"Determination of platinum, palladium, rhodium and gold in platiniferous ores using ICP-MS and microwave dissolution."

Thesis presented in fulfillment of the requirement for the degree of
Masters of Science at the University of Stellenbosch.

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Declaration

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

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Synopsis

The determination of the platinum group metals (PGMs), platinum, palladium, rhodium, iridium, ruthenium and osmium, remains a problem for the low-grade ore samples, and the analysis of these samples in a routine laboratory relies entirely on the fire assay technique. The use of large sample masses to overcome sub-sampling errors has been the greatest advantage of this technique.

The increased economic value of PGMs and recent developments in instrumentation such as inductively coupled plasma-mass spectrometry (ICP-MS) which is capable of trace element detection as low as part per billion (ppb) levels, have led to a search for complementary methods to ensure the accuracy of fire assay results.

This work investigates the feasibility of direct dissolution of ore samples using microwave-assisted dissolution followed by ICP-MS as the measurement technique. Due to the limited sample mass that can be used, a thorough consideration had to be given to sampling errors and analytical errors to assess the overall precision achievable.

Most PGM-bearing minerals occur as sulphides and these are highly resistant to acid dissolution. It was found that roasting the Merensky type samples in air, prior to dissolution gives quantitative recoveries for platinum. Recoveries up to 100% were obtained for platinum, palladium, rhodium and gold for a Merensky flotation concentrate with excellent precision (about 4%) except for gold which had poorer precision (16%). However, ore samples presented a problem due to their lower PGM content and smaller sample masses being used. Precision for all elements improved significantly (from about 20% to about 8%), with the use of 1g-sample aliquot compared to that of 0.25 g-sample.

Acid dissolution, even after roasting proved to be insufficient for the UG-2 chromitite samples. When roasting was followed with reduction under hydrogen flame the solubility of the UG-2 flotation concentrate improved remarkably. The recoveries obtained were approximately 95 ± 5% for platinum, 99 ± 5% palladium, 104 ± 12% gold and 102 ± 5% for rhodium with good precision (comparable to that of Merensky concentrate).

The accuracy and precision of the results depended very much on the sample mass and air-flow in the furnace during the roasting procedure. For this method to be used

successfully, the air flow is very critical, and should lead to a better furnace design which can rotate the crucibles to enable an even flow of air over all the samples during roasting.

Opsomming

Die bepaling van platinumgroep metale (PGM'e), platinum, palladium, rhodium, iridium, ruthenium en osmium is 'n voortdurende probleem vir die lae-graad erts monsters. Die analise van hierdie monsters in 'n roetine laboratorium is geheel afhanklik van die klassieke "fire assay"-tegnieke. Die groot voordeel van hierdie tegniek is die voorkoming van monsternemingsfoute deur die gebruik van groter monster massas.

Die ekonomiese waarde van PGM'e saam met die onlangse ontwikkeling van instrumentasie soos die induktief-gekoppelde plasma-massaspektrometrie (IGP-MS) wat in staat is om spoorelemente in konsentrasies so laag soos dele per biljoen (ppb) te meet, het daartoe gelei na soeke vir komplementêre metodes om die akkuraatheid van klassieke "fire assay"-tegnieke te verseker.

Hierdie werk ondersoek die waarskynlikheid van direkte oplossing van ertsmonsters deur gebruik te maak van mikrogolf-ondersteunde oplossing gevolg deur IGP-MS as opmetingstegniek. As gevolg van die beperkte monster massa wat gebruik kan word, moes deeglike oorweging gegee word aan monsternemingsfoute en analitiese foute, om die oorkoepelende presiesheid te bepaal.

Meeste PGM-draende minerale bestaan in die vorm van sulfiede en bied groot weerstand teen oplossing in 'n suur. Die gloei van Merensky-tipe monsters in lug voor oplossing gee kwantitatiewe herwinning van platinum. Herwinning tot 100% is behaal vir platinum, palladium, rhodium en goud vir 'n Merensky-flotasie-konsentraat met uitstekende akkuraatheid (4%) behalwe vir goud met 'n swak (16%) akkuraatheid. Die erts monsters was problematies as gevolg van die laer PGM inhoud en kleiner monstermassas wat gebruik is. Presiesheid vir al die elemente het beduidend verbeter (van 20% tot 8%) met die gebruik van 1 g- monster massas vergelyk met 0.25 g-monsters. Ten spyte van die gloei van die monster is suur oplossing onvoldoende vir die UG-2 chromatiet-houdende monsters. Wanneer die monster gegloei is onder 'n waterstof vlam (reduksie) het die oplossbaarheid van UG-2 flotasie-konsentraat aansienlik verbeter. Die herwinbaarheid wat behaal is, is 95 +/- 5% vir platinum, 99 +/- 5% vir palladium, 104 +/- 12% vir goud en 102 +/- 5% rhodium met goeie relatiewe presiesheid vergeleke met Merensky-konsentrate.

Die akkuraatheid en presiesheid van resultate hang meerendeels af van monster massa en lugvloei in die oond gedurende gloei. Die lugvloei is krities vir die sukses van hierdie metode en sal moet lei tot beter oond ontwerp wat kroesies kan roteer en 'n gelyke vloei van lug oor die monsters gedurende verbranding toelaat.

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Chapter One

1. Introduction

South Africa has the world's largest reserves of platinum and is the world's biggest supplier (~55%) of platinum-group metals, often referred to as "PGM"s. The PGMs comprise a family of six chemically similar elements namely platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), ruthenium (Ru) and osmium (Os).

The other suppliers include Russia (~16%), Finland (~12%), Zimbabwe (~9%) and USA (~6%) with the remaining 2% coming from four other countries [1,2].

1.1 The Platinum Industry in South Africa

Adolph Erasmus discovered platinum in South Africa as early as 1923. Shortly afterwards mining operations commenced. Exploitation of these deposits proved not to be economically viable because the platiniferrous ore was patchy and difficult to extract. Within the next two years Dr Hans Merensky discovered the Merensky reef and Platreef with the help of farmers Lombaard and Bernstein respectively [3]. This lead to increased mining activity in the area. However, there were few industrial uses for platinum, as it was mainly used for jewellery. In the early 1930s most of the mining operations closed down due to a sustained weakening of the platinum price. This situation did not last long; by 1933 the operations had started following an upturn in the market price. The use of platinum as a catalyst widened remarkably after World War 2.

The growth of South African industry increased in the early 1970s as did the pressure of competition. A substantial number of companies started operations. Between 1973 and 1978 as much ore had been milled as had been processed throughout the preceding 50 years. Growing competition has lead to increased interest in UG-2 chromitite deposits that had been ignored even though they were identified in the 1920s [2,3]. In the recent years, demand for these precious metals has shown an annual increase of about 5%.

1.2 Characteristics and Uses of Precious Metals

Some of the distinguishing features of this group of metals, which mainly give them their utility and favourable properties for use in industry, include:

- good catalytic qualities
- resistance to corrosion
- chemical inertness and
- high melting points.

The rarity of these metals and their increasing industrial importance, has resulted in increased exploration programmes and the growth of secondary refining [4,11].

These precious metals have gained increasing applications in jewellery, chemical, electrical, petroleum refining and automobile industries. The introduction of legislation for stricter vehicle exhaust emission limits has led to the use of platinum, palladium and rhodium in auto-catalysts in the automobile industry [1]. Demand for platinum in autocatalysts rose by 33% in 2001 because of the growth in production and sales of diesel cars due to their improved performance. In 2001, diesel catalysts accounted for 70% of the auto demand for platinum in Western Europe and this raised automobile market share to 36%. The diesel auto catalysts use only platinum, whereas gasoline (petrol) autocatalysts use platinum or palladium, in combination with rhodium. It is expected that the appeal for diesel cars will increase to 40 to 50 percent by 2006 (figure 1.1), because of the fuel costs which are unlikely to decrease significantly. Platinum and palladium jewellery demand, traditionally confined to Japan, has also spread to other regions, most notably China. Ruthenium and iridium are also used in jewellery as components of platinum alloys, to improve machining properties.

In the chemical industry PGMs are used as catalysts in nitric acid production for agricultural use; in petroleum refining industry as well as for the production of ammonia. Platinum is used in coatings for data storage disks in computers. Glass manufacturers producing high-quality glass used in liquid crystal displays (LCD) and in cathode ray tubes for televisions and computers also use these metals. It is also in demand for investment purposes [1,2]. The introduction of fuel cells in automobiles has proved to be economically and environmentally attractive, and this has also led to the increased demand for platinum which is used as a catalyst.

Growth in the production of high quality electronic components has increased the demand for palladium in multi-layer ceramic capacitors (MLCC). In medical technology, palladium is used in dental treatment while platinum-iridium electrodes are used for biomedical devices. Platinum is also used in the manufacturing of cancer combating drugs such as Carboplatin and Cisplatin.

It is expected that the demand for these metals will increase as manufacturers introduce catalysts with higher percentage of PGM, to meet stricter emissions standards in the USA, Japan and Europe [2].

Source: DRI-WEFA Global Automotive Group

Figure 1.1 Sales of diesel passenger cars in Western Europe [2]

1.3 Economic value of the platinum group metals

In the year 2000 the average combined price for platinum, palladium, rhodium, iridium and ruthenium was about 3770 US dollars (which converts to R34 422 when 1$ (US) = ZAR8.60) per ounce, with rhodium contributing about 50% of that total. In 2001 on average this number had decreased to 3280 US dollars per ounce, with rhodium plunging by about 20%, table 1.1 shows individual prices in US dollars per ounce and they are listed in the order according to their market demand and supply. Although these metals occur together, their demand is often independent of each other except in the case of auto catalysts where two or three may be used together or sometimes palladium may be used to substitute platinum. While rhodium is the most costly of all, its demand is only about a tenth that of platinum [2].

Table 1.1 Average PGM price in $ per ounce (oz)[#]

	Pt	Pd	Rh	Ru	Ir
2000	545	682	1998	415	129.8
2001	529	603	1603	413	132

In 2001 platinum supplies rose to 5.86 million oz with the South African supplies accounting for 4% and in that same year the price soared to about R6000 (ZAR) per ounce. This is a significant contribution to the country's economy and as such the financial implications of wrong data are very serious, not only to the producer but to the country, such that an analytical error of 5% converts to a few million rands.

The PGM producers have no control over the price for these precious metals, but the price is controlled by the market (supply/demand). The producers then negotiate sales contracts based on the grade of their products, their mining and processing costs. The initial grade calculation starts from the ore grade, and if this is not determined correctly it could have serious implications in revenue generated[4].

1.4 Occurrence and Mineralogy

In South Africa the PGMs are distributed within various layers of the Bushveld Igneous Complex. The Bushveld complex can be divided into four limbs: eastern, western, northern and southeast areas. Detailed studies and reviews on mineralogy and geology of Bushveld Igneous Complex are available [5-7].

Figure 1.2 is a map showing the geological location of the Bushveld Igneous Complex, the *green* shade represent the Bushveld rocks, the yellow shades show the mining areas, the

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[#] Data obtained from Platinum 2002, PGM review by Johnson Matthey golden colour shows the Gauteng (meaning place of gold) Province (formerly known as Transvaal) and E = eastern limb, W = western limb, N = northern or Potgietersrus limb.

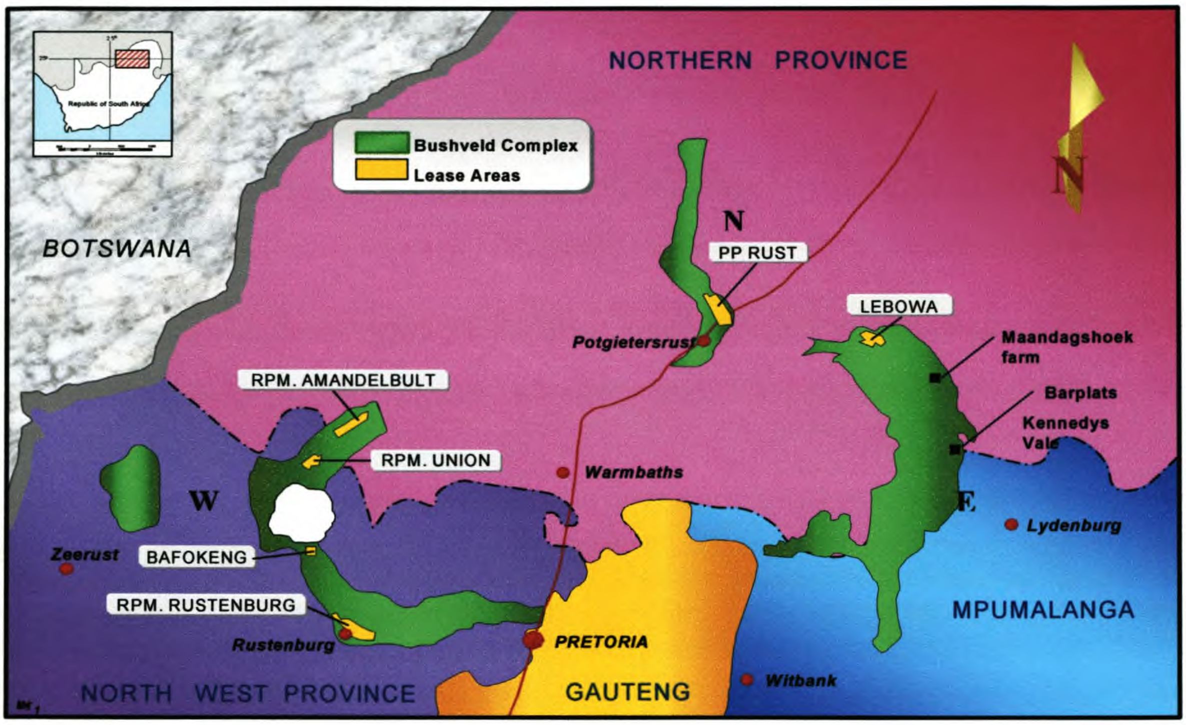

Figure 1.2 Map of Bushveld Igneous Complex [unknown]

The upper *critical zone* of the Bushveld Igneous Complex hosts the world's largest reserves of platiniferous ores. Significant quantities of nickel and copper together with small quantities of cobalt and gold are produced as by-products of the platinum operations.

In the Bushveld Complex, PGMs are mainly associated with three horizons [4]:

- Merensky Reef
- Upper Group Chromitite No.2 (UG-2)
- Platreef

NB: *Zone* refers to a group of rocks

Figure 1.3 illustrates the positioning of UG-2 and Platreef relative to Merensky Reef.

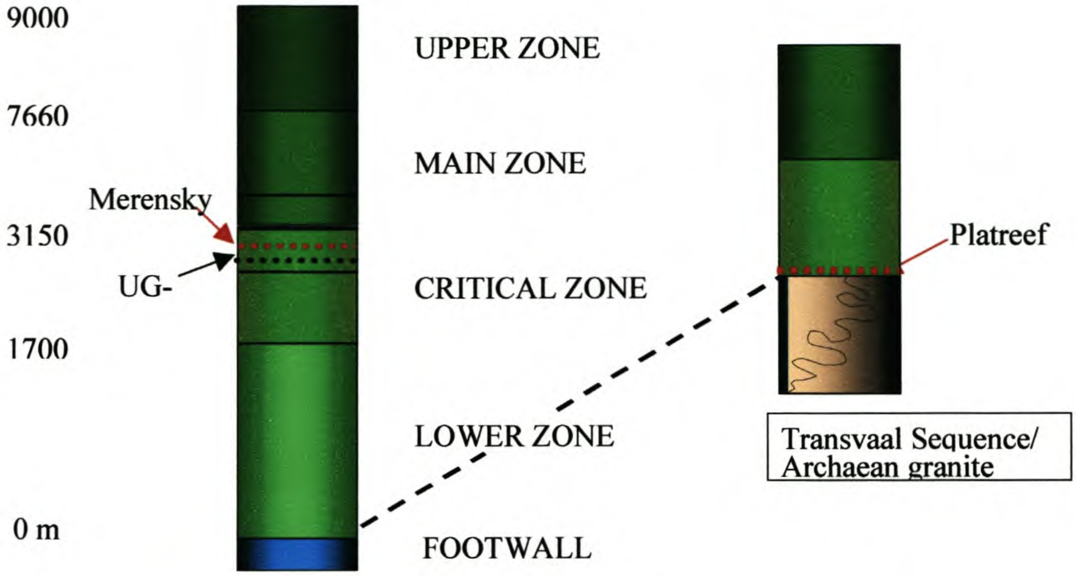

Figure 1.3 **Stratigraphic column showing positions of the 3 platiniferrous reefs [8]**

For many years, production has been confined to the Merensky and UG-2 reefs alone, with only one mine - Potgietersrus Platinum Limited (PPL) operating on Platreef. The UG-2 reef is located below the Merensky reef and both have a distinctive appearance. Platreef occurs only in the northern limb of the Bushveld Igneous Complex.

The precious metals are invariably present at low concentration levels – typical grades at 4 to 20 g/t and are inhomogeneously distributed in the rock as discrete mineral particles. They occur as natural alloys as well as sulphides and arsenides. The principal minerals include: cooperite (PtS), braggite ($(PtPdNi)S$), laurite (RuS_2), sperrylite ($PtAs_2$) and Osmiridium alloy (mainly Os and Ir). The minerals are Pt-rich, with braggite having a substantial amount of palladium and sperrylite having some rhodium [7]. The abundance of the minerals differs from one locality to another. The Platreef resembles the Merensky reef in its mineralization while UG-2 reef is very different from both. The composition of Merensky and UG-2 ores vary significantly with location.

In the context of UG-2 the following terminology will be used:

Chromitite – a rock containing chromite as its major constituent [8]

Chromite – mineral containing 40 – 50% Cr_2O_3

1.4.1 Merensky Reef

The Merensky reef represents the world's largest known reserves of PGMs. It consists of dark pyroxenite (consisting of Mg and Fe-rich silicate minerals) and lighter calcium-aluminium-sodium silicate minerals. The thickness varies from 1.5 m to 3 m. The PGMs usually occur within base metal sulphides, often found between oxide and silicate. The Merensky reef has been traced for about 450 km around the entire outcrop of Bushveld Igneous Complex to depths exceeding 5 km. Major PGM-bearing minerals are cooperite (PtS), braggite ((PtPd)NiS), Moncheite ($(PtPdNi)(TeBiSb)_2$), and Kotulskite ((PdPtNi)(TeBiSb)). This reef also hosts a significant amount of 'base' metals[#] – 0.2% nickel, 0.1% copper and small quantities of cobalt with PGM grade of 3 to 10 g/t [6,7].

1.4.2 UG-2 Chromitite Reef

Lying parallel to and below the Merensky seam (Figure 1.3) are a number of chromite-rich seams consisting mainly of chromitite with lesser silicate minerals. One of these - the upper group no. 2 (UG-2) constitutes a significant potential source of PGMs. This seam varies from 0.9 m to 1.5 m in thickness. UG-2 contains minor amounts of base metal sulphides with which the PGM are associated [8]. The average content of rhodium, the most costly of the PGMs, is about three times higher in the UG-2 reef compared to the Merensky reef [4]. Variable PGM grains are locked in chromite and this affects the theoretical percentage recovery because of the refractory nature of the chromite. Traditionally the grades have been considered to be lower than those of Merensky but recent study [4] have shown that in many areas the PGM concentrations are actually higher than in Merensky.

The composition of UG-2 varies significantly with the region. It consists mainly of chromite with lesser silicate minerals. The PGM-containing minerals are mainly PGM-alloys (Pt-Fe) and PGM sulphides (PtPd-Sulphide and PtRhCu-Sulphide), which have very fine grains. The precious metal content varies from 4 – 10 g/t while nickel and copper concentrations are much lower [5-8].

[#] In the PGM industry the term 'base metals' often refers to copper, nickel, iron and cobalt

1.4.3 Platreef

The Platreef is only mined in the northern limb of the Bushveld Igneous Complex; it consists of lime-rich rocks (calcium-silicates). Base metal mineralization and PGM concentrations are found to be highly irregular, both in concentration as well as distribution.

The major PGM-bearing minerals are Pt-alloys and PGM-tellurides, always in association with base metal sulphides. Estimates of PGM grade range from 7 to 27 g/t, and palladium predominates over platinum. The attractions of the area are that significant tonnage can be recovered from the surface and that copper and nickel can make up to 50% of the by-products [5,6,7,9,10].

In all deposits platinum and palladium are by far the most abundant, while the other four are always by products from exploitation of platinum-palladium deposits. Typically, the proportions of platinum and palladium in the Merensky Reef, UG-2 and Platreef are about 55% and 32%, 46% and 32% and 44% and 46% respectively, with the other metals comprising about 15%.

A summary of minerals as they occur in various reefs is given in Figure 1.4.

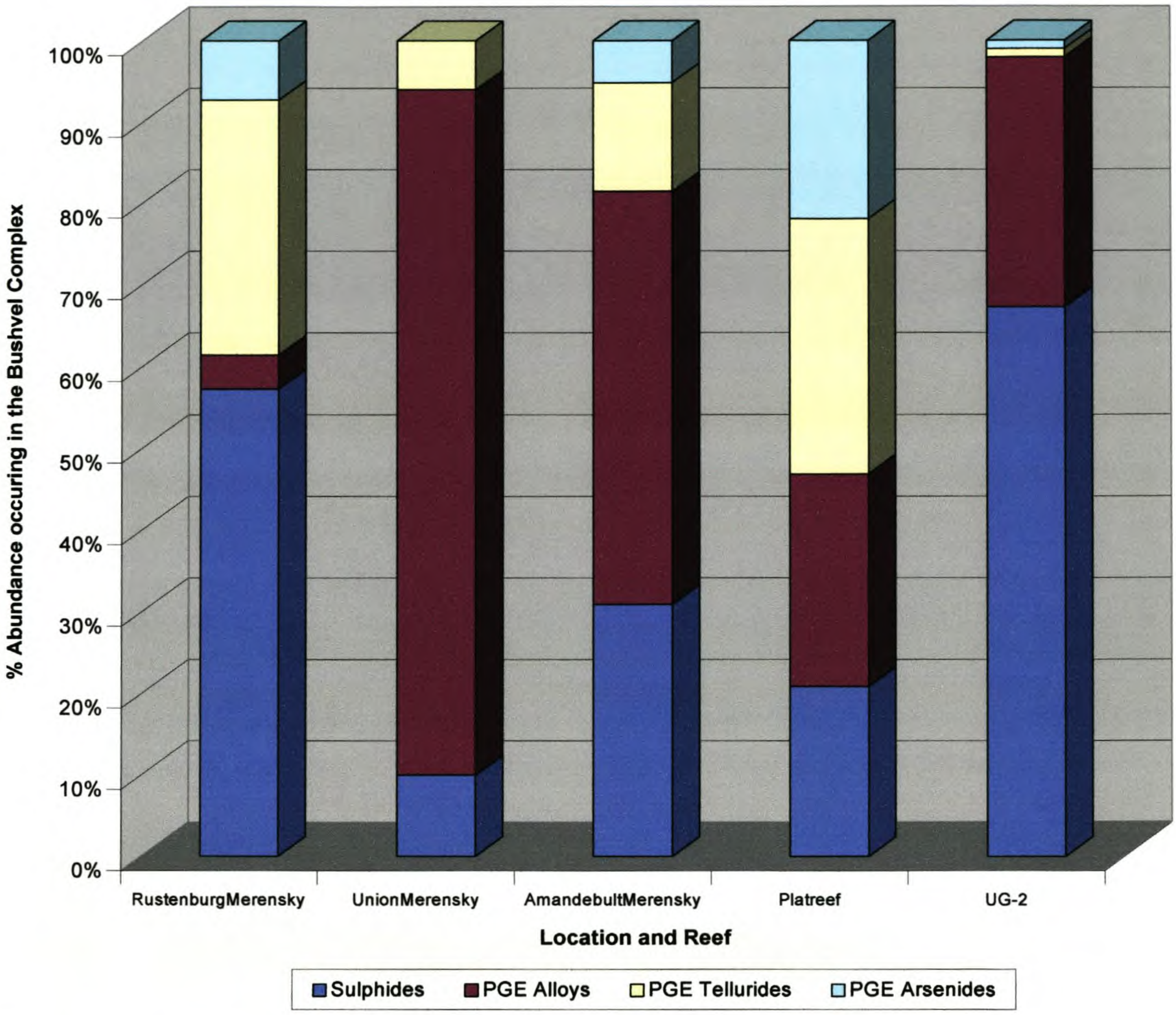

Figure 1.4 **Summary of PGM mineralization in various reefs in South Africa**

1.5 Determination of Platinum Group Metals

Analysis of PGMs remains a very complex process and this limits the number of techniques that can be used. Different techniques are employed depending on the type of sample and grades. Low-grade samples require separation from gangue material and preconcentration prior to any chemical analysis, which is to this day, achieved by fire assay method [11]. High-grade samples can be analysed by classical wet chemical analysis methods such as gravimetry and solvent extraction.

1.5.1 Fire Assay

Fire assay is the 'classical' method for the separation and pre-concentration of PGMs in ores and metallurgical products with the aid of heat and dry reducing and collecting reagents [11]. The method uses larger sub-sample masses and has the possible advantage of reducing sub-sampling errors that are often encountered due to uneven distribution of low-grade PGMs in the rocks and ore samples.

1.5.1.1 Fire Assay Methods

There are two commonly used fire assay methods employed in the South African mining laboratories. The first being known as the "lead fire assay method" where lead (as lead oxide or litharge) is used as the collector. A finely pulverized sample is weighed and mixed with flux (dry reagents). The flux usually contains sodium carbonate (Na_2CO_3), litharge (PbO), silica (SiO_2), sodium tetraborate ($Na_2B_4O_7$), calcium fluoride (CaF_2) and maize meal as a source of carbon which is a reducing agent for PbO to Pb:

$$2PbO + C \rightarrow 2Pb + CO_2$$

The objective is to form a melt of at least two immiscible phases – a complex liquid borosilicate slag and a liquid lead phase of controlled size. The high degree of solubility of the noble metals in molten metallic lead and the high density between lead and the slag allows the separation of precious metals as lead alloys. The lead is subsequently removed as lead oxide by heating the button in a porous vessel known as a cupel, in a high temperature muffle. This process is called *cupellation.* About 98% of PbO is absorbed by the cupel and about 2% is volatilized. The remaining bead or prill containing the PGMs is then weighed [11]. Sometimes this prill can be dissolved and the resulting solution analysed for individual PGMs plus gold. This method provides for a total PGM content, which is taken as a summation of platinum, palladium rhodium and gold, and is determined gravimetrically. Iridium, osmium and ruthenium have only limited solubilities in molten lead and are mainly collected because of their high densities. However, most of these metals (iridium, ruthenium and osmium) are lost during cupellation. Even the four metals (platinum, palladium, rhodium and gold) are not collected quantitatively as losses do occur during the process, particularly rhodium.

These problems have resulted in the development of the second method - the collection by nickel sulphide (NiS). The nickel sulphide is produced by adding nickel carbonate or nickel oxide and sulphur (sulphur substitutes the maize meal) [12]. NiS method employs the same phenomenon as lead method, in which the precious metals are collected as sulphides into a molten nickel to form a NiS button. The NiS button is pulverised in a ring mill and transferred to a beaker and dissolved. The nickel is leached with concentrated hydrochloric acid and the solution is filtered under vacuum through a millipore filter paper. The base metal filtrate is discarded and the black residue of PGM sulphide is digested in *aqua regia* and made up to volume. The resulting solution is then analysed on either ICP-AES or ICP-MS [11-14].

The NiS method has, for some time, been regarded as superior to the lead collection method and while most industrial workers will regard nickel sulphide as being correct this is due more to the lack of a simple alternative technique.

Although the NiS method offers better recoveries and is able to provide quantitative results for all six PGMs, Evidence suggests that gold is incompletely collected during the fusion step [12]. Moreover this method is complex, time-consuming and expensive. It also requires a highly skilled operator, and has a high repeat rate. For every four replicates at least one will be rejected as an outlier, and in every 100 samples prepared about 10 will be repeated. One of the setbacks of this method is the difficulty in obtaining a collector (NiO or $NiCO_3$) which is entirely free of PGMs [12]. For these reasons, lead fire assay is still the preferred method for routine determinations of PGMs.

The efficiency of the fire assay method is critically dependent on the flux composition, which varies according to material type and laboratory. The reactivity of each flux component is a function of temperature and is dependent on the sample composition. Thus to prepare an optimum charge (molten mixture of flux and sample), so as to facilitate maximum recovery of noble metals, it is important to know the chemical and mineralogical composition of the ore [11,14].

In both these methods, the flux composition remains relatively the same depending on the sample mineralogy.

method especially of Rh. This becomes particularly serious in the assaying of UG-2 (chromitite) reef.

1.5.1.2 Sources of Errors in Fire Assay

During lead fire assaying process the PGMs collected in the prill are subjected to varying degrees of poor recoveries or of losses [11]. These losses can be due to:

- entrapment of lead in the slag
- crucible and cupel surfaces entrapping lead
- Volatilisation of certain PGM compounds (particularly ruthenium and osmium).

The extent of losses of the individual PGM metals differs. There are a number of factors that influence the degree of losses. These include:

- concentration of base metals present
- relative ratios of individual precious metals
- the quantity of co-collector present, for example: silver
- size of prill
- cupellation time and temperature.

While losses of PGMs to the slag during fusion in the NiS fire assay are small and can often be overcome by a second fusion of the slag, physical losses are still experienced due to the intense chemical treatment that follows the fusion.

Although use of fire assay has been known for more than 2000 years, extensive use of this technique and the first publication (manual) “De Re Metallica” has been traced back to 1550. However, the creditable works only surfaced in the eighteenth century [11]. Since its inception centuries ago losses of noble metals during fire assay have been, and still are, the subject of much research. Various other collectors such as tin, copper and iron have been studied [12].

Nickel sulphide collection so far remains the only internationally recognised method for the separation and pre-concentration of individual PGMs. Unlike the ‘classical’ lead fire assay, NiS fire assay is a fairly new method and much research is still going into its improvement [16,17].

Despite all these, fire assay remains the practical basis for all routine analyses in the South African gold and platinum mining industry. Although this fire assay method is extensively used, it is clear its shortcomings results in underestimation of the true value of the total PGM content in the samples. In cases where the aliquot mass is not enough to take at least 30 g aliquot (for an ore sample), the use of this method is not advisable, and it is essential that complementary validated analytical methods be developed.

