the glass from the reagent blank (SiO_2).

	Sample Ni	Sample S	Mixture Ni (g)	Mixture S (g)	Sulphide wt.(g)	Glass wt.(g)	Ni conc in Glass	S conc in Glass
G1	0.20%	0.04%	1.02	0.663	0.99	26.85	1.01%*	1.41%
G2	0.20%	0.04%	1.02	0.663	1.18	26.55	0.48%	1.31%
G3	0.20%	0.04%	1.02	0.663	1.21	26.55	0.44%	1.42%
G4	0.20%	0.04%	1.02	0.663	1.12	30.59	0.55%	1.20%
G5	0.20%	0.04%	1.02	0.663	1.15	27.07	0.56%	1.28%
SG1	0.22%	0.55%	1.02	0.715	1.32	27.04	0.24%	1.48%
SG2	0.22%	0.55%	1.02	0.715	1.29	27.07	0.26%	1.33%
SG3	0.22%	0.55%	1.02	0.715	1.33	26.98	0.20%	1.33%
SG4	0.22%	0.55%	1.02	0.715	1.32	27.04	0.26%	1.52%
G10	0.00%	0.00%	1.00	0.66	1.08	22.28	0.88%	1.42%

* Not included in the statistical analysis.

Table 4.10. Summary of experimental Ni partition coefficients for sulphide/silicate at 1050° C.

Sample Name	Total weight of Ni in glass (g)	Total weight of Ni in sulphide (g)	Conc. of Ni in Sulphide$^+$	Partition coefficient
G1	0.21	0.75	75.69%	75
G2	0.13	0.89	75.54%	156
G3	0.12	0.90	74.63%	169
G4	0.17	0.85	75.93%	137
G5	0.15	0.87	75.37%	133
SG1	0.07	0.95	72.28%	296
SG2	0.07	0.95	73.45%	274
SG3	0.05	0.97	72.58%	258
SG4	0.07	0.95	71.95%	277
G10	0.20	0.80	74.07%	84

1 g of Ni and 0.66 g S were added as collector. G1 - G5 are the glasses formed from BF-4, and SG1 - SG4 from SARM-7. G10 is the reagent blank using SiO_2 in place of the sample. + calculated by difference assuming no loss of Ni.

Table 4.11. Summary of experimental partition coefficients of Cu, and Cr at 1050° C.

Sample Name	Conc. of Cu in Glass determined	Conc. of Cu in Sulphide calculated	Conc. of Cr in Glass determined	Conc. of Cr in Sulphide calculated	Partition coefficient of Cu	Partition coefficient of Cr
G1	25	9	1092	1794	0.4	1.64
G2	14	20	1113	1773	1.6	1.59
G3	13	21	1083	1803	1.6	1.66
G4	13	21	989	1988	1.6	2.21
G5	13	21	1061	1825	1.6	1.72
SG1	30	846	2874	3166	28.2	1.10
SG2	29	847	2816	3224	29.2	1.14
SG3	24	852	2839	3201	35.5	1.13
SG4	27	849	2886	3154	31.4	1.09
BF-4	34*		2886*			
SARM-7	876*		6040*			

All concentrations are in ppm. The concentrations in sulphide was found by difference between rock and the glass. * = Rock sample concentration.

1 g of Ni and 0.66 g S were added as collector. G1-G5 are the glasses formed from BF-4, and SG1 - SG4 from SARM-7.

Table 4.12. Concentrations of PGE's and Au in the Sulphide (S) and the Glass (G) phases. All concentrations are in ppb. The < indicates concentration below the reagent blank.

	Ru	Rh	Pd	Os	Ir	Pt	Au
BF-4 G1	0.54	0.18	1.22	< 0.018	<0.006	0.87	0.06
BF-4 S1	21.30	6.67	53.69	14.74	13.79	50.43	9.55
BF-4 G2	0.98	0.64	0.97	< 0.018	0.06	3.13	<0.12
BF-4 S2	18.30	5.38	40.45	15.06	13.35	39.47	7.35
BF-4 G3	0.78	<0.002	1.07	< 0.018	0.04	<0.015	<0.12
BF-4 S3	21.84	6.08	45.01	12.64	13.62	42.36	9.44
BF-4 G4	0.56	0.45	0.68	< 0.018	0.04	0.36	<0.12
BF-4 S4	27.39	7.50	59.28	14.71	13.83	47.03	11.22
BF-4 S5	17.90	4.85	40.83	19.13	13.83	37.60	10.07
BF-4 G6	0.60	0.29	0.13	<0.018	0.08	0.52	<0.12
BF-4 S6	25.33	6.26	51.02	15.91	13.28	43.45	9.50
BF-4 G7	0.45	0.49	<0.019	0.17	0.03	3.47	<0.12
BF-4 S7	22.88	6.33	49.27	13.02	13.85	37.34	6.71
BF-4 G8	0.59	0.16	<0.019	<0.018	0.16	1.79	<0.12

BF-4 S8	130.98*	5.22	42.62	14.69	13.61	30.16	8.31
BF-4 G9	0.42	0.05	<0.019	<0.018	0.12	<0.02	<0.12
BF-4 S9	23.58	6.21	46.19	14.82	14.47	38.63	8.20
SARM-7 G1	4.60	3.40	13.9	0.08	0.40	31.70	2.80
SARM-7 N1	2415.5	1894	12213	97.25	477.90	27572	1431
SARM-7 G2	2.80	1.20	8.4	0.07	0.20	14.20	0.30
SARM-7 N2	1791.5	2071	14054	120.80	340.50	27679	1872
SARM-7 G3	0.90	0.20	1.1	0.02	0.10	11.40	2.50
SARM-7 N3	2515.9	1749	11818	157.60	515.30	28884	2400
SARM-7 G4	4.90	3.30	17.0	< 0.018	0.40	32.90	3.70
SARM-7	2306.6	1810	11743	102.30	493.20	27860	1500
Limit of detection	0.017	0.002	0.019	0.018	0.006	0.015	0.12

G = Glass, and S = Sulphide phase (NiS). The limit of detection (LD) for PGE's was obtained using a calibration reference blank solution made up of a mixture of 0.3 M HCl and 0.4M HNO_3 (1:1).

The calculated partition coefficients of the PGE's and Au are presented in Table 4.13. The partition coefficient values listed with the > sign indicates that the concentration in the glass was below the detection limit. The partition coefficients obtained using SARM-7 were significantly higher than those obtained for BF-4. Sharpe (1982) reported similar D values derived from the Bushveld complex. The D values reported for the UG-2 chromitiite (high PGE contents) were higher than that for Merensky reef. Sharpe reports D values of 4000 (Pd), 3900 (Pt), 6600 (Ir) and 480 (Au) for the Merensky reef parental liquid, and 56,000 (Pd), 21,000 (Pt), 174,000 (Ir) and 860 (Au) for the UG-2 chromitiite.

The computed partition coefficients of the PGE's obtained from this study are not significantly different from those when the model equation was used (Table 4.14). The uncertainty in D values obtained are comparable to the uncertainty in values reported by other workers for similar systems (Table 4.15). Stone *et al.* (1990) have reported sulphide liquid-silicate melt partition coefficients at 1200° C for the PGE's as (90,000 ± 70,000) for Pd, (100,000 ± 70,000) for Ir, (9000 ± 6000) for Pt and (1000 ± 900) for Au. Peach *et al.* (1990) have recorded partition coefficient values of 15,000 - 19,000 for Au, 12,000 - 16,000 for Ir and a range of 500-900 for Ni as deduced from MORB. The significance of the variability in the D's for the PGE's is presently unclear.

Table 4.13. The D values determined from the analysis of the NiS and coexisting glass.

	Ru	Rh	Pd	Os	Ir	Pt	Au
BF-4							
1	40	38	44	> 500	4508	58	169
2	19	9	41	> 500	207	12	>160
3	28	> 67	42	> 500	361	> 130	>160
4	49	17	87	472	333	130	>160
6	42	22	393	> 500	159	84	16
7	51	13	> 80	77	398	11	10
8	222*	32	> 80	132	88	17	> 160
9	56	130	> 80	> 500	120	> 130	> 160
SARM-7							
1	531	561	886	1125	1218	869	508
2	634	1704	1670	1682	2142	1951	6370
3	2876	9659	10626	7046	8304	2531	953
4	4716	5535	6892	>1000	1391	847	406

The D values quoted as >, indicate that the concentration of PGE's in the glass was less than the detection limit. * Not included in the average D calculation.

Table 4.14. The D values determined from the analysis of the NiS and glass, and those derived from the Model (Section 4.1.4.1).

