THE OPTIMIZATION AND CALIBRATION OF SPARK-OPTICAL EMISSION SPECTROSCOPY FOR THE ANALYSIS OF TRACE IMPURITIES IN ULTRA-PURE PT, PD AND RH

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DECLARATION

I declare that this dissertation is my own unaided work, except where acknowledged in the text. It is being submitted for the Degree of Masters of Science at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University.

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ABSTRACT

Since the industrialization of platinum group metals (PGMs), particularly platinum (Pt), palladium (Pd) and rhodium (Rh), the control of trace impurities in these metals has become vital. Reliable analysis of impurities in these metals is, however a difficult task. Nobel metals are difficult to dissolve quickly and quantitatively. Thus, analytical techniques which determine samples in liquid form have become less favourable. They require time consuming digestions and are prone to contamination both from the chemicals and equipment used for the preparation. Direct-analysis techniques are increasingly being used in the platinum group metal (PGM) industry for the determination of impurities in the final products.

Spark-optical emission spectroscopy (Spark-OES) for the analysis of metals offers rapid turnaround times. Since the technique is almost non-destructive, little of the product is lost during analysis. The technique is also well established in the PGM industry. It is routinely used by two of the three largest platinum producing companies for the determination of impurities in their products. It is also used for the determination of PGMs after Fire Assay procedure by Anglo American Platinum. The greatest challenge for this technique remains the availability of certified reference materials (CRM) and calibration standards.

This study investigates the use of the Spark-OES for the determination of impurities in PGMs (notably gold (Au), silver (Ag), iron (Fe), nickel (Ni), copper (Cu), lead (Pb), magnesium (Mg), manganese (Mn), silicon (Si), aluminium (Al), antimony (Sb), chromium (Cr), tin (Sn), titanium (Ti), zirconium (Zr), calcium (Ca), zinc (Zn), boron (B), cobalt (Co), vanadium (V), molybdenum (Mo), bismuth (Bi), arsenic (As), selenium (Se), tellurium (Te), cadmium (Cd) in refined platinum, palladium and rhodium metals). It

is to be used at Anglo American Platinum's final metal's laboratory. A method to be used routinely in the laboratory is also developed. The concentration of the impurities determined is used to quantify the overall purity of the PGMs. PGMs, other than the matrix (the metal whose purity is being quantified), are also determined. The use of Spark-OES was evaluated as an alternative to inductively coupled plasma-optical emission spectroscopy (ICP-OES).

Due to the lack of CRMs and calibration standards, the study included the preparation of in-house reference material (IRM) for calibration and quality control purposes. The standards were prepared by spiking pure PGM metal sponges (produced by Anglo Platinum) with the metal oxides of the elements of interest. These were melted together using a vacuum induction furnace to produce metal disks. The disks were ground and analysed after dissolution using ICP-OES. The metal disks, and the shavings, were distributed to three other independent laboratories and analyzed by ICP-OES, inductively coupled plasma-mass spectroscopy (ICP-MS) and Spark-OES. The assigned consensus values were used for the calibration of the Spark-OES. The method was validated for linearity, accuracy, precision, robustness, bias and the measurement uncertainty of the method.

The metal disks were first tested for homogeneity. It was found that the bottom surface of the rhodium metal was not homogenous. Rapidly cooled moulds, will facilitate almost instantaneous cooling of the metal. This eliminates the migration of elements during cooling. This could assist with homogenizing the metal. Limits of detections (LODs) achieved for the methods ranged from 0.1 $mg.kg^{-1}$ to 4 $mg.kg^{-1}$. The highest LOD was for silicon, which was caused by contamination from the crucibles used. The precision for all impurity elements, except ruthenium (Ru), of the three methods (analysis of platinum, palladium and rhodium) was satisfactory.

Ru showed poor precision in all the matrices due to the channel installed in the spectrometer. Due to the lack of CRMs, the traceability of the method could not be validated and the accuracy could only be validated by comparing it to in-house reference material.

Although the method met the validation criteria, it cannot be used to certify the purity of the product as the traceability could not be validated. It suggests that the method be used for twin stream analysis in conjunction with a primary method. Because of its rapid turnaround time, and its non-destructive nature, the method can be used for plant control purposes, where the level of accuracy required is not as stringent as required on a certificate of analysis.

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CHAPTER 1
INTRODUCTION

1.1 GENERAL INTRODUCTION

The platinum group metals (PGMs) consists of six metals with similar chemical and physical properties. Their distinctive properties such as their very high melting points, chemical inertness, and resistance to corrosion and oxidation have earned these metals their classification as noble metals (Jones, 2005). Unfortunately these properties, as well as the high density of the metals, rendered working with them difficult before the 1700s. Interest in the metals only developed in 1782 after the first successful melting of platinum (Jones, 2005). This growing interest resulted in the description of their catalytic properties during 1823 – 1838 (Jones, 2005). This group of metals gained in popularity in a number of industries and increasing the need for their production in large volumes. The development of extraction and purification methods aided an increase in their production. The increased production of a better quality metal permitted commercial use, which was previously limited by the level of impurities (Free, 2001).

Of the six metals, platinum, palladium and rhodium is most important, due to their extensive applications in industry and their economic importance. These three PGMs are mostly used in their refined form and may be recycled (Hunt & Lever, 1969). Accurate measurement and reporting of impurities and consequently the purity of the metal is required. The purity of the metal is determined by analysing for all the impurities. The percentage impurities are added and the sum is subtracted from 100 to give a final purity of the metal. The control of trace impurities in these metals has in recent years become pivotal; increasing the number of elements, regarded as impurities, to be determined in the pure metals to

more than 27. This raised interest into a more rapid and reliable determination of trace impurities in pure PGM metal (Lincoln & Kohler, 1962). The reliable analysis of impurities (and the subsequent purity of the PGMs) is, however, a challenging task. PGMs do not dissolve easily. Dissolution is time consuming and not always quantitative. Of the three main PGMs, palladium is the only metal which can be dissolved with a single acid (Hillebrand & Lundell, 1929). Rhodium metal is insoluble in most acids and alkali solutions (at standard temperature and pressure), including aqua-regia (Sterliński, et al., 1976). Platinum and palladium sponge can be dissolved with hot aqua-regia, however if this is not done in a pressurized vessel any osmium present in the sample will be volatilized and lost as osmium tetraoxide ($OsO_{4)}$. Volatilization of the element will make its determination as one of the impurities of interest impossible.

According to Hillebrand and Lundell (Hillebrand & Lundell, 1929), rhodium is only slowly attacked by alkaline oxidizing fluxes if the metal is very finely divided. As a result, the determination of these metals by methods that analyze liquid samples can only be done after time-consuming digestions. Digesting the samples increases the risk of contamination from impurities in commercial chemicals. This, due to the time it takes, also makes it impossible to control the final stages of the refining process where the metals are treated as metal powder (sponge) for a specified amount of time. Thus only the final product is analysed. As a result, high levels of impurities caused by contamination from the process are only detected at the final stage of refining. Consequently the sponge has to be dissolved and retreated resulting in the loss of production. This, together with turnaround time for reporting the purity of the metals has made the direct analysis of the metals in solid state more appealing to the PGM industry.

1.2 APPLICATIONS OF PLATINUM GROUP METALS (PGMS)

PGMs were first used to manufacture inert crucibles, wires for telegraphs, touch-holes for flint-lock guns and in sulphuric acid boilers (Free, 2001). However, since the discovery of their catalytic properties, they have become indispensable.

As much as 80 to 90% of the applications of PGMs are for chemical and metallurgical processes. PGMs are also used to a limited extend, for decorative applications (Hunt & Lever, 1969). Platinum, palladium and rhodium have been primarily used in catalytic converters, and also for jewellery. They have also been used in chemical and petroleum refining, fuel cells, glass manufacturing, electrical and electronic applications and in medical and dental applications.

1.2.1 JEWELLERY

The use of platinum for decorative purposes dates as far back as 1400 BC where it was applied in Egypt (Free, 2001). Platinum has been used more than 2000 years ago, by the Indian civilization of South America, where platinum was obtained from river beds as nuggets. The modern platinum jewellery tradition was founded in the 18^{th} century with the European court jewellers. These were further developed during the Edwardian and Art Deco periods (Johnson Matthey, 2002).

Platinum typically used for manufacturing jewellery is of 85 to 95% purity. Pure platinum (100% purity) is rarely used for the manufacturing of jewellery. The metal is too soft to withstand daily wear. The metal is commonly alloyed with other PGMs. Base metals such as copper and cobalt are also commonly alloyed with platinum to optimize its working characteristics and wear properties (Maerz, 1999).

1.2.2 CHEMICAL AND PETROLEUM REFINING

Petroleum refining is achieved through four major processing steps: catalytic reforming, alkylation, catalytic cracking and hydro-processing to refine oil fractions. The catalytic reforming process produces high octane gasoline from gasoline and naphtha. A platinum catalyst embedded on Al_2O_3 has been traditionally used (Pafko, 2000) to facilitate this process.

Platinum group metals have been used extensively for the catalysis of organic reactions in pharmaceuticals. Palladium-catalyzed carbon-carbon bond formation gained popularity as it reduced the need for the use of strong bases and the extensive use of protective groups. There are three dominant reaction types for C-C bond formation reactions, namely: (i) the Heck reaction, (ii) the Suzuki, Ngishi and Kumada coupling reactions and (iii) the Sonogashira reaction (De Vries, et al., 2001). The Heck reaction uses complexes of palladium with Ph_3P or *o*-$Tolyl_3P$, whereas catalysts used for the coupling reactions require phosphine ligands. The Sonogashira reaction also uses palladium/phosphine catalysts, co-catalyzed by copper iodide (CuI) (De Vries, et al., 2001).

1.2.3 FUEL CELLS

Fuel cell systems (particularly polymer electrolyte membrane fuel cells) have in the recent years been considered a source of clean energy. It offers an alternative to fossil fuels consumption that emits greenhouse gases into the atmosphere. Fuel cells are electrochemical devices converting air (or oxygen) and selected fuels to generate electricity directly from chemical reactions. Water vapour and carbon dioxide is the only by-products. These systems produce energy with high efficiency and are used in a variety of applications.

Of the fuels used in these cells, the hydrogen fuelled polymer electrolyte membrane fuel cells (PEMFC) has shown the highest performance. PEMFCs use a thin membrane (solid polymer) as an electrolyte with porous carbon electrodes containing a platinum catalyst. The platinum catalyst is used to aid the conversion of hydrogen (de Wild & Verhaak, 1999).

1.2.4 CATALYTIC CONVERTERS

Catalytic converters, based on heterogeneous catalysis by PGMs, purify automotive exhaust gases. These systems are incorporated more and more into the exhaust systems of automotive vehicles (Lucena, et al., 1999). Catalytic converters were introduced in cars in the U.S. market in 1975 and were since preceded by four generations of converters.

The first generation was the two-way catalytic converters used from ~ 1976 to 1986. These allowed for emissions of hydrocarbons (HC) and carbon monoxide (CO) to be minimized significantly by oxidation to water (H_2O) and carbon dioxide (CO_2), respectively. The converters contained platinum and palladium catalysts (Barbante, et al., 2001), and the following reactions occurred (Mooley, 2007):

$$2CO + O_2 \xrightarrow{Pt/Pd} 2CO_2 \qquad (1.1)$$

$$C_xH_{2x+2} + 2xO_2 \xrightarrow{Pt/Pd} xCO_2 + 2xH_2O \qquad (1.2)$$

The second generation was the three-way catalytic converters that were capable of minimizing the emission of all three products (HC, CO and NO_x) and these were used between 1979 and 1986. The catalysts in these converters were platinum and palladium, for the oxidation of the HC and CO, and rhodium to reduce the NO_x emission to nitrogen and oxygen

(Barbante, et al., 2001). The reduction of the NO_x followed the equation (Mooley, 2007):

$$2NO_x \xrightarrow{Rh} xO_2 + N_2 \qquad (1.3)$$

The third generation, a new generation three-way catalyst, was used from 1986 to 1992. These catalysts were based on platinum and rhodium, and were better suited for the high temperatures of the then-new fuel efficient engines to which the catalysts were exposed (Barbante, et al., 2001).

From 1992 another generation of palladium-rich three-way catalysts were introduced. Catalysts used in these converters vary between palladium-rhodium, palladium only or platinum-palladium-rhodium. These catalytic converters are now used in all motor vehicle exhaust systems, and other engine equipped machines (Barbante, et al., 2001).

1.2.5 GLASS MANUFACTURING

One of the greatest limitations to the manufacturing of homogenous, high quality glass, is the effect of the corrosion of the refractory materials which may also lead to contamination of the glass (Preston, 1960). A sheet of platinum or platinum alloys is therefore used to completely cover certain refractory material to protect them from corrosion and/or reacting with the molten glass.

The process employed for the production of glass fibres involves the rapid flow of molten glass through boxes with serial orifices on their underside (bushings), which must retain their shape, size and alignment. Alloys of platinum and rhodium (10% Rh-Pt) are universally used for the construction of these bushings used for manufacturing glass fibres (Hunt & Lever, 1969).

1.2.6 ELECTRICAL AND ELECTRONIC APPLICATIONS

Due to their electrical conductivity and durability, palladium-containing components are extensively used in electronic devices, largely in multi-layer ceramic capacitors (MLCCs) (Morton, 1982). MLCCs are components of circuits which control the flow of current through other components by storing electrical charge until it is required. Capacitors consist of layers of conductive electrode material, mainly palladium or palladium-silver, sandwiched between insulating ceramic wafers. Palladium is also used in smaller volumes in conductive tracks in hybrid integrated circuits (HIC), where ceramic substrates with electronic components are mounted on them (Morton, 1982). These substrates are linked by conductive silver-palladium tracks, where the palladium is used to hold the silver in place so as to prevent migration of the silver particles.

The increasing need for personal computers with increased disk storage capacity has made computer hard disks the greatest electrical application for platinum. To increase the data storage density of hard disks, a layer of platinum-cobalt alloys is applied. The use of platinum in these disks has resulted in a smaller number of disks in each hard drive.

1.2.7 MEDICAL AND DENTAL APPLICATIONS

The introduction of the two platinum(II) complexes, *cis*-[$PtCl_2(NH_3)_2$] (*cis*-platin) and *cis*-[Pt(1,2-dicarboxycyclobutane)($NH_3)_2$], significantly improved the success rate for the treatment of a wide variety of cancers, notably testicular cancer (Stochel, et al., 1998). Since their introduction, platinum(II) complexes have become some of the most widely used drugs for cancer treatment. However, the effectiveness of (*cis)*-platin is limited

by: its spectrum of activity, the development of resistance in time and its toxicity to normal cells (Sadler & Guo, 1998).

Extensive work has been done on the development of more platinum anticancer drugs to overcome these limitations. An early discovery, that by changing the amine ligands to 1,2-diaminocyclohexane (DACH), allowed cellular resistance to be overcome. This resulted in diaminocyclohexane (DACH) complex and platinum(IV) analogues (Stochel et al., 1998) being of interest to researchers.

Precious metals (gold, platinum and ruthenium) have also been alloyed to Co-Cr, which have been traditionally used for the fabrication of removable partial dentures. These metals are alloyed to achieve better bonding characteristics to ceramic (Reclaru et al., 2005). Reclaru *et al*. (2005) reported that Pt-Ru (in concentrations of the order of 10 wt% each) is soluble in a Co-Cr matrix and their presence does not improve, or deteriorate the corrosive behaviour of the CoCr-based alloys.

1.3 MINING, PROCESSING AND REFINING OF THE PLATINUM GROUP METALS

Platinum was discovered in the Bushveld Complex of South Africa, in 1906. It remains the largest known PGM deposit in the world and contains more than two thirds of the world's known reserves of PGMs, with the Great Dyke in Zimbabwe as the second largest reserve (Jones, 2005). The Bushveld Complex is has economic concentrations of PGMs in three separate extensive layered reefs, each with its own characteristic mineralogy. These reefs are associated with the mafic rocks of the Rustenburg Layered Suite, and they are: the Merensky Reef, the UG2 Chromitite layer and the Platreef (Conradie, 2007). The Merensky Reef and the UG2 Chromitite layer are still the most highly exploited reefs; with

the Platreef, which is palladium enriched, only being marginally exploited. The Merensky and Platreef are metallurgically similar. They both have the PGMs associated with base metal sulphides. The UG2 Chromitite layer has relatively low quantities of base metal sulphides and is rich in chromite (Jones, 2005). The concentration of platinum (grade) in the two highly exploited reefs differs, depending on the mineralogy of the ore, and this has a significant effect on the manner in which they are processed (Conradie, 2007).