1.5.2 'Classical' Wet Chemical Techniques

Most of the reactions of the PGMs employed in wet chemical techniques are not element specific, for example: precipitation of platinum from hydrochloric acid as ammonium hexachloroplatinates - $(NH_4)_2PtCl_6$ where iridium, rhodium and palladium may interfere [15,18]. This means that all these metals must first be separated from each other. PGMs are most often analysed by means of organic and inorganic reagents, which form coloured compounds, under well-specified conditions.

1.5.2.1 Gravimetric Methods

Historically the platinum metals were usually determined gravimetrically, being weighed as the metal after having been precipitated as such or in the form of some compound – sulphide or hydrated oxide [19]. In most cases the gravimetric determinations of PGMs involve weighing in the form of pure metals, which are isolated from solution by means of reducing agents. Most of the precipitation is done by reduction or complex formation with organic reagents or metals for example: Zn and Mg [19].

Despite a wide range of reagents that have been proposed only a few are satisfactory, these include dimethylglyoxime ($C_4H_6N_2O_2$) which is used to precipitate palladium as the insoluble complex ($Pd(C_4H_7N_2O_2)_2$) in acid solution [18]. This reaction is specific, sensitive and unaffected by the presence of other PGMs [20], hydroquinone (($C_6H_4(OH_2)$)) can be used for Au [20] as shown in the equation below:

$$2HAuCl_4 + 3C_6H_4(OH)_2 \rightarrow 2Au + 3C_6H_4O_2 + 8HCl$$

The gravimetric method employs several precipitation and filtration steps and is therefore very time consuming and requires very skilled analysts. Presently these methods have been substituted by instrumental techniques such as atomic absorption and emission spectrometry.

1.5.2.2 Solvent Extraction

This is a novel method of PGM analysis that has formed the basis for the spectrometric determinations [21]. Solvent extraction achieves both separation and concentration of the noble metals from a complex solution. These methods are more specific and applicable to both high and low grade samples. The subsequent solutions can be analysed by atomic absorption spectrometry (AAS), graphite furnace-atomic absorption spectrometry (GFAAS) inductively coupled plasma – atomic emission spectrometry (ICP-AES) or by spectrophotometric methods [18, 19, 20].

These methods, however, require the sample to be in solution, the achievement of which remains the biggest challenge with platiniferrous ore/rock samples.

1.5.3 Total Decomposition – Alkali Fusion and Pressure Acid Dissolution

The introduction of sensitive techniques such AAS, GFAAS, ICP-AES and neutron activation analysis (NAA) has necessitated the extensive use of sample decomposition using fusion methods. Sodium peroxide or a mixture of sodium peroxide and sodium carbonate or sodium hydroxide, is used to convert the precious metals into their soluble sodium salts. The use of lithium metaborate ($LiBO_2$) has also been studied. A list of the salts often used as fluxes for this decomposition method is available [23]. The fusion method does not limit the sample size but often small sample masses ranging from 0.5 g to 5 g are used due to the relatively large amount of flux required. A sample is weighed into a crucible containing sodium peroxide (or the mixture), the crucible is then fused over a burner or in a muffle furnace at 850 °C for 3 minutes and the melt is dissolved in dilute hydrochloric acid. The ratio of sodium peroxide to sample mass is very high (~10). This method is well suited for the determination of major elements such as base metals, when used for trace element determination often co-precipitation with carriers such as tellurium (tellurium collection), which is time – consuming, is necessary. Depending on the type of crucible used for fusion (often zirconium crucibles) serious interferences may also be introduced if the final measurement technique is ICP-MS or ICP-AES.

Acid dissolution under pressure in sealed glass tubes in the presence of oxidising agents such as nitric acid or chlorine has been successfully used for the decomposition of high-grade samples. The acid used is hydrochloric acid and often a little nitric acid is added as an oxidising agent.

The important parameter in the dissolution is the chlorine (Cl_2) or the relation between the amount of hydrochloric acid and the oxidising agent and the metal. The hydrochloric acid is oxidised and chlorine gas is liberated and this is termed 'wet' chlorination.

The other dissolution involves blowing chlorine gas onto a weighed sample, which, is mixed with sodium chloride. The Cl_2 gas is blown onto the mixture for a few hours and the mixture is then dissolved in dilute hydrochloric acid and filtered, this is referred to as 'dry' chlorination.

The acid pressure dissolution (wet chlorination) offers certain advantages over 'dry' chlorination [22], namely:

- it prevents loss of osmium due to the volatility of its chlorides
- it prevents the formation of ruthenium and platinum chlorides which are poorly soluble in hydrochloric acid
- it does not require addition of sodium salts therefore giving a cleaner matrix for the atomic spectroscopy.

1.5.4 Methods of Determination

The determination of individual PGMs after the separation by fire assay has been achieved by use of atomic absorption spectroscopy (AAS) which has been used widely to this day. Its development is described by *Van Loon* [21] as one of the landmarks in the analysis of precious metals. In this technique, the analyte of interest is converted to atoms in the gas phase. Light of a wavelength characteristic of the sought element is passed through a gas, and the amount of light that is absorbed by these gaseous atoms is measured and related to the metal concentration present.

AAS is better suited for Au, Pd, Rh and to a lesser extent Pt. Poor detection limits are obtained for other PGMs. This technique is relatively cheap and easy to operate and this is one of its advantages. However, complex interferences are encountered with the analysis of precious metals leading to the use of "releasing" agents, as well as relatively poor sensitivity [21].

The introduction of inductively coupled plasma - atomic emission spectroscopy (ICP-AES) offered some advantages over AAS of having multi-element capabilities and a wider dynamic range of concentration within the working range, and did not require "releasing" agents.

But, like AAS it also suffers from severe spectral interferences and requires the matrix for the standards to be similar to those encountered in the samples (calibration standards should be matrix-matched). This is often difficult with the geological samples except in cases where samples have been prepared by fire assay, because most of the gangue material is lost and the resulting solutions are cleaner. The detection limits of this technique are still such that the pre-concentration step is essential for most ore, tail and some concentrate samples [21].

Although these techniques are widely available, sample preparation still limits the range of elements, the precision and the accuracy of analytical data that can be obtained from the sample.

Chapter Two

2. Motivation for the Project

The accurate and rapid determination of precious metals in ores, concentrates and tailings is of immense importance to the industry, both in terms of metal accounting and process control. Without accurate and precise figures the extent of losses at various stages of the plants cannot be estimated. Therefore, for business decision-making, faith in the fire assay results is paramount.

Further exploration of new areas through geological boreholes is expensive, and often provides limited material for analysis. The metallurgical bench-scale flotation tests also result in very small sample masses being submitted for assaying.

Moreover, the standard assaying method, lead fire assay, is known to suffer from some inaccuracies and control over some of the furnace parameters in fire assay, which may be critical, such as draft settings are difficult to standardise between sites. However, analyte losses, which occur, are kept as constant as possible by maintaining constant temperature and time in the furnaces, such that the assayers can apply 'correction' factors. These factors are determined from comparisons between uncorrected lead fire assay results and those obtained from the same sample types for fire assay using nickel sulphide collection. The factor between nickel sulphide and lead assay is known to depend on ore type and prill size. If either of these changes there is a danger of using a factor of the wrong magnitude. Therefore, in the situation where there is not enough historical data or where the matrix of the ore material is changing, the use of 'correction' factors is not recommended [23]. The use of 'correction' factors requires that the NiS measurements are accurate. There is therefore, a need for NiS results to be confirmed by other techniques whenever required.

A further problem when determining the efficiency of the assay technique is that any losses to the slag are small and undetectable by most means. The differing types of ore have differing chemical and mineralogical compositions; in some case meaning that complete chemical dissolution in the fusion stage is unlikely. Fire assayers therefore use empirical means to determine if the collection is complete. The basic guides are:

- is the fusion sufficiently fluid to pour?

- has the entire sample dissolved?
- has all metallic lead collected in the button or is there residual lead left in the crucible?
- are the prills formed into a spherical shape?

Given the above shortcomings it is not surprising that doubt exists over the assay of UG-2 materials where the above criteria are often not met.

2.1 Overall Objectives of this Study

The proposed project entails the development of a new analytical method, which will:

- enable the determination of PGMs + Au without resorting to a fire assay preconcentration

  and separation
- improve the analysis turnaround time (i.e. should be rapid and simple)
- give quantitative results with better or at least similar precision and accuracy as fire assay.

It is envisaged that this method may become a reference method against which the standard production techniques may be evaluated. For the purpose of this study only platinum, palladium, rhodium and gold have been examined.

The latest developments in ICP-MS spectroscopic technology potentially allow the determination of the PGMs without the fire assay preconcentration steps. It is desirable to use a highly sensitive and accurate technique, which yields multi-element information even for relatively small samples. One of the techniques that meet these criteria is NAA described as "unequalled for the purpose of submicrogram traces for most metals" [24]. The time-consuming nature, high cost and the technical requirements (reactor) of the method however, make NAA impractical. The short half-lives for other elements such as rhodium (4½ minutes) also presents a limitation. A suitable alternative is inductively coupled plasma-mass spectrometry (ICP-MS) as the option, which allows a compromise between cost and technical requirements.

2.1.1 Approach and anticipated problems

The use of this modern instrumentation together with microwave-assisted digestion techniques limits the sample masses to 0.05 g - 0.5 g. In such cases there is always a risk that the small samples may not be representative of the bulk and this creates sampling errors. This aspect of the technique is seen as a constraint to what the analytical method can achieve.

The reliability of the results depends not only on the quality of the analysis, but also on the degree to which the final sample represents the bulk material. (A detailed discussion on this problem is given in Chapter 3).

Figure 2.1 summarises the possible problem areas identified in sampling and analysis and the suggested solutions:

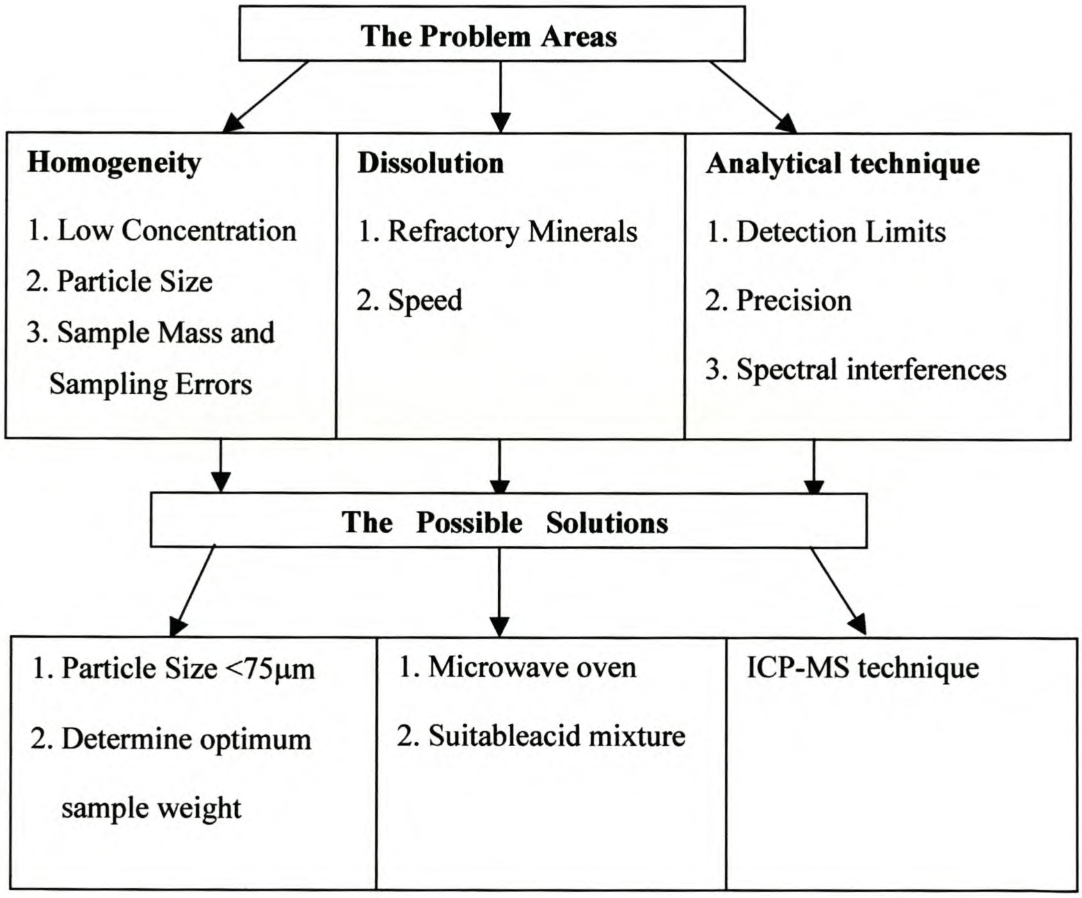

Figure 2.1 **Flowchart to summarise anticipated problems and possible solutions**

2.2 Application of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

The introduction of ICP-MS has shown great potential as a trace element analysis technique. A number of reviews have described both the principles and the applications of the technique [24-30]. The comparative performance of ICP-MS and ICP-AES has also been reported [29,31] and it has been noted that the precision of ICP-MS is poorer than ICP-AES. This could be due to the concentration levels at which the two techniques operate, which is orders of magnitude apart. The ability of ICP-MS to give isotopic information however makes it more attractive. Considerable interest has been shown in the use of ICP-MS for the analysis of geological samples.

Although most of the initial publications focused on the analysis of rare earth elements using ICP-MS [32-34] they have, nevertheless, demonstrated the superior detection power and sensitivity of the ICP-MS and also shown the limitations posed by sample preparation. The low detection limits quoted in most publications ranging from 2 ng/l Rh to 14 ng/l Au depending on the sample introduction system have proved the technique to be suitable for the determination of PGMs.

The ICP-MS allows for various other techniques to be attached as sample introduction systems (for example flow injection or ultrasonic nebuliser). A detailed review on interferences in ICP-MS done by *Evans* [35] showed that desolvation could minimise interfering polyatomic ions due to sample matrix as well as increasing the analyte signal. The application of flow injection to ICP-MS to minimise non-spectral interferences has been studied by, amongst others, *Aggarwa*l [37] and *Eaton* [38] who cite the main areas that are improved by this application as:

- detection limits
- increased sample throughput
- less sample consumption and manipulation and
- reduced matrix suppression effects.

A detailed review of ICP-MS technique is given in Chapter 4.

2.3 Sample Preparation and Terminology

2.3.1 Terminology

In the context of the PGM industry several concepts are used, which are briefly defined below:

Recovery as used in this report means the amount of the element obtained on analysis compared with that given in the references.

Expressed as a percentage: % recovery = $\frac{\text{result obtained}}{\text{consensus value}} \times 100$

Consensus value is the average result (after deleting outliers) obtained after several analyses of the same sample were carried out at different laboratories.

2.3.2 Sample Preparation

While acid mixtures such as *aqua regia* (3 parts hydrochloric acid to 1 part nitric acid) have been used for leaching the PGMs, a combined fusion-acid attack has always been necessary for a number of sample matrices, especially those carrying well-crystallised, refractory minerals. This however, introduces high salt containing matrices to the ICP-MS, with undesirable effects.

The combination of acids is chosen for its efficiency in decomposing the matrix. It is usually desirable for the acid to have oxidising properties and be able to form a soluble salt with the metal ion of interest. For these reasons nitric acid, hydrochloric acid and perchloric acid are commonly used in sample dissolution for chemical analysis [37]. The solvent role of *aqua regia* depends on the presence of nitric acid (an oxidant capable of removing an electron for example: $Pt^0 \rightarrow Pt^{4+} + 4e^-$) and hydrochloric acid, which provides a source of chloride ions to form soluble stable MCl_6^{2-} ($PtCl_6^{2-}$) complexes.

Knowledge of the sample matrix and the presence of other major elements is essential for choosing appropriate acid combination [40].

Other acid combinations, which are widely used, include hydrofluoric acid (to dissolve silicates) and perchloric acid ($HF - HClO_4$) or hydrofluoric acid, perchloric acid and *aqua regia* (HF - $HClO_4$ - *aqua regia*). This approach reduces the sample matrix, since in practice, the addition of HF - $HClO_4$ is followed by evaporation of the solution to incipient dryness and this step is repeated several times (about 5 times). During this process most of the volatile compounds will be lost, for example silica as SiF_4. These dissolutions are usually carried out on a hot plate in open vessels where there is a possibility of losing the volatile elements of interest.

The dissolution of geological samples has also received considerable attention owing to their intractable nature [36-42]. A wide range of dissolution techniques has been developed for the analysis of geological and related samples. The dissolutions are often accomplished by acid attack at atmospheric or elevated pressure. Detailed evaluations of these sample preparation techniques are given [42-44], and all highlight the capabilities of ICP-MS, the potential of this technique for the analysis of geological samples, and the importance of dissolution procedures especially where refractory minerals occur.

Published methods have described the application of ICP-MS for the determination of the precious metals in a wide range of geological materials following acid digestion with or without pre-concentration steps. Some authors have used ICP-MS for the analysis of PGMs after separation and pre-concentration by fire assay [13,16,45,] and good agreement with reference materials has been reported in most instances.

The examination of the NiS preconcentration method has been undertaken and it is believed that most of the losses in the NiS process occur during the dissolution stages. *Parry* [46] used NAA after NiS fire assay collection to bypass dissolution steps and reported yield recoveries around 90% Pt on SARM 7[#]. Similar work was done by *Naldrett* [47], where SARM 7 was used as a tracer (with the chromitite flux) after irradiation yielded between 91 and 112% Pt with most of the other PGM's following a similar trend.

Aqua regia has been used extensively to leach the PGMs, however, it only provides qualitative rather than quantitative results. This is indicated by the low recoveries especially on platinum when aqua reqia alone is used on SARM 7. In the investigation done by *Potts and co-workers* [48] on SARM 7, a 10g sample was digested with *aqua regia* at room

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[#] SARM 7: South African Reference Material for Merensky platinum ore, prepared by Council for Mineral Technology Republic of South Africa.

temperature for 60 minutes. Pd and Au were recovered efficiently, while Pt and Rh showed poor results ~18%. Heating on the other hand improved results on these two analytes (Pt and Rh) and no effect was observed on the amounts of Pd and Au which remained relatively the same. These investigators also observed that the sulphur-rich samples showed lower recoveries, and believed this to be due to the very fine size particles of the sulphide minerals bearing the precious metals which tend to float and are not attacked by the acids.

A search for a rapid dissolution technique and the use of ICP-MS for multi-element determinations, has led to the possible use of a microwave oven as an energy source in a low-temperature closed digestion system. Microwave oven digestions are perhaps the most interesting developments in sample preparation investigated in the last 30 years.

Nowinski [49] used *aqua regia* digestion on SARM 7 using microwave heating and showed very little improvement from the previous results. *Totland et al.* [41] cited three possible reasons why *aqua regia* alone may fail to digest all precious metals:

- some proportion of each element may occur in solid solution within refractory silicate minerals.
- precious metals may be present in discrete, potentially soluble mineral grains, but which may be embedded in an acid resistant matrix such as chromite.
- specific precious metal minerals may occur which are insoluble in *aqua regia*.

A number of such minerals (insoluble in *aqua regia*) have been identified [6,21] and these include sperrylites ($PtAs_2$) and sulphides (cooperite and braggite).

An acid mixture which included hydrofluoric acid and perchloric acid with microwave oven digestion [41], showed significant improvement on Rh recoveries up to 100% and 85% for Pd. Platinum and gold recoveries showed no change from digestion with *aqua regia* only. Taking the experiment further by fusing the residue, the platinum recoveries improved to 90% and 93% for gold while Pd and Rh remained the same. This suggests that the platinum minerals are most resistant to acid attack even after the addition of HF and $HClO_4$ and as such temperature and pressure have no effect on this behaviour, ruling out embedding in silica minerals.

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Although the alkali fusion did bring a significant improvement in the recoveries, it introduces higher dissolved solids, resulting in larger dilutions; by so doing some elements are pushed below the quantitation levels. It is therefore undesirable to introduce more salts to the matrix because of the small sample masses (0.5 g) used.

Losses by volatilisation with HF-$HClO_4$ acid mixture in an open vessel have been investigated by *Bock* [40], and it was found that only ruthenium and osmium are subject to some degree of loss.

Perry et al. [50] describes 'dry' chlorination dissolution method for geological samples, whereby hot chlorine gas is blown onto a weighed sample, which is mixed with sodium chloride. Sodium chloride is required to convert the PGMs to the soluble sodium chloro-complexes. The Cl_2 gas is blown onto the mixture for three and a half hours and the mixture is dissolved in dilute hydrochloric acid; it is then filtered and the precious metals in the filtrate are determined using ICP-MS. This method was developed particularly for low concentrations of PGMs as an alternative to the fire assay technique. The data reported using 15 g sample aliquots shows that only rhodium was "over recovered" (122%) while platinum, palladium and gold results were still lower (80%, 57% and 66% respectively) but significantly higher in comparison to those of *aqua regia* alone. Notably, palladium showed the poorest recovery results. The results indicate the possibility of chlorine resistant material in the sample, which prompted their subsequent study [51] to further treat the residue by microwave digestion which confirmed the existence of a non-metallic fraction not attacked by chlorination, resulting in the encapsulation of some PGMs. Although this method uses fairly large sample masses (and has no mass restrictions), the chlorination time of 3.5 hours is too long and does not meet the requirements for throughput in a routine analysis laboratory. It is also obvious that chlorination alone is not sufficient but requires further treatment of the insoluble material. While the presence of sodium chloride does not pose any limitation as in the alkali fusion method (because of its low ratio to the sample mass), the prolonged use of chlorine gas is dangerous and constitutes a health hazard because of its toxicity.

A comparison of the four preparations: lead and nickel sulphide fire assay, chlorination and acid dissolution is given by *Palmer et al.* [52]. From this work the platinum recoveries from chlorination and acid dissolution were higher (4 to 14%) than those from fire assay for all sample types used, while the other elements (palladium, rhodium and gold) compared well for all preparations, however, the acid dissolution method consistently yielded low recoveries for all four elements on the chromitite ore. The significance of pre-roasting was investigated by these authors and it was found that when samples have been roasted at 600°C, recoveries on chlorination improved from 79 to 96 % Pt; 84 to 96 % Pd and 87 to 98% Rh [52].

The samples were also roasted prior to acid dissolution; however even after digesting a 25 g-sample on a steam bath for 4 hours this method yielded an insoluble residue which required further treatment.

Although the latter two methodologies (chlorination and acid digestion) gave comparable results to fire assay methods (with better recoveries for platinum), they could not be recommended for routine analysis due to the length of time that the preparation takes.

Roasting the samples in the presence of air gives rise to formation of refractory oxides of some PGMs rhodium, iridium ruthenium and sometimes palladium [11]. To overcome this effect it is recommended that samples be reduced under hydrogen.

Hydrogen reduction has also been used [40] to reduce the refractory chromite to a soluble form prior to acid dissolution. Use of phosphoric acid (H_3PO_4) to dissolve chrome ores, iron oxide ores and slags has also been studied [40]. Because of the low vapour pressure of H_3PO_4, relatively high temperatures can be obtained without stressing the microwave digestion vessel [39].

With all this information there should be a way for analysts to develop methods which are applicable to the specific needs and conditions in a routine PGM analysis laboratory, with emphasis on:

- availability of equipment and apparatus
- precision and accuracy required.

2.4 Objectives of this Study

The development of methods for the recovery of precious metals generally requires *complete dissolution* of a *representative sample* together with an *accurate measurement technique*. The aim of this study is to find suitable *rapid* dissolution techniques for the direct determination of platinum group elements in ore or feed (geological) samples of differing mineralogical types, without using an assay pre-concentration procedure. The determination of the PGM plus Au content of the solution will be done on the ICP-MS. This method should be simple to carry out.

As the analytical sample is likely to be much smaller than that used routinely for fire assay, the *sampling and analytical precision* must be determined and taken into consideration.

In order to achieve the above objectives the following approach will be taken:

i. Determine the extent of sampling errors as introduced by small sample masses by estimating the minimum sample weight statistically.

ii. Determine the precision of fire assay by compiling and analysing the data statistically.

iii. Determine the detection limits, precision and the extent of spectral interferences of the ICP-MS technique using synthetic solutions

iv. Determine the effective acid mixture using both synthetic solutions and mine samples.

v. Dissolve the mine sample and check the recoveries. Submit any residue for mineralogical examination.

vi. Evaluate the method by using reference material.

Chapter Three

3. Assessment of Errors

3.1 Statistical Errors

The quality of data obtained from a quantitative chemical analysis depends on sampling, sample preparation and actual measurement of analyte concentration. There are various sources of errors throughout these operations. Errors in chemical analysis may be classified as systematic or random (determinate or indeterminate). Systematic errors cause inaccuracy in the results while the random errors are the cause of imprecision in an analysis.

3.1.1 Systematic or Determinate Errors

Systematic or determinate errors are inherent in the method, these are often independent of the method of sampling, but may depend on the skill of the analyst. They have a definite value and often have 'direction' i.e. causing either high or low results.

These errors may be divided further into constant and proportional errors. Constant errors will become more serious as the size of the quantity measured decreases while the magnitude of proportional error is fixed on fraction of the interfering contaminants in the sample [54].

Systematic errors can be minimised or detected by taking standard rock sample (reference material) through the process, the assumption being that the systematic errors affect the known and unknown samples to the same degree.

3.1.2 Random or Indeterminate Errors

Random or indeterminate errors result from the impossibility of being able to repeat any measurement in exactly the same way. They are due to inherent fluctuations within a repeated method, errors by the analyst, and random sampling error introduced by taking sub-samples from the prepared rock powder.

The uncertainty due to random errors generated by the analytical technique can be reduced by making several measurements on the same solution, such that the distribution of averages is a factor on N1/2 more narrow (each average being the result of N replicates). The uncertainty generated from random errors due to sample variation can be reduced by carrying through several replicates of the sample, taking large sample masses or by ensuring that the sampling error is negligible [53].

3.2 Homogeneity of Analyte Distribution in a Sample

It is apparent that complete uniform analyte distribution (homogeneity) is impossible unless the analyte is distributed completely homogeneously throughout the sample. In practice, complete homogeneity is not obtainable by any physical procedure. The effective homogeneity depends on the physical nature of the noble metal, the size of the ore particle and the size of the sample taken for analysis [23, 53].

The effect of inhomogeneity of analyte distribution is exacerbated when the mineral of interest is predominantly present in discrete minor-phase grains. This effect becomes more serious if the size of these grains is larger and the bulk concentration of the element of interest is lower. This is the case in ores containing precious metals and their minerals.

To improve homogeneity within a sample it is suggested that the minimum mass of material collected of each sample should be at least 1 kg. It is also believed that some of the uncertainties over sample homogeneity effects are overcome by modern standards of rock crushing which normally specify that the rock powders should be milled to pass a 200-mesh sieve (<75 μm).

In most cases, inaccurate results are normally related back to incomplete dissolution or analytical methods. However, the analytical error is often smaller and generally better understood than the sampling error. In his study *Fricke* [53] highlighted the significance of the sampling error, which is often overlooked. This sampling error is dependent on:

- analyte concentration
- physio-chemical characteristics (particle size, shape, density and interaction tendencies)
- precision of the analytical technique.

Due to the known heterogeneous distribution of PGMs in the ore and process samples under consideration, it was essential in this work to examine the effect of heterogeneity on the minimum mass aliquot for further analysis.

3.3 Estimating the Minimum Sample Mass from Sampling Error

Sampling involves taking some part of the lot of material, and it is therefore subject to random errors if carried out correctly and to both random and systematic errors if done incorrectly. As an estimation process subject to random errors, sampling becomes an appropriate field of application of mathematical statistics. Investigations have been carried out on these problems; *Wilson* [55] presented a mathematical derivation of sampling precision. Considering the variance of analyte distributions in terms of particle size, this study concluded that 1 g of rock sample crushed to a mesh size of 200 (<75 µm) - equivalent to 5 x 10^5 uniformly sized particles was adequate for the accurate determination of major elements in most rock types. This then means that for trace elements the problem is more intense.

Kleeman [56] suggests that for sample aliquots smaller than 0.5 g to be used, the powder must be crushed more finely – to pass 230-mesh sieve (<63 µm). A simplified approach has been taken by *Fricke* [53] to estimate the optimum sample mass, assuming only two component particles, one which carries the analyte of interest and that which does not. These authors have used the variance ratio (*F* ratio) which compares two variances to show the contribution of the sampling error to the overall error. They showed that precision increased 10-fold with a 100-fold increase in minimum sample weights. It was observed that samples with larger particle diameters require a very high minimum sample weight, to reduce the "sampling" error.

Knowing the approximate amount of any mineral in the sample powder, and the limits of error that can be tolerated, it is possible to estimate the minimum sample mass for determining an element relative to the abundance of the element and the degree of fineness of the powdered rock sample [53,55], such that the "sampling" error is comparable to the analytical error.

Mass of an object can be given by:

$$\text{Mass} = \text{Volume x Density} \qquad 3.0$$

Because the size of the sample required is expressed in number of particles, therefore the weight of the sample depend on the weight of the particle, such that equation 3.0 becomes:

$$\text{Optimum Sample Mass} = \text{Volume x Density x n} \qquad 3.1$$

Where "**n**" is the number of particles given by equation 3.3

The optimum sample mass is not necessarily the one that gives lowest sampling variance but the one that gives the desired sampling precision. Therefore, where sampling is concerned, the degree of accuracy that is desirable should be considered at the beginning of any method or procedure development and a decision must be made regarding the maximum allowable error due to sampling (σ_E) that can be tolerated [18].

The relationship between the allowable error (standard deviation) and the number of particles required is given by:

$$n = (1 - p) / p\sigma_E^2 \qquad 3.2$$

According to Fricke [53] and Wilson [55], "sampling" error is dependent on several factors: rock type (mineralogy), weight of sample and particle size distribution and these factors are taken into consideration when determining the number of particles - "n" required (equation 3.3) [54]:

$$n = p(1 - p)\left(\frac{d_1 d_2}{d^2_{ave}}\right)^2 \left(\frac{\%P_1 - \%P_2}{\sigma_E \ \%P_{ave}}\right)^2 \qquad 3.3$$

Where: PGM mineral = Grain 1 with density d_1

Gangue = Grain 2 with density d_2

p = Fraction (grade) of PGM Mineral

$P_1\%$ = % of PGM in grain 1

$P_2\%$ = % of PGM in grain 2

d_{ave} = Weighted average density of the rock powder

= $(p \times d_1) + (1 - p) \times d_2$

$P^{\%}_{ave}$ = Weighted average % PGM in all particles

= $(p \times d_1 \times P_1 \times 100) / d_{ave}$

σ_E = the maximum sampling error that can be tolerated.