	SARM-7 determined	BF-4 determined	BF-4 Model
Ru	2189 ± 1734	41 ± 12	63
Rh	4365 ± 3569	42 ± 40	67
Pd	5019 ± 3976	100 ± 120	86
Os	3284 ± 2669	430 ± 220	> 283
Ir	3284 ± 2930	770 ± 140	> 999
Pt	1550 ± 721	64 ± 41	156
Au	2059 ± 2497	> 160	1150
Ni	300 ± 30	150 ± 20	
Cu	31 ± 3	1.6 ± 0	
Cr	1.1 ± 0	1.7 ± 0	

Number of determinations = 4 for SARM-7, 8 for BF-4 (except for Ni, Cu and Cr, where N = 5). BF-4 Model value = the reciprocal of the slope of the Model equation derived in section 4.1.4.1. for the PGE's and Au.

Table 4.15. The D values with their uncertainties from this study compared to Stone *et al.* (1990), and Peach *et al.* (1990).

	Pt ore grade SARM-7	BF-4 determined	BF-4 Model	Stone *et al.*, 1990	Peach *et al.*, 1990
Ru	2189 ± 1734	41 ± 12	63		
Rh	4365 ± 3569	42 ± 38	67		
Pd	5019 ± 3976	105 ± 120	86	9 (±7) x10^4	>23,400
Os	3264 ± 2669	425 ± 220	> 283		
Ir	3264 ± 2930	772 ± 148	> 999	1 (±0.7) x10^5	1.2-1.6 x10^4
Pt	1550 ± 721	82 ± 95	156	9 (±6) x10^3	>2400
Au	2059 ± 2497	>160	1150	1 (±0.9) x10^3	1.5 - 1.9 x10^4

BF-4 Model = the reciprocal of the slope of the Model equation derived in section 4.1.4.1. for the PGE's and Au.

The partitioning of the PGE's and Au between the NiS and the glass, translated as percentage extraction (Table 4.16), shows that 99% of the PGE's and Au were in the sulphide phase for the ore sample, SARM-7 and > 90 % of Os, Ir and Au were extracted into the sulphide for the low level sample, BF-4. About 60% to 75% of Ru, Rh, Pt and Pd were extracted into the sulphide phase for the low level sample. The best estimated of PGE's and Au concentrations in BF-4 from this experiment are listed in Table 4.17. (The best estimate = $[PGE's]_{sulphide} + [PGE's]_{glass}$).

This study indicates that loss of precious metals to the silicate melt is negligible for the sample with high PGE's content. Recovery of Ir, Os and Au in the low level sample BF-4 is also good. Jackson *et al.* (1990); and Hoffman *et al.* (1978) have reported similar PGE recovery for SARM-7 using a larger collector mass. Even though, there was not 100% recovery of Ru, Rh, Pd and Pt from BF-4, when 1 g collector mass of Ni was used, the precision obtained using this collector mass was very good for such low PGE's contents (Table 4.17). Precision for all the PGE's and Au was better than 15% RSD (N = 9, except Ru , N = 8). The consistency of recoveries substantiates the validity of the measured and calculated D's, and suggests that reproducible fractionation can be obtained using the NiS fire assay separations.

Table 4.16. Percentage of PGE's and Au in the sulphide phase in both SARM-7 and BF-4.

	SARM-7, % of precious metals in the sulphide phase	BF-4, % of precious metals in the sulphide phase
Ru	99.4% ± 0.3%	57% ± 8%
Rh	99.6% ± 0.3%	71% ± 8%
Pd	99.7% ± 0.2%	73% ± 8%
Os	99.9% ± 0.2%	97% ± 11%
Ir	99.8% ± 0.1%	91% ± 3%
Pt	99.7% ± 0.2%	73% ± 8%
Au	99.4% ± 0.4%	90% ± 10%

Table 4.17. Concentration of PGE's and Au (ppb) in BF-4 and precision of measurements for 1 g and 5 g Ni mass.

	1 g Ni		5 g Ni		
	Mean	RSD	Mean	RSD	Best estimate*
Ru	2.5 ± 0.3	14%	3.2 ± 0.3	10%	4.49 ± 0.59
Rh	0.68 ± 0.09	13%	0.76 ± 0.05	7%	0.98 ± 0.08
Pd	5.0 ± 0.7	14%	6.24 ± 0.2	3%	7.46 ± 1.67
Os	1.44 ± 0.24	16%	1.05 ± 0.07	6%	1.78 ± 0.27
Ir	1.35 ± 0.06	4%	1.31 ± 0.26	19%	1.78 ± 0.19
Pt	3.9 ± 0.5	14%	4.7 ± 0.5	11%	6.37 ± 1.30
Au	1.23 ± 0.16	14%	1.31 ± 0.28	21%	1.17 ± 0.17

* = $[\text{PGE's}]_{\text{sulphide}}$ + $[\text{PGE's}]_{\text{glass}}$ resulted from the direct analysis of the glass and it's coexisting sulphide. The collector weight used is 1 g Ni.

4.3. DETERMINATION OF THE MINIMUM VOLUME OF HCl TO DISSOLVE A NiS BEAD IN A CLOSED TEFLON VESSEL (TEFLON TUBE).

4.3.1. INTRODUCTION.

In all of the reported NiS fire assay works (Jackson *et al*; 1990, Date *et al.*, 1987), the dissolution of NiS beads was carried out in open vessels. If the dissolution is carried out in a closed vessel (Kerrich, per. comm., 1991), the loss of precious metals could be minimized due to the higher concentration of H_2S generated from the dissolving NiS being retained in solution, which will suppress the solubility of PGE sulphides. Hence, the Te coprecipitation step might be omitted and the solution centrifuged, or the amount of Te used reduced significantly.

This dissolution procedure (closed vessel) with reduced amount of HCl, could also reduce the reagent blank, and the matrix effect due to aqua regia, which is used to dissolve the PGE-S-Te coprecipitate. This method (closed vessel) would also offer the possibility of using more expensive high purity HCl. The minimum volume of HCl needed to dissolve a 1 g NiS bead in a closed vessel dissolution of the bead was therefore studied.

4.3.2. MATERIALS AND EXPERIMENTAL METHODS.

4.3.2.1. REAGENTS AND MATERIALS.

The reagents used were the same as those used in Section 4.1.

Oak Ridge Teflon centrifuge tube (Nalgene™) size 30 mL (Rochester, NY, U.S.A).

The South African National Institute of Metallurgy (NIM) Pt ore reference material, SARM-7, was used in the following experiments.

4.3.2.2. EXPERIMENTAL PROCEDURE.

This experiment investigates the posssibility of dissolving the NiS bead in a closed vessel with smaller volume of HCl. 10 g of sample was fused with a 1 g Ni as a collector. The minimum volume of HCl needed to dissolve a NiS bead resulting from 1 g Ni collector fusion, in a closed vessel was determined.

(1) A 10 g sample was fused with 1 g Ni, 0.66 g S, 13.5 g $Na_2B_4O_7$, 6.7 g Na_2CO_3 and 5 g SiO_2 at 1050° C for 1.25 hours in a clay crucible.

(2). The NiS beads were transferred into 30 mL Oak Ridge Teflon centrifuge tubes and different volumes of concentrated HCl (12M) were added.

(3). The Teflon tube was then tightly capped, placed in an aluminium block holder and placed on a hot plate (at ≈ 150° C).

(4). Dissolution time for various acid volumes was monitored and recorded.

4.3.3. RESULTS AND DISCUSSION.

Preliminary tests were carried out to determine the amount of concentrated HCl needed to dissolve a 1 g NiS bead in a closed teflon centrifuge tube, and the relationship between dissolution time and HCl volume (Table 4.19). Based on these results, 15 mL of HCl was selected to be used for dissolution of the NiS bead in subsequent experiments, even though it did not have the minimum dissolution time.

What is perhaps more significant analytically, is the reduction of the amount of Ru and Rh contributed by the 15 mL HCl to the reagent blank as compared to 600 mL HCl used by other workers. Note that the HCl added to dissolve the bead constitutes >97% of the total HCl used in the whole procedure.

Table 4.18. Determination of volume of HCl (12M) required to dissolve a 1 g NiS bead in a closed system. Number of determinations = 2.

Weight of NiS Bead (g)	Volume of HCl (mL)	Dissolution Time (days)
1	5	> 3
1	10	2.5
1	15	2.0
1	20	Overnight
1	25	Overnight

4.4. DISSOLUTION OF NiS BEAD IN A CLOSED VESSEL AND REDUCTION OF QUANTITY OF TELLURIUM (AND TIN CHLORIDE) FOR THE COPRECIPITATION OF THE PRECIOUS METALS.

4.4.1. INTRODUCTION.

Several investigators have reported losses of precious metals during the parting of NiS beads in concentrated hydrochloric acid (Dixon *et al.*; 1975, Robert *et al.*; 1975, Agrawal *et al.*; 1964). Palmer *et al.* (1971), using radiotracer techniques, reported losses of Au, Ir, Ru and Os of 1.4%, 1.2%, 2.3% and 4.5% respectively, in dissolving the NiS bead using concentrated HCl. Kuznetsov *et al.* (1974) illustrated that losses of Pt and Pd could reach 5 -15% when the insoluble residue is allowed to remain for a long time in contact with HCl solution after most of the H_2S has evolved. Kallmann *et al.* (1983) examined the effect of prolonged heating of sulphide with HCl, and reported no precious metal lost to the leaching solution, except for Au, even when the solutions were evaporated to incipient crystallization of nickel chloride.