Each step of the extraction process is aimed at increasing the grade of the PGMs in the ore, by reducing other metals and minerals in the ore. The ore process described below is that for ore mined from the Merensky Reef.

1.3.1 ORE PROCESSING

Upon mining, the ore is sent to a Concentrator Plant where it undergoes a series of size reduction steps, including crushing and milling. Jaw crushers are employed for the crushing, while milling is carried out with ball mills. A gravity concentrate is separated from the milled ore using shaking tables, and taken directly to the refineries. The remaining ore is concentrated by flotation to recover most of the platinum-bearing minerals. A concentrate, enriched in mainly nickel, copper and iron sulphides and PGMs, result. The concentrate is then dried, pelletized and sent to the smelter.

At the smelter, the concentrate undergoes smelting and conversion, in a series of blast furnaces, producing a PGM-rich copper-nickel matte. The resultant matte is treated at to the Base Metals Refinery. It is crushed and separated into a magnetic enriched concentrate (containing PGMs) and a nickel-copper matte. The nickel-copper matte is refined into pure nickel and copper metal by electrolysis. The magnetic-enriched concentrate is leached to remove any remaining base metals, as well as iron and

sulphur. The final concentrate treated at the Precious Metals Refineries to further separate individual noble metals and purify them. A summary of the process is shown in Figure 1.1.

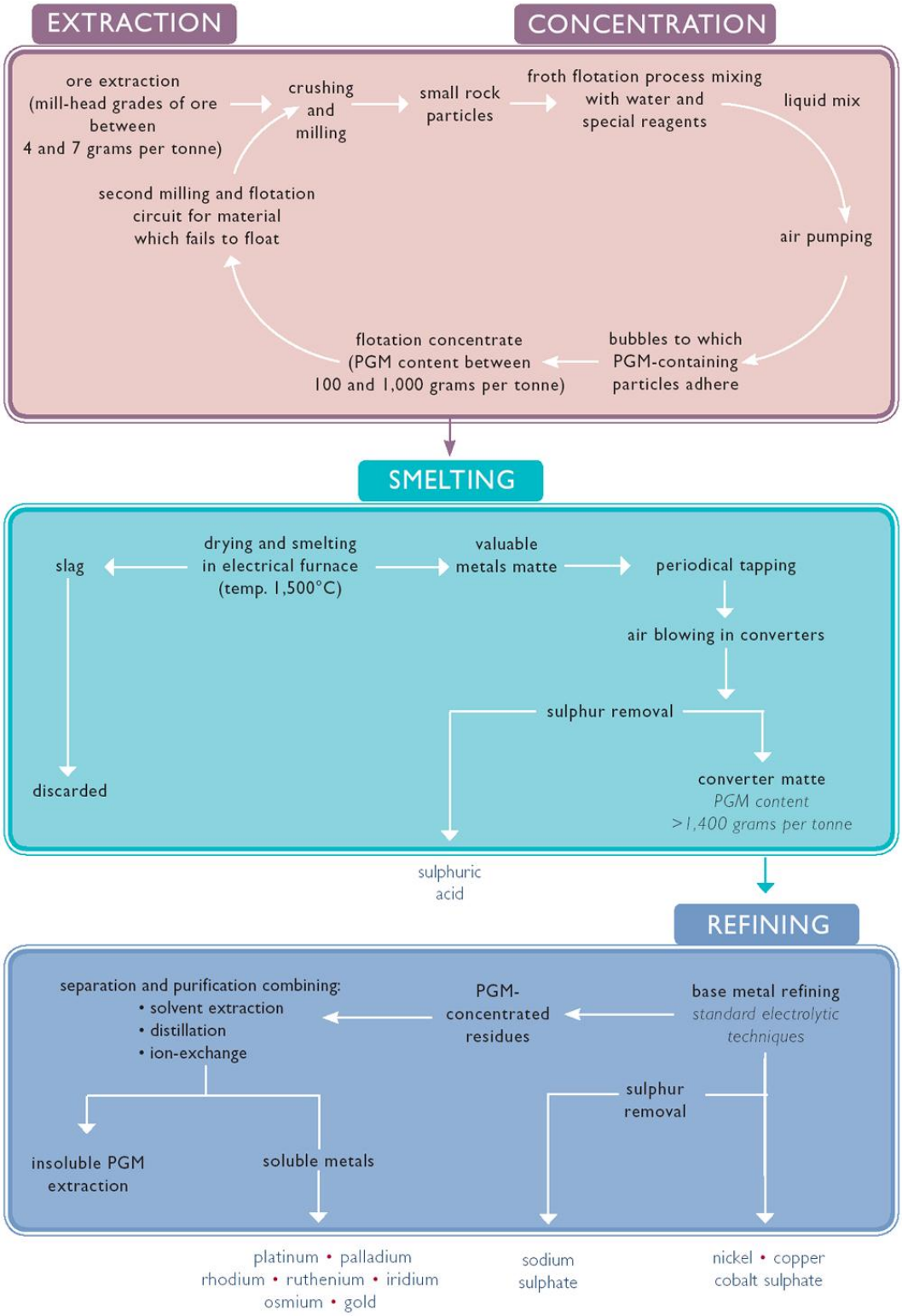

Figure 1.1: Diagram of the overview of the ore processing and refining process (Anglo Platinum, 2007)

1.3.2 CHEMICAL REFINING

The subtle difference in the properties of the PGMs, particularly their nobility, complex forming ability, ligand substitution reactivity and their ion-exchange reactivity, play an integral role in their separation. The separation process of these metals is carried out systematically, taking advantage of the distinctive properties of the metals, for example the formation of volatile tetroxides of certain PGMs (Hillebrand & Lundell, 1929).

The refining of PGMs has been carried out (until the mid 1970s) in a series of precipitation reactions. During the mid-1970s, numerous solvent extractants were introduced and solvent extraction refining methods have since been used. These methods offer higher selectivity, higher metal purity and more complete removal of the metals, reducing production costs and significantly shorter refining time. The process of solvent extraction follows three basic steps, namely: (i) the extraction step, where specific metals are selectively extracted; (ii) a scrubbing step, to remove co-extracted metals and (iii) a stripping step, to remove metal extracted from the organic phase (Robinson & Shackleton, 2002). A summary of the solvent extraction process used is illustrated in Figure 1.2.

The concentrate, as received from the concentrator (after the removal of base metals), is dissolved by suspending the solid in 10M HCl, then agitating at elevated temperatures. This is followed by a chlorine gas sparge to dissolve all PGM present. The solution is boiled, for as long as 8 h, to completely distil and remove any osmium in the solution as osmium tetroxide (Hillebrand & Lundell, 1929).

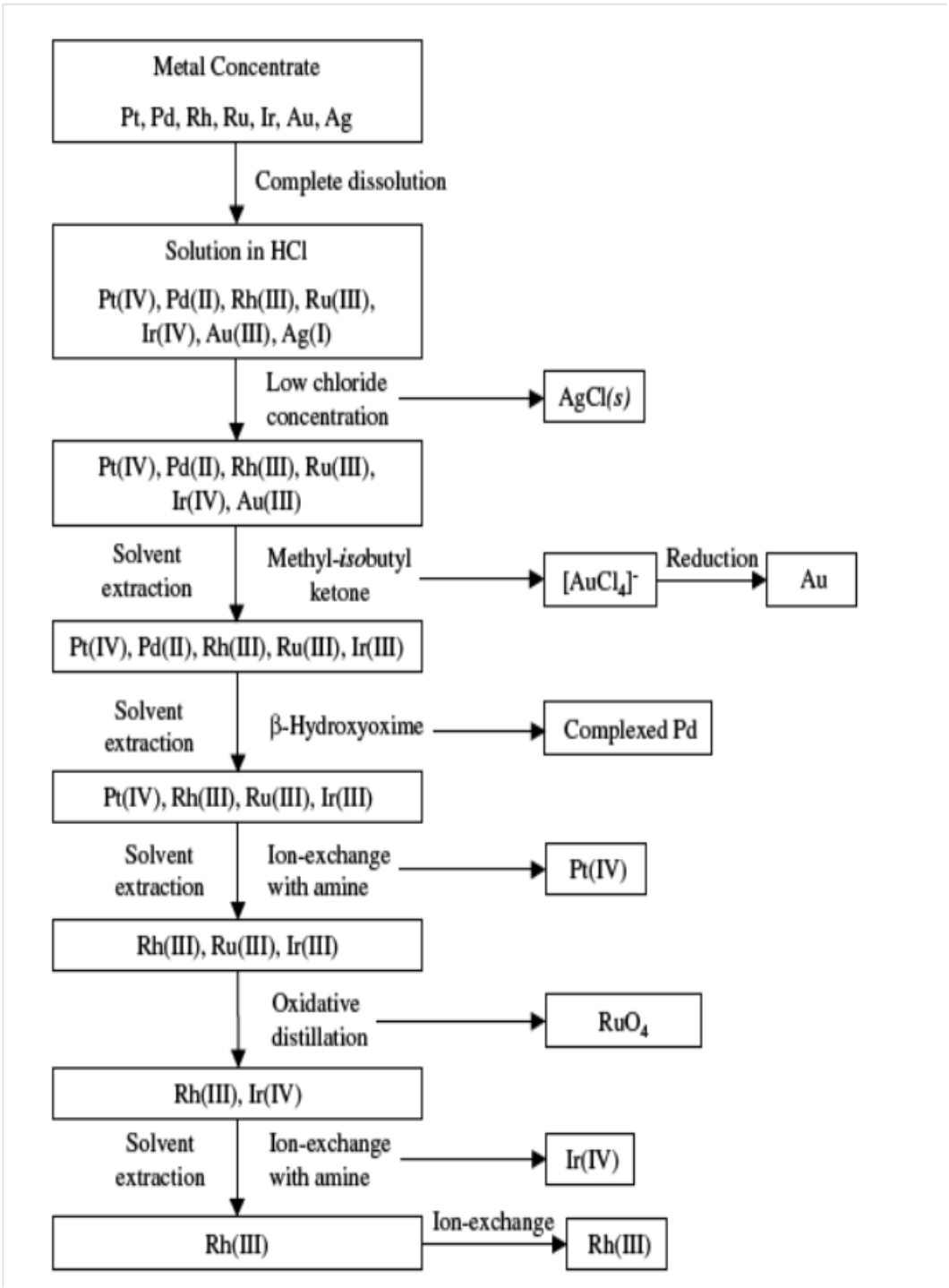

Figure 1.2: Schematic summary of solvent extraction method used for the chemical refining of PGMs (Bernardis et al., 2005)

After the removal of osmium, methyl isobutyl ketone (MiBK) is added to the solution to remove dissolved gold, along with the majority of selenium, tellurium, tin, antimony and iron. The resultant liquor is boiled down to remove any MiBK in the solution, and any lead and silver compounds (Bernardis et al., 2005). The solution is then diluted to its original concentration with 6M HCl.

In the next step palladium is extracted with β-hydroxyoxime(2-hydroxy-5-nonylacetophenome oxime) and the raffinate is boiled to dryness to remove the organic. Boiling 6M HCl is added to generate a solution consistent with the original concentration.

Amberlite LA2 (a secondary amine) is used for the extraction of platinum. The raffinate liquor is boiled to remove any extractant in the solution. The solution is diluted to its original concentration with 11M HCl and the pH adjusted to 1 using caustic. Sodium chlorate is added to volatilize the ruthenium, which is distilled as RuO_4.

Base metals still trapped in the solution are removed by controlling its normality and redox potential. The redox potential of the solution is changed by the addition of H_2O_2. In the next step, an amine is added for the extraction of Ir. The aqueous liquor is boiled to remove any extractant and the resulting solution diluted with 0.15M HCl, leaving a solution containing only rhodium.

Hydrazine is added to remove arsenic, and the lead chloride precipitated. After removal of the precipitate, the rhodium metal is then precipitated using ammonia and HCl.

The wet precipitates of the different PGMs are calcined at high temperature in a muffle furnace under atmospheric air to convert the salts

into metals. In the case of rhodium, they are converted to metal oxides and metal. The metals are allowed to cool and the resultant “bricks” are broken up, ground and screened. These are washed with acid to remove base metals entrained in the metal powder. The resultant metals are reduced with hydrogen gas, in silicon reduction tubes, to preclude metal oxides in the sponge, and cooled under nitrogen gas. To eliminate contamination from the reduction tubes, the sponge is washed with HF and HCl; then thoroughly washed with water. The water is then filtered to produce the pure final metal products.

Palladium and rhodium metals are treated differently due to their high affinity for gasses and their subsequent rapid oxidation during calcinations. Palladium, particular, can absorb up to 900x its own volume of oxygen. To minimize oxidation, rhodium is calcined at a lower temperature than the other metals. Both metals are reduced after calcination. Therefore, these metals undergo two stages of reduction, immediately after calcination and then again after the first acid wash. According to demand, these metals can either be sold as sponge, ingots (metal bricks) or grains (metal granules).

1.4 PURPOSE OF THE STUDY

The three main platinum producers in the country are all compelled to analyze all their products they produce to ascertain that it falls within the customer’s specifications. Currently two of the producers use Spark-OES (Spark Analysis For Traces (SAFT) from Spectro®) (Mtshali, 2008). One of the laboratories used the Spark-OES only for the determination of platinum and palladium while impurities in rhodium are determined with a Jarrel Ash photographic analyzer (Mashike, 2008). Both SAFT instruments are calibrated before it leaves the factory. One standard is used for adjustment of the calibration upon installation. Calibration standards are

not supplied with the instruments. The unavailability of CRMs and/or calibration standards made calibration almost impossible. The use of in-house metal sponge samples for calibrations has been investigated by both laboratories. A pressed pellet produced from sponge is difficult to compact and often breaks. Further grinding is required to homogenize the spiked pressed sponge which reduces the particle size of the sponge. As a result a new set of standards needs to be prepared every time a standardization or calibration is performed. This result in the analysis being unduly delayed and in the loss of material spiked.

The third producer used ICP-OES to perform analyses (Manyako, 2008). Elements such as Si, Al and B are determined using Spark-OES due to the potential contamination from the glassware used in the preparation of liquid samples. Since glass is dissolved by HF, this also introduced a risk of not getting all of the Si in the sample into solution. The other disadvantage in using ICP-OES is the time required to dissolve the PGMs. Rhodium, particularly, is dissolved overnight in closed pressurised tubes.

The purpose of this study was to develop a set of relatively non-destructive methods for the determination of all impurities of interest in refined platinum, palladium and rhodium metals with Spark-OES, which can determine the metals in the solid state. This was to move away from the use of ICP-OES and photographic analysis. If successful it should save on time and material as limited sample preparation is required for Spark-OES. This opens the possibility for samples to be analysed and impurities tracked in the intermediate steps to the final stages of purification. This offers better control of the process, allowing for intervention at any point of the process where it arises.

Spark-OES analyses would mean less loss of product during analysis, and would severely reduce the cost of analysis. The faster analysis would also

accelerate the dispatching of the final product. The purity of the product would be known sooner and the product would be available within hours of its production instead of days as is currently the case. Much fewer chemicals are used in the preparation of the sample. The risk of contamination during the analysis is therefore reduced.

Spark-OES is widely used in automated systems for the determination of PGMs in ore samples, and would be readily accepted in the PGM industry.

1.5 OVERVIEW OF DISSERTATION

The purpose of the research project was discussed in the preceding section, with the main objective being method development for the determination of impurities in solid sample particularly for platinum, palladium and rhodium.

Chapter 2 gives a historical overview of analytical techniques used for the determination of impurities in PGMs. The shortfalls of each method are briefly described, outlining the need for a direct analysis technique. In this chapter, the specific requirements of the project are outlined and discussed.

The techniques used in addressing the specific objectives are described in detail in Chapter 3. These include the technique used for the preparation of matrix matched internal reference materials (IRM) and the analytical technique investigated, namely Spark-OES. Included in Chapter 3 is a literature study on the melting of the PGMs. Equipment best suited for their melting is described as well as the behaviour of the different metals during melting.