Some of these parameters were obtained or calculated from mineralogical data [5] and are given in table 3.1, for each ore type.

If particles are assumed to be spherical then their volume is given by:

$$volume = \frac{4}{3}\pi r^3 \qquad 3.4$$

Where ***r*** is taken as the radius of the average particle size.

The optimum sample masses were calculated assuming different values of σ_E, using equations 3.1 - 3.4 and these are tabulated in table 3.2 (details on calculations are given in Appendix II).

Table 3.1 Mineralogical variables of the three South African Platiniferous Reefs

	Merensky	UG-2	Platreef
Grade (g/ton) - p	4.8	4.04	6.64
Density (g/cm^3) - d_1	10.03	16	10.08
- d_2	3.28	4.04	3.27
- d_{ave}	3.28	4.04	3.27
Total PGM % - P_1	34.2	41	22.64
- P_2	0	0	0
- P_{ave}	6.01×10^{-4}	6.56×10^{-4}	4.62×10^{-4}
Particle radius – r (cm)	12.5×10^{-4}	12.5×10^{-4}	12.5×10^{-4}

Table 3.2 Estimated Minimum Sample Mass for selected tolerable σ_E (sampling error)

Value of σ_E	Estimated Mass (g)		
	Merensky	UG-2	Platreef
1%	57	82	40
5%	2.2	3.3	1.6
10%	0.5	0.8	0.4
20%	0.1	0.2	0.1

The estimates on sample masses given in table 3.2 show that for the contribution of the sampling error to the precision of the analyses to be better (or lower) than 10%, the sample masses used for all three sample types must be at least 1.0 g.

3.4 Evaluation of Overall Analytical Precision

Statistical evaluation of standard analytical error involves two concepts namely: variance and standard deviations. The analysis of variance (ANOVA) is accepted as the most useful statistical treatment for random sources of error in sampling problems.

The overall error $S^2_{overall}$ is estimated by:

$$S^2_{overall} = S^2_{within} + S^2_{between} \tag{3.5}$$

Where: S^2_{within} is the variance within a batch estimating the uncertainty in the analytical results caused by the method of analysis and is given by:

$$S^2_{within} = \frac{1}{k(n-1)}\sum_{j=1}^{k}\sum_{i=1}^{n}(x_{i,j}-\bar{x}_j)^2 \tag{3.5}$$

and $S^2_{between}$ is the variance of the results between batches (days)

$$S^2_{between} = \frac{n}{k-1}\sum_{j=1}^{k}(\bar{x}_j-\bar{x})^2 \tag{3.6}$$

S^2_{within} is taken as the estimate for $S^2_{overall}$ and $S^2_{between}$ is assumed to be equal to S^2_{within} such that the two can be combined to give a good estimate of $S^2_{overall}$.

$$S^2_{overall} = \frac{1}{(nk-1)}\sum_{j=1}^{k}\sum_{i=1}^{n}(x_{i,j}-\bar{x})^2 \tag{3.7}$$

Where:

n	is the number of observations within a batch
k	is the number of batches
x_i	is the ith observation
$x_{i,j}$	is the ith observation in jth batch
$\bar{x}$	is the mean value for all observations
$\bar{x}_j$	is the mean value of the jth batch
S^2	is the variance of the observations

The overall variance of the method is the sum of the total operations involved: sampling and analytical technique:

$$S^2_{overall} = S^2_{analytical} + S^2_{sampling} \qquad 3.8$$

Analytical errors include errors due to crushing, splitting, laboratory subsampling, and instrumental procedures.

The variance between batches ($S^2_{between}$) ideally gives an estimate of the variance within (S^2_{within}) a batch plus the variance due to sampling ($S^2_{sampling}$). As mentioned earlier, $S^2_{between}$ is assumed to be equal to S^2_{within} (assuming that $S^2_{sampling}$ is negligible), but if $S^2_{between}$ is significantly greater than S^2_{within} the difference is taken as the uncertainty due to sampling $S^2_{sampling}$ [57].

From the analysis of variance S^2_{within} and the $S^2_{between}$ are obtained and so $S^2_{sampling}$ can be calculated by taking the difference between the two and dividing by the number of observations:

$$s^2_{sampling} = 1/n\,(S^2_{between} - S^2_{within}) \qquad 3.9$$

3.4.1 Evaluation of Overall Analytical Precision of Fire Assay Data

In order to be able to test the 'new' method against the existing fire assay, it was necessary to first assess the overall precision of the fire assay method, and then set a benchmark for the 'new' method.

A statistical analysis of the lead gravimetric quality control (QC) data was carried out to determine daily precision of results. This data was collected over a number of days. In most cases the samples batches used contained about 20 results. The samples were divided into two categories according to their PGM grades: 2-10 g/t and >10 g/t.

An analysis of variance was performed to differentiate the variation within replicates (S^2_{within}) and that between days ($S^2_{between}$). This was followed by an F-ratio to check the difference between the variances.

$$\text{F-ratio} = S^2_{between} / S^2_{within} \qquad 3.10$$

F-test states that if the experimental F exceeds the critical value given in tables at a certain probability.

A comparison between the two variances (S^2_{within} and $S^2_{between}$) showed no significant differences at 95% confidence level, which implied that the precision within a batch can be a good estimate of the overall precision. In view of the fact that there was no sampling involved between days this could be expected.

The two variances were combined to calculate the overall variance ($S^2_{overall}$) and this variance was compared to the S^2_{within}, and again F-ratio was computed to check difference between $S^2_{overall}$ S^2_{within}, and there was no significant difference at 95% confidence limit between the two variances. Under these conditions, it could be concluded that there is no statistically significant difference between various days and various batches. These variances were expressed as percentage relative standard deviation (%RSD) by dividing the square root of the variances by the mean value ($\overline{x}$) and multiply the result by hundred. The results are shown in Table 3.1.

Outliers were calculated as values falling outside twice the standard deviation of the mean value (2 x $S_{overall}$). A number in the brackets indicates the number of results which were rejected as outliers. The results (after deleting outliers) indicate the estimated precision of the lead fire assay technique, which is set as the benchmark to which the newly developed method in this study must be compared.

Table 3.3 Summary of the Statistical Analysis on Fire Assay QC Results

Grade (g/t)	Average PGM+Au (g/t)	Within Batch Precision (% RSD)	Between Batch Precision (% RSD)	Overall Precision (% RSD)	Total no. of observations (n)
>10	245	4.57	4.92	4.63	259 (25)
3 – 10	4.5	6.39	6.01	6.5	277(12)

The data from the two groups is depicted graphically in Figures 3.1 to 3.2, showing all the data (raw data) reported. These were samples which have been prepared in bulk to be used as quality control samples, they were taken through the fire assay process and analysed with every batch of new samples of similar origin. The samples have been analysed over a period of time such that the mean values and the control limits have been worked out for each one.

Most of the outliers tended to be lower than the mean value. They were found to be mostly due to (1) the brittle prills which often result from the silica or lead adhering to the lead button, and/or (2) a cracked cupel which results in part of the prill being lost into the cupel itself. In some cases the outliers were found to be personal errors where the QC sample was weighed twice into one pot or it was swapped with another sample; this occurred once in each case.

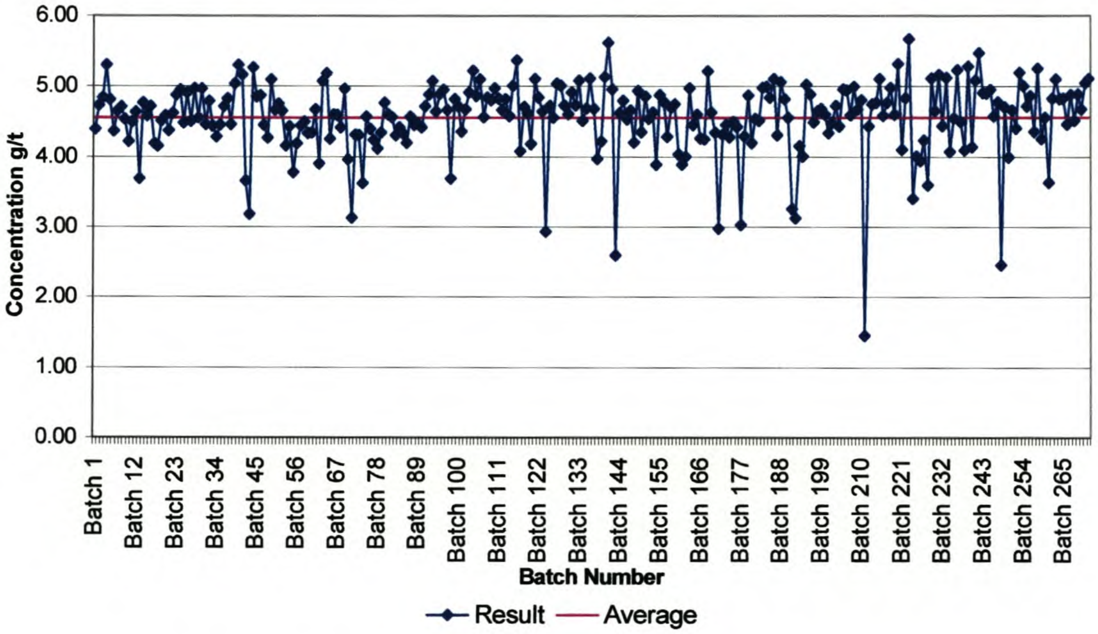


Figure 3.1 Raw Data for Fire Assay QC Results: 2-10 g/t

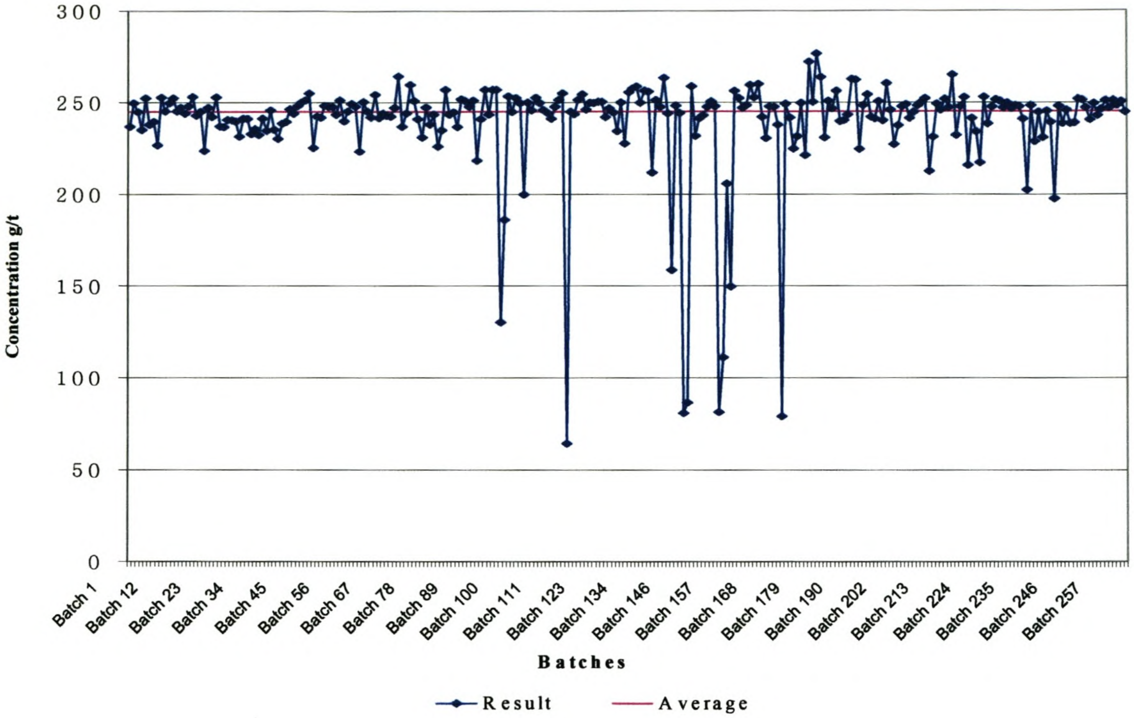


Figure 3.2 Raw Data for Fire Assay QC Results: >10 g/t

3.5 Preparation of Samples for Homogeneity

In view of the above, it was necessary to prepare large homogeneous ore samples from the various reefs to be used throughout this study. For this purpose, three mine samples from each ore type (about 5 kg each) were obtained from Mineral Processing (Metallurgical) department. These were milled to a fine powder by passing the sample through a pulverising machine for about 90 seconds. A particle size analysis was also done using a set of screening sieves (screen size range of 212 µm to 25 µm) in order to estimate the average particle size diameter. The particle size distribution (Figure. 3.4) showed approximately 50% of the sample to be less than 25 µm in diameter, with the largest particle size being 212 µm (Merensky: 0.9%, Platreef: 1.55% and UG-2: 0.05%). The samples were then split into smaller (~1 kg) portions using the 8-way splitter and each container was mixed well using a "Turbula" mixer. To determine the variation between the splits, the samples were analysed for base metals (copper, nickel, cobalt, iron and in the case of UG-2 chromium was included) by means of X-ray fluorescence (XRF), where only the countrates from each split were compared and a statistical analysis was done to check for any significant differences between the splits. The analysis of variance (ANOVA) within and between groups showed no significant difference in the homogeneity of the splits and so it was concluded that the splits were uniform.

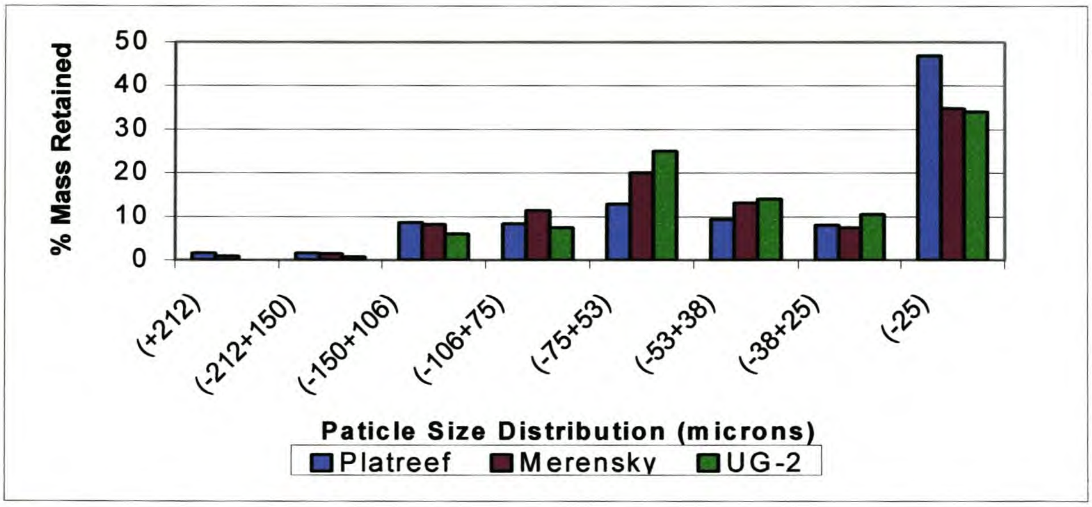


Figure 3.4 Particle size distribution in the 3 reef samples

Chapter Four

4. Inductively Coupled Plasma - Mass Spectrsmetry (ICP-MS)

Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) has become a popular and versatile analytical technique. The first commercial quadrupole based ICP-MS was introduced to the market in 1983. Since then the technique has undergone further developments and has gained worldwide acceptance as a technique for trace element analysis. It is characterised by:

- low detection limits,
- wide linear dynamic range – more than five orders of magnitude,
- multi-element capabilities,
- high sample throughput,
- ability to provide isotopic information.

It is a highly desirable technique for elemental analysis of geological and environmental samples [21-24]. The precision often ranges from 2 to 10% which is poorer compared to ICP-AES (1 to 5%), and is influenced greatly by the concentration levels of the analyte. The benchmark techniques for trace element analysis include graphite furnace atomic absorption spectroscopy (GFAAS) and instrumental neutron activation analysis (INAA). Although these techniques offer better precision [36], the ICP-MS has some distinct advantages over them. The main advantage of ICP-MS over GFAAS is its multi-element capabilities and ability to handle complex matrices better. Its advantages over INAA are: availability, speed of analysis (sample throughput) and element coverage.

ICP-MS is well established as a solution based technique, however the feasibility of slurry nebulisation has been investigated [58-60] and by changing the sample introduction system, solids can also be analysed directly. For example, by electrothermal vaporisation (ETV) [60], or Laser Ablation (LA) [61]. However, ETV-ICP-MS may not cope with complex matrices of geological samples while calibration still remains the limiting factor for accurate measurements using LA-ICP-MS. A number of calibration strategies are still being explored to produce suitable calibration curves for use with unknown samples [36,62]. For the purpose of this study, only the solution-based technique will be reviewed.

4.1 Principle of ICP-MS

A solution is pumped into a nebuliser using a peristaltic pump, where it mixes with argon gas to form an aerosol spray. The aerosol then passes through a spray chamber where heavy droplets (diameter >10 μm) are separated out to drain. Only the light droplets are carried to the plasma where the aerosol is: (a) desolvated, (b) dissociated and (c) atomised and ionised. The positively charged ions are extracted into a high vacuum region through a set of cones. The ion lens forms the ions into an axial beam, through to the quadrupole mass - analyser, which operates as a mass filter along the axis, at which a stable ion path exists, for ions of a given mass per charge ratio at a particular time. Other ions of different masses are deflected away from the axis and are lost. The transmitted ions strike the detector and the number of registered ions from a given isotope is directly dependent on the concentration of the relevant element in the sample. Figure 4.1 illustrates the layout of the VG Elemental PQ2*plus* ICP – MS system.

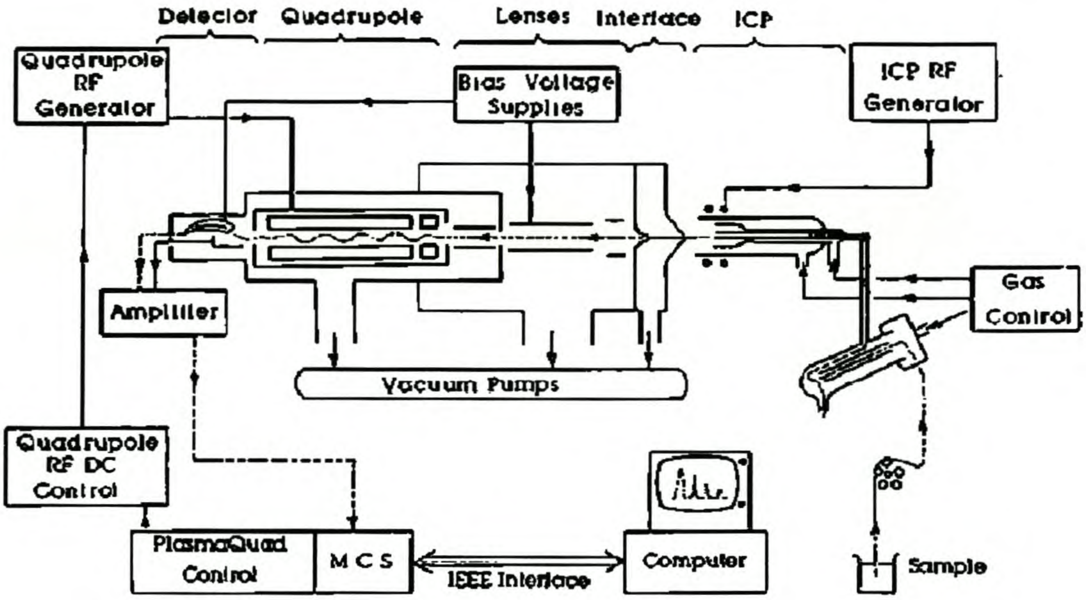


Figure 4.1 **Schematic diagram of an ICP-MS system [63]**

4.2 Various Components of ICP-MS

ICP-MS uses ICP as an ionization source and the quadrupole mass analyser for separation. The performance of the instrument depends on proper optimisation of each component, these components reviewed below and they include: sample introduction, ICP, interface region, ion optics, mass analyser (quadrupole) and a detector.

4.2.1 Sample Introduction System

Comprises:

- Peristaltic pump, used to transport the solution into the plasma. A pump ensures a constant flow rate of sample compensating for the differences in uptake rate due to differing viscosity of samples. It also allows for a controlled uptake rate, which is essential for the calibration of the instrument.
- Nebulizer, producing an aerosol by the interaction of the liquid sample and high velocity argon gas.
- Spray chamber, located between the nebulizer and the torch. It is used to separate the aerosol droplets by size. Heavy or larger droplets that cannot be supported by the carrier gas are removed, ensuring that only finer (lighter) droplets, which are less than 10 μm in diameter pass through into the plasma. This prevents an excessive loading of the plasma, which may give a significant cooling effect. This results in reduced efficiency where only approximately one percent of the aspirated solution goes into the plasma while the rest is pumped out to the drain. The efficiency of the spray chamber is dependent on the temperature. The higher the ambient temperature the less efficient the spray chamber, due to the evaporation of the water vapour that has formed on the walls of the spray chamber. It is estimated that the water transported to the plasma through evaporation is about three times that in the aerosol [64]. Therefore to reduce this overloading the spray chamber inside the torch box is water cooled to about 5 °C or maintained at a constant room temperature outside the torch box to allow the vapour to condense.

4.2.2 Ion Source

From the spray chamber the aerosol is transported to the ICP torch. The torch most commonly used has an outer tube of inner diameter 18 mm and is approximately 100 mm long. Within the outer tube there are two concentric tubes of 13 mm and 1.5 mm inner diameter. Each annular region formed by the tubes is supplied with argon gas. The sample is introduced to the plasma through the centre tube.

The argon stream is seeded with electrons from a high-voltage spark from a tesla coil. The plasma is generated by the interaction of this gas with the radio frequency (RF) magnetic field which is induced by a copper induction coil. The main plasma gas flow is about 10 to 15 l/min, which maintains the plasma and acts as a coolant for the quartz torch. The supporting gas flow (auxiliary) which controls the position of plasma relative to torch (to prevent melting) is about 0.5 - 0.8 l/min. The carrier (nebulizer) gas flows between 0.8 to 1.2 l/min.

The extremely high temperatures of the plasma (6000 to 10000 K) provide excellent dissociation of the chemical species. Ionisation efficiency exceeds 90% for most elements at 6000 K with singly charged positive ions predominating. This is primarily due to argon having a very high first ionisation energy (15 eV) in comparison to other elements.

There are three main regions in the plasma (figure 4.2), characterised by the population of argon ions, as the population decreases the plasma temperatures also decrease [25].

- Induction region: contains the largest number of charged argon ions and is the hottest region.
- Secondary region: in this region the ion density decreases and so does the temperature.
- Analytical region: this is the region used as analytical source due to lower density of argon ions

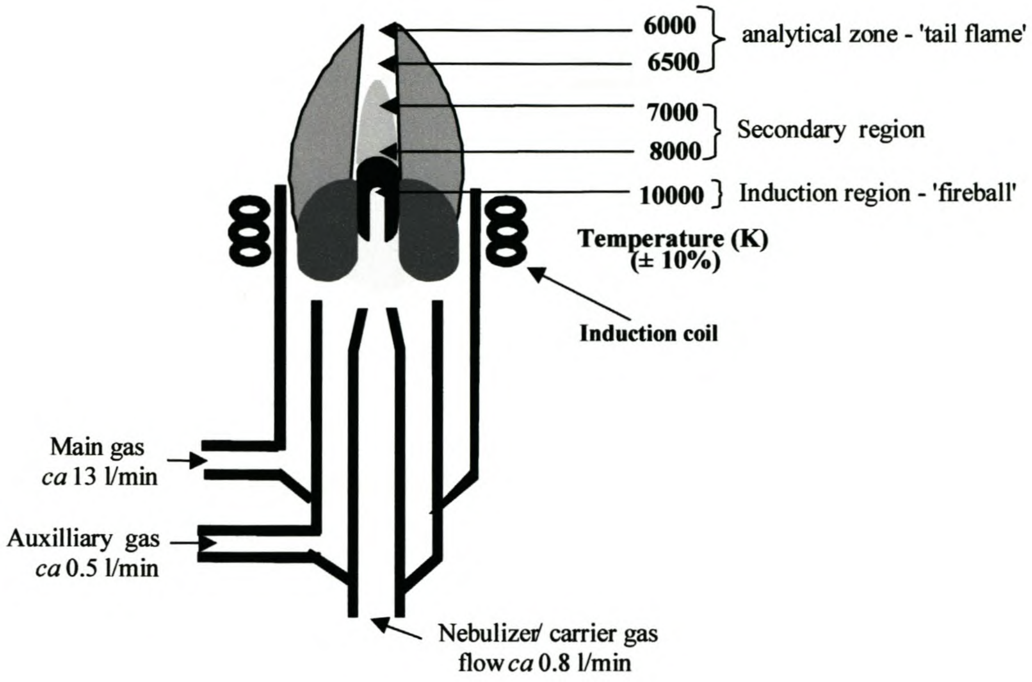


Figure 4.2 **Plasma zones**

A number of reasons have been cited [36] why the argon gas is preferred or used:

- It is inert – does not readily react chemically with samples
- High first ionisation energy (15 eV) – causes effective ionisation of other elements.
- Low thermal conductivity – heat is retained in the plasma enabling stable operation
- Optically transparent

Use of other gases such as nitrogen has been investigated [36] but was found to increase spectral and isobaric interferences.

Ionization takes place in two basic ways:

Electron impact - $M + e^- \rightarrow M^+ + 2e^-$

Penning ionisation - $Ar^+ + M \rightarrow M^+ + Ar + e^-$

4.2.3 Sampling Interface

The function of the interface is to transfer a representative sample of the plasma ion population to a high vacuum region. It consists of sampler cone with about 1 mm aperture followed by a skimmer cone with about 0.7 mm aperture. Both these can be made of pure nickel metal or platinum. Nickel is commonly used because of its affordability while still offering good thermal conductivity, mechanical robustness and reasonable resistance to commonly used acids [65].

A representative material of the plasma central channel (richest in ions) is sampled through the sampler cone into a 1 to 3 torr pressure region (1atm = 760 torr). The sampler isolates the gases from the plasma allowing only the gases richest in sample ions to enter the interface. In this area most of the argon atoms are rejected at the sampler cone and are removed through the vacuum pump.

The ion beam is further sampled through the skimmer cone into a 10^{-5} torr pressure region. The skimmer cone still restricts the flow of gases to the central part of the ions initially coming from the plasma [65]. The condition of the skimmer cone significantly affects the sensitivity of the instrument and the levels of polyatomic species, because the gas flow from the aperture into the low vacuum region depends on the ratio of the aperture diameter and the mean free path (λ) of the gas. The aperture diameter of 0.5 mm or more is considered large enough to provide continuum flow into the vacuum system [66].

Both these cones are water cooled through contact of their bases with water-cooled chambers within the interface. The layout is illustrated in Figure 4.3

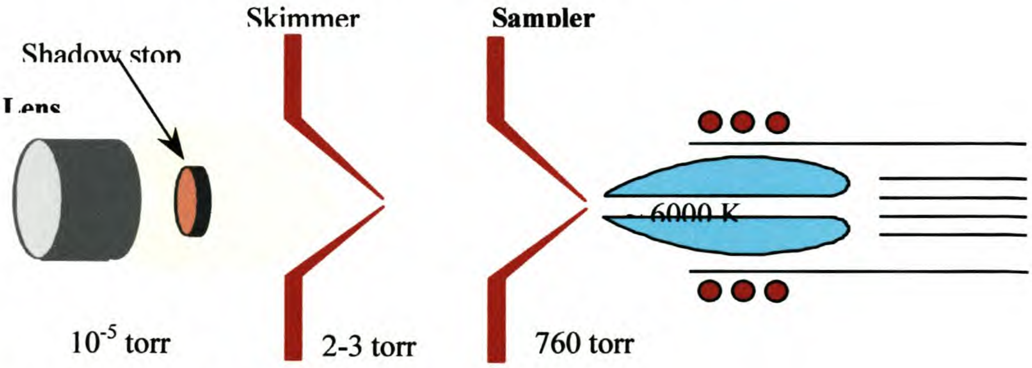


Figure 4.3 Layout of the torch, interface and ion optics.

4.2.4 Ion Optics

Situated on the axis behind the skimmer cone is the shadow (photon) stop (Figure 4.3), which is used to block the photons from passing through to the detector and increasing the background signal.

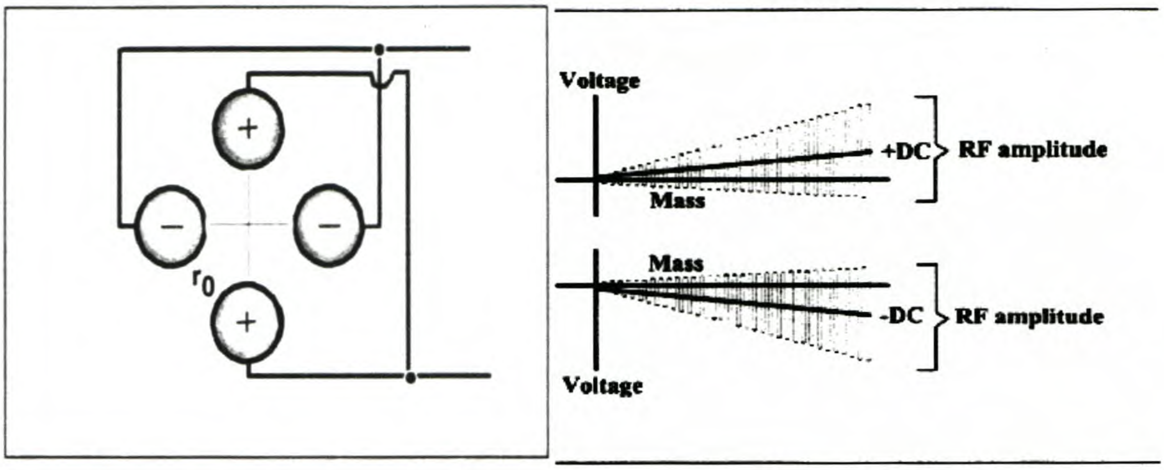
The ion beam that passes through the interface is channelled into the quadrupoles by a cylindrical electrostatic lens. The electrical fields around the lens are carefully controlled. The lens extracts the ions from the neutral species and focuses a broad ion beam coming from the skimmer into a narrow beam using a variable voltage of –24 V to +24 V. By creating a positive field around the ions it forces them back into a beam.