The use of different precipitants to coprecipitate the PGE's from the parted NiS solution has been cited. Fryer and Kerrich (1978) have recorded the use of Te to precipitate the PGE's from HCl solutions. Shazali *et al.* (1987) reported the use of 1 mg of Te to coprecipitate the PGE's and Au from the HCl solution. Recovery by Te precipitation from the filtrate resulting from the dissolution of NiS bead was less than 4% for the all precious metals, except Au; 18% (Shazali *et al.*, 1987). The use of various amounts of Te from 1 mg to 7 mg has been reported.

Generally, PGE sulphides are precipitated by passing H_2S into PGE salt solutions *ie.* from $PtCl^{2-}_4$ and $PtCl^{2-}_6$ are obtained PtS and PtS_2 which are insoluble in concentrated HCl (Cotton and Wilkinson, 1980). Robert *et al.* (1971) and Date *et al.* (1987) recommended bubbling of H_2S through the parted NiS solution before filtration.

The objectives of this present study were to omit or reduce the amount of Te (and $SnCl_2$) used to coprecipitate the PGE's from the parted medium by utilizing the H_2S generated during the dissolution of the NiS bead, and also to replace the filtration step in the Jackson *et al.* (1990) procedure, by centrifugation. These manipulations would have the advantages of reducing the reagent blank and the total dissolved solids in the analytically solution.

A gram of NiS bead was dissolved in a closed 30 mL Oak Ridge Teflon centrifuge tube (Nalgene™), using 15 mL of concentrated HCl. Various quantities of Te solution were used to coprecipitate the dissolved PGE's and Au. The possibility of direct centrifugation to separate the solid (PGE's-S) from the parting medium, and the effect of excess H_2S in the dissolution vessel were also examined.

4.4.2. EXPERIMENTAL PROCEDURES, RESULTS AND DISCUSSIONS.

1. PROCEDURE A.

AIM: To replace the filtration step in the Jackson *et al.* (1990) procedure with centrifugation.

(1). Four 8.9 g NiS beads were prepared, using SARM 7, and labelled herein as beads 1, 2, 3, and 4. A reagent blank was also prepared.

(2). Each bead was broken into pieces by gently hitting with a hammer. (~ size of pieces = 1 g).

(3). 1 g of the broken NiS bead was weighted into a 30 mL Oak Ridge Teflon centrifuge tube (Nalgene™) and 15 mL of concentrated HCl added.

(4). The Teflon tube was tightly capped, placed in an aluminium block holder and placed on a hot plate.

(5). After the dissolution of the NiS bead, the solution was allowed to cool to room temperature. The tube was opened and a volume of 200 ppm Te solution was added (Table A). The solution was diluted with 8 - 10 mL of distilled water and 1 mL of saturated $SnCl_2$ solution was added.

(6). The Teflon tube was capped, the solution boiled for 30 minutes to coagulate the black precipitate formed.

(7). The solution was allowed to cool and then centrifuged. The precipitates formed did not settle. An additional volume of 4 mL of $SnCl_2$ solution was added, the solution boiled, cooled and centrifuged for a longer period of time. Some of the precipitates still did not settle. Hence, the solution was filtered through a Millipore filter system and washed with nanopure water.

(8). The filter paper with the precipitate was returned to the Teflon tube. 5 mL of concentrated HNO_3 and 0.5 mL of concentrated HCl were added, the cap closed and the filter paper and its content were slowly warmed to dissolve.

(9). The solution was allowed to cool to room temperature, transferred to a 50 mL polypropylene bottle (Nalgene™) and diluted to 20 g with nanopure water for analysis.

Table 4.19a. Weight of bead (SARM-7) and quantity of Te used for precipitation of the PGE's. 1 mL Te = 200 μg Te. Trans = wt of broken bead used.

Serial Number	Bead Name	Button wt. (g)	Trans. wt. (g)	Mass of Te (μg)	$SnCl_2$ sol. mL.
A1	Bead-1	8.96	1.02	0	5
A3	Bead-3	8.93	1.04	100	5
A4	Bead-4	8.96	1.00	100	5
A5	Bead-1	8.96	1.00	350	5
A6	Bead-2	8.93	1.00	350	5
A7	Bead-3	8.93	1.04	500	5
A8	Bead-4	8.96	1.02	500	5
A9	Bead-1	8.96	1.02	700	5
A10	Bead-3	8.93	1.02	700	5

RESULTS AND DISCUSSION.

The Te coprecipitation step was performed on SARM-7 (Table 4.19). After the dissolution of the NiS beads, the 30 mL Oak Ridge Teflon centrifuge tubes (Nalgene^{TM}) were not opened and warmed before the Te solution was added. The Te solution was immediately added after the tube was opened and capped again.

The determined PGE and Au concentrations are listed in Table 4.20. The light PGE's values were higher than the certified values for SARM-7, which may be ascribed to mass spectral polyatomic ion interferences due to Ni ($^{61}Ni^{40}Ar^+$, $^{64}Ni^{37}Cl$) and Cu ($^{63}Cu^{40}Ar^+$, and $^{65}Cu^{40}Ar^+$) which were not adequately corrected for. The Ni and Cu are presumably precipitated by the high concentrations of H_2S and remained in the Te coprecipitates.

In summary, centrifugation as a means to separate the precipitates from the parting solution did not work.

2. PROCEDURE B.

The same procedure was followed as in the experiment A, except that 1 mL of $SnCl_2$ solution was used. The filter paper and its contents were dissolved in 1.5 mL of concentrated HNO_3 and 1.0 mL of concentrated HCl. The purpose of this study was to reduce the quantity of Te and $SnCl_2$, while maintaining the filtration step.

Table 4.19b. Weight of bead (SARM-7) and quantity of Te used for precipitation of the PGE's. 1 mL Te = 200 μg Te. Trans = wt of broken bead used.

Serial No.	Bead Name	Button wt. (g)	Trans. (g)	Mass of Te (μg)	$SnCl_2$ sol. mL.
B1	Bead-1	8.96	1.02	100	1
B2	Bead-2	8.93	1.09	300	1
B3	Bead-3	8.93	1.01	500	1
B4	Bead-4	8.96	1.0	700	1
B5	Bead-1	8.96	1.0	0	1
B6	Bead-2	8.93	1.01	100	1
B7	Bead-3	8.93	1.01	300	1
B8	Bead-4	8.96	0.93	500	1
B9	Bead-2/3	8.93	1.16	700	1
B10	Bead-1	8.96	0.56	0	1

In Serial no. B9, 0.65 g of Bead 2 and 0.51 g of Bead 3 were combined.

RESULTS AND DISCUSSION.

Serial numbers B5 and B8 were not analyzed because they were observed to be greenish in colour, possibly due to undissolved NiS (CuS). It was suspected that the high H_2S content inhibited the complete dissolution of the Ni (and Cu) sulphide.

The PGE and Au concentrations measured are presented in Table 4.20. Again, the light PGE's values were higher than the certified PGE's concentrations of SARM-7, attributable to polyatomic ion interferences due to Ni and Cu. In spite of the "abnormal" increase in the light PGE's values, the recovery of PGE's and Au followed the same trend as in the Procedure C (Figure 4.7).

3. PROCEDURE C.

AIM: Study of the effect of opening of the Teflon tube (to release some of the H_2S) before the Te precipitation, and dissolution of the PGE-Te-S coprecipitate with smaller volumes of HNO_3 and HCl.

(1). 10 g sample of SARM-7 was fused with 1 g Ni, 0.66 g S, 13.5 g $Na_2B_4O_7$, 6.7 g Na_2CO_3 and 5 g SiO_2 at 1050° C for 1.25 hours in a clay crucible.

(2). The NiS bead was transferred into 30 mL Oak Ridge Teflon centrifuge tube and 15 mL of concentrated HCl added. The Teflon tube was tightly capped, placed in an aluminium block holder and placed on a hot plate at ≈ 150° C.

(3). After the dissolution of the NiS bead, the Teflon tube was opened and the solution was warmed for about 1 hour. The solution was then allowed to cool until warm. Various volume of 200 ppm Te solution were added (see Table C). The solution was diluted with 8 - 10 mL of nanopure water and 1 mL of SnCl solution were added. The solution was then boiled for 30 minutes to coagulate the precipitate.

(4). The solution was allowed to cool and filtered through a Millipore filter system (Whatman 0.4μ 243m cellulose nitrate membrane filter paper) and washed with nanopure water.

(5). The filter paper was returned to the Teflon tube. 1 mL of concentrated HNO_3 and 0.5 mL of concentrated HCl were added, the cap closed and the filter paper and its contents were slowly warmed to dissolve.

(6). The solution was allowed to cool, transferred to a 50 mL polypropylene bottle and diluted to 20 g with nanopure water.