In Chapter 4, sample preparation procedures are described for wet chemical analysis and direct analysis. in this study the results from wet chemical analysis was used for comparative purposes, as it is the preferred method of analysis at the Anglo American Platinum's Final Metals Laboratory. This technique was also used by one of the laboratories when the of consensus values for the internal reference materials (IRMs) were determined. The principles of the machinery used during sample preparation are also detailed in this chapter.

The results are discussed in Chapter 5. Each specific objective is discussed as a subtitle. The data for calibration evaluation is also in this chapter. The suitability of the instrument is also discussed here.

The evaluation of the fitness-for-purpose of the method can be found in Chapter 6. Figures of merit for this evaluation are described and the results presented. The quality assurance and quality control (QA/QC) procedure, the internal quality system, to be used when applying the newly developed method is presented.

Chapter 8 concludes with a summary of the work done and highlight the results and the application in industry.

CHAPTER 2
LITERATURE REVIEW

2.1 INTRODUCTION

The spectrochemical analysis of PGMs in solid form is one of the oldest techniques for the determination of impurities in these metals. These type of analyses were first carried out to track certain impurities along the refining process. With the increase of analytes that could be measured; the results were then used to quantify the purity of the metals by difference. The early spectrometers used the “point to plane” technique. It was prompted by the complexity of bringing the metals into solution for analysis by wet chemical methods. The methods used then were limited to flame (atomic absorption), arc (solids) and spark spectrometry (Broekaert, 1987).

After the introduction of a plasma sources for the determination of impurities in the late 1960s, the Inductively Coupled Plasma (ICP) became the most explored plasma source. As interest in this technique and the demand for rapid analysis of solid samples increased, sample introduction systems which allow for solid sample analysis including glow discharge, graphite furnace and laser ablation, were incorporated into the ICP technique. This growing interest also resulted in the modernization and improvement of some of the older techniques, bringing these spectrometers back in demand.

The greatest disadvantage of solid sample analysis has been, and still is, the availability of suitable certified reference material with the same matrix composition as the sample. This disadvantage has led to the development and description of calibration standards preparation methods for every method of analysis investigated.

The evolution of the spectrochemical analysis of pure PGMs for impurities and the reported methods for the analyses is discussed in this section, outlining the disadvantages of each method. A full description of the techniques used for the preparation of calibration standards and for the analysis of the samples is also given.

2.2 ANALYSIS OF TRACE IMPURITIES IN PGMS

The quantification of the purity of the PGMs by the determination of their impurities started as early as 1922. It has been improved upon over the years with regards to detection limits and the number of elements that can be determined. In 1922, a list of rhodium lines in platinum was published (Beamish, 1966; Beamish & Van Loon, 1977). This is one of the oldest spectrochemistry techniques used for the analysis of trace impurities in PGMs. The use of a spectrograph for the determination of impurities in PGMs, particularly in platinum, was developed at this time. The technique was first used for the control of impurities in platinum in 1935, where it was used for the determination of minor impurities. In 1945, the first application of the arc method for the spectrographic evaluation of platinum was described, as well as a method for the determination of palladium in platinum. Further work into the determination of the purity of this metal; lead to the publication of a paper describing the determination of 24 impurity elements in 1955. Another publication detailing the determination of 27 elements, at even lower levels appeared in 1962.

Determining the purity of palladium and rhodium metals by the analysis of impurities followed after strides were made in the determination of platinum metal. The determination of impurities in rhodium using a.c. arc spectrometry was only recorded in 1948. Elements determined were iridium, platinum and palladium. During the period 1949 to 1950, the

determination of small amounts of iron, iridium, palladium and rhodium in palladium was described. The determination of 22 impurities was published in 1955.

Vorsatz (Beamish, 1966), described a method in 1957 of incorporating impurities, in the metal, by arcing a filter paper with a known amount of impurities together with a globule of the metal. The method was used for the preparation of calibration standards. It was successful for arc spectrometers but not for all spectrometers. This led to the need for preparation methods calibration standards alongside the need for new methods of analysis.

2.2.1 DIRECT CURRENT ARC-OPTICAL EMISSION SPECTROSCOPY

In 1962 the use of direct current (dc) arc technique was identified as the “preferred” technique for the detection of low level impurities, opposed to other excitation techniques investigated (Lincoln & Kohler, 1962). Initial investigations into this technique, where deep and shallow electrodes were used for platinum sponge analysis, led to remarkably poor precision. This poor precision was attributed to the arc wandering on the surface of the metallic bead during analysis. Attempts to improve the precision and sensitivity of the technique included pelletizing the sample before analysis. A mixture of graphite and sample gave the best results. Other investigations included the use of controlled atmospheres and the use of Stallwood jets.

Dc arc-OES is a “point-to-plane” technique. The sample is placed in a graphite carrier with high-resistance. It acts as an electrode (Perzl, et al., 2003). A current is passed between this electrode and a cathode that is separated by a gap. A high temperature plasma is created between the 2 electrodes. The plasma atomizes the sample and excites the atoms. When

the electrons return to their natural “unexcited” state they release energy that is detected as a spectrum, unique for each element (Skoog, 1985).

Lincoln and Kohler (Lincoln & Kohler, 1962) reported a method for the determination of 27 impurities in platinum using a dc arc-OES. They used 12 A and 300V with a controlled atmosphere of 70% Ar – 30% O_2 in a Stallwood jet.

The standards were prepared by impregnating ammonium platinum chloride with chloride solutions of the required impurities. The product was dried at low temperature (to prevent decomposition), blended thoroughly and reduced in a reducing atmosphere. The samples were mixed with graphite and pressed into pellets, backed with graphite. The pellet was then placed in a cavity in the electrode which allowed for friction fit. The electrode, containing the pellet, was then placed in a Stallwood jet. It formed the anode (the bottom electrode). The Stallwood jet was flushed with a mixture of 70% Ar – 30% O_2 and arced using a graphite cathode. The overall precision obtained was 10%, while the accuracy of the method was not determined and assumed to be similar to the precision.

Disadvantages

- The detection limits of six impurities (zinc, tellurium, osmium, antimony, molybdenum & iridium) exceeded 10 ppm. This resulted in some elements not being reported as the expected concentrations in the samples were below 10 ppm.

2.2.2 DESTRUCTIVE AND NON-DESTRUCTIVE NEUTRON ACTIVATION ANALYSIS

During neutron activation analysis the atomic nuclei of elements present in a sample is irradiated with gamma rays (charged neutrons). It reacts with

isotopes of elements, producing radioactive nuclides. The nuclides then emit characteristic radiation, which can be used for the detection and determination of the concentration of elements. A gallium(lithium) detector is typically used for the detection (Kallmann, 1987). For many elements the sensitivity of the technique for many elements and its ability to carry out simultaneous analysis, made it the preferred technique during the early use of spectroscopy (Maleszewska & Dybczyński, 1976).

Neutron activation had previously been used for the determination of iridium, gold and platinum in rhodium metal using purely instrumental gamma-ray spectrometry. The challenge with this method is that both isotopes of iridium are rich in gamma-ray spectra. It is impossible to analyze other trace elements without sample pre-treatment. Typically the samples would undergo radiochemical separation of trace elements by precipitation and extraction. Thus the samples analyzed were subjected to destructive analysis. According to Sterliński et al. (1976), the sample pretreatment procedure was not suitable for the complete dissolution of rhodium metal. It was a mere “nearly quantitatively” leach out of the traces; while the iridium remained undissolved. They also described a destructive and non-destructive method for the determination of iridium, gold, platinum, palladium and copper, in rhodium metal. They used a sample pretreatment procedure which led to the complete dissolution of the rhodium metal followed by an ion exchange separation procedure. The calibration standards were standards solutions that were pipetted into quartz ampoules, evaporated to dryness and sealed prior to irradiation.
The samples were irradiated at 1 hour intervals, after cooling for 5 to 6. Iridium was measured after an irradiation of 10 to 15 hours and two week of cooling. For the destructive method, the samples were irradiated for 10 to 22 hours and the total period (including completion of measurement) took 32 to 34 hours. The long analysis times were due to the slow

dissolution of rhodium followed by the time consuming radiochemical separation process.

Sterliński et al. (1976) observed that the destructive method determined more elements, and that even more could be analyzed if they are present at higher concentrations (less pure samples).

The destructive method had two main disadvantages: elements with short lived nuclides could not be measured, and the analysis time was quite long.

Maleszewska and Dybczyński (1976) described the use of this technique for the determination of gold, copper, iridium, potassium, lanthanum, manganese, palladium and zinc in 10 mg sample of pure platinum. The method used the same principles as those previously for rhodium, as described by Sterliński (1976), where the sample pretreatment procedure included an ion exchange separation. The same type of resin was used.

The sample was irradiated for 24 hours and cooled for 6 hours before the radiochemical separation. The total analysis time, including counting time, was 8 to 9 hours for all 8 elements of interest.

Disadvantages

- The disadvantage of this method is the long analysis time. For the separation and consequent determination of rhodium and platinum took over 24 hours.
- Not all of the required impurities could be determined by this method.

2.2.3 GRAPHITE FURNACE ATOMIC ABSORBTION SPECTROSCOPY

The atomization of samples in a graphite furnace, as opposed to air-acetylene for AAS analysis, is gaining in popularity, not only because of the much lower detection limits, but also because it allows for the analysis of solids. The technique uses a furnace which is heated in a series of steps. When liquid samples are being analyzed, the steps include a drying, pyrolyzing and then an atomizing step. The instrument is fitted with a light source (hollow cathode lamps or electrodeless discharge lamps) that emits light of a characteristic wavelength and known energy into the atomized sample. If an element is present in the sample, it will absorb light of a certain wavelength in relation to its concentration. The difference in the energy entering and that which exits the sample is used for determination of the concentration of the element in the sample.

Aneva et al. (Aneva et al., 1990) described a method for the separation of iridium, rhodium and ruthenium from platinum, prior to analysis using the graphite furnace. The AAS was calibrated using the method of standard additions. They argued that flame AAS does not have adequate sensitivity for the determination of iridium, rhodium and ruthenium. In addition, the use of lithium sulphate to enhance the analytical signal of iridium will suppress significantly the rate of atomization of rhodium significantly.

According to Aneva et al. (Aneva et al., 1990), the lack of sensitivity for the determination of iridium, rhodium and ruthenium traces in high-purity platinum, has made direct analysis of these elements impossible. A separation is required prior to analysis. *Iso*-amyl alcohol-*iso*-butyl methyl ketone (IAA-IBMK) was used for the extraction of platinum when the matrix was suitable. A double extraction procedure was used. Quantitative removal of the matrix was not possible without the significant loss of analyte. The method of standard addition was used for the calibration to

compensate for the platinum that remained in the aqueous phase after extraction. Other elements that also remained in the aqueous phase did not affect the determination of iridium, rhodium and ruthenium.

Arpadjan et al. (Arpadjan et al., 1990) investigated the behaviour of a number of elements (silver, cadmium, cobalt, iron, nickel, palladium, iridium, lead, ruthenium and manganese) during atomization, in the presence of high platinum and palladium, with different atomizers. The atomizers used were a tungsten-impregnated graphite tube, an uncoated graphite tube and graphite tubes with platforms. They used hollow cathode lamps for all the elements except for cadmium, for which they used an electrodeless discharge lamp. The palladium and platinum samples were prepared by dissolution in nitric acid and aqua-regia respectively. It was introduced into the atomizer with an auto-sampler.

Platinum caused signal depression for iridium, silver, palladium, rhodium and ruthenium. For rhodium and ruthenium the degree of depression increased as the concentration of platinum increased. It remained constant for iridium for concentrations of platinum greater than 0.3 g/l. The signal depression of the base metals, by both platinum and palladium, with the exception of iron was dependent on the atomizer used. Tungsten-impregnated tubes gave the best results (less depression and highest concentration range for interference-free analysis). The depression of the signal by both metals on the iron signal did not depend on the atomizer used. It increased as the concentration of the matrix elements increased.

Disadvantages

- The main disadvantage of this method is that it does not determine impurities resulting from all 29 elements required. Only silver, gold, bismuth, cadmium, iron, molybdenum, palladium, antimony, tin and zinc are extracted with IAA-IBMK. The time it takes for the analysis

to be completed due to the matrix extraction step is also not favourable.

- The excessive dilution of the samples to reduce the concentration of the matrix elements when the tungsten-impregnated tube is used can be time consuming and reduced the concentration of the trace impurities to below the limit of detection.

2.2.4 INDUCTIVELY COUPLE PLASMA-MASS SPECTROSCOPY (ICP-MS)

2.2.4.1 ICP-MS

ICP-MS is mainly used for trace elemental analysis and also to determine the distribution of isotopes. The technique, however, cannot accommodate high concentration of ions. Large dilutions are often needed prior to the analysis.

The technique uses plasma excitation followed by mass spectroscopy for the detection and determination of the elements. The plasma in this case is achieved in ionized gas (Ar) at high temperatures. It contains molecules, neutral atoms, positive ions and electrons. The plasma is formed by passing the gas through a high-intensity electromagnetic field (Kallmann, 1987). When a sample is introduced into the plasma it is atomized and ionized, and the ions are introduced into a quadrupole mass spectrometer where mass resolution and detection occurs.

Kidwell (Kidwell, 2008) used high-purity acid to dissolve a sample, which was diluted to 2-5% acid with high-purity water and sprayed through a nebulizer into the desolvation chamber then into the plasma. The ICP-MS used employed a desolvation chamber to remove most of the water from the small droplets of the sample after the nebulizer. The high resolution

ICP-MS had a resolution greater than 10000. It was capable of resolving many, but not all, adduct ions (ion-atom recombination that occurs after extraction from the plasma). The ICP-MS can irreversibly be contaminated by high concentrations ($mg.L^{-1}$ level) of elements. It often requires the concentration of the matrix element to be reduced prior to analysis. Kidwell (Kidwell, 2008) suggested a method to reduce the palladium matrix by extraction with dimethylglyoxime (DMG). The dissolved sample was mixed with a 14% excess DMG (over a 2:1 stoichiometric DMG-palladium ratio) and shaken overnight at room temperature. To separate the supernatant and the DMG-palladium complex, the sample was centrifuged before the analysis.

At the acid concentration used (below 0.6 M) the extraction resulted in final palladium concentrations smaller than levels of $<1\ mg.L^{-1}$. This allowed for the analysis of samples without the need for dilution. It increased the sensitivity and precision of the analysis.

Disadvantages

- The samples have to be left overnight to decrease the concentration of the palladium in the sample matrix. The DMG is also known to precipitate Ni which can be an impurity element of interest.

2.2.4.2 LASER ABLATION ICP-MS

Laser ablation ICP-MS (LA-ICP-MS) has the lowest limit of detection of the solid-state mass spectrometric techniques in the determination of impurities. The greatest challenge with this technique is the lack of standard reference materials with a significant number of certified elements in the same matrix as the samples to be analyzed. A laser beam ablates the sample surface to volatilize a portion of the sample that is

introduced into the plasma. After ionization the sample is analysed with the MS.

To overcome the deficiency of standards, Becker et al. (Becker et al., 2001) reported a method for the determination of impurities in high purity platinum using solution calibration. The MS detector used in his investigation was a quadrupole-based LA-ICP-MS. He used a collision cell for the elimination of adducts. An ultrasonic nebulizer (USN) was coupled directly to the laser ablation chamber. During nebulization using the USN, the metal was simultaneously ablated with a focused laser beam. A standard addition mode of calibration was used. The nebulized sample was transported into the ablation chamber with Ar nebulizer gas. It was observed that there was a loss in the intensity for all elements when ablation of the pure platinum sample was done. Correlation coefficients of 0.99 were achieved for all elements investigated (11 elements).

Disadvantages

- Not all elements of interest can be analyzed.

2.3 DISCUSSION

Throughout the history of the use of spectroscopic analysis, the major problem with solid samples remained the same. While the main disadvantage of techniques which analyze liquid samples is the time–consuming sample preparation, the main disadvantage of direct analysis in solids is the lack of commercially available calibration standards or CRMs. While the work done on liquid sample analysis are accompanied by safer digestion methods or using less acid with fewer steps, direct analysis of solids are accompanied by the preparation of working standards and/or reference material.