The lens can gradually become contaminated by a build-up of deposits over time. This is indicated by a steady increase in the optimum voltage [65].

4.2.5 Quadrupole Mass Filter

The focused ions are directed into the quadrupole mass spectrometer. This is constructed of four parallel conductive rods that operate in a vacuum of 10^{-5} torr. The shape of the rods and the spacing between them are held at a high tolerance so as to produce a hyperbolic field. Each opposite pair of the rods with radius $\mathbf{r_0}$ has an overall positive or negative potential (figure 4.4a).

The mass filtering action is achieved by applying AC and DC voltages. Polarity is switched around at a frequency of 2.5 MHz. At a given RF/DC ratio only ions of a given mass per charge ratio can pass through the quadrupole. Ions that are not of the correct mass per charge ratio will have unstable trajectories and are lost by colliding with the rods or exiting out of the path and are pumped out (4.4b)



(A) (B)

Figure 4.4 Quadrupoles : A shows alignment and B shows the effect of changing polarity

DC voltage U and RF voltage V are applied to each pair of quadrupoles. DC is negative for one pair and positive for the other. The RF voltages on each pair of quadrupoles have the same magnitude but opposite in signs. The ion trajectories and transmission properties of a quadrupole can be determined from U, V, m/z, radius between the rods - $\mathbf{r_0}$, and RF frequency – $\boldsymbol{\omega}$. (r_0 and ω are fixed parameters). By changing U and V and maintaining U/V ratio constant, a scan line can be generated and the operating points of differing m/z will move into the stable region and a mass spectrum can be obtained [25].

Quadrupoles performs best with ions that have low kinetic energies as:

KE = $\frac{1}{2}$ mv^2, high value of KE implies high velocity (v).

If ion energy is high the ions move too quickly through the mass filters and do not experience enough RF cycles for proper resolution. The entire mass range 5 to 270 atomic mass units (amu) may be scanned in about 100 milliseconds.

The front end of the mass spectrometer is equipped with a valve to allow the change of cones and lens without losing the vacuum.

4.2.6 Detector

Ions are transmitted from the quadrupole mass filter to the dual mode detector (fig. 4.5) producing an amplified signal that is processed by the detection electronics and sent to the computer for signal processing. The detector is situated in the vacuum chamber. It comprises 21 dynodes (metal plate supplied with high voltage between 2500 V and 1300 V), which carry out the electron multiplying process.

From the quadrupoles the ions strike the first angled dynode and secondary electrons are emitted from the surface of the dynode and as they descend down the dynodes, they are multiplied. The position of successive dynodes result in multiplying cascade effect of the secondary electrons.

Should the pulse count exceed 2 million counts an isolated dynode is switched to ground potential, disabling the pulse section of the detector. The analogue section (less sensitive) of the detector will then measure the current produced from the first 13 dynodes [65].

The angled dynode causes the ions to flow in a curved path, separating the signal ions from the background noise, which consist of neutral species, and the electromagnetic radiation from the ion source.

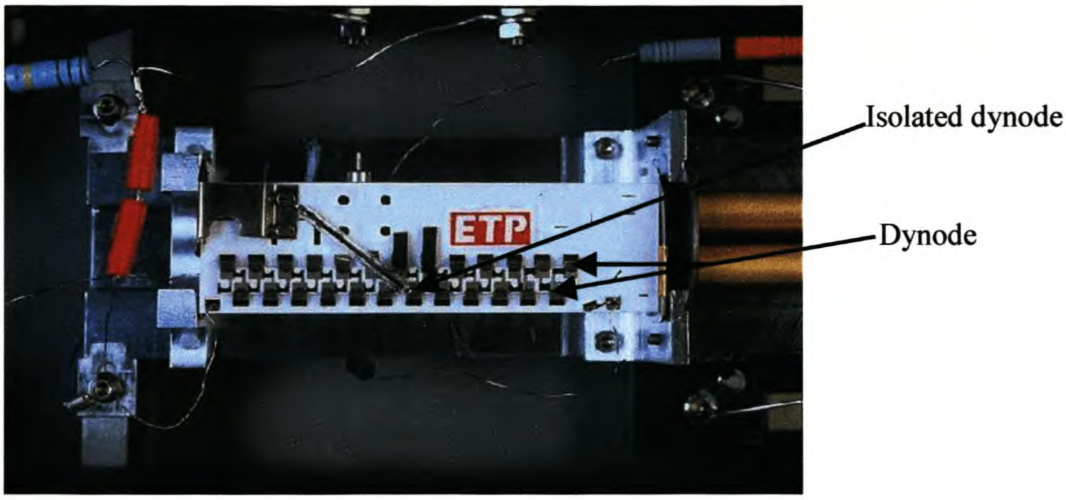


Figure 4.5 Dual stage discrete dynode detector

4.2.7 Vacuum System

Mass spectrometry requires movement of the ions without collisions, therefore a mass spectrometer is contained in a high vacuum (10^{-5} torr) chamber. In this high vacuum system, gas atoms collide with the walls of the chamber more frequently than collisions between gas atoms, they then bounce off the walls and diffuse out into the pump. The pump functions as a gas trap – gas flows from the chamber into the pump where it is compressed and exhausted [25].

A three-stage vacuum system is used to reduce the pressure gradually from atmosphoric (at ICP) to 10^{-5} torr using different pumps.

First stage – a rotary (mechanical) pump is used with a relatively low speed. It is used to evacuate the interface region and as a backing pump to carry off the exhaust from the high vacuum pumps.

Mechanical pump, has a hollow metal cylinder which contains a rotor, and the rotor has two grooves which hold spring-loaded vanes. As the rotor spins the vanes move with it by doing so they can compress or expand the volume of gas that they enclose [25]. Figure 4.6 shows the operating principle of the rotary pump.

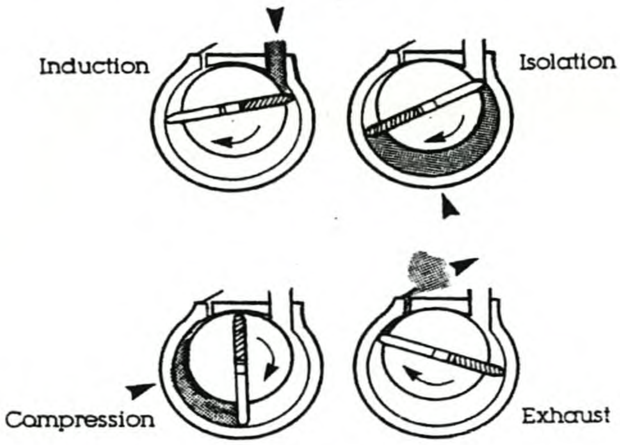


Figure 4.6 Operating principle of the mechanical pump [63]

Turbomolecular pump, is a large metal cylinder with a wide inlet and a narrow outlet, (fig. 4.7a) it contains a turbine which is spun at a very high speed (~300000 rpm). The turbine has blades which intermesh with the stationary blades mounted on the inner wall of the cylinder. The gas molecules are deflected from one plate to another and fall out at the bottom into the rotary backing pump and are exhausted (fig. 4.7b)[25].

The turbo pumps do not use oil vapour in the pumping mechanism, however they require cooling and lubrication for the turbine bearings.

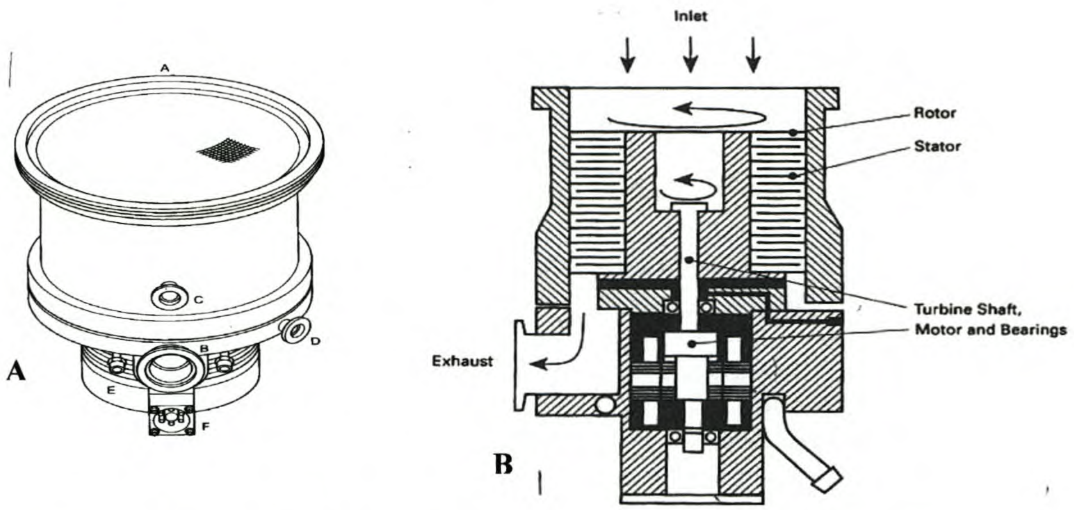


Figure 4.7 **Picture of the turbomolecular pump (A) outside and (B) inside [25]**

4.3 Advantages and Disadvantages

4.3.1 Advantages

ICP-MS has very low detection limits and outstanding sensitivity for elements above mass 80 amu. This sensitivity makes the technique particularly attractive for the analysis of precious metals. It offers rapid, multi-element determinations and this makes it highly cost effective. In comparison with other spectral techniques ICP-MS gives simple spectra even in complex matrices and has less spectral interferences. Although the ICP-MS is a sequential instrument, it behaves like a simultaneous instrument due to the speed at which it scans – scans through a periodic table within 100 ms. This enables measurement of transient signals, allowing use of only microlitres of a sample. It also provides isotopic information.

4.3.2 Disadvantages

ICP-MS has a number of significant limitations. The allowed amount of total dissolved solids (TDS) in the ICP-MS is limited to 0.2% to minimise signal drift due to blocking of cones in order to maximise precision. This is a limiting factor in the use of ICP-MS as this demands large dilutions. The increased dilutions invariably result in some trace element concentrations in solution being below the limit of determination. The acid content in the solution also has to be kept minimal (about 5%) to avoid corrosion on the cone surface. In order to minimise interferences due to chloride ions, nitric acid is preferred over hydrochloric acid and also because HNO_3 can be produced at a higher purity.

The technique also suffers from a number of interferences, and in order to achieve the optimum performance of the ICP-MS, it is necessary to be aware of the existence of spectral interferences, as well as quantification of such interferences on specific sample matrices. It is equally important to determine the impact of the matrix on various masses. These interferences are briefly discussed.

4.4 Interferences

It has been demonstrated that quadrupole ICP-MS suffers from interferences, despite earlier claims that ICP-MS is free from interferences [26]. This is due to the inability of quadrupoles to resolve masses below 1 amu apart. For example $^{56}Fe^+$ (actual mass m/z 55.847) is interfered by $^{56}ArO^+$ (m/z 55.947). The double-focusing magnetic sector high resolution ICP-MS (HR-ICP-MS) is able to resolve these masses [30] at a loss of some sensitivity. Spectral interferences are however, well characterised and can be avoided or minimised. Fortunately the PGMs are not heavily affected by interferences as they occur above 80 amu and have more than one isotope with two exceptions, gold and rhodium which are monoisotopic.

There are two main types of interferences, namely: spectroscopic and non-spectroscopic matrix effects.

4.4.1 Spectroscopic interferences

These are caused by atomic or molecular ions having the same nominal mass as the analyte of interest, causing an increase in the signal at the mass per charge ratio (m/z) of interest. These can be divided further into four categories according to their origin.

4.4.1.1 Isobaric Interferences

These are caused by two isotopes of different elements having the same mass. They are often anticipated and well documented, and can be avoided by choosing alternative isotopes or by applying mathematical corrections. Table 4.1a shows the isobaric interferences that occur on some PGMs and all of them can be avoided.

Table 4.1a Isobaric Interferences occuring on some PGMs

[1]Isotope (analyte)	% Relative Abundance	Isobar	% Relative. Abundance
^{102}Pd	1.02	Ru	31.6
^{104}Pd	10.97	Ru	19.54
^{106}Pd	27.33	Cd	1.22
^{108}Pd	26.71	Cd	0.88
^{110}Pd	11.81	Cd	12.39
^{190}Pt	0.01	Os	26.4
^{192}Pt	0.79	Os	41.0
^{198}Pt	7.2	Hg	9.97

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[1] Only isotopes which have relative abundance above 1% have been considered

4.4.1.2 Polyatomic Interferences - MX^+

Polyatomic ions that form in the plasma result from a reaction between the most abundant ions in the plasma. Most commonly occurring combinations involve the plasma gas argon (Ar) and the solvent acids, for example ArO^+, ArH^+ in water or nitric acid. $ArCl^+$ and ClO^+ are examples of interferences due to the presence of HCl. Often the sample matrix that contains high levels of sodium or copper also result in the formation of $ArNa^+$ and $ArCu^+$ respectively. The formation of these polyatomic interferences is unavoidable in all ICP-MS systems, although plasma conditions and other parameters may be optimised to minimise their formation they can never be completely removed [67]. These interferences become more serious in cases of ^{75}As, ^{51}V ($^{40}Ar^{35}Cl$, $^{35}Cl^{16}O$), where there are no alternative isotopes, which are free from interferences and their determination is therefore compromised. The choice of acid matrix is critical depending on the analytes of interest. In the case of high sample matrices, high dilutions are inevitable. Table 4.1b shows some of the polyatomic interferences that affect PGM determinations.

Table 4.1b Examples of Polyatomic Interferences affecting PGM analysis

Isotope	% Abundance	MX^+ ($X = {}^{40}Ar$)	% Abundance of M
^{103}Rh	100	$^{40}Ar^{63}Cu$	69.09
^{105}Pd	22.23	$^{40}Ar^{65}Cu$	30.91

4.4.1.3 Doubly Charged Ions - M^{++}

Although most ions (90%) which form in the plasma are singly charged, there are still some doubly charged ions (M^{++}) formed. If the second ionisation energy of the element is lower than the first ionisation energy of argon then the result is a doubly charged ion. In this case a signal is seen at half the mass of a parent ion. The instrument can however, be optimised to give the low levels of M^{++}. None of these pose any problems for PGM determinations. However, in fire assay preparation, if lead (Pb) is not efficiently volatilised, the solutions will contain high amounts of Pb and the existence of Pb^{++} may be a nuisance in the determination of the mono-isotopic rhodium ($^{103}Rh^+$) as a result of $^{206}Pb^{++}$.

4.4.1.4 Oxide Formation - MO^+

The recombination can also occur in the plasma tail flame resulting in oxide formation. If the nebuliser gas flow rate is too high, the aerosol is pushed through the plasma quicker resulting in increased oxide formation. This can also be kept minimal during optimisation. For these interferences to emerge the parent analyte must be present in reasonably high concentrations (above 100 ppm). Some of the possible oxides that can interfere with PGM analysis are tabulated in table 4.1c.

Table 4.1c Oxide Interferences on a PGM Determination

[2]Isotope (analyte)	% Rel Abundance	MO^+ ($O = {}^{16}O$)
^{103}Rh	100	^{87}Sr, ^{87}Rb
^{105}Pd	22.23	^{89}Y
$^{106,108,110}Pd$	27.33, 26.71, 11.81	$^{90,92,94}Zr$
$^{194,195,196}Pt$	32.9, 33.8, 26.3	$^{178,179,180}Hf$
^{197}Au	100	^{181}Ta

These interferences can be predicted from the knowledge of sample matrix and method of sample preparation and where possible alternative isotopes can be selected.

4.4.2 Non-spectroscopic Matrix Effects

The matrix can cause non-spectroscopic interferences. The high dissolved solids in the samples will reduce the sensitivity significantly by clogging the cone orifices and reducing the precision. Any element present in significant concentrations can potentially cause ionisation suppression especially those with ionisation potentials below 8 eV (easily ionisable).

The presence of a heavy element like uranium causes significant signal suppression. This is believed to result from physical scattering of lighter ions by the heavy matrix ions (positively charged ions repelling each other), as the ion cloud enters the ion

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[2] Only isotopes with relative abundance above 1% have been considered

optics [28, 29]. Sodium matrix also causes apparent signal suppression, this could be due to the fact that sodium is easily ionisable and when the density of easily ionisable atoms increases, the degree of ionisation of the analyte atoms decreases.

Some commonly used strategies for overcoming these non-spectroscopic effects include use of internal standardisation and high dilutions. These can also be overcome by using standard additions or isotope dilution for calibration.

There are different strategies to overcome both spectroscopic and non-spectroscopic interferences that can be employed by the analyst and the manufacturer:

Analyst:

- Alternative sample preparation
- Preconcentration, precipitation or solvent extraction
- Alternative sample introduction: flow injection, desolvation, thermal vaporisation or laser ablation.

Instrumental:

- Instrumental optimisation
- Interface design
- Multivariate correction methods
- High mass resolution magnetic sector
- Collision / reaction cells

The latest developments in ICP-MS technology such as reaction or collision cells have provided a solution for most spectral interferences due to argon gas and/or the solvent by providing chemical resolution. Collision cell based systems are working on kinetic energy discrimination to reduce the background, collision gases are fed into the cell and these cause collisions and reactions between various species, polyatomic ions are broken into their constituent parts or converted into ions that do not interfere with the analyte of interest [68]. However, these collisions and reactions may still generate more unwanted combinations (species). The reaction cell systems on the other hand use gas-phase reaction chemistry (thermochemistry to predict the reactions that may occur) and this chemistry is mostly controlled. However, without control of the chemistry in the cell, undesirable reactions will also result in the unwanted species [67,69]. The resolution of a reaction cell system has been found to be much higher than most systems with the right chemistry (without loss of sensitivity), it has been possible to achieve the resolution of ^{87}Rb from ^{87}Sr using CH_3F gas which is not attainable in a normal ICP-MS system where a resolution of about 300000 would be required [70]. The cell gases that are commonly used in both systems include the highly reactive ammonia and methane and the less reactive gases such as hydrogen and helium.

In this study a PE Sciex Elan6100 quadrupole based ICP-MS by Perkin Elmer was used, details of the instrumental parameters are given in chapter 5.

4.4.3 Internal Standardisation

The internal standard is used to compensate for variations in instrument sensitivity caused by electronic drift, nebuliser and transport efficiency and other matrix effects. More than one internal standard can be used. The internal standard must behave much like the analytes, must occur at very low and preferably constant levels in the samples, they must be readily available in suitable purity and at a reasonable cost. The internal standard must not suffer isobaric overlaps or from other interference and not generate them on isotopes of interest.

Chapter Five

5. Experimental Procedures

5.1 Instrumental Details and Settings

All determinations were carried out using a PESciex® Elan™ 6100 ICP-MS spectrometer using the operating parameters in Table 5.1. A range shows how some parameters changed over the entire experimentation.

Table 5.1 Operating Parameters

RF Generator	40 MHz free-running
Nebuliser:	Cross-flow
Spray Chamber:	Ryton
Interface:	Nickel cones
RF Power (W)	1125 – 1150
Plasma (cooling) gas (L/min)	15
Neb. Gas flow rate (l/min)	0.81 - 0.89
Lens voltage (volts)	6.4 – 8.0
Acquisition mode	peak hopping
Sample uptake (ml/min)	1.2
Running vacuum (torr)	$1.06 \times 10^{-5} – 1.45 \times 10^{-5}$

The instrument was optimised using indium (^{115}In). Indium was used as an internal standard for palladium and rhodium, while rhenium (^{185}Re) was used for platinum and gold. The two internal standards were used to minimize any mass dependent effects that may occur. Cerium (^{140}Ce) was used to optimise for the oxide ions and this was done by maintaining the ratio ^{156}CeO^{+} / ^{140}Ce^{+} below 4% (<4%), and the doubly charged ions were monitored using ^{69}Ba/^{138}Ba ratio and this was kept below 3%.

Table 5.2 shows the elemental isotopes which were used for analysis

Table 5.2 Elements and Isotopes used and Relative %Abundances

Element	Isotope(s) used	Relative Abundance (%)
Platinum	^{195}Pt	32.9
	^{196}Pt	33.8
Palladium	^{105}Pd	22.33
	^{106}Pd	27.33
	^{108}Pd	26.46
Rhodium	^{103}Rh	100
Gold	^{197}Au	100
Internal Standards:		
Indium	^{115}In	96.7
Rhenium	^{185}Re	37.4

5.2 Reagents and Glassware

The acids (32% HCl, 65% HNO_3 and 40% HF) used were ultra pure from Merck and the ultra pure certified solutions for base metals were also purchased from Merck. The perchloric acid (70%) and boric acid (H_3BO_3) were "Analytical" grade. Ultra pure water was obtained from Millipore (Milli-Q) water purification system (18 MΩ.cm). All glassware used was "A"-grade and these were acid washed in *aqua regia* and rinsed in ultra pure water. The pipettes and the volumetric flasks were calibrated by weighing the volume of water contained at a given temperature.

5.3 Preparation of Test Solutions for Optimisation of ICP-MS

5.3.1 Precious Metal Solutions

A mixed stock solution of 50.00 mg/l PGMs was prepared from 1.000 g/l individual PGM solutions prepared from pure metals. From this a 10.0 µg/l PGM standard was prepared for the determination of the detection limits and a set of calibration standards was also prepared. The concentration range of PGM calibration standard in µg/l was as follows: 0.0; 0.25; 0.62; 2.5; 6.25; 12.5; 25.0 and 50.0.

The synthetic PGM solution used for determining instrumental precision was obtained from monthly quality control mixed stock solutions prepared from pure metals and analysed over a period of time.

5.3.2 Base Metal Solutions

Standard solutions of 0.50 g/l individual base metals (copper, nickel, iron, cobalt and chromium) were prepared from 1.00 g/l ultra pure standards purchased from Merck and these were used as matrix for the determination of detection limits.

5.4 Apparatus, Equipment and Instrumentation

Samples were weighed on a 'Sartorius' chemical balance, registering four decimal places. The balance was checked against known weights daily. For filtration, the 'witts' filtering apparatus was used with a 'Sartorius' 0.45 µm cellulose nitrate filter papers.

A commercial microwave digestion system, the Milestone Ethos 1600 microwave unit was used for the dissolution, the oven has variable power up to 1000 W, an exhaust and a HPS 1000/6 rotor which takes six high pressure PTFE vessels. It is provided with a capping station to tighten the caps reproducibly to a specific torque, thereby allowing maximum pressure within the vessels to be maintained without venting.

The comparative ICP-AES work was done on a Jobin Yvon JY 70 Plus instrument fitted with a cross flow nebulizer. During the initial test work some of the microwaved and leached residues were submitted on the cellulose nitrate filter paper for qualitative scans using a Philips PW2400 x-ray fluorescence spectrometer. Some residues were submitted for mineralogical examination where PGMs are detected using an automated 'bright particle search' routine on JEOL scanning electron microscope (SEM). The composition of each particle detected is checked using energy dispersive spectroscopic (EDS) techniques.

Samples were roasted in the Carbolite LMF muffle furnace and compressed air was connected from the wall. Air was bubbled into an absorbing flask containing water and then into an empty flask before delivering it to the muffle, this was done to make the air flow visible, to ensure a constant uninterrupted flow of air.

A 'Leco' sulphur and carbon analyser, SC-144DR was used for sulphur analysis.

5.5 Sample Preparation

The samples were subjected to pretreatment steps prior to acid dissolution by microwave digestion.

5.5.1 Roasting of Samples

Sample aliquots were carefully weighed into vitreosyl (silica) crucibles and transferred to a muffle furnace which has been heated to 850 °C. A small hole was drilled into the door of the furnace through which a stream of compressed air was carefully blown into the furnace at about 1.4l/min. Two absorbing flasks were connected (in series) to the air inlet, the first flask contained water such that the air bubbled through and then passed into the empty flask (to avoid water passing into the furnace) and then through to the furnace using a quartz L-shaped delivery tube. This was done in order to have an indication of continuous flow of air into the furnace. The furnace is fitted with an extraction fan which provides effective expulsion of sulphur dioxide (upon oxidation of sulphur). The samples were roasted for about one hour after which they were cooled in the dessicator before being transferred to microwave vessels.

5.5.2 Thermal Hydrogen Reduction

Thermal reduction of the roasted samples is effected by placing the hot crucibles from the muffle onto the hydrogen reduction manifold. A lid with a hole in the middle is placed on each crucible and hydrogen gas is delivered to the crucibles using an 'L'-shaped delivery tube. From the tip of the delivery tube, the gas is ignited and brought into contact with the sample through this hole in the lid. The crucible is heated from underneath with liquid petroleum gas (LPG) flame using Bunsen burner for about 10 minutes and the burners are switched off leaving the hydrogen burning for another 20 more minutes. Thereafter, hydrogen is switched off and the crucibles are placed in the dessicator to cool.

5.5.3 Microwave Acid Dissolution

After completion of the roasting/reduction treatment the samples in the crucibles were then transferred to the microwave vessels. However, in cases where roasting was omitted the samples were weighed directly into the microwave vessels. The vessels were capped and assembled onto a rotor and tightened before being transferred to a microwave oven. The rotor assembly was allowed to twist to provide even and effective heating.

A microwave unit is controlled through a computer and once the rotor is in the microwave, a program that has been pre-determined is activated. When the cycle is completed the contents were allowed to cool before uncapping the vessels.

The acid mixture that was used contains hydrofluoric acid therefore to protect the glassware 28 g/l (saturated) boric acid is added to the vessels to complex the excess fluoride ions, before the solution was transferred to the volumetric flasks.

The samples were analysed on the ICP-MS using an 8-point external calibration. (Details given in Appendix III).

5.6 Factorial Design Experiments

Factorial experiments were designed to investigate the effect of having HF and $HClO_4$ acids in the acid mixture on the individual PGMs using both synthetic PGM solutions and the mine samples (see Appendix III). The designs enables the analyst to study more than one parameter in a given batch of samples. The software also provides a means to analyse the data given.

A “Stat-Easy” (Design-Expert 5, v. 6.0.9 by Stat-Ease Corporation) program was used to compute the analysis of variation (ANOVA).

5.7 Samples and Reference Materials

Two well-prepared Anglo Platinum in-house Merensky flotation concentrate sample and UG-2 flotation concentrate were used. The samples were prepared at one laboratory and distributed to six other group laboratories for analysis. Although all the laboratories used fire assay technique for the determination of PGMs, the Pb fire assay technique varied significantly from one laboratory to another, while other laboratories used NiS method. The *pooled standard deviations* were calculated and these were used to determine the uncertainty on the results, and the consensus values in this case were treated as reference values.

Three feed samples from different reefs were used for mineralogical studies. Method evaluation was carried out using the South African Platinum ore Reference Material – SARM 7.

Definition:

Flotation Concentrate - metallurgical term for the ore that has been put through a flotation cell to separate PGM minerals from gangue material. Ground ore is mixed with water to form pulp, introduced into a flotation cell and the cell is agitated, reagents are added and air is blown into the cell. PGM-bearing minerals collect into a froth, which overflows out of the cell and is collected, filtered and dried. The typical total PGM grade range for a flotation concentrate is 80 – 300 g/t.

Feed (flotation)– ore that has been crushed and milled to a smaller particle size in order to prepare it to be fed into the plant for processing.

Chapter Six

6 Results and Discussion

6.1 Performance of the ICP-MS

The analysis of trace elements requires good detection limits, good precision and ideally no interferences. The first part of this chapter looks at how well these can be achieved using the ICP-MS by employing synthetic standard solutions to determine:

- detection limits
- precision and accuracy
- matrix tolerance (interferences)

6.1.1 Determination of Detection Limits and Limits of Determination

The limit of detection (L_D) is described as the smallest signal that can be observed and be considered as being caused by the analyte to be measured at a given confidence limit. These can be determined by a number of methods, but is usually obtained by repeatedly measuring signals from a blank solution and a single standard solution containing all the analytes. At least eleven replicates (n = 11) are recommended [56].

The detection limits were calculated from the standard deviation of the blank signal using the following equation:

$$\text{Detection Limit } (L_D) = \frac{k \times s_{(blk)} \times 10000 \text{ ng/l}}{N_{std} - N_{blk}} \qquad 6.1$$

where: k = numeric constant often taken as 3 (99.87% confidence limit)

$s_{(blk)}$ = standard deviation of the blank

N_{std} = mean countrate (cps) of the standard

N_{blk} = mean countrate (cps) of the blank

10000 ng/l = concentration of the standard in ng/l

The limit of quantitation (L_Q) which is described as the smallest signal that can be quantitatively measured at a satisfactory level of confidence (99.99%) [46] is calculated with the value of $k = 10$

Table 6.1 shows the detection limits in a clean blank solution of 2% nitric acid and in the presence of individual base metals. The results that were significantly affected by the presence of a base metal matrix are marked with an asterix (*).

Table 6.1 Detection Limits (L_D) and Limits of Quantitation (L_Q) in ng/l (n = 11)

Isotope(s)	Matrix 2% HNO_3		Matrix 0.5 g/l Cu		Matrix 0.5 g/l Ni		Matrix 0.5 g/l Cr		Matrix 0.5 g/lCo	
	L_D	L_Q	L_D	L_Q	L_D	L_Q	L_D	L_Q	L_D	L_Q
^{195}Pt	3.8	12.5	6.6	18.5	10	33	6.5	18.2	6.5	18.2
^{196}Pt	4.6	16.2	7.5	24.8	12	39.6	8.1	26.7	18	59.4
^{105}Pd	8.3	27.4	298*	983.4*	9.5	31.4	52*	171.6*	18	59.4
^{106}Pd	3.1	10.2	23	76.9	7.6	26.1	22	72.6	23	76.9
^{108}Pd	2.3	7.6	10	33.0	6.8	22.4	15	49.5	17	56.1
^{103}Rh	2.5	8.3	224*	739.2*	1.8	6.9	31	102.3*	3.5	11.6
^{197}Au	13.8	46.5	15	49.5	13.6	44.9	25	82.5	18	59.4

The detection limits of palladium and rhodium are undoubtedly affected by the presence of some base metals due to the existence of polyatomic interferences which form in the plasma. Copper interferes with one isotope of palladium (^{105}Pd) and that of rhodium (^{103}Rh) by combining with argon (^{40}Ar) to form $(^{40}Ar^{65}Cu)^+$ and $(^{40}Ar^{63}Cu)^+$ respectively. The increased detection limits on ^{105}Pd in the presence of chromium matrix seem to be due to possible copper contaminants in the chromium solution because a similar effect is observed on ^{103}Rh.