Table 4.19c. Weight of bead (SARM-7) and quantity of Te used for precipitation of the PGE's. 1 mL Te = 200 μg Te. Trans = wt of bead used.

Serial No.	Button wt. (g)	Trans. (g)	Mass of Te (μg)	$SnCl_2$ sol. mL.
C1	1.10	1.10	0	1
C2	0.93	0.93	100	1
C3	1.04	1.04	300	1
C4	1.10	1.10	500	1
C5	0.96	0.96	700	1
C6	1.02	1.02	300	1
C7	1.02	1.02	0	1
C8	8.65	1.13	100	1
C9	8.65	1.0	300	1
C10	8.65	1.04	700	1

* Serial numbers C8, C9 and C10 were from the same NiS bead, the sample blank prepared in experiment A.

Note: Some of the 1 g pieces of the NiS beads were found to take 3 -4 days to dissolve compared to the 2 days dissolution time period observed in Section 4.3.

RESULTS AND DISCUSSION.

In procedure C, the sample was concentrated in a 1 g NiS bead instead of a 8 g bead and the Teflon tube was opened and the solution warmed for approximately 1 hour before the addition of Te solution. The results (Figure 4.7 and Table 4.20) indicate that 100 µg of Te is sufficient for quantitative recovery of the leached PGE's. (N.B. Jackson *et al.* (1990) used 2500 µg of Te). The maximum recovery was attained at 500 µg of Te (Figure 4.7b)

Warming of the solution to expel some of the generated H_2S eliminated the polyatomic interference problems observed in procedures "A" and "B". *ie.* the Ni and Cu dissolved completely. Note that PGE sulphides dissolve when the H_2S is released and therefore the Te coprecipitation is required for quantitative recovery.

Table 4.20. Variation of PGE's and Au concentration with Te volume added to precipitate the leached PGE's.
SARM-7

Procedure	Ru	Rh	Pd	Os	Ir	Pt	Au	Quantity
"A" 1	665*	398*	2227*	57	83	3134	169	0
2	639*	433*	2281*	39	84	3232	194	100
3	634*	410*	2286*	45	80	2933	191	350
4	603*	408*	2171*	40	79	2983	183	500
5	661*	405*	2238*	49	80	2995	176	700
"B" 1	501*	323*	1887*	51	80	3299	205	100
2	506*	328*	1881*	53	82	3626	190	300
3	506*	321*	1858*	55	85	3737	243	500
4	469*	320*	1773*	49	84	3413	200	700
"C" 1	36	17	109	3	5	200	13	0
2	384	259	1445	41	62	2818	210	100
3	385	288	1597	43	68	3097	337	300
4	495	291	1606	50	77	3279	444	500
5	469	266	1476	50	76	2878	396	700

* marginal high values.

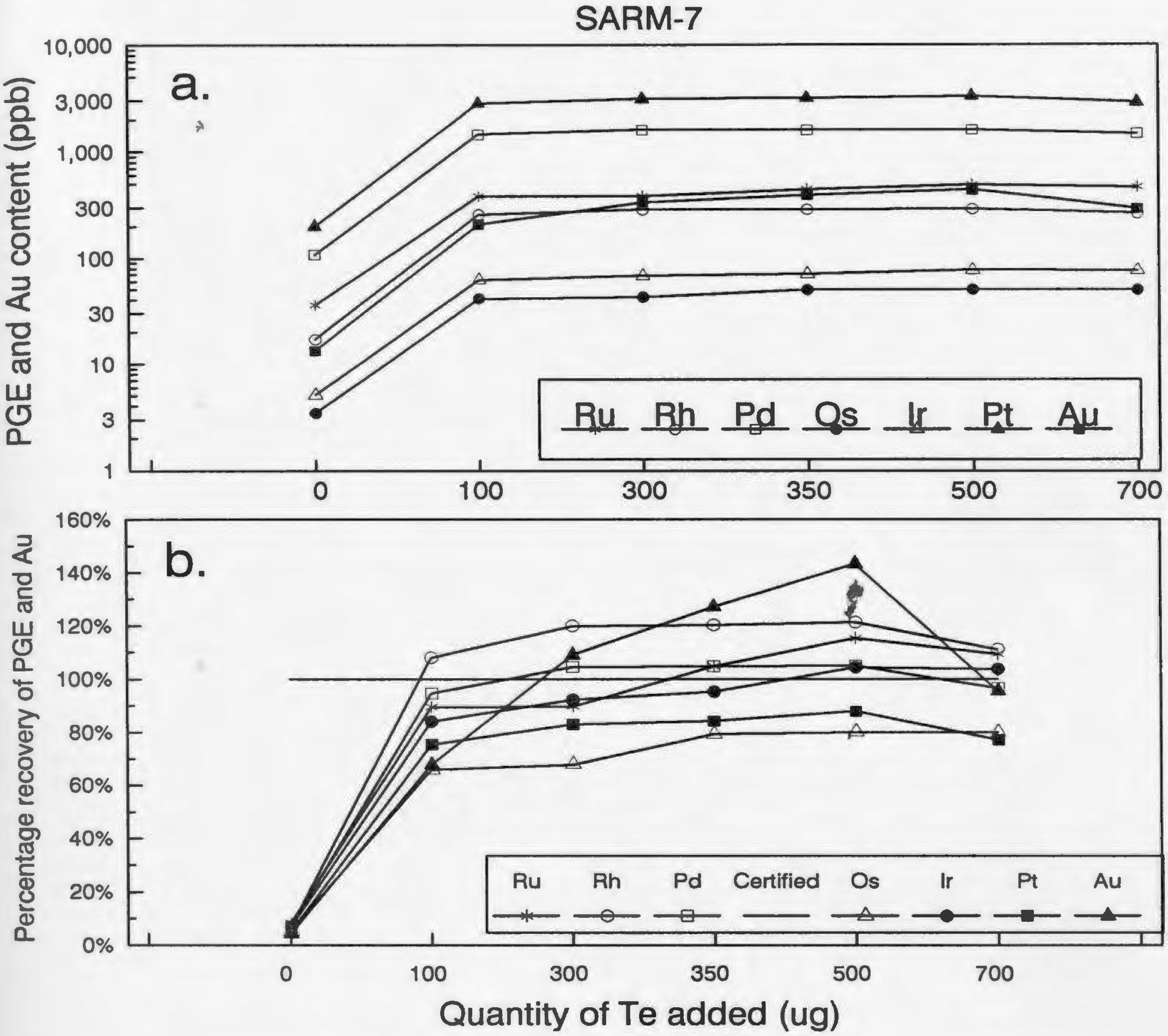


Figure 4.7. Relationship between PGE and Au contents measured and quantity of Te utilised to precipitate the dissolved PGE's. (a) The result indicates that 100 μg of Te is sufficient for a recovery of the leached PGE's. (b) The maximum recovery is attained at 500 μg of Te.

SUMMARY

The results of this chapter indicate that:

1. The one gram Ni collector mass offers a quantitative recovery of all the precious metals from the Pt ore grade sample, SARM-7, and Os, Ir and Au from the low to sub ppb sample, BF-4.
2. The derived model indicates that the recovery of PGE's and Au is collector mass and D dependent.
3. The reduction of glass mass relative to Ni mass as a means to improve PGE recovery is not practicable. For fluid slag to form, a sample to flux ratio of at least 1 to 1 should be maintained.
4. The determined D's values vary markedly with PGE and Au concentrations. The D's values for the PGE's and Au were higher for the Pt ore sample, SARM-7 than those for the low to sub ppb sample, BF-4. There is a good agreement between the model D's and those from direct experiment. This gives credence to the proposed model equation.
5. For the dissolution of the NiS bead in a closed vessel, the HCl is reduced 40 times less than that of Jackson *et al.* (1990), and also the quantity of Te reduced by a factor of 5.

CHAPTER 5. AN IMPROVED PROCEDURE FOR THE DETERMINATION OF THE PRECIOUS METALS IN GEOLOGICAL MATERIALS.

5.1. GENERAL DESCRIPTION OF THE IMPROVED METHOD.

Methods having lower reagent blank and higher sensitivity are needed to study the geochemistry of low concentrations of Platinum-Group Elements and Au. Using the results of the previous chapters, an improved method has been developed for the analysis of PGE's and Au in geological materials.

This procedure utilises : {i} 1 g Ni as collector, {ii} 15 mL concentrated HCl to dissolve the NiS bead in a closed Teflon centrifuge tube, {iii} 2.5 mL of 200 ppm Te solution and 1 mL of saturated $SnCl_2$ solution to precipitate leached PGE's and Au, {iv} 1 mL concentrated HNO_3 (16M) and 0.5 mL concentrated HCl (12M) to dissolve the PGE-Te coprecipitate in the same closed tube, and dilution to a final volume of 20 g, and {v} ICP-MS quantification, using Cd and Tl as internal standards.