Most of the methods which are available for the determination of impurities in PGMs do not determine all the analytes required. Thus, the defining suite of analytes required for the quantification of the purity of PGMs has made the analysis of these products difficult.

2.4 OBJECTIVES

This study intended to use Spark-OES for analysis of platinum, palladium and rhodium metals instead of the laborious ICP-OES method. Due to the unavailability of certified reference PGM material, in-house matrix-matched reference material will have to be prepared for the evaluation of the Spark-OES for the determination of impurities in these PGMs. These materials are intended for use in calibration as well as for quality control (QC). The advantage of using matrix-matched reference material for calibration is that any matrix effect of the samples and, to a large extent background effects, are compensated for in the calibration. This makes the method more suited for the samples intended for analysis.

The main objective of developing a Spark-OES method for the determination of impurities in platinum, palladium and rhodium were:

- To prepare full sets of calibration standards for the different matrices.
- To optimize the melting conditions for preparation of palladium, platinum and rhodium metal, using an ultra-high temperature vacuum induction furnace.
- To develop and optimize a suitable surface preparation method.
- To validate the calibration standards prepared (e.g. through the use of statistical inferences).
- To calibrate the Spark-OES, with the prepared standards.
- To validate the methods of analysis (Spark-OES and ICP-OES).

- To compare the developed method to the current method (i.e. Spark-OES vs. ICP-OES) and establish the fitness-for-purpose of the method.

CHAPTER 3
SPARK-OPTICAL EMISSION SPECTROSCOPY THEORY

3.1 INTRODUCTION

Spark-OES is a non-destructive analytical method. It ablates only micro grams of a sample at a time. Because of its extensive use in the metal industry, it is well suited for the determination of impurities in PGMs. However, there is a lack of certified reference materials for the required elements regarded as impurities in these metals at the levels required. Therefore, a procedure for the preparation of matrix matched calibration standards had to be investigated.

This section details the theory of Spark-OES. The method used for the preparation of the reference material used for calibration is also discussed and a brief review on the work done on melting platinum, palladium and rhodium is given.

3.2 SPARK-OPTICAL EMISSION SPECTROSCOPY

There are four main components in the spectrometer system: An energy source, a spectrum generator, a device for spectrum determination and a spectrum processor (Slicker, 1981). Three of these components can be used to distinguish the different spectroscopic instruments:

- Energy source: This distinguishes the spectrometer systems according to the way energy is supplied for the vaporisation and excitation of samples. There are two main sources of energy: non-electrical and electrical. Non-electrical sources includes lasers, chemical flames, and purely thermal sources, while electrical sources include inductively coupled plasma, arc, spark, direct

current plasma, low-pressure discharge and capacitive microwave plasma.

- Spectrum generation: distinguishes the spectrometer according to the way in which the light generated at the source, is dispersed into its characteristic wavelengths. The basic elements in all spectrometric instruments are: a primary slit, a spectral disperser and secondary slit. The dispersion is carried out using gratings.
- Spectral determination: distinguishes the spectrometers according to the way the light is detected. Different types of detectors are available for this, ranging from detectors that allow sequential determination of various wavelengths and those for simultaneous determination of the various wavelengths at the same time.

Spark-OES uses electrical discharge where the sample is an electrode (Slicker, 1981). It analyzes solid samples “point to plane”, with the electrode as the point and the sample the plane. There are a number of electrical discharges, where the sample is the electrode. These are differentiated by the discharge current density (McIntosh, 2004). They include, in decreasing order of current density: arc- and spark discharges, which operate at atmospheric pressure, glow discharge and Townsend discharge. Of these, the spark source has plasma temperatures that are higher, as the power converted in the analysis gap per discharge duration, is greater. Spark spectra, therefore have more lines that include ionized atom lines. It also has better precision and is less prone to effects from sample composition, structure and matrix.

The basic phenomenon of the electrical sources is that of avalanche breakdown, a form of electron avalanche. Electrons in the transition region are accelerated by the electric field to energies sufficient to free bound electrons upon collision (McKay, 1954). These electrons are rapidly decelerated upon collision with the sample, releasing energy into the

sample surface and heating it. The heat ionizes the chamber gas and ablates material from the sample. At transient high temperature plasma, containing atoms, ions and high energy molecules are generated (McIntosh, 2004). The electrons in the transition region (the gap between the electrode and the sample) are accelerated from the electrode. Characteristic radiation is emitted from the excited species and it is diverted through the light guide in the spark stand, into the spectrometer.

The spectrometer disperses the light and the characteristic wavelengths are measured with detectors. An electronic system converts the light into count rates. The count-rates (the instrument response) are used to calculate a calibration from standards with a known concentration, concentration in unknown samples can be determined by comparison to the calibration.

The instrument uses the same energy for vaporizing and exciting the sample, thus it is separated into two parts: the energy source where the spark and the spectrum are generated, and the optical system where the spectrum is determined.

3.2.1 ENERGY SOURCE

The spark is generated in an electrical circuit. Externally ignited “point-to-plain” spark generators are popular as they have better LODs (Slickers, 1993). The period and shape of the spark generated is determined by the supplied voltage, the capacitance, resistor and inductor.

A basic principle spark generator circuit are given in Figure 3.1. The capacitor C_L is charged through the resistor R_L with a charge U_1 from a direct current source. As soon as the analysis gap AG is made conductive, C_L discharges itself, through R_B, L and AG, and through the sample. The

analysis gap is made conductive by the ignition unit which ionizes some of the gas in the chamber. The ignition unit has the same circuit set-up as the spark generator.

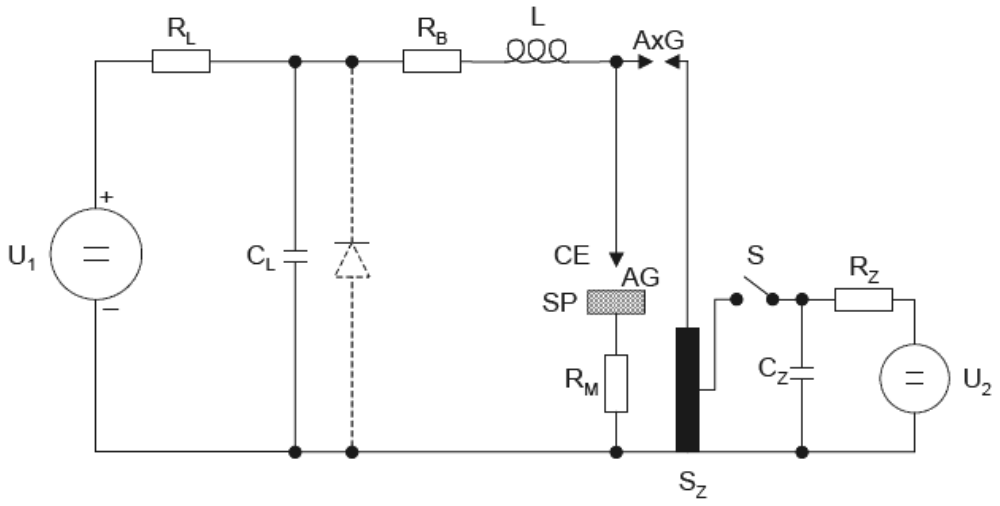

Figure 3.1: Spark generator circuit with external ignition (McIntosh, 2004)

Where:

U_1 = Applied voltage	U_2 = Applied voltage	SP = Sample plane
R_L = Charging resistor	R_Z = Ignition resistor	AG = Analytical gap
C_L = Capacitor	C_Z = Ignition capacitor	AxG = Auxiliary gap
R_B = Discharge resistor	S_Z = Ignition coil	S = Switch
L = Inductor	CE = Counter electrode	
R_M = Measuring resistor		

By selecting a low R_B and L value, a high spark current density (“hard” spark) and peak current intensity can b the R_B and L value produce a weaker current and a “soft, arc-like” spark.

R_M is a resistor for measuring the current in the circuit using an oscilloscope. It has a small resistance, usually ≈ 0.1 Ω.

High voltage spark generators produce oscillating discharges. The current oscillate, after the initial discharge, as a result of limitations in the components of the circuit. The critical resistance determining the current curve of a circuit is defined by (McIntosh, 2004):

$$R_C = 2\sqrt{L/C_L} \qquad (3.1)$$

The oscillating circuit is damped aperiodically (Slickers, 1993). A limiting case for critical damping is ideal. If $R_B < R_C$, the resultant circuit will be oscillating. A critically damped circuit results when $R_B = R_C$. An over-critically damped circuit results when $R_B > R_C$. This implies that the inductor and the capacitor control the current curve.

The resistors in the circuit are connected in series; hence the transition resistance at the sample surface affects the circuit. Changes in the composition, temperature and the dimensions of the sample will affect the resistance of the circuit.

In modern instruments spark generator circuits that controlled digitally. The discharge is electronically monitored and adjusted to keep the current discharge constant. Thermo ARL has developed a current controlled source (CCS), which uses the same principle as the circuit, described above although more complicated, for spark generation. The operator can now no longer adjust values of the components of the circuit. The circuit components settings are optimized and electronically entered by the manufacturer. The parameters are set by the software to default values.

Sparking and excitation of the sample occurs in two steps. A high energy pre-spark (HEPS) followed by an integration (analytical) spark (Figure 3.2). The HEPS is often used for homogenization of the sample before

integration. The high energy heats and melts a thin layer of the sample. It is achieved by increasing C_L up to 5 times and setting $R_L = R_C$ in the circuit (Figure 3.1). The melted surface solidifies, creating a more homogenous surface. It is then ablated by the analytical spark. After the pre-spark, the analytical spark strikes a previously homogenized area of the sample. Inclusions on the surface of the metal are attacked first.

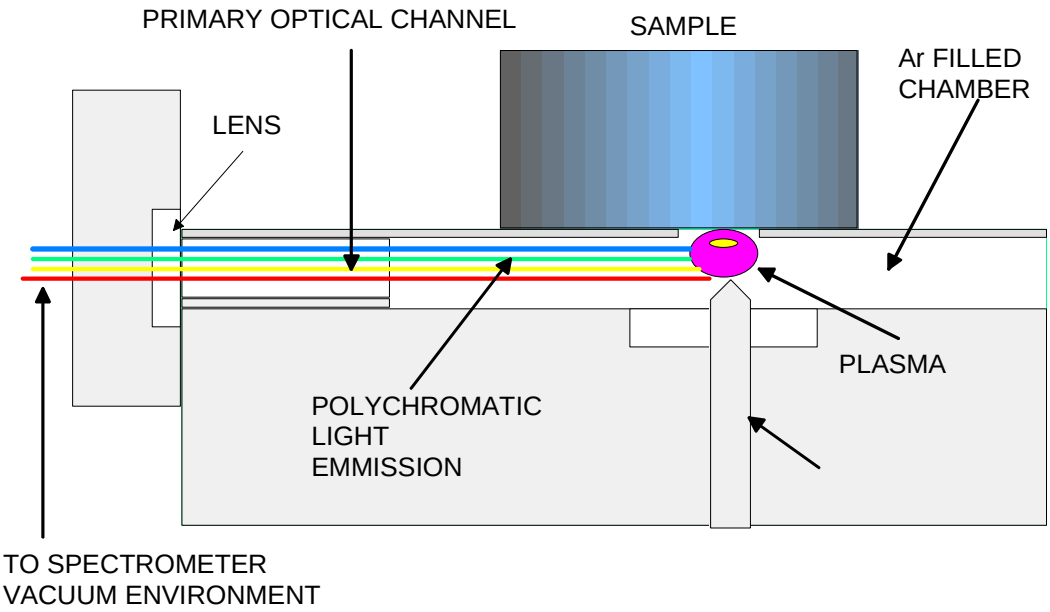

Figure 3.2: Diagram of spark stand (Halász, 2004b)

The chamber can be filled with gasses depending on the data required from the instrument. Gasses which have been used for the spark chamber include air, inert gasses and a mixture of air and inert gasses. Air may lead to the oxidation of samples during spark discharges. This leads to the energy in the discharge wasted to break down the metal oxides formed, reducing the energy available for vaporization and excitation. As a result, small variations in the sample matrix can produce anomalies in the analysis. This is reduced by using graphite electrodes as a counter electrode and/or oscillating discharges. The use of Ar or N_2, instead of air, also eliminates the oxidation of the metal samples during sparking.

When the spark chamber contains air, the oxygen in the air forms metal oxides at the point of impact of the spark. The oxide then becomes the preferred point of attack. If sufficient oxygen is available, the process of oxidation repeats with every spark, resulting in the discharge remaining diffuse, never melting and homogenizing the sample. The discharge in a mixture of air and nitrogen creates single craters where the sample is not melted or homogenized. The oxidation depends on the metal's affinity for oxygen.

The oxygen in the spark chamber may come from leakages in the system, or may be released from the decomposition of oxides in the sample. The negative effects of oxygen can be curbed by using counter electrodes (made of graphite) or oscillating discharges. The presence of hydrogen can prevent the oxidation of the analytical surface, although it might give rise to the formation of metal hydrides. The oxidation effect can also be eliminated by using inert gasses.

The use of argon in the chamber creates profound cathode fall, while negligible fall is noticed on the anode. An electrode with anodic polarity is not attacked.

Electrodes traditionally used on spark source instruments are made up of graphite or tungsten. Graphite electrode generates a reducing "carbon-atmosphere". The sample is melted and vaporized, with large amounts of carbon in the discharge space. This effect is also observed when the electrode is used in an oscillating discharge made with anodic discharge. Carbon electrodes need to be sharpened after every measurement. When used in nitrogen and air atmosphere it creates extra work and a blackish carbon-rich deposit.

Tungsten electrodes, due to the hardness of the metal, do not overheat during sparking but have low temperatures (less than 960°C). Thus the electrode can be used for many measurements before the tip needs to be renewed, making them attractive for metal analysis. Metal brushes are used for cleaning the electrode between analyses.

3.2.2 OPTICAL SYSTEM

The radiation created during the spark is passed into the spectrometer optics through the entrance slit. In the spectrometer it is dispersed and passed through the exit slit into the radiation receiver where it is measured. Although components may differ for different spectroscopes, the optical system is composed of basic elements: the slit and spectral dispersion.

The optical system of the Spark-OES is known as a Pashen-Runge mount where the components are arranged on a Rowland circle (Halasz, 2004). The spectrometer casing is made of cast iron and is temperature controlled to ±0.1 °C at 38 °C to prevent thermal expansion that might affect the spectrometer.

The radiation created at the spark stand passes through a collimator with a shutter. The light is collected by a vacuum ultra violet (VUV) primary lens which focuses it on the primary slit of the spectrometer. The primary lens is used for the analysis of carbon, nitrogen, oxygen, phosphorus and sulphur. It is a calcium fluoride lens that is transparent to light in the region of 160 to 190 nm (McIntosh, 2004). The lens is heated to prevent a temperature gradient between the spectrometer and the stand.

The spectrometer is under high vacuum. The ARL 4460 is using a dual pump system. The first stage of generating the high vacuum is carried out

with a dry membrane pump, to eliminate the introduction of hydrocarbons from pump lubricants. This pump generates a vacuum of 20 mbar. The second stage is carried out with a high-speed molecular drag pump, reaching a final vacuum better than 10^{-4} mbar.

The spectrometer has a Rowland circle geometry. The light enters on the circumference of the circle (through the primary slit) and falls on a concave grating on the opposite side of the circle. A 1080 grooves/mm concave diffraction mirror disperses the light according to Bragg's Law (Slickers, 1993):

$$n\lambda = 2d \sin\theta \qquad (3.2)$$

Where:
n = order of diffraction
λ = wavelength (nm)
d = spacing of the grooves
θ = angle of diffraction

The dispersed light is isolated into its different wavelengths, reflected and focused onto the exit slit (secondary slit) on the Rowland circle (refer to Figure 3.3). The secondary slit has to be correctly aligned. This is done at the factory. The movement of the position of the primary slit on the Rowland circle adjusts the spectrum in the spectrometer. This also adjusts the position of the secondary slit.