The low detection limits (instrumental) obtained in this study indicate the potential for the determination of trace elements. These are comparable and in most cases better than those achieved in many other publications [16,41,45,49] with the standard pneumatic nebulisation (this instrument is relatively new). However, these figures are obtained in relatively clean solutions, which is not the case in the geological environment, where the sample matrices contain high quantities of dissolved solids requiring very high dilution factors.

In practice, the limits of quantitation which are given often depend on the sample preparation technique, for example in alkali fusion, they can be pushed up by a factor of about 2000, compared to acid dissolution where they can be pushed up by a factor of 500.

6.1.2 Determination of the ICP-MS Precision

Two solutions containing known amounts of PGMs and gold were analysed against the synthetic PGM standards, to assess the precision of the technique. The results were acquired over three months and a summary of these is given in table 6.2 showing the overall precision obtained for each element.

Table 6.2 Precision Test Results of the ICP-MS (n= 20)

	Platinum (mg/l)		**Palladium (mg/l)**		**Gold (mg/l)**		**Rhodium (mg/l)**	
	Solution 1	Solution 2	Solution 1	Solution 2	Solution 1	Solution 2	Solution 1	Solution 2
Nominal	**22.0**	**30.0**	**13.5**	**15.0**	**1.7**	**1.0**	**3.1**	**3.1**
AVE	21.9	30.0	13.2	15.1	1.63	0.96	3.15	3.2
STDDEV	0.3	0.60	0.2	0.30	0.07	0.04	0.06	0.09
%RSD	**1.5**	**2.0**	**1.6**	**2.0**	**4.0**	**4.6**	**1.9**	**2.9**

Where:
AVE = Average result
STDDEV = Standard deviation of the results
% RSD = Percentage relative standard deviation

The reproducibility of the measurements, expressed as a percentage standard deviation of the mean value varied from one element to another. This was around 2% RSD for Pt, Pd and Rh, while Au was consistently around 4% showing the poorest precision. Gold has the lowest concentration compared to the other elements and has shown the worst precision, therefore, the precision of the ICP-MS is also dependent on the concentration levels as expected. The quoted precision (%RSD) in the literature [36,42,43] for these elements ranges from 2 - 10%, therefore the instrument used is well within the commonly obtained range.

The analysis of variance was computed to check the precision within and between months. Using the statistical F-ratio, the variances within months and those between months were compared. The results for all elements (Pt, Pd, Rh and Au) showed no significant difference at the 95% confidence limit. That meant that the within variance could be used as an estimation for the overall precision. (Data is shown Appendix III).

6.1.3 Calibration of the ICP-MS

External calibration was performed immediately prior to the analysis of samples by acquiring seven standard solutions and a blank each time. Internal standards (^{115}In for Pd and Rh and ^{185}Re for Pt and Au) were also used to compensate for any instrumental drift during the analysis. The curves were made to go through the origin and an eight point linear graph was obtained between 0.0 to 125 µg/l on all four elements. Statistical features of typical calibration graphs are shown in Table 6.3

The countrate per second (cps) is directly proportional to the concentration of the analyte such that from the countrate of each standard a calibration graph is generated.

Table 6.3 Features of the Calibration Graphs for all the Elements.

Isotope	Slope of the Graph $Y^a = mX^b + C$	Correlation Coefficient (R^2)	Calibration Range (µg/l)
^{195}Pt	0.047	0.9999	0.25 – 125
^{196}Pt	0.041	0.9999	0.25 – 125
^{105}Pd	0.019	0.9999	0.25 – 125
^{106}Pd	0.020	0.9999	0.25 – 125
^{108}Pd	0.022	0.9999	0.25 – 125
^{103}Rh	0.077	0.9999	0.25 – 125
^{197}Au	0.065	0.9999	0.25 –125

Figures III.1A to III.1D in appendix III show the typical calibration graphs for the four elements where the standard concentrations are plotted against the intensity. The intensity in this case is the ratio of counts per second for each isotope to that of the internal standard.

6.1.4 Base Metals Interferents on Selected Isotopes

As described in section 1.3 (page 15 - 16), most PGM minerals occur in association with base metal sulphides, which implies that unless base metals are removed, they are always present as part of the matrix in the PGM solution. However, as indicated in table 6.1, the determination of palladium and rhodium is significantly affected by copper interference. When solutions containing high amounts (500 mg/l) of copper were aspirated a significant signal enhancement was observed on ^{105}Pd and ^{103}Rh (table 6.1). To quantify this effect of base metals on these isotopes (^{105}Pd and ^{103}Rh) and determine a 'correction' factor to minimise uncertainties associated with these interferences, three copper standards with different concentrations (100.0, 250.0 and 500.0 mg/l) were prepared and analysed for palladium and rhodium with a full calibration.

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[a] Y = ratio of the countrate to that of the internal standard

[b] X = concentration in µg/l

The obtained *apparent* concentrations (due to the presence of copper) on palladium on ^{105}Pd and rhodium on ^{103}Rh were plotted against the copper concentration. Figures 6.1A and 6.1B show the plot of the *apparent* rhodium and palladium concentrations against that of copper, showing essentially a linear relationship.

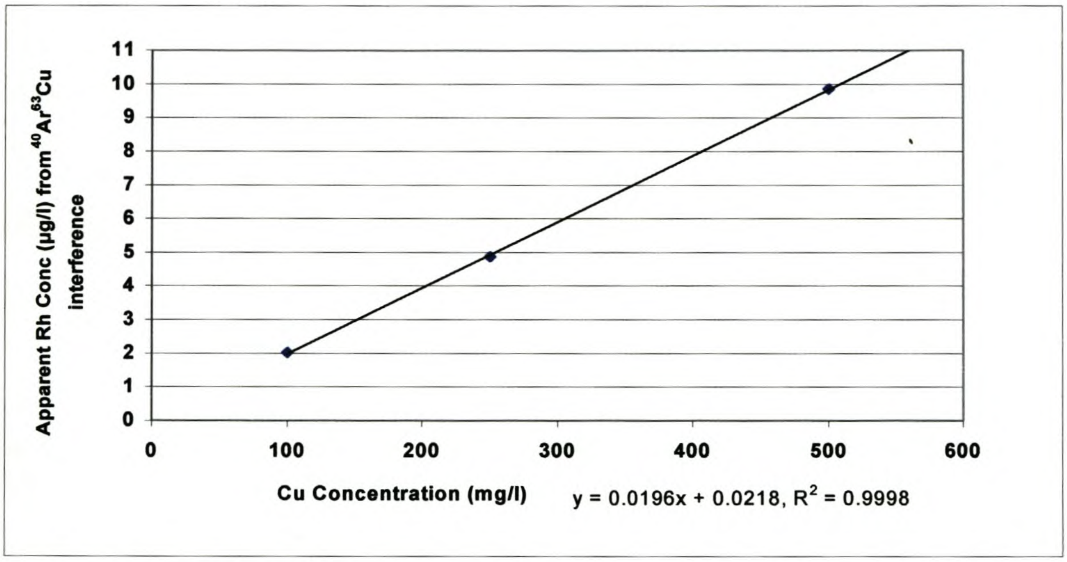


Figure 6.1A Effect of ^{63}Cu interference as $(^{40}Ar^{63}Cu)^+$ on ^{103}Rh (100 mg/l Cu = 2.0 µg/l ^{103}Rh)

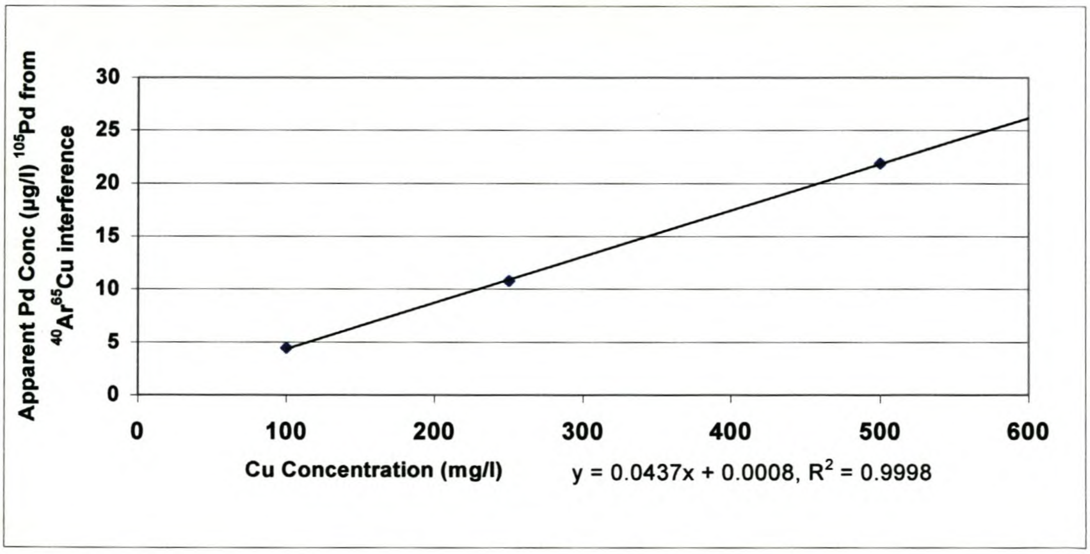


Figure 6.1B Effect of ^{65}Cu interference as $(^{40}Ar^{65}Cu)^+$on ^{105}Pd (100 mg/l Cu = 4.4 µg/l Pd on ^{105}Pd)

From the slopes of the lines it can be calculated that each 1 mg/l of copper contributes 0.02 µg/l apparent concentration of rhodium and 0.044 µg/l of palladium, if conditions remain the same. That is, when a solution containing 100 mg/l of copper is aspirated a signal is observed on ^{103}Rh which is equivalent to that of 2 µg/l of rhodium and a signal is also observed on ^{105}Pd which is equivalent to 4 µg/l of palladium. Thus if copper concentration in the aspirated solution is known, then it can be multiplied by 0.02 to give the total copper contribution and this will be subtracted from the observed rhodium concentration.

The presence of copper (in excess of 25 mg/l) in the sample matrix thus is a problem in the determination of low amounts (~1-2 µg/l) of rhodium (which has only one isotope). However, the fact that copper interference occurs on two isotopes - ^{103}Rh and ^{105}Pd a comparison can be made between the results of ^{105}Pd with those of ^{106}Pd or ^{108}Pd. In principle, the excess amount of palladium on ^{105}Pd can be corrected by subtracting the palladium intensity on ^{108}Pd (or ^{106}Pd) from that of ^{105}Pd, the difference is expressed as a ratio of the observed signal on ^{108}Pd this ratio is multiplied by 2.246 (% abundance of ^{63}Cu divided by % abundance of ^{65}Cu) and the number obtained is taken as the 'correction' factor (**F**) for copper on rhodium. The signal due to copper interference on rhodium is given by (**F** x observed intensity on ^{103}Rh), and this can be subtracted from the observed value on ^{103}Rh to obtain a 'true' intensity due to rhodium. This factor is employed in section 6.1.5 to check its effectiveness. An illustration of how the rhodium correction can be worked out from palladium isotopes is given in Appendix II.

6.1.5 Comparison of PGM determination on Matte Samples as done by ICP-MS and ICP-AES

In order to confirm that the presence of base metals in the sample solutions does not impact on the analysis of platinum, palladium and gold on the ICP-MS; a test was done on plant (matte) samples which have a high content of base metals (20% copper, 40% nickel and 4% iron), and a substantial amount of PGMs (100-1500 g/t Pt; 50-1000 g/t Pd; 5 – 150 g/t Rh and 5 – 300 g/t Au).

The sample solutions for ICP-MS were prepared by open-vessel acid digestion of 0.5 g-sample and diluting to 250 ml, this is equivalent to 2 g/l total dissolved solids. Some of these solutions were then diluted 5-fold prior to analysis, to bring platinum results within the calibration range and to reduce the base metal content (to avoid instrument contamination). On average these solutions contained about 400 mg/l copper, 1000 mg/l nickel and 80 mg/l iron. The solutions were analysed on the ICP-MS and the results were compared with those obtained by ICP-AES on PGM solutions obtained after removal of the base metals. For ICP-AES preparation, a 20 g sample was leached with hydrochloric acid to remove the base metals, with the insoluble PGM residue subsequently being dissolved in *aqua regia* and diluted to 50 ml.

The comparison of the results from the two techniques is not intended to assess the two techniques, because there are orders of magnitude difference between the detection limits of the two techniques, but to compare the ICP-MS with a well-established technique to highlight the matrix tolerance of the ICP-MS instrument. Figures 6.2A to 6.2E show a comparison between the PGM results that were obtained by the ICP-MS in high base metal solutions and those that were obtained by ICP-AES in base metal-free matrix. Figures 6.2D and 6.2E show the effect of using the correction factor for rhodium results.

For simplicity, these samples may be grouped into two categories: low grade and high grade, these groups are easily identifiable on the graphical display of the results. Although the PGM grade was varying, the base metal content was relatively similar for all samples.

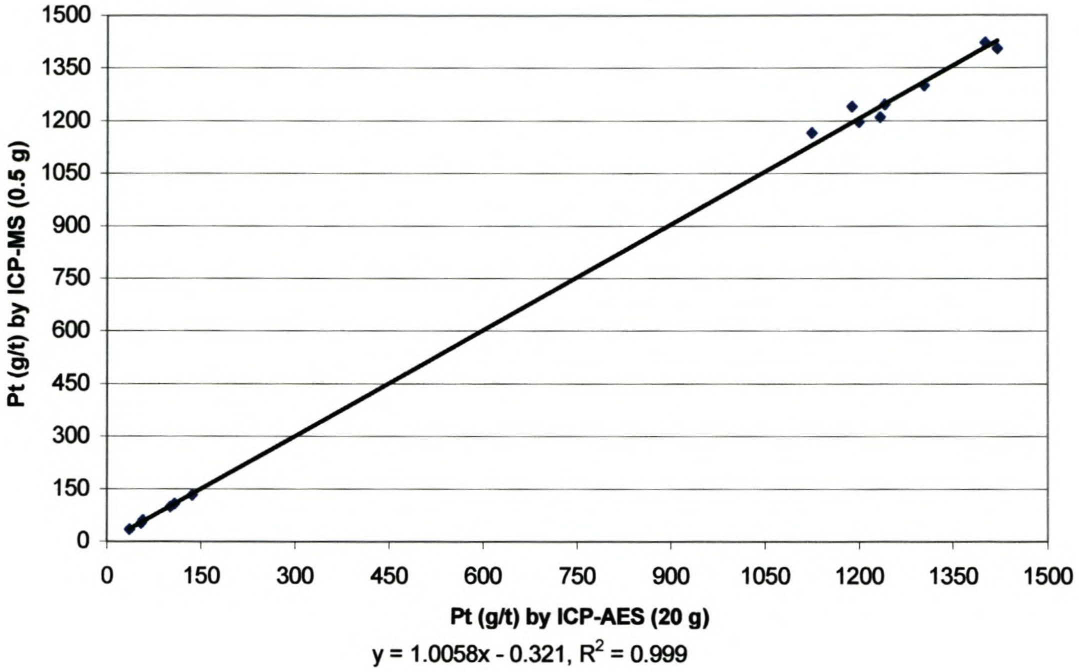


Figure 6.2A Pt results: 20 g Sample by ICP-AES vs. 0.5 g sample by ICP-MS

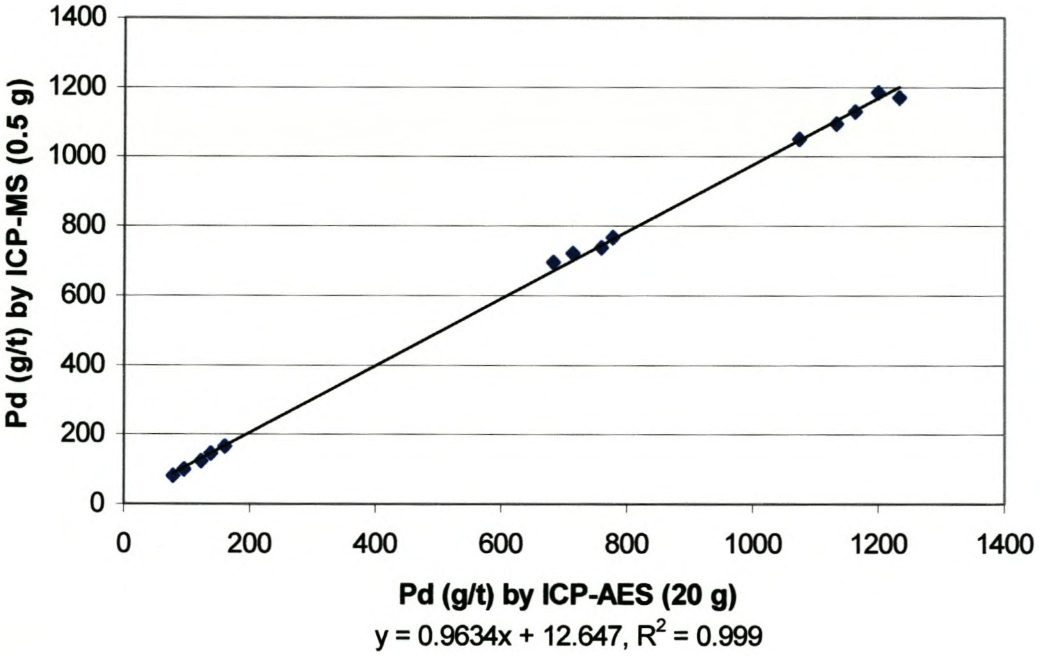
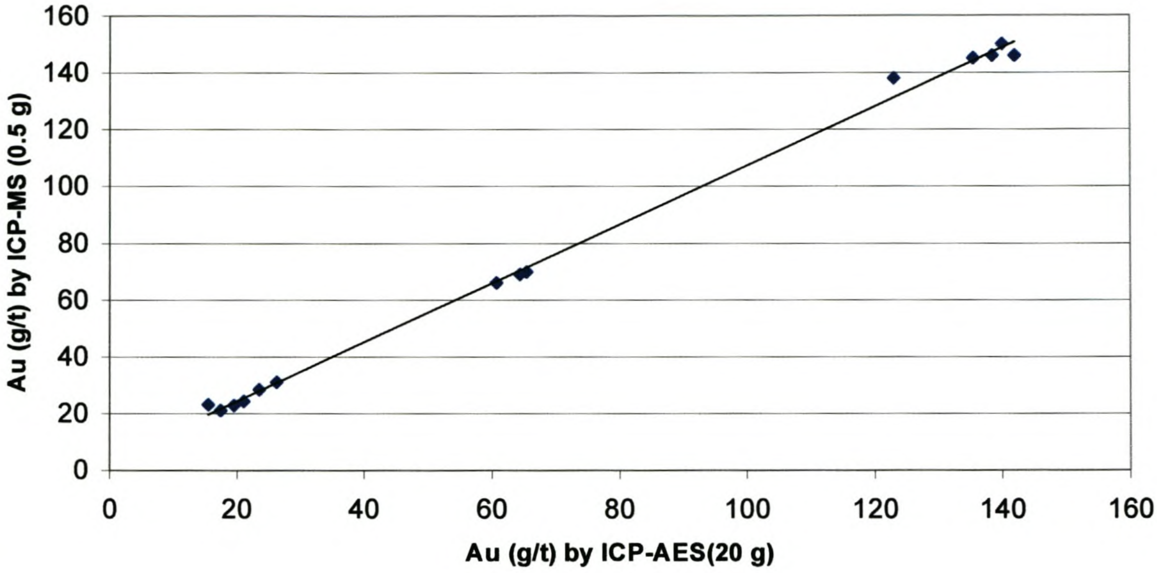
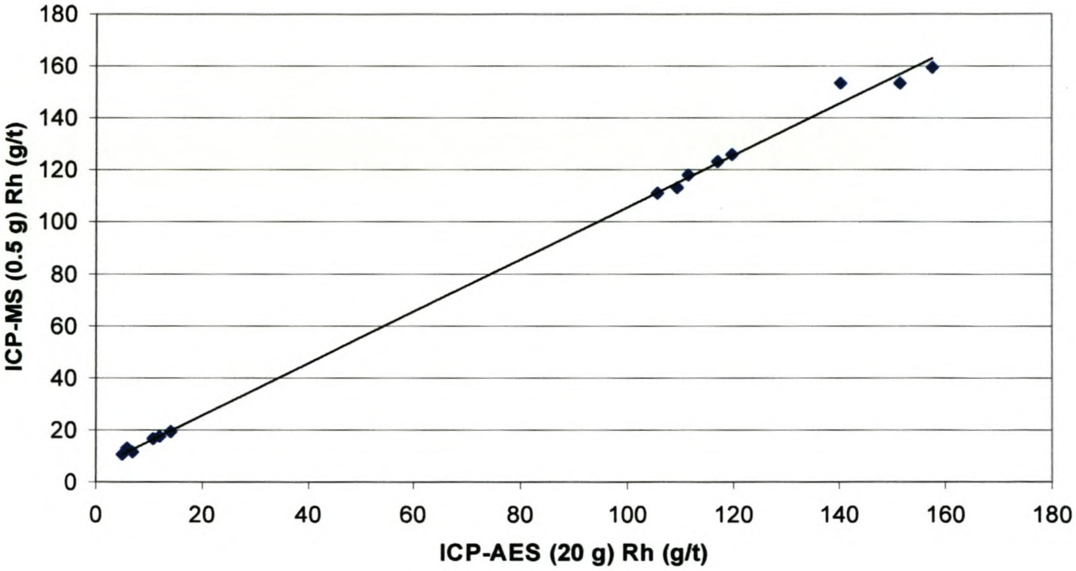


Figure 6.2B Pd results: 20 g Sample by ICP-AES vs. 0.5 g sample by ICP-MS



y = 1.0363x + 3.7713, R^2 = 0.9977

Figure 6.2C Au results 20 g Sample by ICP-AES vs. 0.5 g sample by ICP-MS



y = 0.9978x + 5.797, R^2 = 0.9981

Figure 6.2D Rh results 20 g Sample by ICP-AES vs 0.5 g sample by ICP-MS (uncorrected)

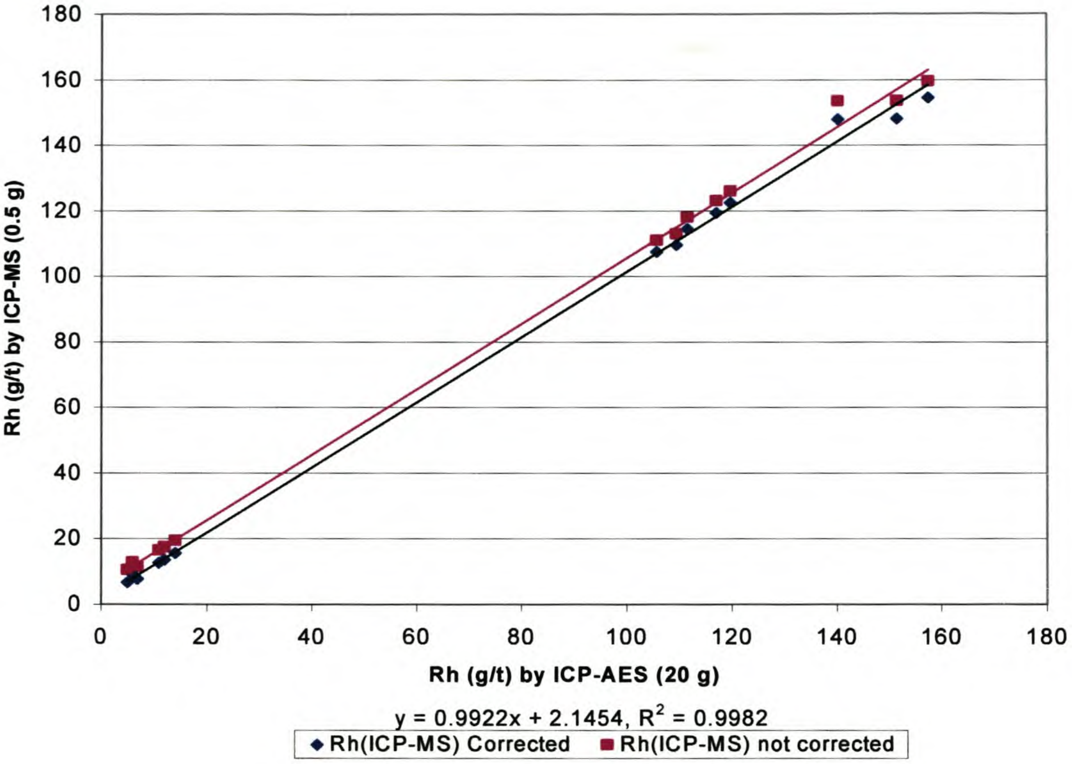


Figure 6.2E **Rh results: 20 g sample by ICP-AES vs. 0.5 g sample by ICP-MS (corrected and uncorrected)**

The above results show a good correlation between the two techniques and provide a check for the calibration graphs on the ICP-MS. It is often difficult or not possible to check the data from the ICP-MS using other techniques, because these are always at trace levels. The slope of the graphs should ideally be one and 0.95 was obtained for palladium and rhodium while that of platinum and gold were 1.02 and 1.03 respectively.

A significant difference between the two sets of data was observed on rhodium results below 100 g/t. For concentrations below 20 g/t the ICP-MS data for Rh was about 40% higher than that from ICP-AES (and in some cases the results were almost double). For Rh concentrations around 100 g/t the difference between the two techniques was about 5% and those concentrations above 100 g/t (in the solid) the difference between the two techniques was below 2% with a random scatter. This was not apparent in the displayed graph figure 6.2E, it is however clearly shown in the data in table III-3 (appendix III).

Using the known concentration of copper in these solutions, a correction factor obtained as described in Section 6.1.4 was applied to the rhodium results. The contribution of $(Ar^{40}Cu^{63})^+$ was calculated by multiplying the concentration of copper in solution by 0.02 (from 6.1.4) and subtracting the product from the apparent concentration of rhodium in solution. In order to give a better picture the two graphs (the corrected and uncorrected) are plotted together in figure 6.2E. A noticeable bias was observed in the results, this is seen in the change in the slopes of the graphs, a change was also seen in the y-intercept (y = mx + c), which decreased from 5.8 to 2.1 (getting closer to the origin) signalling a better agreement between the ICP-MS data and that of ICP-AES.

From these results it can be concluded that the polyatomic ion of $ArCu^+$ interferences impact significantly on rhodium isotope if the concentration of rhodium is much lower than the interfering element. As was observed in low grade mattes where the concentration of rhodium was below 20 g/t and that of copper being 27% (about 40 µg/l rhodium in solution and 500 mg/l copper). However, as the concentration of rhodium decreases the impact of the interference is more pronounced.

Having confirmed the capabilities and the limitations of the quadrupole based ICP-MS, the possible uncertainties and limitations posed by the sample preparation were also investigated in the next section.

6.2 Microwave Acid Dissolution

Although the overall objective of the study was to develop an analytical method for flotation feed samples, it was necessary to start with a flotation concentrate sample which contains a reasonable amount of precious metals (typically 200 g/t total PGMs compared with a feed of about 5 g/t PGMs). This was done in order to get a clearer understanding of the sources of errors in both the preparation and the analytical technique.

From previous studies [32], it was found that the most effective acid mixture for microwave-assisted dissolution was that of HCl – HNO_3 – HF – $HClO_4$. After preliminary investigations, the ratio for these acids was optimised and maintained as 3:1:1:1 (vol:vol) of concentrated acids. (Details of sample preparation are given in appendix III). For each 1ml HF acid used, 25 ml of 2.8% boric acid [23] is added to complex the free hydrofluoric acid.

However, it was equally important to establish the extent to which the reagents (acid mixture) may affect the reproducibility and the accuracy of the results, and to examine the effect (if any) of the acid mixture on each element (Pt, Pd, Rh and Au) to be determined. This was achieved by using clean PGM synthetic standards as samples and taking them through microwave dissolution steps followed by PGM analysis with ICP-MS.

6.2.1 Microwave Acid Dissolution on Synthetic Solutions

Before 'real' mine samples were studied, it was necessary to investigate the possible matrix effects that potentially affect the analyte signal. Matrix effects can be due to the presence of heavy elements, easily ionisable elements. These interferences can cause suppression or enhancement of the signal.

Preliminary work was done on synthetic solutions with PGM concentrations similar to those in a real production concentrate sample, to check the effect of the acid mixture on the PGM determination by ICP-MS. Aliquots of these solutions were pipetted into the microwave vessels, the acid mixture was added, the solutions were placed in the microwave oven and the microwave program was activated – the total microwave heating time was 20 minutes. After cooling, the solutions were uncapped and transferred to volumetric flasks and 5ml aliquots of these were taken, internal standards were added and solutions were analysed by means of ICP-MS. The recovery of PGMs was good except for platinum whose results were consistently lower than expected by comparison to Pd, Rh and Au.

In order to investigate the possible cause of this negative bias for the platinum results, a factorial experiment was designed where the microwave heating time, the PGM concentrations (volume of solution), volumes of HCl and HNO_3 acids were kept constant, while the composition of the acid mixture was varied by omitting either hydrofluoric acid or perchloric acid and in some cases both acids. After microwave heating the solutions were cooled, boric acid added accordingly, made up to volume and again analysed on the ICP-MS, the results are tabulated in table 6.3, showing the variable acid mixture and the individual absolute PGM concentrations in g/t.

Table 6.3 Factorial design and results for synthetic solutions

Nominal value expected				**124.5**	**76.5**	**7.14**	**16.7**
Design	Run order	*HF (ml)	$HClO_4$ (ml)	Pt (mg/l)	Pd (mg/l)	Au (mg/l)	Rh (mg/l)
1	4	**0**	0	**124**	77	**7.15**	17.9
2	6	**0**	0	**126**	78	**7.23**	18
3	7	1	0	116	76	6.67	16.9
4	9	1	0	117	76	6.77	17.3
5	1	**0**	2	**124**	77	**7.16**	17.5
6	10	**0**	2	**124**	76	**7.18**	17.2
7	8	1	2	115	74	6.71	16.7
8	2	1	2	115	72	6.61	16.2
9	3	0.5	1	118	75	6.74	16.9
10	5	0.5	1	119	76	6.88	17.2

*2.8% boric acid was added to those runs that had HF acid: 25 ml to 1 ml HF.

The results showed that the platinum and gold results were lower in the presence of hydrofluoric acid, and it can also be seen that the absence of HF was marked by almost 100% recovery of platinum and gold. The omission of HF also implies that no boric acid was added prior to the sample prior to dilution. The presence of HF has a significant suppressive effect on platinum and gold. It is very interesting to note that at high concentration of HF this suppressive effect has similar magnitude for both elements, which could suggest that the problem could be related to the internal standard ^{185}Re which is used for both elements.