The above modifications were adopted as reduced amounts of Ni and HCl offer a significant reduction in the inherent reagent blank associated with the NiS fire assay. A Ni collector mass of 1 g produces acceptable recoveries of PGE's and Au. The dissolution of the bead in a closed vessel allows the use of smaller quantities of Te and Sn, which invariably decreases the total dissolved solids in the final analytical solution.

A systematic description of the method is given below.

REAGENTS

Nickel - carbonyl nickel powder, 99.8% Ni (INCO powder T-123)

Sulphur - precipitated sulphur powder (United States Pharmicopia (U.S.P) (B.D.H. B30317)

Sodium carbonate - anhydrous granular (B.D.H. ACS)

Borax - disodium tetraborate (B.D.H. ACS)

Concentrated HCl - (E.M. SCIENCE)

Concentrated HNO_3 - (B.D.H ACS)

Aqua Regia - A mixture of 75% concentrated hydrochloric acid and 25% concentrated nitric acid by volume.

Te solution - 200 ppm in 10% HCl. Prepared by dissolving 0.2 g Te metal (99.999%, SPEX Industries, Metuchen, New Jersey, U.S.A) in 15 mL aqua regia followed by two evaporations to dryness with concentrated HCl, then diluted to final volume with 1.2M HCl.

$SnCl_2$ solution . 110 g of stannous chloride ($SnCl_2.2H_2O$) (Fisher) dissolved in 150 mL concentrated HCl and diluted to 500 mL with water.

Teflon screw-capped Tubes - Oak Ridge centrifuge tube, size 30 mL Nalgene™ Company, Rochester, NY 14602-0365, U.S.A.

EXPERIMENTAL PROCEDURE.

(1). Weigh 10 g of rock powder, 6.70 g of Na_2CO_3, 13.30 g $Na_2B_4O_7$, 5.00 g silica and the collector (1.00 g Ni + 0.66 g S) into a clay crucible and mix thoroughly with a spatula.

(2). Fuse the mixture in a preheated oven at 1050° C for 1.25 hours. Remove and allow the crucible to cool to room temperature.

(3). Break open the crucible and retrieve the NiS bead and weigh.

(4). Transfer the NiS bead into a 30 mL Oak Ridge screw-top Teflon centrifuge tube, and add 15 mL of concentrated HCl. Cap the Teflon tube tightly, place in an aluminium block holder and heat on a hot plate at ≈ 150° C to dissolve the bead.

(5). After dissolution of the NiS bead, open the Teflon tube, and warm the solution for ≈ 1 hour. Allow the solution to cool until warm. Add 2.5 mL volume of 200 ppm Te solution, and dilute the solution with 8-10 mL of nanopure water. Warm and add 1 mL of $SnCl_2$ solution. Cap the tube again and boil the solution for 30 minutes to coagulate the precipitate.

(6). Cool and filter the solution through a Millipore filter system (using Whatman 0.4μ 243m cellulose nitrate membrane filter paper) and wash the precipitate with nanopure water.

(7). Transfer the filter paper to the Teflon tube, and add 1 mL of concentrated HNO_3 and 0.5 mL of concentrated HCl. Cap the tube and warm slowly to dissolve the filter paper and its content.

(8). Cool and transfer the solution to a 50 mL polypropylene bottle. Rinse thoroughly the teflon tube into the polypropylene bottle. Dilute to 20 g with nanopure water.

5.2. ANALYSIS OF GEOLOGICAL MATERIALS.

The improved procedure was used to analyze a suite of ore grade samples, namely SARM-7, PTM-1, PTC-1 (Table 5.1), and the low to sub ppb samples BF-2, BF-4 and BF-5 (Table 5.2), as well as reagent blanks. BF-2, BF-4 and BF-5 are komatiitic rocks from Munro Township, Ontario. 2 g sample size was used for the PTM-1 and PTC-1 analyses.

The measured PGE and Au concentrations were slightly higher than the recommended values for SARM-7, except for Os and Au (Table 5.1). The Os concentration found is in reasonable agreement with other data (Asif *et al.*, 1989). Elwyn van Wyk *et al.* (1983), have also reported higher values for SARM-7 *ie.* Σ[PGE's + Au] of 5.987 to 6.008 ppm, versus the recommended Σ[PGE's + Au] of 5.71 ppm. They attribute the difference to the way the certified values were obtained. The certified value for SARM-7 was obtained from a total of 88 determinations of which 73 were obtained by fire assay, 65 of them with lead as the collector. Beamish *et al.*(1977) have reported that except for Au, the NiS procedure is superior to Pb fire assaying. Branch and Hutchison (1986) have also reported lower values for Pt in PTC-1 and PTM-1, and Pd in PTC-1 as compared to the certified PGE and Au concentrations.

The PGE and Au concentrations of sample BF-4 were found to be higher than those found when an open beaker procedure (1 g Ni mass) was used (Table 5.3). The improved procedure is quantitative for Os, Ir, and Au, and provides generally better recovery for Ru, Rh, Pd, and Pt as compared to the open beaker procedure using 1 g Ni (Figure 5.1).

The marginal increase in this work's values may also be ascribed to the elimination of crushing of the NiS bead. The crushing of the NiS bead before dissolution as advocated by other workers was avoided, and the whole bead was dissolved in this work. Jackson *et al.* (1990) suggest that the loss during crushing could be corrected by weight difference measured before and after crushing. Strictly, this correction procedure may not be adequate since the precious metals are not homogeneously distributed in the button (Wilson *et al.*, 1991) and some may be in metallic forms, which may be preferential lost through crushing of the bead.

Table 5.1. Concentrations (ppb) from this work, Jackson *et al.* (1990) and the certified or recommended values (± 95% confidence intervals) for geological reference standard SARM-7 (Steele *et al.*, 1975), PTC-1 and PTM-1 (Steger, 1983).

SARM-7

	Certified	This Study (N=3)	Jackson *et al.*
Ru	430 ± 57	462	397
Rh	240 ± 13	319	212
Pd	1530 ± 32	1892	1353
Os	63 ± 7	42	53
Ir	74 ± 12	75	71
Pt	3740 ± 45	3815	3395
Au	310 ± 15	246	253

Jackson *et al.*, N = 29 and N= 7 for Os.

PTC-1

	Certified	This Study (N=1)	Jackson *et al.*
Ru	(650)	483	442
Rh	620 ± 70	556	606
Pd	12,700 ± 700	10,934	11,438
Os	(240)	245	303
Ir	(170)	156	165
Pt	3000 ± 200	2470	2,582
Au	650 ± 100	303	466

Jackson *et al.*, N = 22 and N= 5 for Os.

cont. **Table 5.1.**

PTM-1

	Certified	This Study (N=1)	Jackson* (N=10)
Ru	(620)	654	612
Rh	900 ± 200	1020	1086
Pd	8100 ± 700	9081	8191
Os	(140)	164	83
Ir	(450)	291	341
Pt	5800 ± 400	5004	5127
Au	1800 ± 200	1006	1609

Jackson* (personal communication).

Table 5.2. PGE and Au contents of 3 low to sub ppb level Komatiite samples and their measure of precision (N = 3). BF-2, BF-4 and BF-5 are komatiites from Munro Township, Ontario.

	BF-2		BF-4		BF-5	
	Mean ± σ	RSD	Mean ± σ	RSD	Mean ± σ	RSD
Ru	1.68 ± 0.17	9.9%	2.6 ± 0.30	11.5%	2.5 ± 0.23	9.5%
Rh	1.14 ± 0.07	6.1%	0.68 ± 0.09	13.2%	0.9 ± 0.04	4.6%
Pd	9.49 ± 0.43	4.5%	5.3 ± 0.70	13.2%	6.5 ± 0.40	6.1%
Os	0.32 ± 0.08	26.3%	1.44 ± 0.24	16.7%	0.84 ± 0.16	18.4%
Ir	0.59 ± 0.0	0.6%	1.35 ± 0.06	4.4%	0.88 ± 0.04	5%
Pt	7.80 ± 0.12	1.5%	4.00 ± 0.50	12.5%	5.20 ± 0.07	1.4%
Au	1.38 ± 0.05	3.9%	1.38 ± 0.21	15.5%	1.22 ± 0.26	21.4%

RSD = relative standard deviation.

Table 5.3. Comparison of concentration of PGE's and Au in a low-ppb sample (BF-4) determined using the modified and the open beaker procedures (N = 3).

BF-4

	Modified procedure 1 g Ni mass as collector.	Open beaker procedure, 1 g Ni mass as collector.	Open beaker procedure, 5 g Ni mass as collector.	Best estimate*
Ru	2.60 ± 0.30	2.19 ± 0.17	3.20 ± 0.30	4.49 ± 0.59
Rh	0.68 ± 0.09	0.52 ± 0.02	0.76 ± 0.05	0.98 ± 0.08
Pd	5.30 ± 0.70	3.71 ± 0.67	6.24 ± 0.20	7.46 ± 1.67
Os	1.44 ± 0.24	1.04 ± 0.13	1.05 ± 0.07	1.78 ± 0.27
Ir	1.35 ± 0.06	1.28 ± 0.11	1.31 ± 0.26	1.78 ± 0.19
Pt	4.00 ± 0.50	3.07 ± 0.25	4.70 ± 0.60	6.37 ± 1.30
Au	1.38 ± 0.21	1.43 ± 0.10	1.31 ± 0.28	1.17 ± 0.17

* See Table 4.17.