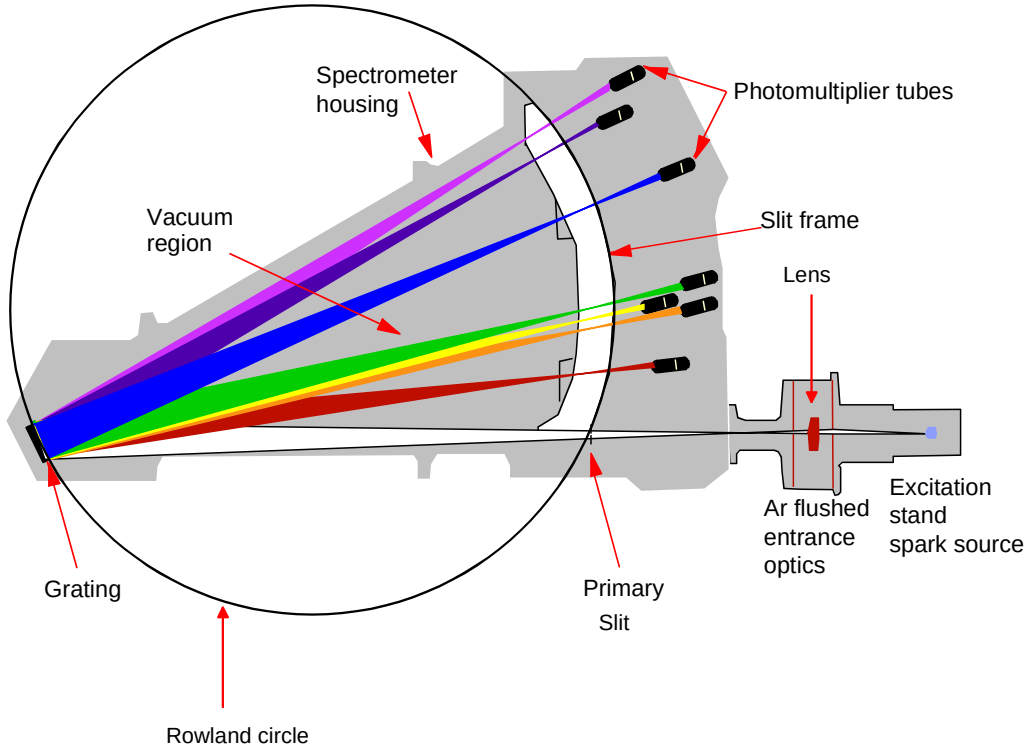

Figure 3.3: Optical system of the Spark-OES spectrometer system (Thermo Fisher, 2007)

From Bragg's law it can be derived that the angle of diffraction increases with an increase in wavelength as sin θ is directly proportional to λ. It can also be seen that higher order reflection may occur. These have the potential to interfere with the measured analytical lines (McIntosh, 2004). Second order reflections are usually measured in the ARL 4460, for higher dispersions, by placing a phototube at an equivalent wavelength. The phototube measures the same light in second order. Filters are used for the removal of possible first order interferences.

Two different kinds of filters can be used, namely transmission and interference filters. The transmission filter only transmits the desired wavelength while absorbing the others. It is made up of a coloured glass. The interference filter reflects light several times, between two partly-

transparent mirrors separated by a thin layer, according to the Fabry-Perot etalon-principle described by equation 3.3 (McIntosh, 2004). This interference only permits a narrow range of wavelengths to be transmitted.

$$I_{max} = {}^{2d}/_{n} \qquad (3.3)$$

Where:

I_{max} = maximum intensity

d = optical layer thickness

n = order

If the optical spacing is 600 nm (d = 600 nm) the maximum intensity that will be transmitted from the filter will be: 1200 nm for first order, 600 nm for second order and 300 nm for the third order. All these occur at the same position, allowing for the first order wavelength to be separated from the rest. This type of filter is used on lines with interferences from higher or lower order reflections. The ARL 4460 mostly measures lines in the second order because of its configuration. Some are, however, measured in the third or first order; depending on the required spectral resolution.

From the filters, the light falls onto concave mirrors focusing it from the horizontal onto the side entrance of a photomultiplier tube. The mirrors can reflect the light either up or down. The phototube may cover the window slightly with a mask allowing only light from the analytical mirror to enter. The mask prevents light that is reflected from mirrors, screws or adjacent tubes from entering the phototube.

The light is amplified and converted to an electronic pulse in the phototube. The electronic pulses are recorded by the instrument. The cathode of the phototube is coated with a metal to which a voltage can be applied. All the dynodes in the phototube are connected at various

voltages. The cathode (photocathode) absorbs a photon of light and releases an electron. The electron is accelerated and strikes the first anode that releases more electrons and so on. This occurs under voltage, until the required amplification has been obtained. When current flows, the signal from the phototubes is converted into counts and it is measured. The concentration of the analyte is a function of the counts. The software calculates the concentration using the calibration of the standards.

3.3 MATRIX-MATCHED IN-HOUSE STANDARDS

The preparation of metal standards was preferred over that of pressed powder pellets. Challenges with pressed pellets include:

- The sponge used for the preparation of the standards has to be homogeneously mixed with the impurities used for spiking.
- The samples and standards must have the same particle size, and the impurities added to spike the standards, must have the same particle size as the metal sponge to allow for effective mixing. However, platinum and palladium sponges are usually coarse.
- The form in which the impurities are added has to be the same as the elements in the samples to minimize matrix effects.

3.3.1 MELTING PLATINUM GROUP METALS

Attempts to melt the PGMs started in the late 1700's, where a homogeneous molten metal could not be produced but 'partial agglomeration is achieved. The agglomeration which was used for artefacts was produced by hot forging the powdered metal (Griffith, 2009). The early methods of melting platinum and other PGMs include:

- directing a stream of oxygen (possibly mixed with hydrogen) onto powdered platinum in hot hollowed-out charcoal (1782),

- oxy-hydrogen or oxy-propane blow pipes and
- the use of coal gas-oxygen to fire up a furnace with two large hollowed-out blocks of lime in which the metal was placed.

The last remained the method of choice until the introduction and availability of induction furnaces in the early twentieth century (Griffith, 2009). Currently, three principal methods are used for the melting of PGMs. All these use electricity as heating source and can be used for large scale melting:

a) Induction heating: The metal sample is placed in a refractory crucible that is surrounded with a water-cooled copper coil through which a high frequency alternating current is passed.
b) Electron beam heating: uses a refractory cathode (tungsten or molybdenum). The sample is placed in a refractory container and acts as the anode. A high-voltage current source accelerates electrons, steered by a magnetic field, from the cathode to the anode.
c) Arc melting: the metal is rested on a water-cooled copper anode and an arc is struck between the metal and a tungsten cathode. This is done under argon, using a direct current potential of 50 to 80 V.

Induction melting is the quickest and most effective for melting platinum and palladium.

3.3.1.1 INDUCTION MELTING

Induction melting is based on the principle of electromagnetic induction discovered first by Michael Faraday in 1831. This principle states that the magnetic movement of a circuit (secondary circuit) is affected by the flow of alternating current (AC) through a circuit close to it (primary circuit). The circuit to which current is applied is called the primary circuit. The circuit to which current is induced is the secondary circuit. Thus, electromagnetic induction is when the alternating current of one circuit produces an electric

current in a closed circuit close to it. If the secondary and primary currents are in direct proportion, in accordance to turn ratio, losses result from the resistance of windings. When the two circuits have the same number of turns, the link coefficient between the two circuits is 1, and the magnetic current leakage can be ignored. Where the secondary circuit has only one turn and is short-circuited, significant heat is lost as a result of the augmented load current (secondary current). The two circuits are depicted in Figure 3.4.

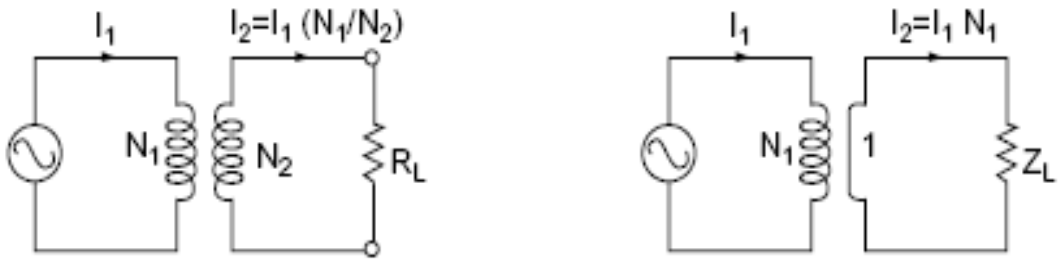

Figure 3.4: a) Equal primary and secondary circuits, b) Short secondary circuit

During induction heating, the induction coils serves as the primary circuit while the material being heated represents a single turned, short-circuited secondary circuit. The material being heated has to be electrically conductive. A large alternating current is driven through the primary coil from an intense electricity source creating an intense and rapidly changing magnetic field in the space within the coil (Burnett, n.d.). The material to be melted (load) is placed in the middle of the coil, separated by a small aperture. The primary current in the coil causes induced currents in the sample, called eddy currents, to flow through the load. The current's density decreases towards the centre of the metal, creating what is known as the skin effect. This significantly increases the heating effect of the

induced current that is converted to heat energy, as it is concentrated on the skin depth of the load.

3.3.1.2 PGM CASTING

Jewellery, the second largest application of PGM, is the only application which involves the melting of large quantities of metal. The melting of these metals has consequently been for jewellery applications. As a result, the work that has been done and recorded is on the melting and casting of platinum. Very little work was done on casting palladium and almost no work on the casting rhodium. Romanoff (Romanoff, 1999) has reported on possible casting problems for platinum and the solutions to each.

Platinum Casting

According to Normandeau (Normandeau, 1996), electric induction heating is the best method for melting any amount of platinum, as platinum sponge does not “interact well with high velocity torch gasses”. He also mentions that carbon containing crucibles (graphite and silicon carbide) react with platinum, making the resulting metal brittle. Ceramic crucibles, or those that do not contain carbon, should be used for melting. However, these crucibles (ceramic) have to be backed with rammed ceramic powder and an additional protective sleeve to counter a tendency towards thermal shock that causes cracking.

Normandeau (1996) explained that ceramic crucibles and implements are required for melting of PGMs, due to the reactivity of the metals and the rapid rate of heating which occurs when using electric induction. Magnesium oxide, aluminium oxide, thorium oxide and zirconium oxide have also been tested. Zirconium silicate or alumina silica mixtures cannot withstand temperature above 2000°C (Normandeau, 1996).

Normandeau (1996) found that molten platinum is prone to contamination. Due to its high melting point it will melt most materials it comes into contact with. Molten platinum reacts with silicon and phosphorous to form intermetallics, which results in the embrittlement of the metal. In his report, Normandeau (1996) suggests that platinum be melted under oxidizing conditions as reducing conditions causes any silicon dioxide in the crucible to be reduced. Elemental silicon will then react with the molten pool. In oxidizing conditions, any silicon, iron or phosphorus will react with free oxygen in the air to form oxides which remain stable in the flux as a slag layer.

Suitable moulds for the melting of platinum can be made from materials with a high conductivity at high melting temperatures. Poor conductivity lowers the solidification rate, compromising the physical properties of the ingot. Graphite and copper moulds offer good heat dispersion conductivity and shock resistance, but graphite suffers from oxidation deterioration.

Palladium casting

Forschungs institutedelmetalle and metallchemie (FEM) together with other institutes conducted a study on the casting of palladium metal (Zielonka & Klotz, 2007). They found an optimum feed-sprue system to avoid shrinkage porosity when casting palladium to be a pre-requisite. Palladium has a strong tendency to absorb oxygen. It is prone to gas porosity and, unless other parameters are optimized, it will be sensitive to poor feed-sprue systems. Palladium reacts with residual gases in the melting chamber before pouring, during cooling and during solidification. The gas solubility, of gas in the metal, decreases rapidly with decreasing temperature releasing the gases. If the feed-sprue supports directional solidification, the gases will escape mainly via the direction into the fee-sprue system.

Palladium promotes the decomposition of refractory materials at high temperatures. Excessive heating of the melt would increase the metal's reaction with the crucible material. This would promote crucible breakage. Crucibles which have been successfully used and showed long term stability for the melting of platinum and palladium are those made of silicon-oxide, possibly with stabilisers. Forschungs institutedelmetalle and metallchemie successfully used crucibles with a base material made of Si+Al-oxide, coated with zirconium-oxide, which proved more resistant to decomposition.

The atmosphere during the casting of the metal has to be free from oxygen, to avoid the risk of the metal absorbing oxygen. It also should not be done under vacuum even though vacuum can remove the air. Casting under vacuum, increases the inclusion of decomposition products from the crucible; especially silicon. Forschungs institutedelmetalle and metallchemie suggested a process of eliminating the air. A vacuum extracts the air and then it is filled with argon, prior to melting. They argued that pyrometers are not suitable for controlling casting temperatures if reproducible castings are to be made.

Discussion

From the results it is obvious that each of the metals have unique properties in the molten state. Palladium requires an environment free from oxygen to minimize absorption by the metal. Platinum on the other hand requires the presence of oxygen to decrease the reaction of the molten pull with the silicon in the crucible. While palladium requires the use of a feed-sprue system, this is not necessary for casting platinum.

The similarities in the physical properties of the metals, however, make the use of the same material possible. The metals should ideally be melted by induction, in a closed chamber due to their reaction with gasses. Both

platinum and palladium have been melted successfully with the same crucible material (Si+Al-oxide, coated with zirconium-oxide). They are both prone to contamination, because of their high melting temperatures, and should not be excessively heated.

While there are similarities in the melting of the metals, it is obvious that the conditions for each matrix need to be optimized for the preparation of the standards.

CHAPTER 4
EXPERIMENTAL PROCEDURES

4.1 INTRODUCTION

Samples of the pure metals from in Anglo American Platinum's Final Metals Laboratory (FML) are submitted in two forms: as a powder (referred to as sponge) or metal, referring to lollipop samples (Figure 4.1). The lollipop samples owe their name to the shape of the sample. It has a metal stem supporting a round metal disk.

Figure 4.1: Lollipop sample with metal stem and round disk

Lollipop samples originates when molten metal is sampled with a sample tool designed at Anglo American Platinum. Only platinum and palladium lollipop samples are submitted as these are the only two metals with both ingot and grain final products. Rhodium is sold only as a sponge. Both sample types are digested prior to ICP-OES analysis. For Spark-OES analysis, no digestion is necessary. The sponge samples are pelletized. In

the metal samples, the lollipop only was milled. The milled samples were analysed “as is” and were not pelletized. In the following section, the methods and procedures for sample preparation are briefly discussed. The chemical reagents and chemicals used are also briefly outlined.

4.2 REAGENTS AND CHEMICALS

All reagents used for sample preparation and sample pre-treatment were analytical grade (AR) chemicals supplied by Merck, South Africa. 32% hydrochloric acid was used for sample treatment, digestion and the preparation of 10% hydrochloric acid. 65% nitric acid was used for digestion. Demineralised water was prepared using an Elga Micromeg dionizer, and used for all sample preparation.

Melting was done on powdered material. The PGMs were used as pure metal sponge, of which platinum, palladium, rhodium, iridium, osmium and ruthenium were produced by Anglo American Platinum. It was analyzed and a certificate of analysis was issued. Certified ultra-pure Au was purchased from Rand Refineries. Base metals oxides were used for spiking the matrices. These were added as composites (Table 4.1), supplied by De Bruyn Spectroscopic Solutions (SA). Analytically pure graphite was also used for the serial dilution of the contaminants, with matrix specific degassing fluxes. The fluxes were supplied by Ergoxo Products (SA). The composition of the fluxes is proprietary.

Table 4.1: Certified concentrations of base metal oxides

Group	Base metal oxide	Certificate mass% of base metal
Group B	PbO	10.4
	CuO	12.9
	NiO	12.3
	Fe_2O_3	13.8
	Bi_2O_3	10.8
	Cr_2O_3	14.1
	ZrO_2	13.0
	Co_3O_4	13.4
Group C	MgO	14.2
	SnO_2	10.8
	ZnO	10.5
	Ag_2O	9.24
	Al_2O_3	16.1
	MnO_2	13.1
	TiO_2	14.2
	CaO	11.9
Group D	As_2O_3	21.2
	SeO_2	22.2
	TeO_2	19.7
	CdO	18.0
	Sb_2O_3	18.9
Group E	B_2O_3	40.3
	V_2O_3	18.4
	MoO_3	18.8
	K_2O	22.7

4.3 SAMPLE PREPARATION

4.3.1 WET CHEMICAL DIGESTION

Metal samples were analyzed by both Spark-OES and ICP-OES. The lollipop head was used for Spark-OES analysis and the stem for ICP-OES analysis. Melted standards ingots were also analysed by ICP-OES. The stem of the lollipop, and the standard ingots were ground using a Metabo

GE700 grinder fitted with tungsten carbide burrs. The grinder was used at maximum speed. The metal shavings were collected into a 50 ml beaker. To remove any surface contamination, the shavings were gently boiled in ± 20 ml 32% hydrochloric acid. The acid was slowly decanted. The excess acid was then washed with ± 20 ml de-mineralized water. This was repeated three times. The sample was boiled in 20 ml de-mineralized water. The water was slowly decanted, and the beaker placed on the hot plate to dry the shavings.