From the above observation three questions needed to be answered:

i) was the suppressive effect proportional to the amount of HF?

ii) was the suppression due to the occurrence of spectral overlap (spectroscopic interference) such as polyatomic or oxide ions on rhenium isotope, resulting in the enhanced signal of rhenium thus causing lower recoveries. Or due to poor ionisation in the plasma because of the operating parameters (non-spectroscopic)?

iii) would the presence of dissolved silica have an effect?.

Each of these were investigated and discussed below.

6.2.1.1 The influence of HF acid concentration on suppression of Pt and Au signals

To check if the suppressive effect of HF on platinum results was proportional to the amount of HF added, a further test was done where all the other parameters (1 ml $HClO_4$, 3 ml HCl, 1 ml HNO_3 and microwave time: 20 minutes) were kept constant and the concentration of HF acid added was varied. The volume of saturated boric acid varied according to HF acid present (25 ml of 2.8% H_3BO_3 to 1 ml HF).

This experiment indicated that the suppression increased with the increasing amount of HF acid, suggesting that the effect was approximately proportional to the amount of hydrofluoric acid added or perhaps boric acid added. These results are shown graphically in figure 6.3.

6.2.1.2 Effect of the HF acid on platinum using different internal standards

Because there are two isotopes of rhenium namely ^{185}Re and ^{187}Re (with 37.4% and 62.6% relative abundances respectively), it was necessary to check if the suppressive effect of HF was due to spectral (isobaric or polyatomic) interferences on ^{185}Re which is used as an internal standard for the heavier elements (platinum and gold). This was done by changing the internal standard to ^{187}Re, (there was no osmium in the standards nor in the synthetic solutions, otherwise this would have an isobaric overlap on ^{187}Re). The results calculated using ^{187}Re looked exactly like those calculated on ^{185}Re, this ruled out the possible spectral overlap on ^{185}Re, because it would be unlikely to have the spectral overlap with similar magnitude on both isotopes because of their occurring abundances.

Due to the fact that platinum and gold use the same internal standard – rhenium, while palladium and rhodium use indium (section 5.1). The possibility of omitting rhenium as an internal standard and using indium for all elements was checked by reprocessing the same data (6.3.1.1) using indium (instead of rhenium) as the internal standard for platinum and gold. These results are also shown graphically in figure 6.3.

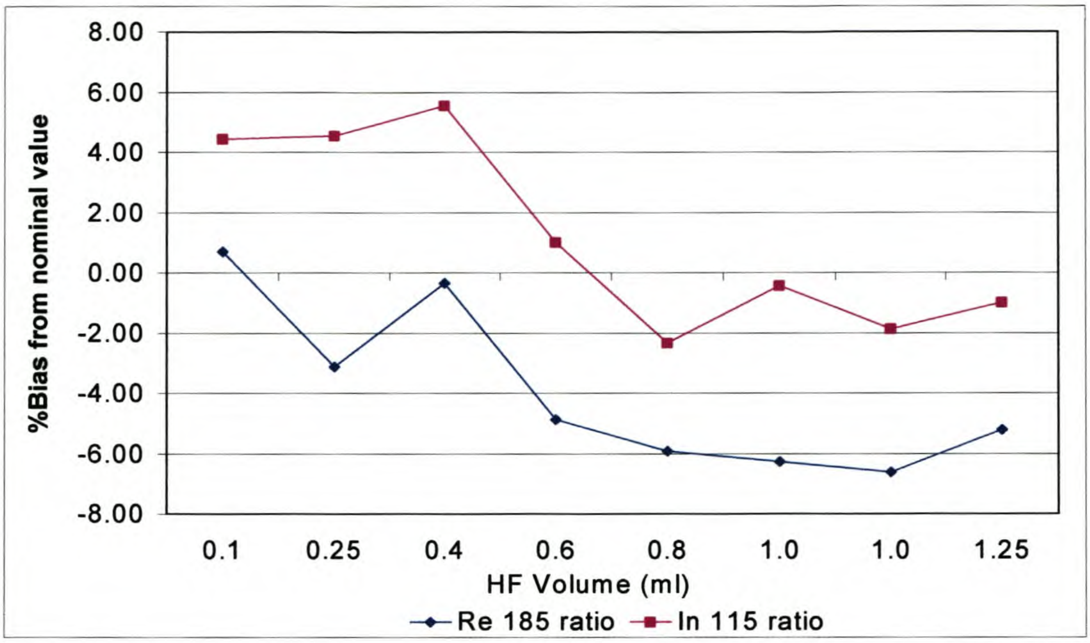


Figure 6.3 **Effect of increasing HF concentration on Pt results calculated using both internal standards (^{185}Re and ^{115}In)**

The platinum trends were similar for both internal standards (figure 6.3) although the magnitude of the suppressive effect is different for both internal standards. This suggested that platinum is the element most affected. While the platinum results obtained using rhenium are lower than the expected value, indium on the other hand gives much higher results than those expected. This also highlighted the importance of minimising mass-dependent matrix effects by using internal standards with atomic masses closest to that of the analyte. These results confirm the possibility of mass-dependent matrix effect due to the instrumental operating parameters.

The next section examines the possible solution to this problem by using matrix-matched standards to calibrate the instrument.

6.2.1.3 Effect of using matrix-matched standards on platinum recoveries

The previous tests have indicated the possibility of mass dependant matrix effects due to HF acid and in order to confirm that the above problem is due to a matrix effects generated from the instrumental operating parameters, the same solutions were analysed against the matrix-matched standards. The standards were matched by adding an aliquot of the blank solution which contained HF, $HClO_4$, *aqua regia* and water. The blank had also been taken through the microwave digestion stage together with the synthetic solutions. Table 6.4 shows the results obtained after reading the above solutions against matrix-matched standards. The results are expressed as percentage recoveries of the nominal platinum, palladium, gold and rhodium concentrations. Table 6.4 shows both these results (*matchstd column*) and the original results (shown in table 6.3) obtained using clean standards (*cleanstd column*), they have also been expressed as percentage recoveries of the nominal concentrations.

Table 6.4 Platinum recoveries on synthetic solutions obtained using clean standards and matrix-matched standards expressed as percentage recoveries.

*HF	HClO4	cleanstd	matchstd	cleanstd	matchstd	cleanstd	matchstd	cleanstd	matchstd
(ml)	(ml)	% Recovery Pt		% Recovery Pd		% Recovery Au		% Recovery Rh	
0	0	99	**109**	100	100	98	**108**	103	101
0	0	101	**110**	101	104	100	**112**	105	103
1	0	95	99	98	101	94	103	101	104
1	0	93	100	98	102	92	102	101	103
0	2	100	**106**	101	99	102	**106**	104	100
0	2	98	**106**	99	102	99	**111**	102	102
1	2	92	98	103	98	95	100	98	100
1	2	93	101	98	102	94	103	99	103
0.5	1	95	102	98	99	94	102	98	101
0.5	1	94	103	102	104	99	**108**	103	**105**

It is clear that using the matrix-matched calibration standards gives better recoveries. It is also apparent that the observed suppressive effect of HF is probably due to matrix effect. The relatively high recoveries obtained for platinum and gold when there is no HF added indicated that the presence of HF causes signal suppression mainly on these two elements (Pt and Au). These results also confirm that the problem can be overcome by using the matrix-matched standards to some extent.

6.2.1.4 Effect of adding silica to the synthetic solutions

In practice the actual mineral production sample has a complex matrix the bulk constituent being silica. The addition of HF acid is mainly to dissolve the silicate minerals. Therefore, the suppressive HF effect was again examined in the presence of silica.

It was estimated that a typical Merensky feed sample contains about 45% silica, so if 100 mg of sample is used about 45 mg of that will be silica. Pure silica was thus added to the synthetic solution by weighing 50 mg of silica into the microwave vessels, followed by the same procedure as described in section 6.3.1.1. The results, showing the trends observed on platinum results when solutions contained no silica (6.3.1.1) compared to those for which silica was added, are shown graphically in figure 6.4

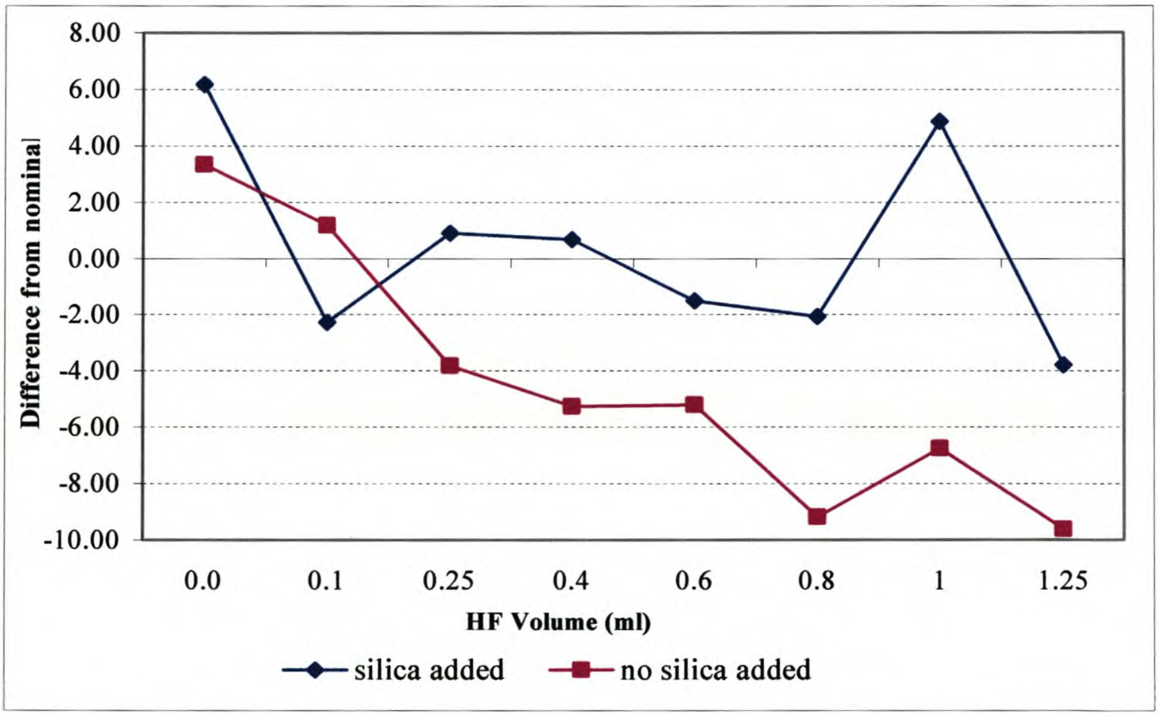


Figure 6.4 **Comparison between observed trends on platinum results as the HF concentration increases, in solutions that contained silica and those that had no silica**

The presence of silica in the solution showed a different trend; evidently when the solutions contain silica, the downward trend disappeared. This suggested that the problem arose from having free or excess HF acid despite having boric acid in the solution.

It was observed that 0.1 ml of HF acid was not enough to dissolve 0.05 g silica, because there were still visible traces of silica left undissolved in the solution, but this was not the case from 0.25 ml, suggesting that 0.25 ml was enough to dissolve 0.05 g silica such that 1.25 ml HF acid used in the experiment described above was 5 times more than required. Therefore, the experiment also highlighted that if the correct amount of hydrofluoric acid is used then there should be little free HF left. This in turn means that the minimum amount of HF acid required must be estimated to avoid excessive amount of HF.

The reason for adding HF to mineral samples is to dissolve silica. It is generally accepted that HF reacts with silica to form silicon fluoride complex:

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \qquad 6.1$$

It can also be concluded that this trend that was observed initially (section 6.3.1.1) may not exist in the actual mineral sample which has a lot of silica.

The amount of HF acid required for a given mass of a sample was estimated assuming equation 6.1

Thus a 100 mg sample of Merensky feed containing about 45% silica will require about 0.25 ml of HF acid, similarly, about 300 mg of a concentrate sample containing 33% silica requires about 0.5 ml hydrofluoric acid. (Details on this calculation are given in appendix III).

Having identified the potential problems that can be generated by the acid mixture and possible solutions thereof, experiment was then performed using the actual mine/mineral samples and this is explained in the next section.

6.2.2 Microwave –assisted acid dissolution of a Merensky flotation concentrate sample

The flotation concentrates used in this section were known in-house quality control samples used in the laboratory.

Microwave safety procedure stipulates that the sample mass for a sulphide ore or concentrate should not exceed 300 mg [39]. Initially, about 100 mg of concentrate samples were weighed directly into microwave vessels and digested using high pressure microwave vessels. This was done to check for complete dissolution and to examine the residue (if any) for any PGM minerals.

Complete dissolution of the samples was not achieved using the optimum HF-$HClO_4$-HNO_3-HCl acid mixture and the microwave parameters shown in table III-1. A small amount of insoluble black residue was observed in each trial. Solutions were filtered using the 'witts' filtering apparatus with a 'Sartorius' 0.45 µm cellulose nitrate filter paper and analysed by means of ICP-MS. Average recoveries obtained ranged from 90% to 95% for Pd, Rh and Au, while platinum showed much poorer recoveries of only 71%. The gold recoveries were erratic ranging from 62% to 140% (4 g/t to 9 g/t) with high RSDs – 23%; this could have been due to low concentration of gold in the sample particularly in view that only 100 mg sample was used. In most cases gold occurs in particulate form as a results it is most affected by the use of small sample masses. However, comparing the precision obtained on gold in the fire assay method where a larger sample mass was used, it is noted that this was still poorer in comparison to other elements. Therefore, this confirms that the problem may be due to the nature in which gold occurs (alluvial).

The residues were submitted for mineralogical examination using energy dispersive analysis (X-ray diffraction), which showed that the residue predominantly contained sulphide minerals, namely cooperite (PtS) and braggite (PtPdS) which occur in abundance in this sample type, and one grain consisting of laurite (RuIrSCu) and irasite (IrAsS) was also observed in this residue.

From the mineralogical examination it was considered that some form of pretreatment step was required to break down the sulphide minerals prior to the dissolution. This was done by roasting samples in a stream of air to oxidise sulphur to a volatile sulphur dioxide. The compressed air was carefully blown in from the front of the muffle at about 1.4 l/min using an L-shaped quartz delivery tube [5.5.1). The samples were then digested with the same acid mixture in the microwave oven and analysed on the ICP-MS.

The results showed remarkable improvement for platinum recoveries (above 95%) and the RSDs reduced from 9% to 4%. While recoveries for palladium and gold showed a slight improvement and well within the expected range also with improved RSDs. The recovery for rhodium decreased significantly, presumably due to the formation of refractory oxide.

Results from these investigations are shown graphically in figure 6.5, showing the average recoveries obtained for the untreated samples compared to those of the roasted samples. The spread of the results for 16 runs is indicated by the error bars, which were calculated as one standard deviation of all the results, expressed as a percentage of the average result.

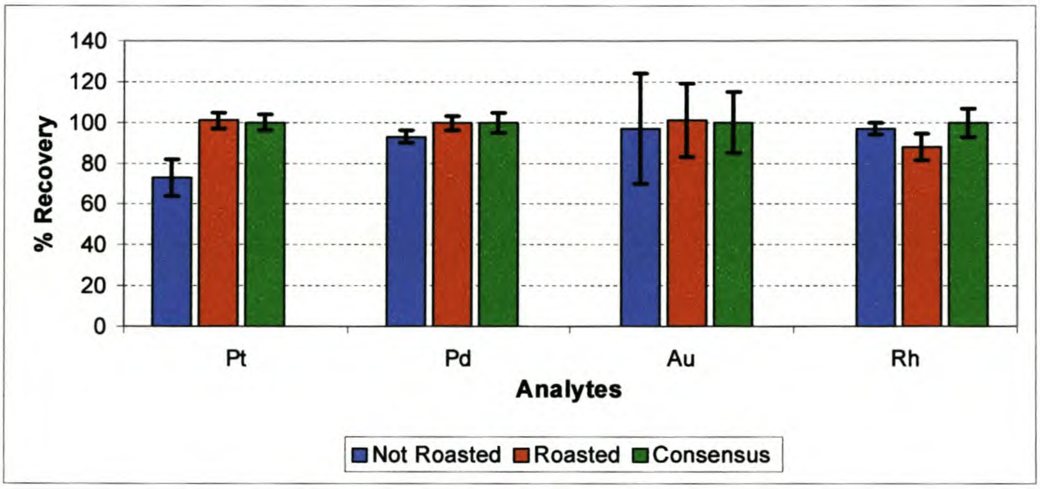


Figure 6.5 Percentage recoveries obtained on roasted samples with error bars calculated as 1s compared to those of non-roasted samples.

The recoveries for samples that were not roasted were all below the consensus value that has been obtained from fire assay technique. However, precision (shown by error bars) on palladium and rhodium is comparable to that of fire assay, while that of platinum and gold is poorer. However, after roasting the samples, the recoveries for platinum, palladium and gold were all around 100% (102% Pt; 99.6% Pd and 103% Au). The recoveries above 100% particularly on platinum could be an indication that fire assay technique underestimates the total PGM content in the samples, as these recoveries were calculated using fire assay results. Although only 300 mg sample aliquots were used these results were well within the 1s of the consensus value (for which 3 – 10 g sample masses were used) with similar precisions. Because the mean results from both methods are within one standard deviation (1s) of each other, it can be concluded that difference between them is statistically insignificant at 95% confidence level. This undoubtedly satisfies the criteria set out for the method. The roasting process however, does not favour rhodium as the recoveries were much lower. The possible solution to this problem would be to determine rhodium on unroasted samples particularly in view of the good precision that was obtained on these results.

The actual metal concentration ranges of the elements in the concentrate sample are given in table 6.5. Gold has the lowest concentration (~ 6 g/t), and the need to maintain the total dissolved solids at maximum 2 g/l often results in lower gold concentration (5 μg/l) in solution, with poorer precision.

Table 6.5 Summary of Results on Merensky Concentrate Sample (g/t)

Sample	Pt ±1s (g/t)	Pd ±1s (g/t)	Au ±1s (g/t)	Rh ±1s (g/t)
Not roasted	94 ± 9	73 ± 2	6.3 ± 1.7	13.1 ± 0.4
Roasted	132 ± 6	78.6 ± 3	6.7 ± 1	11.9 ± 0.5
Consensus[ϕ]	129.8 ± 5	78.9 ± 4	6.45 ± 1	13.5 ± 1

The dissolution of Merensky concentrate sample was successfully achieved using microwave-assisted digestion of the roasted samples with good precision (similar to that given on consensus values).

[ϕ] Consensus value is the average result done by both Pb and NiS fire assay methods from five group laboratories.

6.2.3 Influence of HF and $HClO_4$ acids on sample dissolution and PGM recoveries on roasted concentrate sample .

A partial factorial design experiment was performed to study the significance of HF and $HClO_4$ acids in the acid mixture and their effect on the actual PGM results. This was done by omitting either hydrofluoric acid or perchloric acid or both of them together. This investigation also served to optimise the acid mixture on different sample masses.

The muffle temperature was kept at 800 °C, the roasting time was also maintained at one hour and the microwave conditions remained the same. The acid mixture and the sample masses were varied as shown in table 6.3, 'low level' indicates the minimum amount used and 'high level' shows the maximum amount used. Two results were used as response indicators - % residue (insolubles) to indicate the influence of the three variables on dissolution and % Pt recovered from the filtrate was used to indicate the influence on the actual PGM results.

A "Stat-Easy" program was used to compute the ANOVA on the results.

Table 6.6 Parameters for the experimental design showing the variables and the amounts varied

Variable Parameters			
Variable	Low level	Mid point	High level
HF (ml)	0	0.5	1
$HclO_4$ (ml)	0	1	2
Sample mass (g)	0.1	0.3	0.5

From this experiment the following observations were made:

Using amount of residue present (expressed as a percentage of the original sample mass) as a factorial design response indicator:

- The absence of HF was marked by the presence of a dense reddish residue, which indicated incomplete dissolution.
- The absence of $HClO_4$ resulted in the formation of a fine white precipitate. An XRF scan showed that the white precipitate is mainly due to magnesium and calcium. This was confirmed by the SEM/EDS results which further classified those as calcium and magnesium oxides.
- A combination of all these acids (HF-$HClO_4$-HCl-HNO_3) gave the least amount of residue - maximum 1% for a 0.5 g sample.

In spite of the fact that there was still some insoluble material left after the microwave dissolution with the optimum acid mixture, the filtrates were analysed on ICP-MS to check the recoveries on four PGMs (Pt, Pd, Rh, and Au). From these results the platinum recoveries were used as the response indicator instead of the residue.

Using platinum recoveries as a factorial design response indicator:

- The platinum was quantitatively recovered except in the case of high mass; high $HClO_4$ and no HF which had lower results (table 6.6).

The overall results of this factorial design experiment are displayed graphically in figure 6.6 showing the amount of residue (expressed as a percentage of the original sample mass) obtained with different acid combinations, as well as the platinum recovery from the filtrate of the same test.

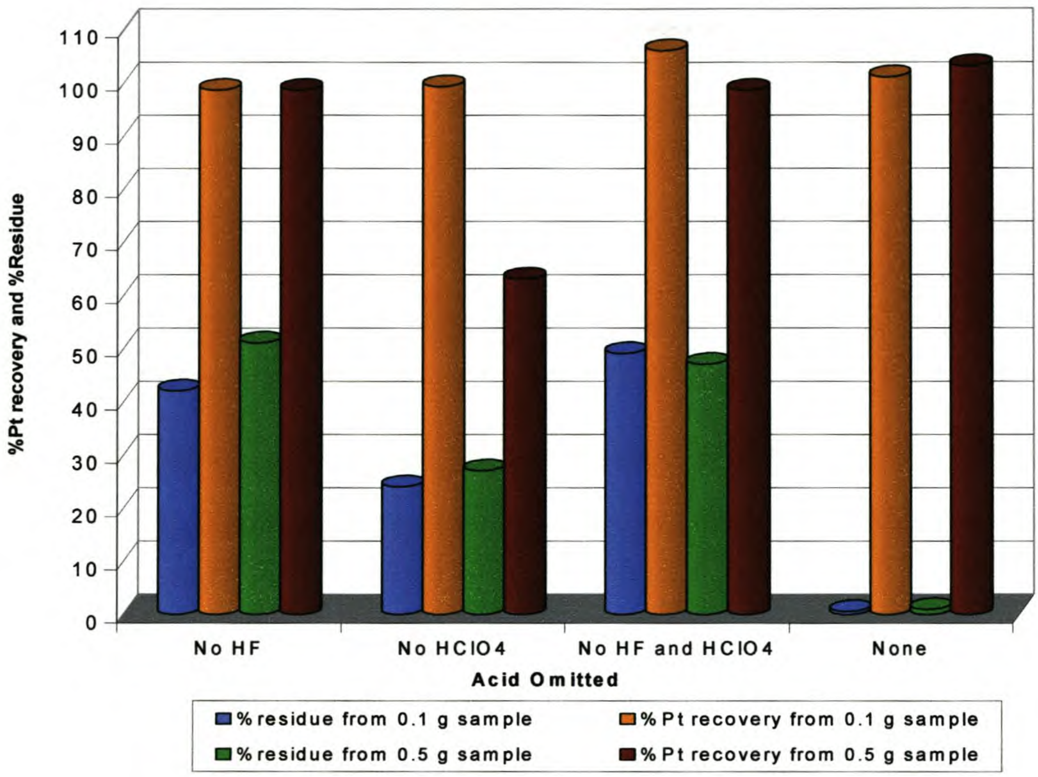


Figure 6.6 **Effect of omitting HF and $HClO_4$ acids on dissolution and Pt recovery on different sample masses.**

Increasing the amount of HF from 0 ml to 1 ml had no significant effect on platinum recovery at 95% confidence level, but significantly reduces the amount of insolubles.

Although the absence of hydrofluoric acid (HF) and perchloric acid ($HClO_4$) resulted in a large amount of residue, it was found that this has no effect on the platinum recoveries, as these remained close to 100% (97–105%). A combination of all these acids ($HF-HClO_4-HCl-HNO_3$) resulted in the least amount of residue maximum; 1% for a 0.5 g sample, suggesting that both HF and $HClO_4$ are essential for the almost complete dissolution of the sample.

For these sample types, roasting was found to be the most important step to ensure satisfactory platinum recoveries. Presumably roasting of samples results in the conversion of the acid-resistant platinum-bearing sulphide minerals into a form which is soluble in *aqua regia*.

Gold on the other hand has higher recoveries for larger sample masses. This could be due to the improved limits of determination. The rhodium recoveries were consistently lower by about 25% confirming the findings in 5.5.1. This factorial experiment also confirmed the presumption made in section 6.3.1 that the suppression effect that was observed on platinum results due to the excess HF acid when synthetic solutions were used, may not be observed with the mineral samples that contain silica.

Table 6.7 Conditions for the experimental design and results obtained for Pt, Pd, Rh and Au

Experimental parameters				Results			
Design	Mass (g)	HF (ml)	$HClO_4$ (ml)	Pt ± 1s (g/t) #	Pd ± 1s (g/t) #	Rh ± 1s (g/t) #	Au ± 1s (g/t) #
Consensus values				129 ± 5	78.9 ± 5	13.5 ± 1	6.45 ± 1
1	0.1	0	0	138	75.9 ± 5	8.4 ± 0.9	6.2 ± 0.5
2	0.5	0	0	127	73.5 ± 0.7	7.8 ± 0.4	7.2 ± 0.3
3	0.1	1	0	127 ± 7	83.2 ± 4.5	10.4 ± 0.2	5.5 ± 0.4
4	0.5	1	0	129 ± 6	74.4 ± 0.5	9.3 ± 0.1	6.3 ± 0.03
5	0.1	0	2	122 ± 10	78.0 ± 3	9.4 ± 0.6	7.0 ± 0.8
6	0.5	0	2	81 ± 2	71.9 ± 0.8	6.8 ± 0.2	7.5 ± 1.2
7	0.1	1	2	132 ± 11	76.7 ± 2	10.5 ± 0.2	5.7 ± 0.5
8	0.5	1	2	126 ± 11	76.7 ± 0.2	10.5 ± 3.5	6.8 ± 0.2
0	0.3	0.5	1	134 ± 9	77.9 ± 0.2	9.6 ± 0.3	6.8 ± 1

[#] Each design was done twice and analysed four times.

These previous experiments have confirmed that roasting is the most critical stage of this process, and it is vital that the muffle furnace conditions be optimised. Initially the roasting temperature was arbitrarily set at 800 °C. The next section looks at the optimum roasting temperature.

6.2.4 Determining the optimum roasting temperature using the Merensky concentrate

Most PGM minerals in Merensky and UG-2 ores are associated with sulphides and these are resistant to normal acid attack. For effective roasting, the optimum roasting temperature must be determined. This was done by roasting 300 mg sample aliquots at various temperatures for one hour and determining the residual sulphur content using the 'Leco' sulphur analyser. Four replicates were roasted at each temperature; two crucibles were removed from the muffle at 30-minutes intervals; cooled and the samples were gently ground to break down any lumps that had formed and then put back into the muffle for another 30 minutes. This is done to check if there could be a 'baking' effect which could hinder effective roasting by not preventing smooth air flow through the sample. The samples were cooled and then analysed for sulphur on the 'Leco' – sulphur analyser. Results for this test are shown in figure 6.7

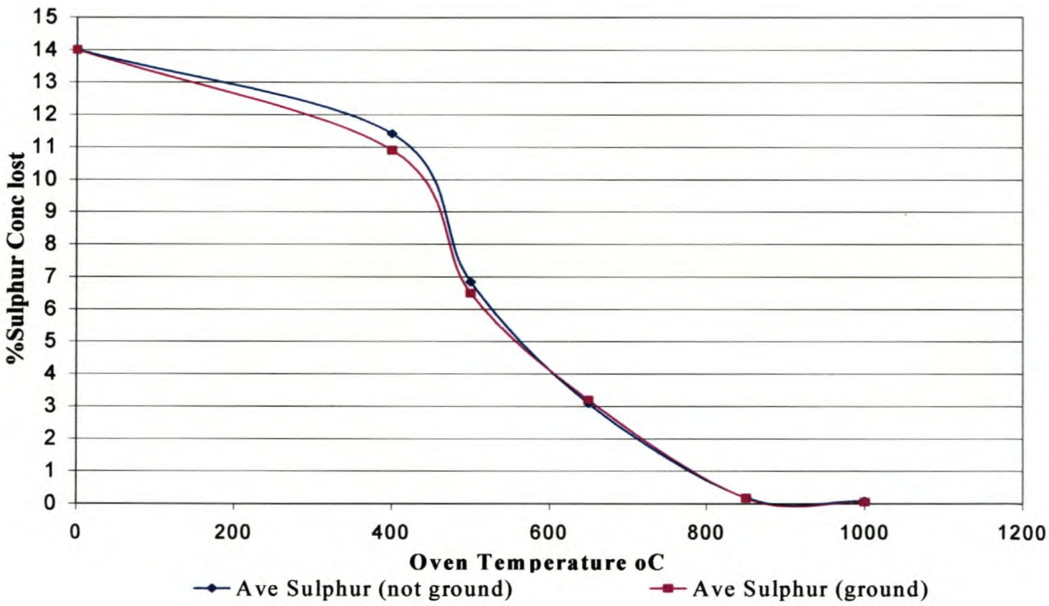


Figure 6.7 **Sulphur results (%) obtained after roasting the samples at different temperatures**

As the temperature increases the amount of sulphur that gets volatilised also increased.

A two – stage roasting process which included partial grinding did not liberate additional sulphur and therefore had no advantage over the non-ground samples.

Roasting at 850 °C converts about 98% of sulphur and at 1000 °C more than 99% sulphur has volatilised. However, at 1000 °C some samples adhered (baked) onto the walls of the crucibles and this will make it difficult to transfer the sample quantitatively for further dissolution. Although 1000 °C would be the ideal temperature for roasting, for safety and ease of handling the samples the roasting temperature was set at 850 °C, and a roasting time of one hour.

Having established the optimum conditions and good analytical performance for a concentrate sample, the next step was to examine the effectiveness of this dissolution procedure and the PGM recoveries on a ‘real’ feed sample with much lower PGM concentrations and a more complex matrix.

6.2.5 Dissolution of a Merensky ore sample

For this study, a certified reference sample SARM 7 was chosen to assess the microwave dissolution procedure.