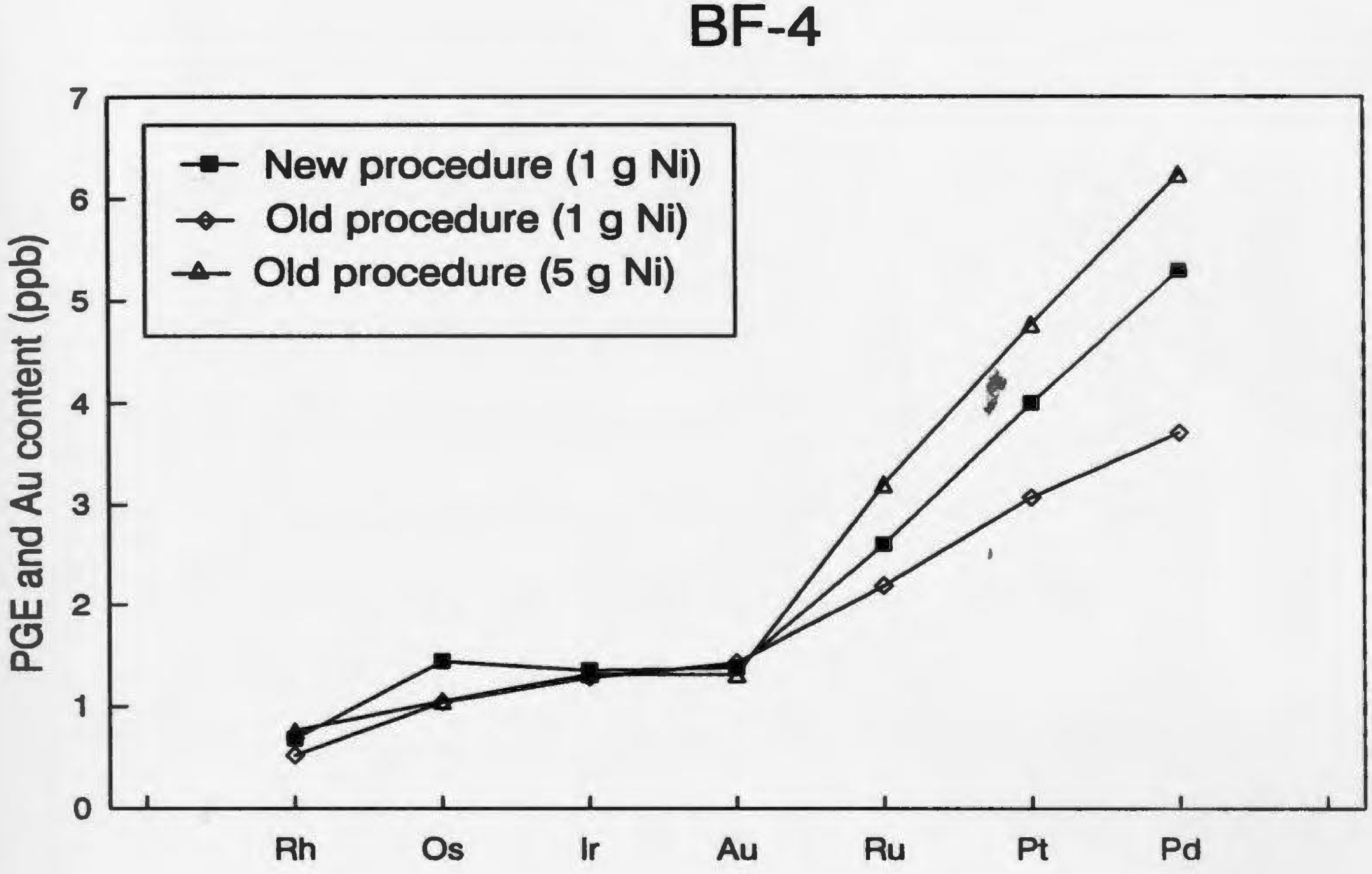


Figure 5.1. Comparison of PGE and Au recovery by the modified procedure, and the open beaker method after Jackson *et al.* (1990). The improved procedure offers quantitative recovery for Os, Ir, and Au, and better recovery for Ru, Rh, Pd, and Pt, as compared to the open beaker procedure (1 g Ni).

The elimination of the crushing step provides other benefits such as (i) general cleanliness of the blanks (and the laboratory), and (ii) elimination of cross contamination. Generally, an elimination of an analytical step is very useful for any analytical procedure development.

5.3. PGE CONTENTS OF THE REAGENT BLANK.

The impurities in the reagents were measured using blank fusions. The blank fusions were prepared and analyzed using the same procedure as for rock fusion, with acid washed silica powder as the sample. Table 5.4 compares the concentration of PGE's and Au measured in blank samples using 1 g Ni (this work), 5 g Ni (Jackson *et al.*, 1990), and 0.5 and 10 g Ni (Asif *et al.*,1989). This work's reagent blanks are lower than both Jackson *et al.* and Asif *et al.*, based on sample size used. (Note: Jackson *et al.* "clean" blanks were obtained using much cleaner acids). This work uses 10 g sample, compared to 15 g (Jackson *et al.*, 1990) and 25 g (Asif *et al.*, 1989). It is clear that the use of a reduced amount of Ni significantly decreases the reagent blank, because Ni is the predominant contributor of PGE's to the reagent blank.

Table 5.4. Concentration of PGE's and Au in reagent blank (ppb) of this study (1 g) compared to "A" & "B" (Jackson *et al.*, 1990), and "C" & "D" (Asif *et al.*, 1989).

	This Study, 1 g Ni collector	A All	B Clean	C 0.5 g Ni	D 10 g Ni
Ru	0.08 ± 0.02	0.16	0.40	≤ 16*	≤ 7*
Rh	0.03 ± 0.32	0.03	0.00	0.85	≤ 0.6*
Pd	0.26 ± 0.01	0.56	0.12	≤ 12*	≤ 20*
Os	0.09 ± 0.28	0.01	0.01	5.5	≤ 0.8*
Ir	0.08 ± 0.01	0.02	0.04	0.34	0.15
Pt	0.32 ± 0.07	0.37	0.09	≤ 9*	≤ 4*
Au	0.60 ± 0.15	1.21	0.51	5.6	0.07*

Number of determination (N) for this study = 6, except for Au, N = 5. * = Average of the reported values.

This blank reduction can also be ascribed to the smaller amount of concentrated HCl used to dissolve the bead as compared to other workers. (15 mL of HCl was used instead of 600 mL by Jackson *et al.*, 1990; and Date *et al.*, 1987). The HCl used to dissolve the bead is > 97% of the total HCl utilised in the procedure, and its reduction yields a smaller contribution of PGE's to the blank.

5.4. PRECISION AND ACCURACY.

The precision of this technique is good for both high and low to sub ppb levels, as seen for the low ppb samples BF-2, BF-4, and BF-5 (Figure 5.2 and Table 5.2). (Note relative standard deviation is inversely related to analyte concentration). There is good agreement between the values found in this work and previously published values for SARM-7, PTC-1 and PTM-1 (Figures 5.3a, b).

5.5. EVALUATION OF THE IMPROVED PROCEDURE.

The improved method is quantitative for ore grade type samples. For low to sub ppb level samples, Ir, Os and Au recoveries are quantitative, while those of Ru, Rh, Pd and Pt are comparable to any other method. PGE's and Au yields of ≥ 70% have been reported by other workers using much larger collector masses for Pt ore grade samples (Hoffman *et al.*, 1978, Date *et al.*, 1984, Asif *et al.*, 1989, Jackson *et al.*, 1990). Generally, the recovery of an analyte is influenced by factors such as concentration of the analyte in the sample, and sample homogeneity and matrix. In low to sub ppb levels, the concentration of the analyte is the major factor affecting recovery (Keith *et al.*, 1983). Hence, the achieved recovery of PGE's and Au is very good, considering the PGE and Au concentrations (low to sub ppb levels). The NiS fire assay method is adequate for collection of PGE's and Au from low to sub ppb level samples.

The use of more expensive high purity reagents is also possible without increasing analytical cost due to the smaller amounts of reagents employed in this method. The reagent blank and the total dissolved solids in the final analytical solution are considerably reduced. Cross contamination of samples during crushing is eliminated.