One gram of the shavings was accurately weighed, to four decimal places, into polytetrafluoroethylene (PTFE) vials. All samples were done in duplicate. Separate vials were used for each different matrix to avoid cross-contamination. Hydrochloric acid and nitric acid were added to the vials to dissolve the sample on a hot plate.

The dissolved samples were allowed to cool to room temperature. The cool sample was transferred into clean 25 ml plastic volumetric flasks with a labelled funnel, and filled to the mark with 10% hydrochloric acid. The samples were subjected to ICP analysis.

Preparation of insoluble metals

0.5000 ± 0.0003 g of the metal shavings were weighed accurately to four decimals into a clean and dry glass pressure tube. This was done in duplicate. The tube was placed in ice water to slow the reaction acids down when added, and decrease the amount of chlorine gas lost. 5 ml of 32% hydrochloric acid and 0.3 ml of 65% nitric acid were added. The tube was sealed with a jeweller's torch. The sealed tube was wrapped in aluminium foil and inserted into a steel sleeve; the threads at the top of the sleeves were greased with nickel paste. The cap was secured by hand. The sealed samples were placed overnight in an oven at 250°C. After cooling the samples the sealed sample tube was removed. If the sample

was not completely dissolved, it would be wrapped with aluminium foil and inserted into the sleeve and the process repeated.

The glass tube containing the dissolved sample was rinsed with demineralised water, before opening with a jeweller's torch. The contents of the tube were transferred to a clean 25 ml volumetric flask with the funnel dedicated to a specific matrix. The flask was filled to the mark with 10% hydrochloric acid. The sample was submitted to ICP-OES for analysis.

4.3.2 SOLID SAMPLE PREPARATION

Preparation of sponge samples

A specified amount of samples (Table 4.2) was accurately weighed out to four decimal places. The mass was transferred to the dye chamber of a 100 ton press and levelled off with a plastic stirrer. The dye was then sealed with a lid and the dye-securing arm closed and tightened by hand. The sample was progressively pressed at 40, 70 and 100 TSI. The sample was removed and the forged pellet analysed by Spark-OES.

Table 4.2: Mass of samples used for pressed pellets

Matrix	Weight (g)	Required Pressure (TSI)
Pt	15.0005	40; 70 then 100
Pd	10.0005	40; 70 then 100
Rh	10.0005	40; 70 then 100

Preparation of metal samples

Degassing flux was weighed (Table 5.2 in preceding chapter) into a crucible followed by 35 g metal powder. An additional 15 g metal powder was weighed separately and compacted into a disk. The disk was broken in smaller pieces and placed on top of the existing sample. The crucible

was place in the centre of the induction coil in the melting chamber of the furnace. The mould and the catch mould were placed on the ramp. The chamber was sealed. The furnace settings were then adjusted to the optimum melting conditions (Table 5.2). The melting process was visually observed and casting was done automatically. The metal was left in the chamber under Ar purge, until the glow subsided. The sample was then quenched with cold water.

4.4 INSTRUMENTATION

4.4.1 RETSCH MM301 MIXER MILL

The Retsch MM301 Mixer Mill from Retsch, a Verder company in the Netherlands, was used for mixing and homogenising of the solid master mixes. The mixer mill allows for the mixing of two sample jars at a time. 50 ml plastic (polyethylene) sample bottles and 5 mm polyamide mixing balls were used.

The MM301 allows two adjustments, the vibrational frequency of the mixing jars and the time of mixing. The frequency can be set from 3 to 25/30 Hz and the mixing time from 10 s to 99 min. Nine combinations can be stored. It has electronic speed control to keep the set vibrational rate constant during the mixing process.

Principle of operation

The Retsch MM301 is an impact ball mill. It mixes and homogenizes samples by impact and friction. The mixing jars oscillate in a horizontal position, resulting in two types of forces being generated between the mixing balls. The force of inertia of the mixing balls causes them to impact the sample, with high energy. This happens at the rounded ends of the jars. It results in the breaking of any lumps or segregation of the sample.

The frictional force between the mixing balls, on the other hand, results in intensive mixing of the sample. To increase the degree of mixing, the frictional force in the jars should be increased. This can be achieved by using a larger number of smaller balls. The MM301 allows for up to 1800 impacts per minute through the adjustment of the vibrational frequency (refer to Figure 4.2).

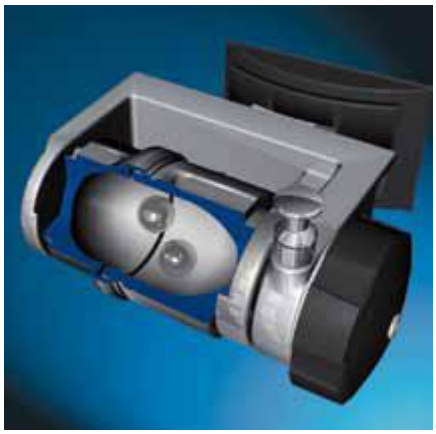

Figure 4.2: Illustration of a mixing jar with balls

4.4.2 100 TON PRESS

The 100 ton press was used for pressing powder samples to compact disks. Dedicated matrix specific die sets were used to prevent cross-contamination between the matrices.

4.4.3 ICON IRM VACUUM INDUCTION FURNACE

The ICON IRM (Hot Platinum, South Africa) is an ultra high temperature (UHT) vacuum induction melting and casting system. It is fitted with a three phase 15 kW three phase high frequency induction generator. It is filled with a variable frequency control algorithm which allows it to couple energy to almost any metal. This system operates at a melting and casting

temperature range of 600 to 2800 °C, and can cast up to 250 g Ir at 2450 °C in less than two minutes. It features an automated casting mechanism. The crucibles employed were fused silica (SiO_2) crucibles and casting was done into graphite moulds (Figure 4.3).

Principle of operation

Induction heating is a contact free process to heat conductive material. A large alternating current applied to the induction coil by a high frequency source. The current generates an intense and rapidly changing magnetic field in the space around the coil, where the material to be heated is placed.

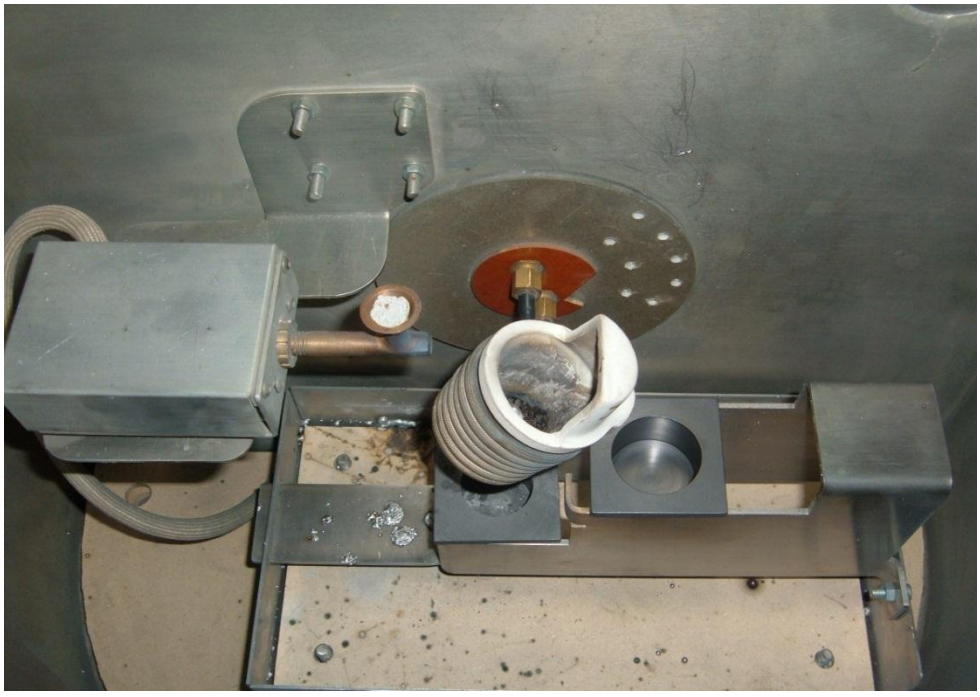

Figure 4.3: Induction coil and crucibles used (fused silica and alumina)

4.4.4 GE 700 METABO710W ELECTRONIC STRAIGHT GRINDER

GE 700 Metabo 710 W electronic straight grinder, from Metabo International, was used to make metal filings. It has an extended grinding spindle with double ball bearing, ideal for grinding, while vertically mounted (up right) on a drill stand. The grinder has VC full-wave electronics and a robust Metabo marathon motor, with a rated input power of 710 W and an output power of 430 W. It grinds at speeds up to 20,000 rpm, and is fitted with a thumbwheel for pre-selection of the required speed. The grinder was fitted with routers, to shave metal off the sides of a lollipop stem or disks.

Principle of operation

The motor of the grinder turns clockwise at very high speed, causing the routers (blades) to rotate in the same direction and at the same speed. The blades pressed against solid material and cut and trim the material. The routers are classified according to their total length, flute length, shank (D) and nominal diameters (D1). The routing depth is determined by the total length of the router (Figure 4.4) (Wulf, 2007). The efficiency of these routers is dependent on the routing depth, pattern of the teeth and the carbide content of routers.

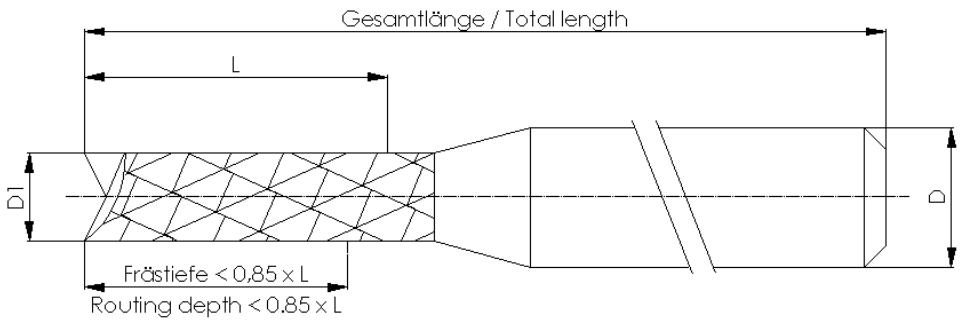

Figure 4.4: Specifications of a router (Wulf, 2007)

Routers can either have diamond-patterned, or spiral-patterned teeth. Both come in either up or down cut. The routers have different applications such as flute or burr-free routers. Diamond-patterned teeth routers and spiral-patterned teeth routers (Figure 4.5) were used in this study for the routing of platinum, palladium metal sticks and disks as well as rhodium metal disks. Due to the hardness of the metals, tungsten carbide routers were used. They are less prone to wear, and neither tungsten nor carbon are of interest as trace elements in the PGMs.

Figure 4.5: Teeth patterns of routers (a) diamond-patterned up cut, (b) spiral-patterned up-cut (Wulf, 2007)

4.4.5 HERZOG HS-FF MILLING MACHINE

A Herzog HS-FF automatic vertical milling machine (Herzog, Oldenburg), was used for the production of a smooth even surface on palladium and platinum metal samples. It was fitted with a motor driven cutting tool spindle with milling cutters. Metal samples milled had to have a height greater than 8 mm. A milling spindling with four cutters was used. Tungsten carbide cutters were fitted on the spindles. Again tungsten

carbide spindles were used. A variable speed belt sander was used to prepare the surface of smaller metal samples (platinum and palladium as well as rhodium).

The Herzog HS-FF is an automatic vertical milling machine, with milling parameters which can be adjusted to all material grades. It is fitted with two independently operated milling spindles for precision milling (Herzog, 2008). It is allows for the storage of 16 different parameter defined programs in the controller. The machine uses different milling cutters and different materials of construction which are optimally matched to the material grades. Milling is the process of creating a smooth even surface from irregular surfaces that would snugly fir onto the spark table. The metal is pressed against a rotating cutter fitted with a number (4) of cutting edges. The mill consists of a motor driven cutting tool spindle which houses the milling cutters. It has an adjustable work table for the work piece. Milling machines can be either horizontal or vertical, according to the orientation of the spindle. They are further classified by their mechanical set-up and the criteria on which they are focused (Figure 4.6).

Figure 4.6: Illustration of the Herzog HS-FF milling cutting tools (Herzog, 2008)

CHAPTER 5
SPARK-OPTICAL EMISSION SPECTROSCOPY ANALYSIS

5.1 INTRODUCTION

Spectrometers which are used to analyse samples on the point-to-plane are extensively used in the metal industry due to their short analysis time, and the “non-destructive” nature of the analysis. Little of the sample is lost during analysis. Despite the strides that have been made in improving these techniques, the greatest challenge is the lack of suitable solid CRMs of most pure metals. ISO/IEC 17025:2005 standard clause 5.6.2.1.2 states that when calibrations cannot be strictly made in SI units, consensus standards that are clearly described and agreed by all parties concerned, should be established (ISO Committee, 2005). This applies when traceable measurement standards, such as certified reference materials provided by a competent supplier, are not available or the use of specified methods is not possible. Thus, the preparation of calibration standards often has to be included in the description of a method to be used for such analyses. In this section the preparation of calibration standards and the assignment of their values are briefly described. The method to be used described in full.

5.2 PREPARATION OF CALIBRATION STANDARDS

Calibration standards were prepared by melting metals with low levels of impurities. They were then spiked with the required metal oxides and analysed for homogeneity. They were distributed to three independent laboratories for the assignment of a set of consensus values that could be used for calibration. The concentrations of the impurities are listed in Table 5.1.

Table 5.1: Spiked impurities concentrations ($mg.kg^{-1}$)

Element	Std 10	Std 9	Std 8	Std 7	Std 6	Std 5	Std 4	Std 3	Std 2
Pt	305.0	152.5	76.25	38.13	19.06	9.53	4.77	2.38	2.38
Pd	305.0	152.5	76.25	38.13	19.06	9.53	4.77	2.38	2.38
Rh	610.0	305.0	152.50	76.25	38.13	19.06	9.53	4.77	4.77
Ir	305.0	152.5	76.25	38.13	19.06	9.53	4.77	2.38	2.38
Ru	305.0	152.5	76.25	38.13	19.06	9.53	4.77	2.38	2.38
Os	610.0	305.0	152.50	76.25	38.13	19.06	9.53	4.77	4.77
Au	61.00	30.50	15.25	7.63	3.81	1.91	0.95	0.48	0.48
Pb	40.37	20.19	10.09	5.05	2.52	1.26	0.63	0.32	0.32
Cu	40.37	20.19	10.09	5.05	2.52	1.26	0.63	0.32	0.32
Ni	40.37	20.19	10.09	5.05	2.52	1.26	0.63	0.32	0.32
Fe	40.37	20.19	10.09	5.05	2.52	1.26	0.63	0.32	0.32
Bi	40.37	20.19	10.09	5.05	2.52	1.26	0.63	0.32	0.32
Cr	40.37	20.19	10.09	5.05	2.52	1.26	0.63	0.32	0.32
Zr	40.37	20.19	10.09	5.05	2.52	1.26	0.63	0.32	0.32
Co	40.37	20.19	10.09	5.05	2.52	1.26	0.63	0.32	0.32
Mg	35.13	17.57	8.78	4.39	2.20	1.10	0.55	0.27	0.27
Sn	35.13	17.57	8.78	4.39	2.20	1.10	0.55	0.27	0.27
Zn	35.13	17.57	8.78	4.39	2.20	1.10	0.55	0.27	0.27
Ag	35.13	17.57	8.78	4.39	2.20	1.10	0.55	0.27	0.27
Al	35.13	17.57	8.78	4.39	2.20	1.10	0.55	0.27	0.27
Mn	35.13	17.57	8.78	4.39	2.20	1.10	0.55	0.27	0.27
Ti	35.13	17.57	8.78	4.39	2.20	1.10	0.55	0.27	0.27
Ca	35.13	17.57	8.78	4.39	2.20	1.10	0.55	0.27	0.27
As	65.97	32.99	16.49	8.25	4.12	2.06	1.03	0.52	0.52
Se	65.97	32.99	16.49	8.25	4.12	2.06	1.03	0.52	0.52
Te	65.97	32.99	16.49	8.25	4.12	2.06	1.03	0.52	0.52
Cd	65.97	32.99	16.49	8.25	4.12	2.06	1.03	0.52	0.52
Sb	65.97	32.99	16.49	8.25	4.12	2.06	1.03	0.52	0.52
B	52.01	26.00	13.00	6.50	3.25	1.63	0.81	0.41	0.41
V	52.01	26.00	13.00	6.50	3.25	1.63	0.81	0.41	0.41
Mo	52.01	26.01	13.00	6.50	3.25	1.63	0.81	0.41	0.41

Std: Standard

The calibration range prepared was determined such that the top standard was 150% of the analyte values. Base metal impurities were added in excess to make provision for the loss incurred during melting. The concentration of each metal varied in accordance with the mass percentage of the metals in the oxide composites. Ten calibration standards for were prepared each matrix (Table 5.1). Std 1, the lowest standard, was not spiked but prepared by melting the matrices as is. No blank standard (zero) was included in the calibration.