From section 3.3 it was estimated that if the overall tolerable relative precision is set at 5% then the minimum sample mass for the Merensky feed type sample should be at least 2 g and for a 10% error the mass should be at least 0.5 g (table 3.2). Several sample aliquots of SARM 7 of differing masses which included those calculated (estimated) in section 3, were used in this experiment, ranging from 250 mg to 1000 mg. This was done to check the usefulness of the estimated minimum sample masses on the basis of Fricke's [53] method. Weighed samples were transferred to a pre-heated furnace at 850 °C and roasted in air for an hour, the roasted samples were cooled and transferred to microwave vessels. The samples were digested in the microwave with a mixture of *aqua regia* (hydrochloric and nitric acids), hydrofluoric acid and perchloric acid (the mixture which has been established earlier 3:1:1:1, vol : vol).

After dissolution, the solutions were transferred to volumetric flasks and aliquots were taken and analysed on the ICP-MS. The average results obtained on individual element (Pt, Pd, Rh and Au) were compared with the reference values and the differences are plotted as a percentage of the expected value against the sample mass.

Table 6.9 shows the actual individual metal concentration ranges in the sample. Each trial at different mass had six replicates that is, n = 6 for each mass.

Table 6.9 Summary of results for SARM 7

	Mass (g)	Pt ± 1s (g/t)	Pd ± 1s (g/t)	Au ± 1s (g/t)	Rh ± 1s (g/t)
SARM 7	0.25	3.7 ± 1	1.76 ± 0.07	0.3 ± 0.1	0.28 ± 0.01
	0.30	3.9 ± 0.6	1.8 ± 0.2	0.27 ± 0.05	0.26 ± 0.03
	0.50	3.6 ± 0.3	1.7 ± 0.2	0.27 ± 0.06	0.26 ± 0.03
	1.00	3.8 ± 0.3	1.6 ± 0.1	0.28 ± 0.03	0.26 ± 0.02
Reference		3.74 ± 0.043	1.53 ± 0.032	0.31±0.015	0.24 ± 0.013

Figures 6.8 to 6.11 compare the spread and closeness of the average values obtained to the consensus value (table 6.9). The error bars have been calculated as one standard deviation expressed as a percentage of the average result.

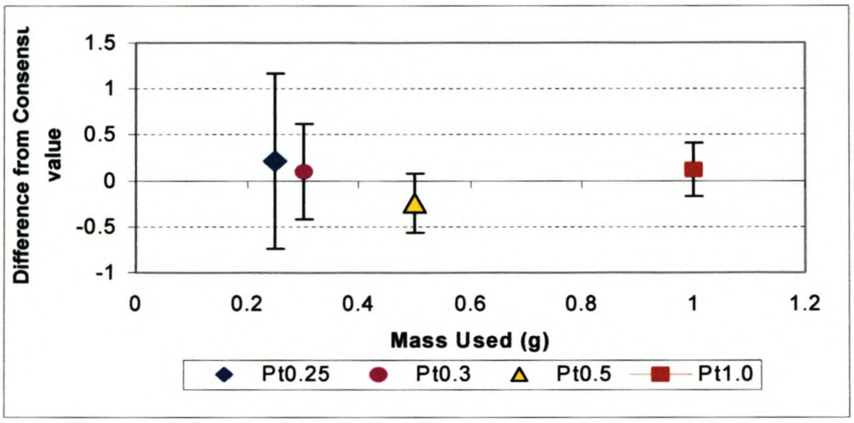


Figure 6.8 Platinum results on SARM 7 expressed as % difference from consensus value with error calculated as 1s

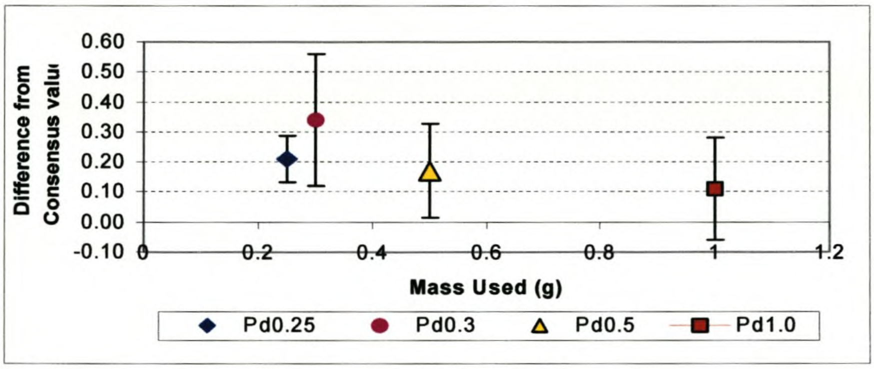


Figure 6.9 Palladium results on SARM 7 expressed as % difference from consensus value with error calculated as 1s

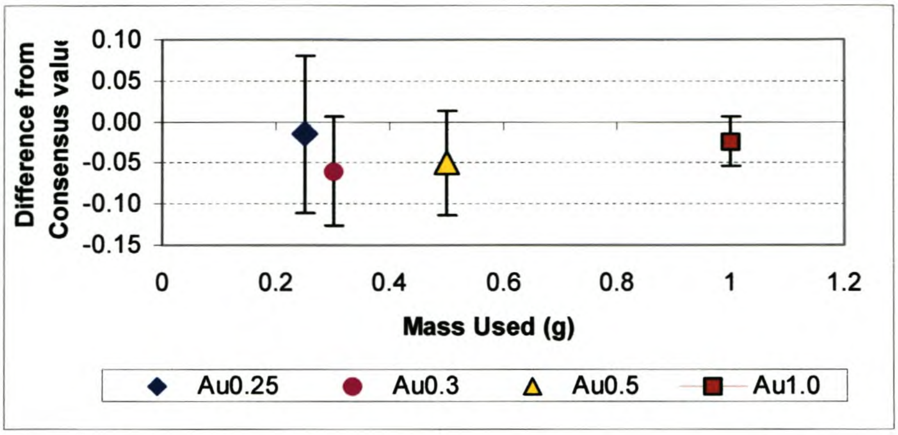


Figure 6.10 Gold results on SARM 7 expressed as % difference from consensus value with error calculated as 1s

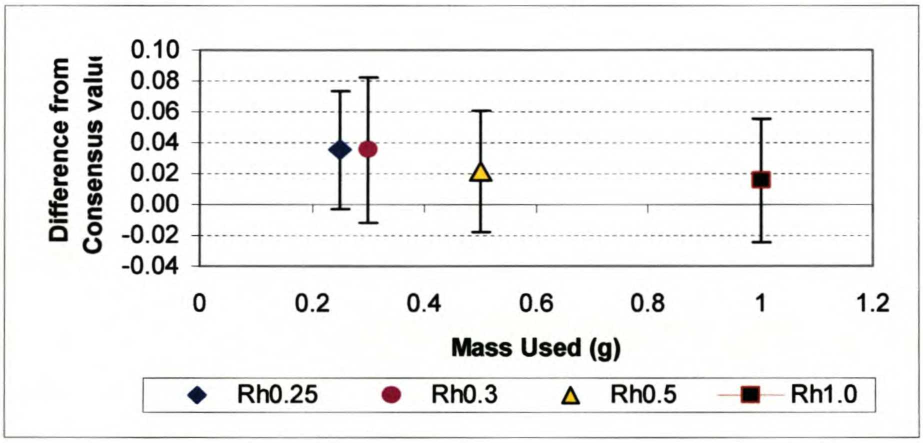


Figure 6.11 Rhodium results on SARM 7 expressed as % difference from consensus value with error calculated as 1s

The precision on platinum results improved from 27% RSD for 250 mg to 8% RSD for 1000 mg sample. This precision obtained compares very well with that estimated in chapter 3 using Fricke's [53]

The graph for gold results has a similar pattern to that of platinum with the spread narrowing significantly at higher sample mass. The larger the mass of the sample the better the precision and the closer the result is to the reference value, at higher sample mass (1000 mg), the concentration levels of the metals in solution increase and this improves the limits of determination particularly for gold.

For palladium and rhodium the scatter does not show any particular trend, although as the sample mass increases, the average results get closer to the consensus value (improved accuracy) as in the case of platinum. It can however be expected that because the concentrations for these elements are lower than that of platinum, the precision will be poorer than that observed for platinum. This is apparent in the case of rhodium where 1000 mg is still not enough to improve the precision of results.

For a more comprehensive study on the minimum sample weight and the tolerable error the optimum sample weight should be estimated using all four elements or using the element with the lowest concentration in the sample [55]. This was not done in this study, but platinum was used (has a higher concentration) in order to check the relevance of this estimation. (Detailed results are tabulated in Appendix III).

The work done on Merensky type samples has shown that PGM recovery on microwave acid dissolution is achievable with roasting and with the appropriate acid mixture. The uncertainties caused by taking small sample masses have to be given attention, hence the need to estimate the minimum sample mass required for any desired precision and accuracy.

This investigation was extended to UG-2 type samples which have a very different mineralogical composition but similar form of PGM mineralisation.

6.2.6 Acid Dissolution of a UG-2 Flotation Concentrate Sample

For this study, again an in-house quality control sample of a UG-2 flotation concentrate was used. Following from the Merensky samples, an initial UG-2 flotation concentrate sample of mass 300 mg was taken through the roasting and microwave digestion procedure using the same acid mixture (3:1:1:1 vol:vol). A black heavy residue, believed to be mainly chromite was left undissolved. The sample mass was then reduced to 100 mg, however about 25% of sample was still left as a black residue.

Following from the theory that reducing the chromite helps in its solubility [38], a further step was introduced during pretreatment; a 100 mg sample was roasted and then thermally reduced under hydrogen (section 5.6) to reduce the chromite. After this treatment almost all the sample was dissolved and no visible residue was observed. The samples were then analysed on the ICP-MS and the results are shown in figure 6.11.

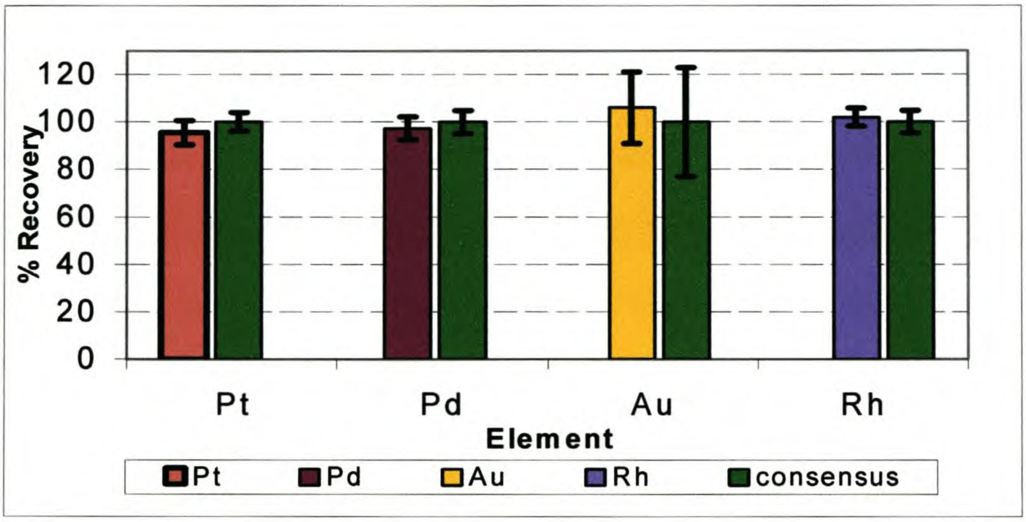


Figure 6.12 **Percentage recoveries obtained on UG-2 concentrate after roasting the samples followed by hydrogen reduction; with error bars calculated as 1s**

The results obtained in this work for a chromitite sample were very good, gold and rhodium yielded recoveries just above 100%, Au: 106 ±12% and 102 ± 5% Rh, while palladium recoveries were 97 ± 5%. These were considered good because they were better than the lowest results obtained by fire assay technique. However, platinum recoveries were about 92 ± 5%, which is slightly lower than the recoveries obtained by fire assay technique (96 ± 4%).

Most importantly it was observed that the precision obtained with 0.1 g sample was very similar to that of the set limits which were generated from fire assay method where sample masses were larger ~ 3 – 10 g. A summary of these results showing the exact concentration ranges of each element is given in table 6.10

Table 6.10 Summary of the results for the UG-2 flotation concentrate

	Mass (g)	Pt (g/t)	Pd (g/t)	Au (g/t)	Rh (g/t)
This work – Ave ± s	0.1	**92.4 ± 4.6**	**45.0 ± 2.0**	**0.80 ± 0.09**	**17.6 ± 0.7**
Ave + 2s		101.6	49.0	0.98	19
Ave – 2s		83.2	41.0	0.62	16.2
Reference ± 2s		**96.7 ± 3.8**	**46.0 ± 1.6**	**0.77 ± 0.18**	**17.8 ± 0.8**
Recom + 2s		100.5	47.6	0.94	18.6
Recom – 2s		92.9	44.4	0.59	17.0

Basic statistics stipulates that if the averages of the two analyses are within a range of 2 standard deviations from each other it can be concluded that any difference between the two averages is not statistically significant. In the above case, all the results are within 2 standard deviations of each for all the elements except platinum, therefore it can be concluded that any difference between the two averages has no statistical significance for Pd, Rh and Au. However, the same cannot be said for platinum as the average result (92.4) falls just outside the 2s (92.9) of the reference value.

A Student's t-test was applied to check the significance of the observed difference between the mean values in this test work and the reference values.

Hypothesis: $\bar{X}_{\text{this work}} = {}^{\phi}\mu_{\text{reference}}$, this is true if:

$$t(½\alpha, n-1) \leq \sqrt{n}\,|(\bar{X} - \mu)|/s \leq t(½(1-\alpha), n-1)$$

where : α = significance level in this case taken as 0.05

n-1 = degrees of freedom

s = standard deviation

[ϕ] reference value treated as μ because it was not generated from just one method cf. section 5.7

Table 6.11 Comparison between the observed difference between mean values and the consensus values and the computed "t" value.

	Pt	Pd	Rh	Au
computed "t"	3.58	2.06	1.18	0.91
$\lvert(\bar{X} - \mu)\rvert$	4.3	1.0	0.2	0.02

When the observed difference between the means and the consensus values is less than the computed t-value, it suggests that there is no significant difference between the means and the reference values and therefore it can be accepted that : $\bar{X}_{\text{this work}} = \mu_{\text{reference}}$.

From table 6.11 it can be seen that the difference between the mean values is lower than the computed "t"-values for Pd, Rh and Au, suggesting that there is no significant difference (at 95% confidence level) between these results and those obtained by fire assay technique. For these three elements the microwave dissolution gives good results with excellent precision even with smaller sample masses. However, the same cannot be said for platinum where the difference between average result and the consensus value is greater than the computed t-value. This means that the $\bar{X}_{pt}$ is significantly different from μ_{pt} and also indicates the existence of some determinate error. There could possibly be some formation of a platinum hydride complex which is not readily soluble in mineral acid.

Chapter Seven

7. Conclusion and Recommendations

This work consisted of three major investigations; the first part evaluated the uncertainties introduced by taking small sample masses of a heterogeneous solid sample. Due to the nature of occurrence of the precious metals and the levels at which they occur, the area of concern lies in the ability in taking the representative sample thereby reducing the sampling error. If the precision of the method is pre-defined it is possible to estimate the minimum sample mass that would give negligible sampling error relative to the overall error. Knowing the fraction of the analyte element in a mineral species; the specific gravity of such mineral species and the particle size distribution, then the optimum sample size can be estimated at that given precision. Minimum sample weights were determined in the early chapters of this work and it was clear that for good precisions on the results, the sample weights must be reasonably high depending on the concentration of the elements of interest. Using platinum grade, particle size and other mineralogical information on the samples, it was estimated that if 20% RSD is the desired precision then the optimum sample weight required on a Merensky (silicate) feed sample was about 100 mg and 200 mg for a chromitite feed sample. To improve this precision to 5% the estimated optimum sample mass increased to about 2000 mg for a silicate and 3000 mg for a chromitite.

The relevance of these estimated masses was checked during the dissolution of SARM 7, the precision obtained on platinum results compared very well with the estimated values. This highlighted the relevance and importance of these calculations in evaluating any new method development and the need to perform these calculations each analyte to obtain a full evaluation of the new method.

The second part investigated the potential of using the ICP-MS as the trace element technique for the determination of platinum, palladium, rhodium and gold at very low levels in the presence of complex matrices. ICP-MS has proved to be a very sensitive technique offering very low detection limits about 4 ng/l Pt; 3ng/l Pd; 3 ng/l Rh and 14 ng/l Au. However, one of the most important factors governing the detection limits that can be achieved is the purity of the reagents. In addition, the existence spectral interferences (polyatomic ions from copper and argon) overlapping the only rhodium isotope and one of palladium isotopes could be seen in the presence of base metals. These interferences enhance the signal on these isotopes (^{103}Rh and ^{105}Pd) leading to a decrease in detection power of these elements by ICP-MS particularly so for rhodium which has no alternative isotope, but palladium has alternative isotopes (^{106}Pd and ^{108}Pd) that can be used. Although the instrumental detection limits are often very low, the true detection limits (limits of quantitation) depend on sample preparation.

The occurrence of these spectral interferences of copper argide on two isotopes enables the analyst to estimate the magnitude of copper argide on ^{105}Pd and use it to correct for that on ^{103}Rh. Or alternatively the pre-determined factor can be worked out. This pre-determined correction factor was checked on the PGM analysis that was done on the matte samples which contained high base metals. These results were compared with those obtained by ICP-AES, the agreement between these two techniques was found to be very good for platinum, palladium and gold, with the maximum percentage differences obtained on the lowest concentrations, these were: [‡]5% for Pt, 4% for Pd and 17% for Au. However, the agreement between the rhodium results was very poor with the maximum percentage difference being 50% for those concentrations below 10 g/t. After applying the correction factor, the agreement improved such that the highest percentage difference was about 20%. No doubt that given exactly the same conditions for the measurement the correction factor will work.

The precision of the ICP-MS on each element was checked using the synthetic PGM solution and these proved to be very low at about 2% RSD for platinum, palladium and rhodium and 4% RSD for gold.

The microwave dissolution tests done on clean synthetic PGM solutions showed that the presence of free hydrofluoric acid caused signal suppression on heavier elements like platinum, gold and rhenium on the ICP-MS. However, when silica was added to the solutions the suppression effect disappeared. Although this was a cause for concern it was found that in the presence of silica or 'real' samples this trend is not necessarily displayed. This could be due to the reduced amount of free HF acid after its reaction with silica

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[‡] percentage difference calculated as (ICP-MS –ICP-AES)/ICP-MS multiplied by 100

resulting in dilute acid medium. This however, indicated the existence of matrix effects on the ICP-MS, and emphasized the importance of ensuring that the matrix for the synthetic sample matches that of the 'true' sample as closely as possible before any conclusions are drawn. It is equally important that the stoichiometric reaction of HF acid and silica be used to estimate the required amount of HF acid and avoid excess amount of acid. The use of single standard addition can also be employed as an alternative to matrix-matched standards to minimise the matrix effects.

The third part formed the core of this work which involved the microwave dissolution of the actual mine/production samples. Direct microwave assisted dissolution yielded low recoveries on platinum and this was consistent with the observations by Totland and Nowisnki [41,49]. Mineralogical examination of the residue from these dissolutions confirmed the presence of undissolved platinum minerals in the residue, and these were mainly platinum sulphides. From these observations, it was apparent that the PGM minerals, which occur predominantly as sulphides, are highly resistant to attack by common acids or combinations of these acids. About 20% of platinum is associated with these minerals, which implied that platinum would be the least recovered when acid dissolution alone is used even at high temperatures and elevated pressures. Introducing the pre-treatment step of roasting samples prior to microwave digestion proved to be of utmost importance. Roasting oxidises the sulphide and converts it to a volatile sulphur dioxide, leaving behind the acid-soluble minerals of platinum (presumably metal alloys – PtFe). Air was blown into the muffle furnace to facilitate the oxidation process. The flow of air into the muffle furnace has to be even and sufficient to ensure adequate conversion of sulphur to the volatile oxide.

Although total dissolution of the samples can not be claimed because of the small (<1%) residue present (figure 6.7), using the microwave preparation, it has been clearly demonstrated in this study that by roasting the samples in the presence of air, more than 95% of the PGMs can be leached out of a Merensky concentrate sample with *aqua regia*. However, there is a need to keep the amount of insolubles to a minimum to avoid losses of analytes by entrainment into the residue, and for this reason use of HF to break down silicate material is still desirable.

The optimum roasting temperature was determined by roasting the samples at different temperatures and analysing them for sulphur and this was set at 850 ºC.

Excellent recoveries were obtained for Merensky concentrate sample after roasting in air, followed by microwave acid dissolution. The highest recovery was obtained on gold (104 ± 15%) followed by platinum (102 ± 5%), palladium (99.6 ± 4). Rhodium was negatively affected by roasting giving only 88 ± 4% recovery, compared to 97 ± 3% obtained on the non-roasted samples. Although gold had the highest recovery, the precision obtained was poorer compared to other elements due to the low concentrations.

The results obtained for the ore samples were not as good as those obtained for a concentrate, because of the poor precisions. The recoveries on different sample masses (from 250 mg to 1000 mg) for the SARM 7 ranged from 99 ± 27% to 102 ± 8% for platinum; 114 ± 4% to 104 ± 6 for palladium; 97 ± 33% to 90 ± 11% for gold and 117 ± 4% to 108 ± 8% for rhodium. The precision obtained especially on platinum was consistent with Fricke's observations that the smaller the sample mass the wider the spread of the results. Accuracy also improved with the increase in sample mass.

Interestingly, the precision obtained on this method with a 1g sample is about ~ 8% RSD for all elements (except gold at 11%), this is very close to that obtained on the usual fire assay procedure (~ 7% RSD for 50 g sample). Looking at the difference in sample masses used between these methods, it can be acknowledged that with a little more work on this microwave digestion method improved PGM recovery and more precise results can be obtained, such as increased sample mass or improved sample introduction system on the ICP-MS, to improve the limits of quantitation.

Due to the difference in mineralogy between Merensky and UG-2 reefs, the pre-treatment step of roasting alone was not sufficient for the UG-2 Chromitite sample but incorporating hydrogen thermal reduction after roasting in air produced very good results for the UG-2 concentrate sample. The recoveries obtained were in good agreement with the consensus values and excellent precision was also obtained (table 7.1).

Although the sample masses that could be used for UG-2 sample were lower than those for Merensky samples, surprisingly, the PGM recoveries in some cases were as good and sometimes even better than those obtained for a Merensky concentrate sample. A lower recovery was obtained on platinum the difference was statistically significant at 95% confidence level.

Table 7.1 Recoveries obtained on flotation concentrates

Sample type	% Recovery			
	Pt	**Pd**	**Rh**	**Au**
Merensky concentrate -silicate	102 ± 5	99.6 ± 4	88 ± 4	104 ± 15
UG-2 concentrate - chromitite	95 ± 5	97.5 ± 5	102 ± 5	106 ± 12

Thermal hydrogen reduction served two purposes:

- to reduce the chromite to a soluble form and
- to reduce the refractory oxide of rhodium formed during roasting – this is shown in the good recovery yield of rhodium.

The overall microwave program takes 20 minutes and with 30 minutes allowance for the contents to cool, the total dissolution time is about 60 minutes. The roasting time is kept at one hour to ensure sufficient airflow and this brings the total preparation time to about two hours and one more hour for analysis. This certainly provides a very quick turnaround time.

However, further refinements to the method are essential to improve platinum recoveries on a chromitite sample before the method can be used routinely.

In order to achieve lower limits of quantitation for all elements, it will be necessary to change the sample introduction system to accommodate the high total dissolved solids and avoid high dilution factors. This will undoubtedly improve the precision of the results.

7.1 Recommended Future Work

1. In order to improve precision and accuracy on gold and rhodium in particular, the following investigations are recommended:

- use of single standard addition to overcome matrix effects
- use flow injection as a sample introduction system to avoid large dilutions due to the high dissolved solids.
- In order to increase the sample masses, one may also have to look at different microwave units that can be used because the present unit may not handle masses above 1000 mg.

2. To increase the number of samples, which can be roasted efficiently at one time, replace the current muffle with:

- a muffle that has a rotating carousel within, to hold the crucibles or a muffle with uniform air circulation.

3. In order to compare the effect of homogeneity of the daily mine samples to that of SARM 7:

- Analyse different sample masses (from different sources) including the calculated optimum sample mass and compare the standard deviations to those obtained for a well prepared reference sample (SARM7).

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Appendices

Appendix I Safety

The chemicals and equipment used in this work are all hazardous to various degrees; therefore extra care has to be exercised at all times. Work should be carried out in the fume cupboards with necessary protective apparel.

1.1 Chemicals

Special attention needs to be given to hydrofluoric acid and perchloric acid, as they can be extremely dangerous.

1.1.1 Hydrofluoric Acid (HF acid))

HF is corrosive and highly toxic. This acid attacks glass even in dilute concentrations and should not be used in glass or quartz unless boric acid is added. Even so, the solutions should not be stored in glass containers. Freshly prepared calcium gluconate paste should be kept in the fridge closest to the working station.

It will readily burn the skin and if fumes are inhaled will cause serious damage to the lungs. HF acid attacks the calcium in the bones and unlike other acids its effect is not immediately felt or seen. Contact with the skin should be washed with running water immediately and calcium gluconate paste should be applied to the affected area. Pain is a signal that damage has occurred and therefore a professional help should be sought.

1.1.2 Perchloric Acid ($HClO_4$)

This is a very strong oxidising agent and contact with organic material can result in explosive reaction. Small quantities of nitric acid are added to oxidise the more reactive components at lower temperatures, thereby reducing the potential of explosive oxidation [21].

1.2 Microwave Unit

Safety is a prime concern when using acids under pressure and so chemical and mechanical considerations have to be made.

1.2.1 Capping and Uncapping

If the total volume of the mineral acids in the vessel is about 10 ml the reaction should be allowed to subside before capping the vessels, to prevent violent reactions.

It is very important that the contents of the vessels are allowed to cool to room temperature before the vessels can be opened.

1.2.2 Sample Mass, Time and Temperature

It is recommended that:

a) the sample mass of sulphide ores and concentrates should not exceed 300 mg.

b) dissolution time in the microwave should not exceed 30 seconds at 700 W

1.2.3 Digestion Vessels

Routine inspection of the vessels for flaws or fissures is strongly recommended as a safety feature to prevent accidents. Vessels are designed to withstand certain temperature and pressure (110 bar / 250 ºC in the case of high-pressure vessels used in this work). The microwave vessels are equipped with a pressure spring which will deform when the pressure increases over maximum spring working pressure, and the entire cover will lift up and release overpressure. However, if this spring is not in good condition then exceeding the pressure and temperature limits will deform vessels and cause them to lose essential properties.

Appendix II Estimation of Optimum Sample Mass and other Calculations

1.1 Optimum Sample Mass

In order to estimate the contribution of the sampling error to the overall error of the analysis the simplified approach given by Fricke [52] was used (section 3.2). This statistical calculation adopts some assumptions: i) there are two mineralogical grains -one with PGM minerals and one without any PGM-bearing minerals and ii) that particles are spherical.

To ensure that the contribution of the sampling error to the overall variance of the method is negligible; a decision has to be made on the precision that would tolerable, This is calculated by equations 3.1, 3.2 and 3.3 given in section 3.2. Some of the parameters that influence the sampling error such as density, grade and mineralogy are obtained from mineralogical data. This information is presented in table 3.1 and is used to calculate the minimum sample mass on the three ore types. The particle size is estimated from the particle size distribution.