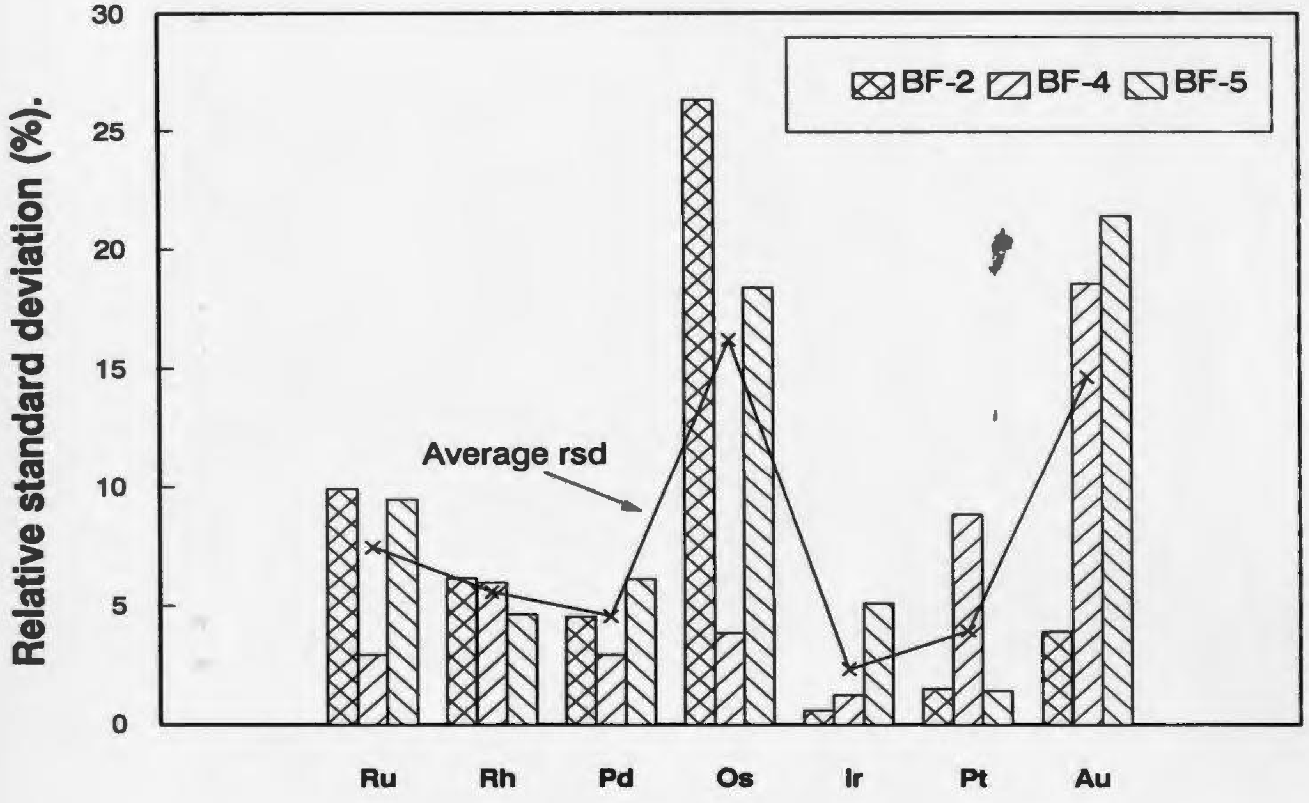


Figure 5.2. Precision of the modified NiS fire assay procedure is demonstrated for three sub-ppb level PGE's samples.

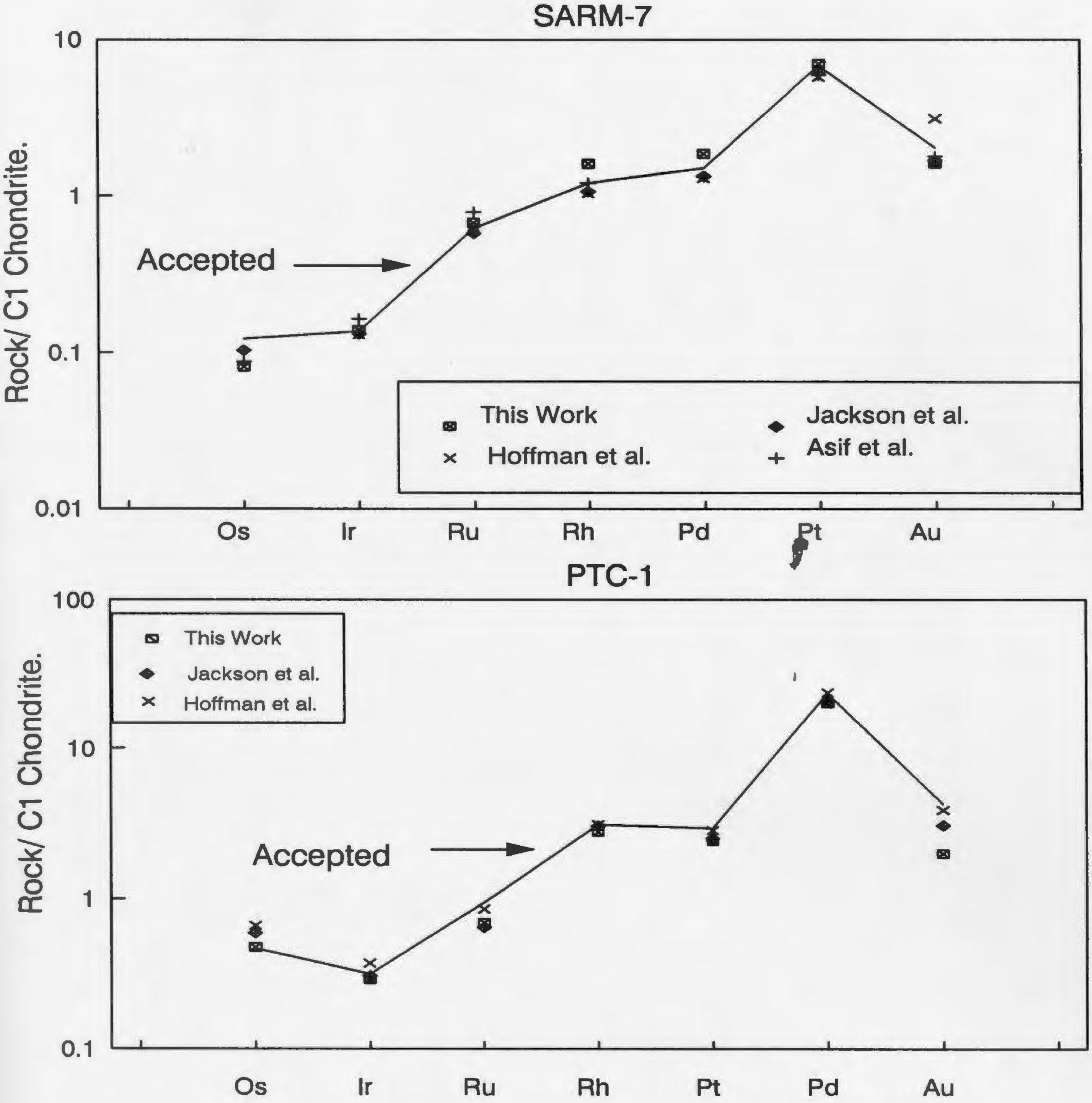


Figure 5.3a. The accuracy is shown by the measured PGE's contents of the international reference materials: SARM 7 and PTC-1.