5.2.1 OPTIMIZATION OF MELTING PARAMETERS

The ICON IRM was used for the melting of the PGMs in this study. The furnace included the option to use a vacuum pump, which allows for melting with or without vacuum. It also allowed melting under an inert environment by removing the air and refilling the chamber with the inert gas. The casting speed (in rpm) at which the coil rotates through 90 degrees during casting as well as the angle at which the crucible should be when the power is switched off could be adjusted. All these parameters were investigated in the development of a robust melting method with which to produce metals with surfaces conducive to spark analysis.

Quartz (fused silica) crucibles were used for the melting due to their ability to withstand thermal shock. Graphite moulds were used for casting. Melting tests were conducted on sponge material; a final product in all the PGMs. It was also convenient to use the sponge for all the pre-treatment required. It was observed that when sponge samples were melted, the sample coupled perfectly and gave a characteristic glow. However, spaces between the finely divided particles of the sponge sample caused gaps in the final sample. This prevented effective flow of current in the sample and prevented the metal to melt properly. Previously pressed sample and/or pieces of solid metal had to be layered on top of the sponge for to serve

as an initial conductor to initiate melting. The melt flowed to the bottom of the crucible, forming a conductive mass that resonded to the inductive heating and resulted in a successful melting of the sample. Optimization tests were conducted on the features of the ICON IRM furnace.

Optimization of melting temperature

Melting was started in normal atmosphere at the theoretical melting points of the respective metals; 1770 °C for platinum, 1555 °C for palladium and 1965 °C for rhodium. Tests were conducted using 10 °C increments.

Palladium and rhodium casts were lumpy, with bubbles forming on the top surface of the metal. The metals also displayed a blackish hue on the surface due to oxidation (Figure 5.1). Oxidation occurred during cooling in atmospheric air.

The melts displayed cavities on the bottom surfaces where the metal contacted the mould. It was concluded that the bubbles on the top surface were caused by entrapped gasses that escape during cooling. As the metal cools it expels absorbed gas. The gas rises to the surface as bottom and sides in contact with the mould cool first. If the surface solidifies before the gas can escape, bubbles form at the top surface of the metal. Air may still be trapped in the metal depending on the rate of cooling and the amount of gas absorbed. Palladium, ruthenium and to a lesser extent rhodium have a high affinity for gasses which exacerbate bubble formation.

Figure 5.1: Rhodium (left) and palladium (right) metal after melting in atmospheric air

This phenomenon was illustrated with ruthenium metal, where the passage of the gas that escaped could be clearly seen. Ruthenium metal showing a bubble cavity on the top surface is shown in Figure 5.2. The sample was split. The right hand picture shows the two halves of the metal. The inside of the metal, clearly shows the channelling formed by gas bubbles travelling, from the bottom and the sides of the metal, converging on the top surface.

Figure 5.2: Ruthenium metal broken in half

To reduce the porosity of the sample, different melting conditions were evaluated. The conditions included melting under inert atmosphere and melting under partial vacuum.

Melting under inert atmosphere

When melting in an inert atmosphere, the air in the melting chamber was first removed with a vacuum pump. The chamber was evacuated to negative 850 mbar and filled with analytical grade argon. This exercise (flushing) was repeated three times to ensure the chamber was filled only with argon.

This greatly improved the quality of both palladium and rhodium and no lumps were seen on either metal. The reaction of the metal with the mould was reduced for rhodium and eliminated altogether for palladium. The metals also improved with an increase in the number of flush cycles performed prior to melting. The efficiency of expelling air from the chamber

increased with each flush cycle. However, even in an inert environment rhodium metal reacted with the mould, producing holes on the bottom surface of the metal. The holes observed in the metals obtained melting under an inert atmosphere did not pass through the metal, and were shallow.

Melting under pressure

The ICON IRM allowed for the melting chamber to be kept under vacuum, at normal and/or positive pressure during melting. For melting at normal pressure, the air in the chamber was removed with a vacuum pump, and filled with argon. To melt under positive pressure, argon had to be continually pumped into the chamber. It was achieved by purging the gas through the chamber after flushing, creating an increased pressure, which would stabilize at approximately 100 mbar. This pressure was maintained for the duration of the melt.

The use of normal pressure resulted in the metal overheating (rhodium). When casting, the superheated metal did not fill the base of the mould but spread out across the wall of the mould forming a cup-like object (Figure 5.3). However, the use of positive pressure showed an improvement on all the metals as the air was continually removed from the chamber during the melting.

The use of flush cycles and positive pressure lead to improvement on the palladium, with no surface oxidation or lumps.

Figure 5.3: Rhodium metal cup

Since the reaction of the mould with the rhodium could not be completely eliminated, the use of degassing fluxes was investigated. Tailor-made degassing flux for the different PGM i.e. platinum, palladium and rhodium, were bought from Ergoxo Products cc (composition of the flux proprietary). It was noted that the flux made the melt more fluid, creating the impression that the melting point had been reduced. The pseudo-melting lead to premature casting; resulting in the cooling of the metal during casting. Visible layers formed in the cast. However, this greatly reduced the reaction of the melt with the mould and consequently eliminated the formation of holes in the metal. The addition of the degassing flux also increased the lifetime of the crucible and reduced the formation of slag. The optimum melting conditions establish for melting of platinum, palladium and rhodium metals are summarised in Table 5.2.

Table 5.2: Optimum melting conditions of all PGM

Parameter	Optimum Settings		
	Pt	Pd	Rh
Flux type	Pt	Pd	Rh
Mass% Flux	0.50	0.60	0.25
Casting Temperature (°C)	1780	1570	1980
Max Applied Power (%)	55	55	55
Vacuum Level (mBar)	-850	-850	-850
Argon Restore (mBarr)	0	0	0
No of Flush Cycles	3	3	3
Purge Time After Cast (s)	60	60	90

5.2.2 MELTING CALIBRATION STANDARDS

From the evaluation of reference material that is commercially available it was postulated that 100% recovery for the impurity elements of interest would not be achieved during melting. Commercially available reference materials are only relatively pure (with 99.9% purity). This is, however, expected as the melting point of the PGMs is higher than the boiling points of some of the impurities of interest. Some elements are lost during the high temperature melting. Another factor which could result in the low recovery of impurities is slag formation. The solubility of the metals in the matrix will also affect the recoveries.

All impurities were added as metal oxides. To dilute pure metals to the required range would result in numerous dilutions. To improve the recovery of the analytes, metal oxides need to be reduced to metal during the melting process. Ways of creating a reducing environment were evaluated. The reduction would allow for the base metals to dissolve into the matrix at the high temperatures at which the PGM metals are melted.

The reduction will also cut down on slag formation during melting. The following methods of reduction were investigated:

a) The addition of carbon,

   Carbon is a constituent of Fire Assay fusion fluxes. It is added tp reduce of lead oxide to metallic lead at high temperatures. Due to the reduction properties of carbon it was added as graphite to reduce base metal oxides in our study.

b) The reduction of the material prior to melting

   The mixture of the matrix and the master mix was reduced in a reduction manifold with hydrogen, while heating over a Bunsen burner. It was cooled under nitrogen prior to melting.

c) The addition of excess degassing flux. Degassing flux act as oxygen scavengers. The fluxes were added in excess to determine how they would react with the oxides.

Two of these methods involve the addition of extra materials to the samples (carbon and the degassing flux). These materials were tested for contamination. Palladium metal was used in these tests as it has the greatest ability to absorb oxygen in the melt, and was prone to reacting with the crucible as well as material added to the melt (Zielonka & Klotz, 2007). Three different metal disks were prepared and analysed by ICP-OES:

- Pure matrix, with nothing added.
- Matrix with the degassing flux.
- Matrix with degassing flux and excess C.

It was observed that the addition of the flux made the molten metal more fluid. The metal with excess carbon resulted in a rough and dull surface. A crystal pattern could be seen on the surface of the metal.

The ICP-OES method used was not accredited for the analysis of silicon. Obtained silicon values were however used as an indication of what is present in the sample as. The results obtained for the three metals were compared to the sponge blank (matrix). Negative values are for results which are smaller than those in the matrix. The deviations in the results are mostly slag forming elements and some refractory elements (Figure 5.4).

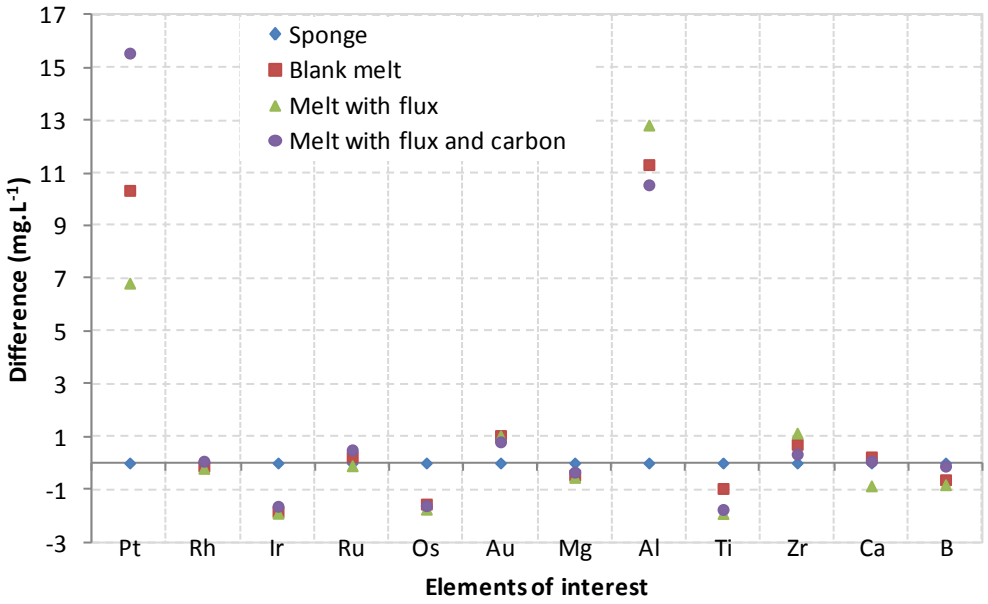

Figure 5.4: The absolute difference in mg.kg^{-1} between pure sponge and metals disks melted from the sponge

The difference between the sponge and the metal disks was less than 2 mg.kg^{-1} for all analytes except for platinum and aluminium. The high platinum values were attributed to cross contamination at the grinding station, before chemical digestion. This is confirmed by the high standard deviations obtained for the replicates (Figure 5.5).

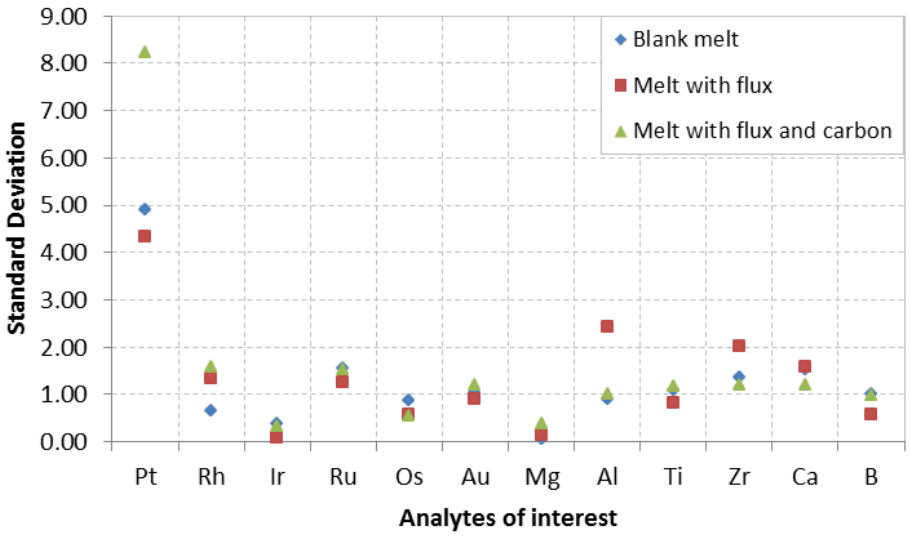

Figure 5.5: Standard deviations for four replicates of each metal per analyte.

When comparing the results from the 3 metals disks, 8 of the 30 impurity elements analyzed, gave lower values than compared to the two other standards. Silicon had a difference of 380 $mg.kg^{-1}$; arsenic had a difference of 2 $mg.kg^{-1}$. The remaining elements (including those not in the plot) had a differed of 1 $mg.kg^{-1}$ or less.

Table 5.3: Statistical evaluation of the contamination introduced by the addition of flux and graphite

Element	Average (mg.kg^{-1})			Average	Stdev	Two-way ANOVA	
	Blank	Blank + C	Blank + Flux			F	F crit
Pt	20.3	21.9	16.8	19.7	2.60	1.29	5.14
Rh	2.88	3.24	2.80	2.97	0.23	0.63	5.14
Ir	0.26	0.22	0.09	0.19	0.09	6.14	5.14
Ru	2.24	2.30	1.90	2.14	0.22	1.59	5.14
Os	0.33	0.46	0.25	0.35	0.11	2.22	5.14
Au	2.04	1.80	2.03	1.96	0.13	1.47	5.14
Ag	1.68	1.52	1.58	1.59	0.08	1.44	5.14
Cu	3.81	2.94	3.31	3.35	0.44	8.80	5.14
Ni	2.42	1.56	1.65	1.88	0.47	4.53	5.14
Fe	8.16	4.21	6.03	6.13	1.97	10.6	5.14
Pb	2.10	4.70	3.31	3.37	1.30	6.17	5.14
Mg	1.54	1.48	1.45	1.49	0.05	2.73	5.14
Mn	0.93	0.86	0.92	0.90	0.04	0.87	5.14
Si	13.1	397.5	70.0	160.2	207.4	105.8	5.14
Al	13.3	12.07	14.8	13.4	1.38	3.13	6.94
Sb	0.87	0.64	0.99	0.83	0.17	1.78	6.94
Cr	0.22	0.44	0.40	0.35	0.12	11.18	5.14
Sn	0.31	0.11	0.39	0.27	0.15	1.51	5.14
Ti	1.03	0.10	0.08	0.41	0.54	0.83	5.14
Zr	3.39	2.84	4.14	3.46	0.65	64.21	6.94
Ca	5.00	3.76	3.93	4.23	0.67	35.21	6.94
Zn	1.78	0.33	0.23	0.78	0.87	9.43	5.14
B	1.36	1.46	1.18	1.33	0.15	0.62	5.14
Co	3.70	3.74	4.90	4.12	0.68	18.17	5.14
V	0.03	0.08	0.04	0.05	0.03	4.18	5.14
Mo	0.00	0.00	0.04	0.00	0.44	9.49	5.14
Bi	1.26	1.47	1.51	1.42	0.13	25.3	5.14
As	5.33	6.99	3.60	5.30	1.70	0.76	6.94
Se	0.59	0.63	0.89	0.70	0.16	0.28	6.94
Te	1.13	1.25	0.89	1.09	0.18	2.18	5.14
Cd	0.17	0.21	0.37	0.25	0.11	6.01	5.14

A two-way ANOVA analysis was performed on the results to determine the statistical significance of the difference between the three means. The calculations were done under the assumption that there is no interaction between the two factors. This is justified as the two additives were added separately. The results of these are summarized in Table 5.3. 43% of the impurity elements (13 elements) had statistically significant differences between the averages of the three different samples (indicated in red). Of the elements that failed the ANOVA test; platinum and silicon are the only elements with a pooled standard deviation (standard deviation between the three standards) greater than 2. The pooled standard deviations of all the other elements were less than 2, which was acceptable.