Minimum Sample Weight - Platreef

Minerals				Densities
Eustatite	16.2%	⎫	Pyroxene	3.265 g/cm^3
Diopside	47.2%	⎭	63.4%	3.275 g/cm^3

$$\text{Weighted density of pyroxene} - d_2 = \left(3.265\,\mathrm{g/cm^3} \times \frac{16.2}{63.4}\right) + \left(3.755\,\mathrm{g/cm^3} \times \frac{47.2}{63.4}\right)$$

$$d_2 = 0.834\ \mathrm{g/cm^3} + 2.438\ \mathrm{g/cm^3}$$

$$d_2 = 3.272\ \mathrm{g/cm^3}$$

Precious Metals

Grade: 6.64 g/ton

Minerals:

Pt tellurides [Pt: 14%, Pd: 19%, Te: 47, Bi: 20] – 60%, density ~ 8.5 g/cm^3

Pt alloy [often Pt: 89% – Fe: 11%] – 16%, density ~ 16.00 g/cm^3

$$\text{Weighted density of PGM grain - } d_1 = \left(8.5\,\text{g/cm}^3 \times \frac{60\%}{76\%}\right) + \left(16\,\text{g/cm}^3 \times \frac{16\%}{76\%}\right)$$

$$d_1 = 6.71\ \text{g/cm}^3 + 3.368\ \text{g/cm}^3$$

$$d_1 = 10.08\ \text{g/cm}^3$$

Total %Pt in the PGM grain is given by:

Pt tellurides - $\text{Pt} = \frac{14}{100} \times 60 = 8.4\%$

Pt alloy - $\text{Pt} = \frac{89}{100} \times 16 = 14.24\%$

Total %Pt $= 8.4\% + 14.24\% = 22.64\%$

Calculate the number of particles – n (from equation 3.3)

$$n = p(1-p)\left(\frac{d_1 d_2}{d^2_{ave}}\right)^2 \left(\frac{\%P_1 - \%P_2}{\sigma_E\ \%P_{ave}}\right)^2$$

$$d_{ave} = (p \times d_1) + (1-p) \times d_2$$

$$= (6.64 \times 10^{-6} \times 10.08) + ([1-6.64 \times 10^{-6}] \times 3.272\ \text{g/cm}^3)$$

$$\cong 3.272\ \text{g/cm}^3$$

$$P^{\%}_{ave} = (P \times d_1 \times P_1 \times 100) / d_{ave}$$

$$= (6.64 \times 10^{-6}) \times 10.08\ \text{g/cm}^3 \times 0.226 \times 100$$

$$\cong \; 3.272 \text{ g/cm}^3$$

$$= \frac{\underline{11.51 \text{ x } 10^{-3}}}{3.272} \quad = \quad 4.62 \text{ x } 10^{-4}\%$$

Assume: There are no PGM minerals in particle 2

Substitute:

$$n = (6.64 \text{ x } 10^{-6})(1 - 6.64 \text{ x } 10^{-6})\left(\frac{10.08 \text{ x } 3.272}{(3.272)^2}\right)^2 \left(\frac{22.64 - 0}{\sigma_E \, 4.62 \text{ x } 10^{-4}}\right)^2$$

$$= (6.64\text{x}10^{-6})\left(\frac{10.08}{3.272}\right)^2 \left(\frac{22.64}{\sigma_E 4.62\text{x}10^{-4}}\right)^2$$

$$= (6.64 \text{ x } 10^{-6}) \times 9.5 \left(\frac{4.89 \times 10^4}{\sigma_E}\right)^2$$

$$= 6.308 \times 10^{-5}\left(\frac{4.89 \times 10^4}{\sigma_E}\right)^2$$

For: σ_E = 1%

$$n_{0.01} = 6.308 \times 10^{-5}\left(\frac{4.89 \times 10^4}{0.01}\right)^2$$

$$= 1.508 \text{ x } 10^9$$

For: σ_E = 10%

$$n = 6.308 \times 10^{-5}\left(\frac{4.89 \times 10^4}{0.1}\right)^2$$

$$= 6.308 \text{ x } 10^{-5} \text{ x } 2.391 \text{ x } 10^{11}$$

$$= 1.508 \text{ x } 10^7$$

Estimated average particle diameter -d (from figure 3.1) = 25 µm = 25 x 10^{-4} cm

Radius (r) = 12.5 x 10^{-4} cm

Assume particles are spherical :

⇒ Volume of particles (equation 3.2): $V = \frac{4}{3}\pi r^3$ or $\frac{1}{6}\pi d^3$

$$V = 4.19 \text{ x } (12.5 \text{ x } 10^{-4} \text{ cm})^3$$

Therefore from equation 3.1: mass = volume x density x n

$$\text{Mass} = {}^3/_4\, \pi r^3 \text{ x } d_{ave} \text{ x n}$$

$$m = 4.19 \text{ x } (12.5 \text{ x } 10^{-4} \text{ cm})^3 \text{ x } 3.272 \text{ g/cm}^3 \text{ x n}$$

For: $n_{0.01}$ (1%): $m = 4.19 \text{ x } (12.5 \text{ x } 10^{-4} \text{ cm})^3 \text{ x } 3.272 \text{ g/cm}^3 \text{ x } 1.508 \text{ x } 10^9$

$= 40{,}38$ g

$n_{0.1}$ (10%): $m = 0.404$ g

$n_{0.05}$ (5%): $m = 1.615$ g

1.2 Rhodium Correction Factor from Palladium in ICP-MS

Rhodium (^{103}Rh) has one isotope at mass 103, and in cases where there is copper in the sample matrix there is an apparent signal enhancement which is due to the combination of copper ($^{63}Cu^+$) and argon ($^{40}Ar^+$) ions which occurs in the plasma to give $^{103}CuAr^+$. Several approaches have been taken to correct for this interference (cf. section 6.2.3)

The copper interference is also observed on one palladium isotope ^{105}Pd, and by comparing the signal on this isotope with that of other palladium isotopes: ^{106}Pd or ^{108}Pd the enhancement can be estimated and related back to the one on ^{103}Rh.

The equations below illustrate how the rhodium correction can be worked out from palladium isotopes.

$$I_{105,Pd} = I_{105,total} - \left(I_{108} \text{ x } \frac{\theta(Pd105)}{\theta((Pd108)} \right)$$

where: **I** = intensity and **θ** = % relative abundance of the isotope.

$$I_{105,Pd} = I_{105,total} - \left(I_{108} \text{ x } \frac{22.33}{26.46} \right)$$

$$I_{105,excess} = I_{105,total} - I_{105,Pd} \text{ x } 0.8439$$

$$I_{103,Rh} = I_{103,total} - \left(I_{105,excess} \text{ x } \frac{\theta(Cu63)}{\theta(Cu65)} \right)$$

$$I_{103,Rh} = I_{103,total} - \left(I_{105,excess} \text{ x } \frac{69.17}{30.83} \right)$$

$$I_{103,Rh} = I_{103,total} - 2.2436 \text{ x } I_{105,excess}$$

1.3 Stoichiometric calculation of silica and HF acid

Silica reacts with HF acid to form a silicate complex.

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$

1 mole of SiO_2 requires 6 moles of HF

1 mole of SiO_2 = 60 g and Merensky (AM) concentrate sample contains 33% SiO_2

$\therefore$ 0.3 g of AM sample contains $300 \text{ x} \frac{33}{100} = 0.1$ g SiO_2

$$\frac{0.1}{60} = 0.00167 \text{ moles} = 1.67 \text{ mmoles of } SiO_2 \quad \text{and} \quad 1 \text{ mole HF} = 20 \text{ g}$$

$\therefore$ 6 x 1.67 = 10.0 2mmoles of HF are required $\Rightarrow$ 10.02 x 20 =200 mg (0.20 g) HF.

1ml of 40% HF with density = 1.13 contains: $1.13 \text{x} \frac{40}{100} \text{g} = 0.452$ g (452 mg)

$\therefore$ 200 mg $\cong \frac{200}{450} \times 1 = 0.44$ ml of 40% HF

$\Rightarrow$ 0.3 g of this concentrate sample requires about 0.5 ml HF

Appendix III Detailed Sample Preparation and Results

1.1 Microwave oven power calibration

Microwave energy is a non-ionising radiation that causes molecular motion by migration of ions and rotation of dipoles, but does not cause changes in molecular structure.

Microwaves heat all the fluid without heating the vessel, and the solution reaches its boiling point very quickly. It has proved to be a rapid and inexpensive method of decomposing rocks for multi -element determinations and it is more useful for volatile analytes that are often lost during the normal open vessel procedures [37]. There is also less chance of contamination because small amounts of acids are used and the sample handling is minimal.

In order to evaluate the available power for heating, the actual power output is measured regularly by measuring the initial temperature (T_0) of 1 kg (1000 ml) water, heating for 2 minutes at 1000 watts. Immediately another temperature is measured (T_1), and the power is calculated by this equation as recommended by the manufacturer [32]:

$$P = 34.86 \text{ x } (T_1 - T_0)$$

The total power output was found to be 935 ± 10 watts (n = 3).

1.2 Determination of the instrument precision

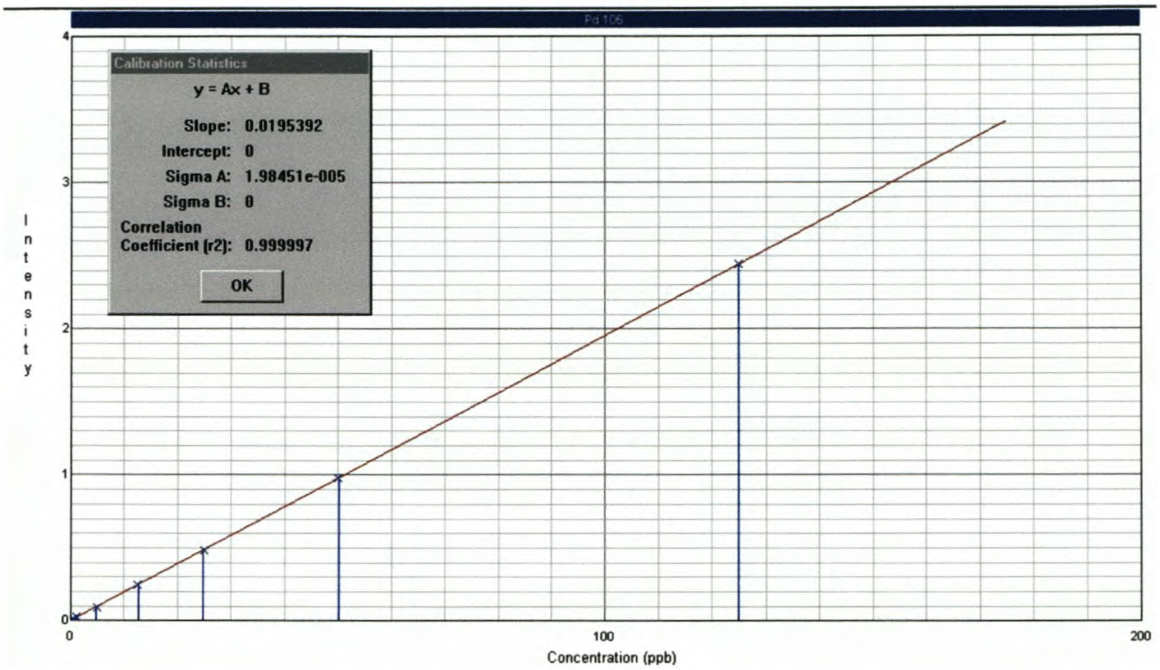
Table III -1 Data obtained on one solution to check the precision of the ICP-MS

	Pt 22.0 mg/l			**Pd 13.5 mg/l**			**Au 1.69 mg/l**			**Rh 3.1 mg/l**		
	July	Aug	Sept	July	Aug	Sept	July	Aug	Sept	July	Aug	Sept
Day 1	22.55	21.54	21.4	13.60	13.60	13.5	1.65	1.584	1.53	3.19	3.169	3.12
Day 2	22.07	21.6	21.99	13.25	13.47	13.3	1.53	1.68	1.61	3.13	3.11	3.14
Day 3	21.87	22.2	22.05	13.37	13.3	13.2	1.62	1.55	1.71	3.13	3.12	3.09
Day 4	21.85	21.9	21.9	13.52	13.6	13.6	1.66	1.71	1.57	3.17	3.18	3.18
Day 5	22.02	21.6	22.4	13.54	13	13.3	1.60	1.57	1.71	3.18	3.02	3.26
Day 6	21.81	21.34	21.9	13.63	13.26	13.7	1.64	1.69	1.57	3.18	3.17	3.27
Day 7	22.50			13.80			1.73			3.24		
Day 8	21.96			13.82			1.77			3.09		
Average	**22.08**	**21.70**	**21.94**	**13.57**	**13.37**	**13.43**	**1.65**	**1.63**	**1.62**	**3.16**	**3.13**	**3.18**
Std dev	**0.29**	**0.31**	**0.32**	**0.19**	**0.23**	**0.20**	**0.074**	**0.070**	**0.077**	**0.048**	**0.061**	**0.074**
Variance	**0.08**	**0.094**	**0.104**	**0.038**	**0.053**	**0.039**	**0.005**	**0.005**	**0.006**	**0.002**	**0.004**	**0.006**
%RSD	1.31	1.41	1.47	1.43	1.73	1.46	4.49	4.31	4.74	1.50	1.95	2.34

Table III-2 Summary of ANOVA on the ICP-MS precision results

	Average	Variance Within	Variance Between	Overall	F-value	F-critical
Pt	21.9	0.093	0.25	0.11	2.7	3.59
Pd	13.4	0.043	0.069	0.045	1.63	3.59
Au	1.63	0.0054	0.018	0.0051	0.33	3.59
Rh	3.15	0.0037	0.0037	0.0037	1.02	3.59

1.3 Calibration of ICP-MS showing typical calibration graphs for Pt, Pd, Rh and Au



y = Ax + B

Slope: 0.0195392

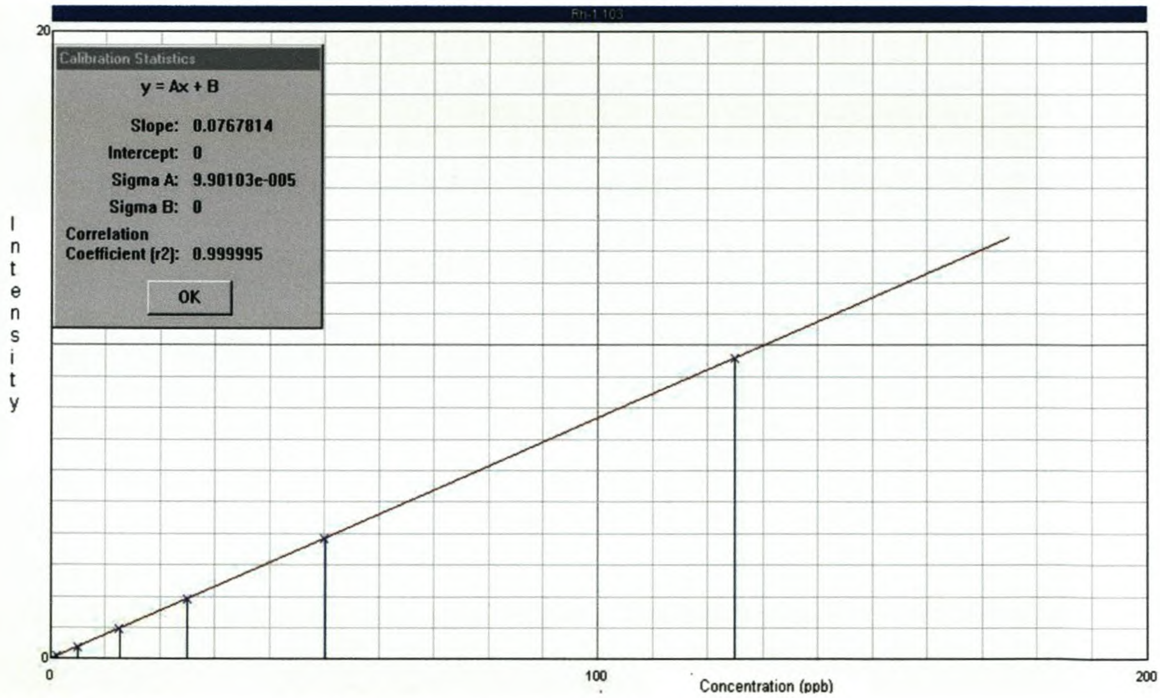
Intercept: 0

Sigma A: 1.98451e-005

Sigma B: 0

Correlation Coefficient (r2): 0.999997

Figure III-1A A typical calibration graph for Pt^{195}



y = Ax + B

Slope: 0.0767814

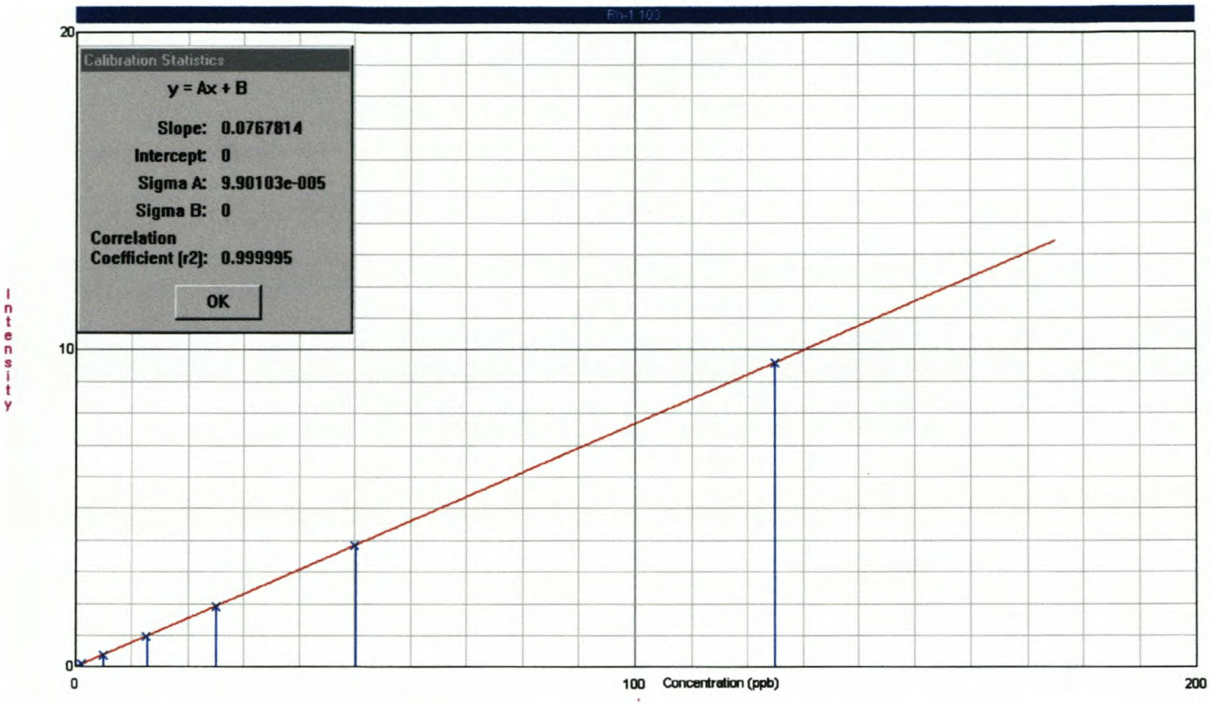
Intercept: 0

Sigma A: 9.90103e-005

Sigma B: 0

Correlation Coefficient (r2): 0.999995

Figure III-1B A typical calibration graph for Pd^{106}



y = Ax + B

Slope: 0.0767814

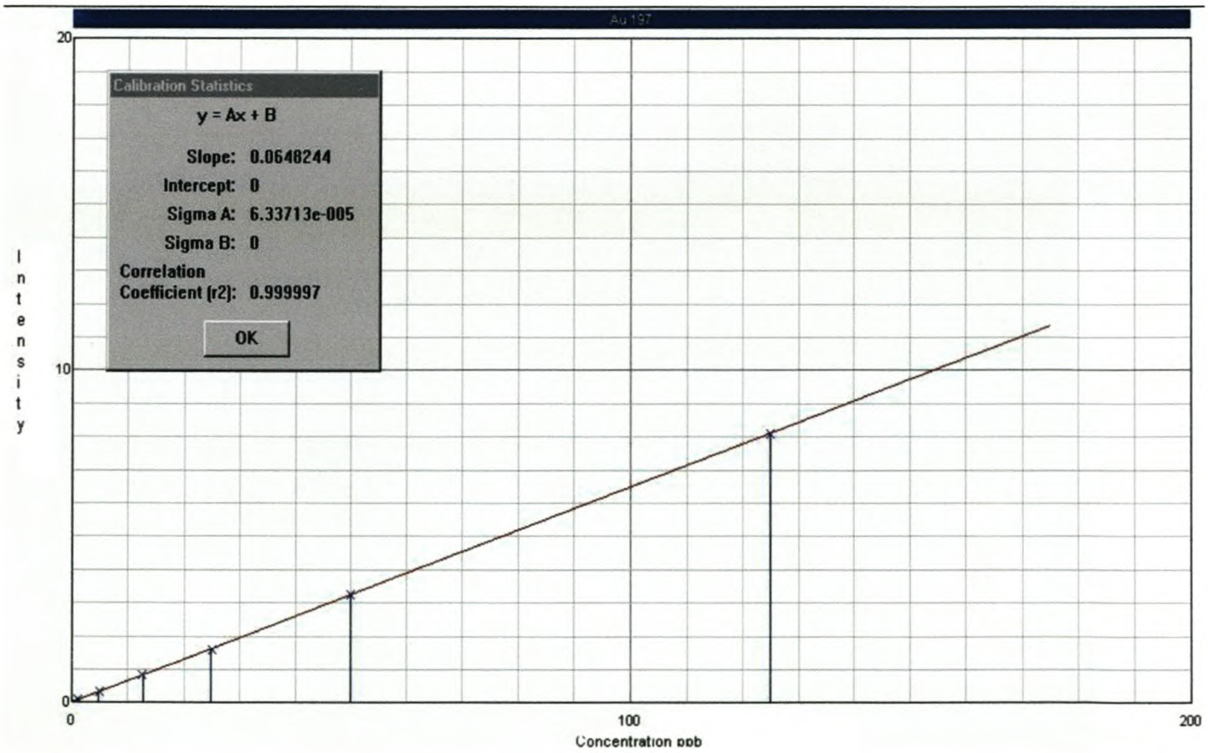
Intercept: 0

Sigma A: 9.90103e-005

Sigma B: 0

Correlation Coefficient (r2): 0.999995

Figure III-1C A typical calibration graph for Rh^{103}



y = Ax + B

Slope: 0.0648244

Intercept: 0

Sigma A: 6.33713e-005

Sigma B: 0

Correlation Coefficient (r2): 0.999997

Figure III-1D A typical calibration graph for Au^{197}

1.4 Comparison of PGM determination as done by ICP-MS and ICP-AES on matte sample

Table III-3 Comparison results from ICP-AES and ICP-MS on matte samples

Sample ID	Platinum g/t		Palladium g/t		Gold g/t		Rhodium g/t		
	ICP-AES	ICP-MS	ICP-AES	ICP-MS	ICP-AES	ICP-MS	ICP-AES	ICP-MS	ICP-MS
								Uncorrected	Corrected
Matte 1	1242	1245	1074	1050	123	128	110	113	109.5
Matte 2	1402	1422	1200	1185	140	150	120	126	122.5
Matte 3	1305	1300	1163	1130	139	146	112	118	114.4
Matte 4	1234	1210	1133	1095	136	135	106	111	107.4
Matte 5	1421	1405	1234	1170	142	146	117	123	119.3
Matte 6	136	134	161	166	26.3	31	14	19.5	15.6
Matte 7	108	108	138	145	23.5	28.5	10.8	16.5	12.7
Matte 8	58	61			15.5	23.2	5.89	13	9.2
Matte 9	55	52	95.7	100	19.5	23	6.86	11.5	7.7
Matte 10	36	34	78.2	81.5	17.3	21	4.94	10.5	6.7
Matte 11	101	99	122.5	124	21.0	24.5	11.9	17.5	13.5
Matte 12	1190	1240	778	768	65.4	70	158	160	154.5
Matte 13	1200	1195	760	738	64.4	69	152	154	148
Matte 14	1125	1165	714	721	60.7	66	140	154	147.9

1.5 Experimental Parameters

The experimental parameters in table III-2 were used throughout the investigations in this work. In cases where factorial designs were used some parameters were changed and those are shown in the relevant sections.

Table III-4 Experimental parameters used in this study

		Acid Mixture		Microwave Parameters	
		Acid	Volume (ml)	Power (W)	Time (min)
Oven temperature (°C)	850	HF	1	250	5
Roasting time (hr)	1	$HClO_4$	1	400	5
Air flow	1.4 l/min	HCl	3	650	5
		HNO_3	1	250	5

1.6 Sample Digestion Procedure

i. 300 mg aliquots of a well mixed sample were weighed into the microwave vessels.

ii. 1 ml HF, 1 ml $HClO_4$, 3 ml HCl and 1 ml HNO_3 (Acid mixture) were added.

iii. The vessels were capped, assembled onto a rotor, and tightened to a specific torque

iv. Placed in the microwave unit and program activated.

v. The vessels were allowed to cool and opened.

vi. 25 ml of 2.8% boric acid was added to the sample solution - to complex any free HF

vii. Filtered through a 0.45 μm filter paper and the residue submitted for mineralogical examination and XRF qualitative scans.

viii. Filtrate transferred to 100ml volumetric flasks

ix. Analysed on the ICP-QMS

ICP-QMS Preparation

- 2.5 ml aliquot of each sample is pipetted into a 25 ml vial
- 10 ml of 20 ppb In/Re internal standard and 5 ml water are added using 10 ml dispensers.
- The same preparation is done with the calibration standards each time an analysis was performed.

1.7 Sample Digestion with Roasting

The pre-treatment step was introduced to breakdown the acid resistant sulphide minerals.

i An empty crucible is weighed

ii. About 300 mg sample is weighed into the crucible and the total mass is recorded

iii. crucible is placed in a preheated muffle and air is blown in at about 1.4 l/min

iv. roasted for 1 hour, placed in a dessicator to cool to room temperature

v. crucible is re-weighed (change in mass noted)

vi. contents of the crucible are transferred to the microwave vessel

vii. empty crucible is re-weighed

viii. steps **ii** to ix in **1.3** were followed

1.8 Sample Digestion with Roasting and Hydrogen Reduction

i. An empty crucible is weighed

ii. About 100 mg sample is weighed into the crucible and the total mass is recorded

iii. Crucible is placed in a preheated muffle and air is blown in at about 1.4 l/min

iv. roasted for 1 hour at 850 °C

v. transferred to the hydrogen reduction manifold (immediately from the roasting furnace)

vi. place the crucible on a silica triangle and place the lid on (with a hole in the middle), open the LPG gas, light the Bunsen burner and place it under the crucible, open and ignite the hydrogen gas it then place the hydrogen flame into the crucible (through the hole in the lid) to bring sample into contact with hydrogen and a burner under the crucible. Heat for about 20 minutes and cool under hydrogen flame for another 20 minutes.

vii. Place the crucible in the dessicator and follow steps from **v.** in **1.4**

1.9 Raw data obtained on the three samples used

Table III-5 Results of the Merensky concentrate

	Pt (g/t)		Pd (g/t)		Au (g/t)		Rh (g/t)	
Ref.	129.8 ± 5		78.9 ± 4		6.45 ± 1		13.5 ± 1	
N	AVE	SD	AVE	SD	AVE	SD	AVE	SD
1	137.5	6.4	76.6	0.9	6.40	0.68	11.95	0.9
2	143	6.7	80.9	0.1	6.68	0.64	12.7	0.1
3	126	0.0	80.0	3.0	4.40	0.25	11.2	0.3
4	*189.5	2.1	*90.8	0.8	7.30	0.04	12.75	0.5
5	144	4.2	83.4	0.2	6.59	0.45	11.95	0.5
6	124.5	4.9	79.2	1.0	7.80	0.57	12.05	1.1
7	137.5	0.7	77.7	2.7	6.89	0.21	11.7	1.3
8	*152	0.0	77.1	3.0	7.22	0.20	12.25	1.8
9	128	0.0	76.3	2.5	8.54	0.25	11.35	0.2
10	129	1.4	81.0	3.1	*10.75	0.21	11.5	0.7
11	134.5	0.7	76.2	1.8	6.66	0.24	11.8	1.1
12	129	1.4	79.7	0.7	6.66	0.22	12.3	1.6
13	133	1.4	76.9	1.1	6.8	0.21	11.85	1.3
14	127	2.8	83.1	0.9			11.15	1.2
15	133.5	6.4	74.2	6.4	6.02	0.10	12.6	1.4
16	124	0.0	78.5	1.3	7.68	0.25	11.4	1.0
Ave	**132.18**		**78.6**		**6.6**		**11.9**	
SD	**6.50**		**2.7**		**1.1**		**0.5**	
%RSD	**4.92**		**3.4**		**16.1**		**4.0**	

---

* Results falling outside 2sd and discarded as outliers.

Table III-6 Results of the Merensky feed sample - SARM 7

	Pt (g/t)			Pd (g/t)			Au (g/t)			Rh (g/t)		
Ref.		3.74	0.043		1.53	0.032		0.31	0.015		0.24	0.013
Mass-g	**Pt**	**Aver**	**SD**	**Pd**	**Aver**	**SD**	**Au**	**Aver**	**SD**	**Rh**	**Aver**	**SD**
0.25	3.69	3.65	0.96	1.70	1.76	0.07	0.31	0.32	0.11	0.30	0.28	0.01
	2.99			1.70			0.23			0.29		
	4.63			1.73			0.23			0.27		
	2.43			1.77			0.32			0.26		
	*			1.81			0.50			0.27		
				1.86						0.28		
0.3	4.54	3.87	0.57	1.85	1.80	0.17	0.31	0.27	0.05	0.21	0.26	0.03
	3.73			1.80			0.21			0.30		
	3.25			1.51			*0.16			0.28		
	4.61			*2.32			*0.18			0.25		
	3.66			1.96			0.26			0.26		
	3.46			1.86			0.30			0.28		
0.5	3.53	3.62	0.31	1.81	1.74	0.16	0.19	0.27	0.06	0.27	0.26	0.03
	3.36			1.55			0.20			0.26		
	3.32			1.73			0.23			0.25		
	3.45			1.73			0.32			0.19		
	3.29			1.46			0.36			0.25		
	4.07			1.70			0.30			0.32		
	3.93			1.99			0.32			0.28		
	4.00			1.80			0.29			0.29		
	3.58			1.84			0.23			0.25		
1.0	3.28	3.83	0.35	1.64	1.64	0.13	0.27	0.28	0.03	0.23	0.26	0.02
	3.83			1.46			0.28			0.24		
	3.77			1.55			0.31			0.23		
	3.49			1.58			0.26			0.29		
	4.15			1.74			0.32			0.26		
				1.90			0.32			0.29		
	4.14			1.60			0.27			0.26		
	4.17			1.65			0.22			0.27		
Averag	**3.74**			**1.72**			**0.28**			**0.27**		
Stddev	**0.52**			**0.14**			**0.06**			**0.03**		

---

[*] Results falling outside 2sd limits - discarded as outliers

Table III-7 Results for UG-2 Concentrate

	Pt (g/t)		Pd (g/t)		Au (g/t)		Rh (g/t)	
Ref.	**96. 7 ± 3.8**		**46.0 ± 1.6**		**0.77 ± 0.18**		**17.8 ± 0.8**	
	AVE	SD	AVE	SD	AVE	SD	AVE	SD
1	91.1	1.9	43.3	0.9	0.99	0.054	18.7	0.60
2	90.2	0.3	43.1	1.0	0.77	0.020	18.3	0.58
3	86.3	0.4	41.3	0.5	0.76	0.072	16.7	0.16
4	91.4	0.5	47.5	0.1	0.68	0.017	18.5	0.34
5	91.5	0.8	42.9	0.1	0.69	0.018	18.1	0.46
6	104.2	0.2	47.0	1.7	[¶]10.71	0.953	18.6	0.39
7	90.8	0.3	45.9	1.1	[¶]1.43	0.264	17.8	
8	98.1	0.1	45.8	1.6	0.83	0.049	17.9	0.27
9	91.8	0.4	49.0	0.1	[¶]2.09	0.058	16.9	0.40
10	92.4	0.7	45.5	0.5	0.81	0.063	17.4	0.69
11	91.3	0.7	46.3	1.3	0.78	0.055	17.1	0.61
12	94.4	0.6	44.1	1.5	0.81	0.051	16.6	0.73
13	86.9	0.2	41.8	1.3	0.98	0.058	16.1	0.57
14	91.9	1.1	44.2	0.8	0.80	0.017	17.1	0.61
15	88.8	1.0	44.5	0.3	0.73	0.020	17.8	0.42
16	97.9	0.5	46.4	0.3	0.80	0.035	17.9	0.54
17	91.4	0.8	46.0	1.2	0.79	0.023	17.6	0.67
Ave	**92.4**		**45.0**		**0.80**		**17.6**	
SD	**4.3**		**2.0**		**0.086**		**0.74**	
%RSD	**4.6**		**4.4**		**10.75**		**4.2**	

[¶] Results discarded as outliers