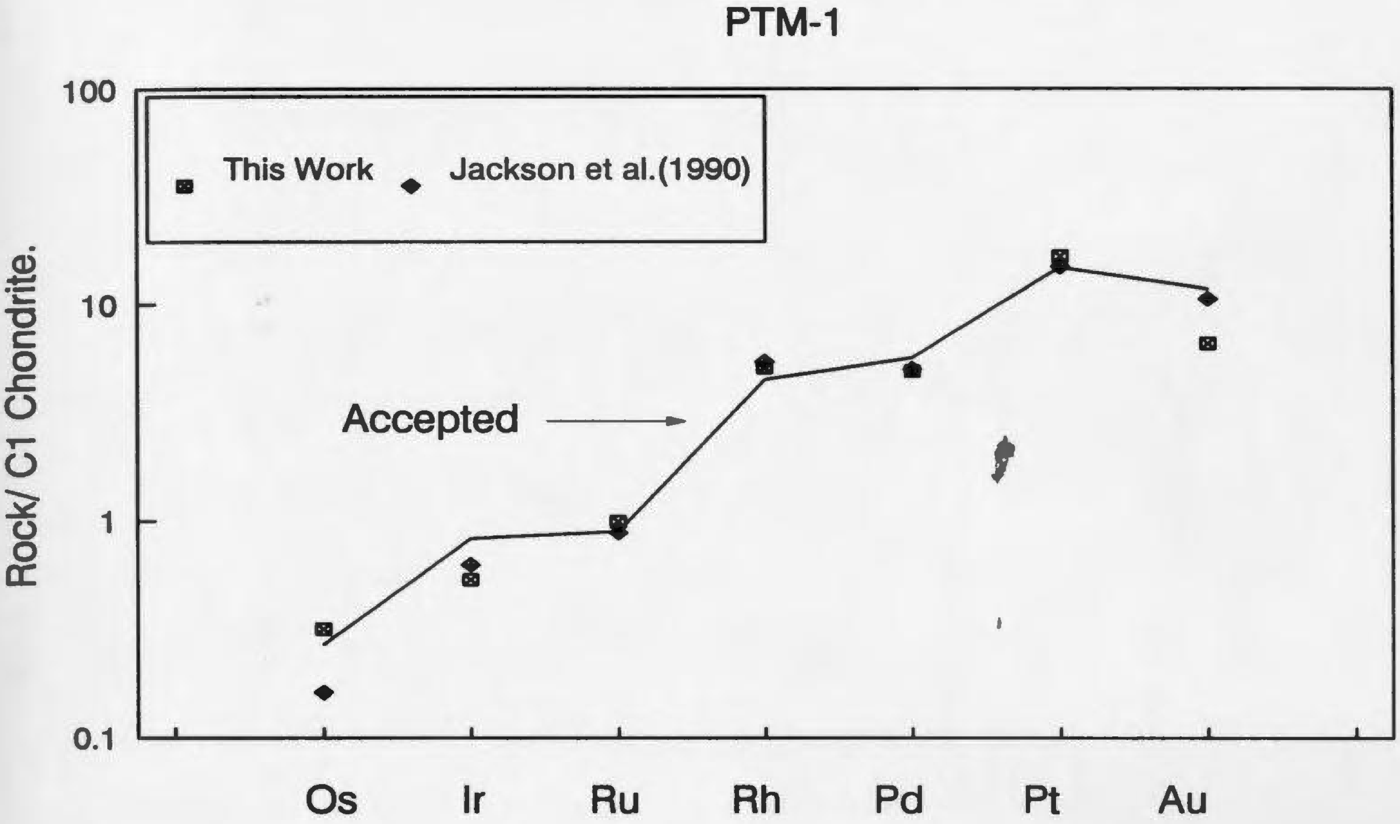


Figure 5.3b. The accuracy is shown by the measured PGE's contents of the international reference material PTM-1.

CHAPTER 6. CONCLUSIONS.

Results from this study indicate that loss of precious metals to the silicate melt is analytically insignificant, for ore grade samples (higher PGE and Au contents), which lends support to the contention that NiS fire assay procedure is an effective preconcentration step for all the six PGE's and Au for ore grade samples. The use of reduced amounts of Ni as a collector potentially affords a significant reduction in the reagent blank. The precision of the 1 g Ni procedure is good.

This work has also shown that the recovery of Ru, Rh, Pd and Pt in low ppb level samples is affected by reducing the mass of Ni (and S) relative to the silicate glass. The recovery of Au, Ir and Os is not significantly affected by reducing the collector mass.

The measured partition coefficients of the PGE's and Au ($[PGE]_S/[PGE]_G$) vary markedly with the total concentration of precious metals. The D values increase with PGE and Au contents of the samples. The uncertainty associated with the determined D values presented here is less than the uncertainties in previously published values determined from magmatic sulphide and coexisting silicates.

The distribution of Ni between the sulphide and silicate melt also varies with the PGE concentration in the sample. A higher D_{Ni} value was obtained for the sample with higher PGE and Au concentrations. *ie.* D_{Ni} obtained for SARM-7 is twice that for BF-4. Similar results were obtained for D_{Cu}. However, the distribution of Cr shows no preference in both sample types. The presence of Cr in the NiS bead suggests that there may be other phase(s) in the bead, since Cr is not a chalcophile element. The amount of sulphur found in the glass was independent of the total sulphur content of the mixture (sample + flux).

With judicious application of calibration strategies enumerated by Jackson *et al.* (1990) and Longerich (1987, 1990) and reduction of hydrochloric acid concentration; from 0.6M to 0.2M in the final solution, the limit of detection of the precious metals by the ICP-MS could be improved 15% to 25%. However, this is not a particularly useful increase in the method sensitivity. The internal standards (Cd and Tl) do provide adequate measure and correction for the matrix and drift effects.

Due to lack of any large change in Beta value (the ratio of count rates of the internal standard(s) in blank and sample) over the range of concentrations studied (a range of concentration over which a practical analytical scheme could be developed), there is no advantage to change the Te coprecipitation step, except that the amount can be reduced to 500 μg instead of the 2500 μg used by Jackson *et al.* (1990). 500 μg Te was found to offer maximum recovery of the leached PGE's and Au during the bead dissolution step.

An improved NiS fire assay procedure has been developed from the results of this study (chapters 3 and 4). The procedure offers precision and accuracy tolerable for geochemical applications considering the sampling and determinative uncertainties encountered in studies of PGE distributions.

The advantages of using reduced amounts of Ni, Te and HCl are (i) reduction of matrix effect due to HCl on the sensitivity of the PGE's and Au; (ii) reduction of reagent blank; (iii) a saving in the cost of chemicals and labour; (iv) a smaller volume of acid, reducing filtration time.

The crushing of NiS bead; a potential contamination source, before acid dissolution has also been eliminated. This procedure also utilizes smaller amounts of the other components of the flux and a 10 g sample.

It should be noted that the 30 mL Oak Ridge Teflon centrifuge tubes (Nalgene™) must be opened and warmed to expel some of H_2S before the Te precipitation step, to eliminate any possible polyatomic ion interferences from undissolved Ni and Cu on the light PGE's.

Further study is needed to analyze samples of intermediate PGE's concentrations to formulate a model to correct for the loss of PGE's and Au. Other sample dissolutions such as straight analysis of the fused glass should also be examined as initial work on the fire assay glasses has shown the potential for these types of analyses. Other ICP-MS sample introduction methods such as laser ablation should also be investigated, as this mode of sample introduction will eliminate the use of HCl and bead crushing which have been demonstrated to be serious contamination sources in the NiS procedure.

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APPENDIX 1. Concentration of the major and trace elements of BF-4 and SARM-7 measured in this study (N = 4) using XRF. Major elements are %, and trace elements in ppm.

	BF-4	SARM-7
SiO_2	44.94 ± 0.06	46.25 ± 0.15
Na_2O	0.39 ± 0.00	0.84 ± 0.00
MgO	34.13 ± 0.09	23.53 ± 0.08
Al_2O_3	5.33 ± 0.01	8.77 ± 0.03
P_2O_5	0.02 ± 0.00	< 0.01
K_2O	0.06 ± 0.00	0.21 ± 0.00
CaO	4.87 ± 0.02	6.12 ± 0.01
TiO_2	0.25 ± 0.00	0.23 ± 0.00
MnO	0.16 ± 0.00	0.20 ± 0.00
Fe_2O_3	10.89 ± 0.02	12.59 ± 0.01
S	358 ± 11	5455 ± 64
Cl	181 ± 2	206 ± 2
Sc	20 ± 1	24 ± 2
V	118 ± 3	148 ± 0
Cr	2886 ± 31	6039 ± 64
Ni	2010 ± 5	2211 ± 7
Cu	34 ± 1	876 ± 5
Zn	43.0 ± 0.5	81.0 ± 0.6
Ga	< 3	7.0
As	< 2	14.0 ± 1.6
Rb	1.5	5.6 ± 0.0
Sr	12.6 ± 0.3	109.0 ± 0.3
Y	5.7 ± 0.4	4.9 ± 0.1

Zr	10.0 ± 0.5	18.1 ± 0.5
Nb	0.6 ± 0.0	0.9 ± 0.1
Ba	< 21	62.0 ± 0.2
Ce	39 ± 2	< 37
Pb	< 4	20.0 ± 3.4
Th	< 3	< 3
U	< 4	< 4

Uncertainty (1σ) = reproducibility of the measured value.

APPENDIX 2. Weight of sample, flux, NiS bead, and concentration of PGE's and Au recovered using different collector masses. All weights are in g, and concentrations are in ppb.

BF-4

Sample	10	10	10	10	10	10	10	10	10	10
Ni used	0.5	0.5	1.0	1.0	2.0	2.0	3.3	3.3	5.0	5.0
S used	0.33	0.33	0.66	0.66	1.22	1.22	2.0	2.0	3.3	3.3
NiS formed	0.35	0.38	1.05	1.08	2.38	2.33	4.26	4.14	6.71	6.70
Ru	1.13	1.61	2.10	2.43	2.62	2.39	3.37	3.76	3.52	2.88
Rh	0.25	0.48	0.54	0.59	0.67	0.70	0.91	0.65	0.90	0.79
Pd	2.29	4.16	3.27	4.61	5.20	5.21	7.37	4.88	6.98	6.56
Os	1.17	0.91	0.67	1.53	0.93	1.76	1.42	0.96	1.12	0.99
Ir	1.49	1.08	1.17	1.40	1.16	1.25	1.40	1.02	1.63	1.12
Pt	2.25	3.58	3.42	3.93	3.79	3.89	5.04	3.70	5.23	4.12
Au	1.64	1.40	1.54	1.33	3.37	2.85	2.19	1.56	1.59	1.01

Glass weight = 26.46 g.