The concentration of silicon increased drastically with the addition of both the flux and carbon. However, the metal containing both the flux and C was melted last, using the same crucible. It was expected that the deterioration of the crucible that is made of fused silica had worsened considerably due to the high temperature by the time the third melt was done. A combination of the deteriorating crucible and the reactivity of palladium could have led to the increase in silicon concentration.

To establish whether the increase in the silicon concentration of the metal with flux and C was due to the presence of C, two other standards with varying amount of C were prepared. The amount of graphite had to be kept at a minimum as C renders the metal brittle. The metal disks were prepared; one using the same amount of graphite added in the original sample, and 0.05 g C was added to the second standard.

The samples were then analyzed by ICP-OES. A non-linear relationship between the amount of C added to the mixture and the concentration of Si was observed (refer to Table 5.4) as the correlation coefficient obtained was not close to 1. The significance F is also less than the F critical value,

indicating that there is no significant linearity between the C added and the concentration of Si in the metal. This suggested that the Si observed in the metal is not dependent on the amount of C in the sample but on the state of the crucible.

Table 5.4: Regression analysis for carbon added to blank sample and concentration of silicon obtained

Regression Statistics	
Multiple R	0.8235
R Square	0.6781
Adjusted R Square	0.5172
Standard Error	110.7
Observations	4.0000

ANOVA					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	51604	51604	4.214	0.1765
Residual	2	24494	12247		
Total	3	76098			

Since no proof could be found that the suggested additives would contaminate the metal disks, the three reduction methods were evaluated to establish which would lead to greater recoveries. These tests were done on platinum metal, as it is the easiest of the three metals to melt. The results are illustrated graphically in Figure 5.6.

The recoveries when graphite was added were lower for some selected metals (calcium, aluminium, vanadium and titanium). The recoveries of all the PGM (except gold) were low. This trend is seen for all impurity elements. Only 5 elements have recoveries higher than that of the “blank”.

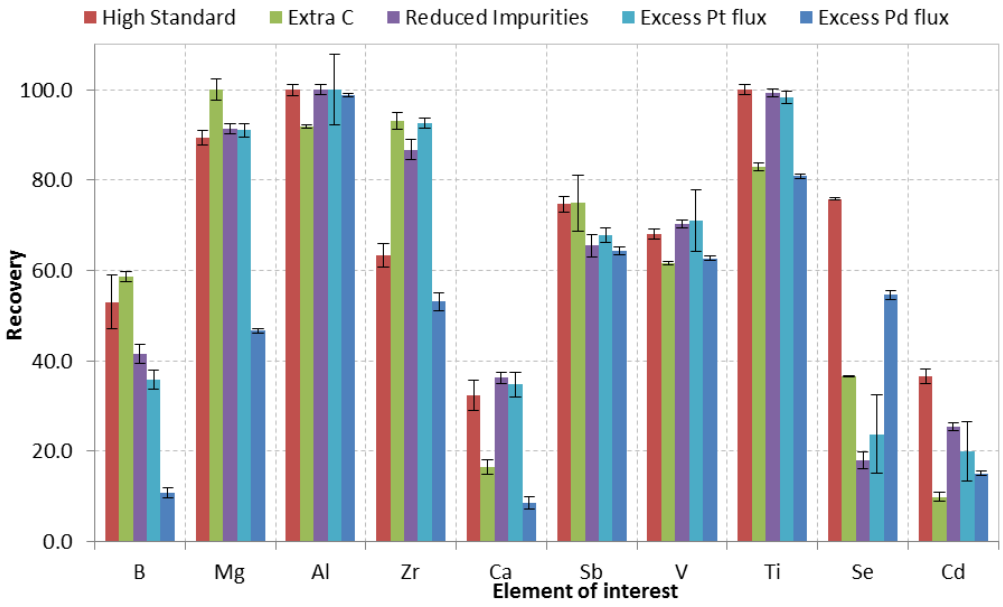

Figure 5.6: Recoveries (%) for different reduction methods on platinum standards

The plot in Figure 5.6 shows that the recovery for most of the base metals was the greatest when a reduction method was used. The reduction method gave an average recovery of 78.65% compared to the 77.59% obtained for the addition of excess C method. The method resulted in only selenium with a recovery of less than 20% while the C method resulted in two elements with recoveries of less than 20% (calcium and cadmium).

It was noticed that in 25 out of the 30 elements, the recoveries closely matched the recoveries obtained for the addition of excess flux. The recovery of silicon in both these methods was lower than that obtained for the reference standard and also for the method when extra C was added. In this case the reduced impurities method gave a lower silicon concentration than that of excess platinum flux method. However, both recoveries were of the same order of magnitude. Since the reduction of the impurities before melting is time-consuming, the method of adding of

excess degassing flux was chosen for the preparation of the full range of standards.

Preparation of master mixes (m-mix)

The impurities were mixed together in powder form to produce a master mix (m-mix) which was used to spike the pure metals. PGM and base metals (BM) m-mixes were prepared separately. It was prepared just before sample preparation.

For the PGM m-mix, 1 g of each of platinum, palladium, iridium and ruthenium were added to 2 g of rhodium, osmium and gold. All metals were accurately weighed out and placed in a 50 ml plastic sample bottle. The bottle was mixed with 7 mm polyamide mixing balls for 15 min at 25 Hz using the Retsch MM301 Mixer. For the BM m-mix, 1 g of each group of base metal oxides (refer to Table 4.1) and 1 g analytically pure graphite was accurately weighed and places in a separate sample bottle. The sample bottle was also mixed for 15 min at 25 Hz.

Melting of calibration standards

For the preparation of the standards, the m-mixes prepared for the calibration standards were diluted to make m-mixes for each standard. The serial dilution was done by weighing and mixing 1 g of each of the m-mixes (PGM and BM) for the highest standard, and mixing 1 g of the preceding and m-mix 1 g matrix of a typical sample. The concentrations of the impurities in the matrix were added to the matrix of the m-mixes to determine the final theoretical concentrations of the standards. 0.5 g of each standard's m-mix was weighed out per 100 g of standard. 150 g standards were prepared for platinum, as platinum metal disk were smaller than those of palladium of the same mass of sponge used due to its high density. 150 g standards were prepared for rhodium is slightly more dense than palladium. And 100 g palladium standards were prepared. Two drift

correction standards of 200 g with concentrations similar to Std 2 and Std 8 were prepared for each metal. All the metal sponge was compacted into pellets prior to melting.

Half of the optimum mass of flux was weighed for every matrix and placed at the base of the crucible. The other half was mixed with 10 g matrix for palladium and rhodium and 15 g for platinum, 0.5 g m-mix for palladium and 0.75 g for platinum and rhodium and pressed into a pellet. Different masses were used for the different metals according to their density. The pellet was snapped and layered in the middle of the pelletized metal sponge. The crucible was then place in the centre of the induction coil in the melting chamber of the furnace, with the mould and the catch mould placed on the ramp. The chamber was then sealed. Melting was conducted using the optimum melting conditions described in the preceding section (Table 5.2). The melting process was done manually, but casting was done automatically. The metal was left in the chamber, under Ar purge, until the glow disappeared. It was quenched with cold water.

5.2.3 HOMOGENEITY TESTING

The standards, for homogeneity testing were prepared differently from the calibration standards. These standards were assumed to have an even distribution of elements. Metal melted with induction heating are subject to convection heat transfer, which stirs up the metal during melting. All the standard was subjected to the same form of stirring. Care was taken to ensure the same melting conditions were employed throughout calibration standards and samples preparation. Three standards were prepared for each matrix: two blank standards and one standard spiked with 20 $mg.kg^{-1}$ of impurity elements.

Melting of homogeneity testing standards

The crucible could only fit a maximum of 150 g pressed powder or sponge. To prepare standards greater than 150 g smaller masses had to be melted and then combined and re-melted. Therefore, for blank standards nothing was added to the metals. The 20 $mg.kg^{-1}$ standards pressed pellets (for each matrix) were prepared and added to the melt.

The pellets were prepared from degassing flux, metal sponge, 0.1400 g PGM m-mix and 0.8271 g base metal m-mix per 100 g of standard. The mass of degassing flux used in the preparation of the pellet was calculated using the optimum melting parameters (Table 5.2). The same amount of degassing flux was weighed out into the bottom of the crucible. This resulted in double the optimum amount being added to the melts. The pressed pellets were layered on top of the flux, then three 50 g metal samples were placed on top of the pellets before the samples were melted.

The flux at the bottom of the crucible was added to reduce the reaction between the melt and the crucible. It was observed in earlier tests that adding the flux at the bottom of the crucible seemed to prolong the lifespan of the crucible.

For platinum and rhodium, two extra 20 g pellets were added to the crucible and 200 g standards prepared. Only 160 g standards were prepared for palladium. The difference in the mass of the standards was due to the difference in the density, and hence the volume of the resultant metal pieces. The crucible was place in the centre of the induction coil in the melting chamber of the furnace, with the mould and the catch mould placed on the ramp. A 40 mm mould was used for platinum and palladium, while a 35 mm mould was used for rhodium. The chamber was then sealed. The furnace settings were adjusted to the optimum melting

condition (Table 5.2). The melting process was done manually to visually determine when to cast. The casting was done automatically. The metal was left inside the chamber, under argon purge, until the glow disappeared. It was then quenched with cold water.

Analysis of homogeneity

The analysis of homogeneity was carried out as per ASTM E826 'Standard Practice for Testing Homogeneity of a Metal Lot or Batch in Solid Form by Spark Atomic Emission Spectrometry' (ASTM International, 2008). This standard is designed for the elemental homogeneity measurement of metals by Spark-AES, with the primary intent of being used in the development of reference materials. The procedure described in this standard is based on J. W. Tukey's HSD (honestly significant difference) procedure for pair wise comparisons of means (ASTM International, 2008). This procedure uses ANOVA to separate the components contributing to variation in the results using the following model (ASTM International, 2008):

$$\mathcal{X}_{ij} = \mu + \beta_i + \mathcal{T}_j + \varepsilon_{ij} \qquad (5.1)$$

Where:

$\mathcal{X}_{ij}$ = the result of the *i* th burn on the *j*th position

μ = the "true" mean of the population of all possible burn results,

β_i = the variation in the *I* th burn due to the measurement process,

$\mathcal{T}_j$= the variation in the *j* th position due to heterogeneity, and

ε_{ij} = the variation due to random or randomized processes.

The data is evaluated with row wise statistics to allow for the estimation and elimination of the variation in the measurement process, leaving only the variation due to the heterogeneity and random processes. The maximum contribution of random error is estimated and a critical value (w)

determined. If the difference between any two pairs of means is greater than the critical value, then the pair is considered heterogeneous. The critical value is defined as (ASTM International, 2008):

$$w = qs/\sqrt{b} \tag{5.2}$$

Where:
q = is a constant dependent on the number of positions (t) and degrees of freedom (n)

$$s = \sqrt{(SST - SSb - SSt)/(b-1)(t-1)} \tag{5.3}$$

Where:
b = number of burns

The standard requires a minimum of four burns per position for “good statistics”. To determine the homogeneity of the standards, heterogeneity was evaluated for two dimensions; across the face of the metal disk and as a function of depth. Each homogeneity standard, from the different metals platinum, palladium and rhodium were treated the same.

Both sides of the metal disks were shaved, by milling for platinum and palladium and/or grinding for rhodium. Both sides were mapped (assigned positions). Due to the size of the homogeneity testing standards (platinum and palladium were 40 mm diameter and rhodium 35 mm) and the spark size, the metals had different numbers of positions on each face. Platinum and palladium had seven positions on each face, while rhodium had four positions (Figure 5.7). The positions were sparked in a random order across each face. The analyzed surface was milled and the analysis was repeated. For platinum and rhodium, four sets of analysis could be

obtained on both sides of the metals. Six sets of results were obtained for palladium.

For each element, the data of the different metals was arranged in a b by t matrix table. The following were calculated on the tables (Table 5.5): T_j = the sum of row j; B_i = the sum of column i; X_j^2 = the sum of the squares of row j, t_j = the mean of row j and G = the sum of T_j; b = number of burns per position; and t = number of positions.

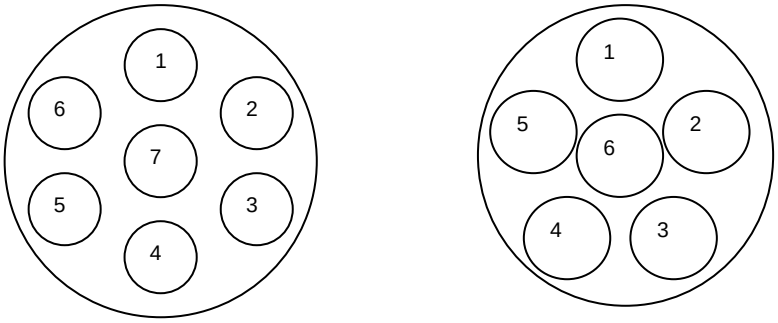

Figure 5.7: Map of the positions on a) platinum and palladium metal phase and b) rhodium metal phase

From the table the following contributions to random error were determined. The value of s and the critical value were then calculated:

- The sum of squares due to positions (ASTM International, 2008):

$$SSt = [\sum T_j^2/b] - (G^2/tb) \quad (5.4)$$

- The sum of squares due to burns (ASTM International, 2008):

$$SSb = [\sum B_j^2/t] - (G^2/tb) \quad (5.5)$$

- The sum of squares of all the measurements in the ANOVA and subtract G^2/tb (ASTM International, 2008):

$$SST = \sum\sum X_j^2 - (G^2/tb) \quad (5.6)$$

Table 5.5: The homogeneity testing b by t matrix table of rhodium element in palladium metal

Pos	Number of burns per position						Ave	T_j	T_j^2	X_j^2
	1	2	3	4	5	6				
1	19	19	19	19	19	19	19.0	114	12981	2164
2	19	19	18	18	19	19	18.8	113	12782	2132
3	19	19	19	19	19	19	19.0	114	13021	2170
4	20	19	19	20	19	19	19.3	116	13391	2233
5	19	20	19	18	19	19	19.2	115	13313	2220
6	19	19	19	19	18	19	18.8	113	12772	2129
7	20	19	19	19	19	20	19.3	116	13376	2230
B_i	135	134	132	133	132	134	G	801		
B_i^2	18327	17838	17525	17668	17563	17987	G^2	641409		

Pos: the position of the spark on the metal

Ave: the average of the row

For the analysis of heterogeneity across faces of the pellet, the row wise data analysis was carried out for each side of the metal disk (top and bottom). Critical values for each side were calculated and the difference between the highest and lowest mean (called T) compared against this value. Elements which had T ≤ w, were considered homogeneous. For those elements were T > w, the metal was considered heterogeneous. For the heterogeneous standards the differences between the means were then calculated for each pair to determine the positions on the face of the standard which were not homogenous. A summary of the data obtained for the top surface of the spiked metal is presented in Table 5.6 above. The elements for which T >w are highlighted in red.

Only two analytes in the palladium matrix showed heterogeneity across the top surface of the metal (silicon and aluminium). Six analytes showed heterogeneity in the rhodium matrix. The pair wise comparisons of the two elements in palladium are showed in Table 5.7 and 5.8 respectively.

Table 5.6: Summary of analysis of heterogeneity across face (top surface) for the spiked metal disks of platinum, palladium and rhodium

Element	Pt 20 mg.kg^{-1} Metal		Pd 20 mg.kg^{-1} Metal		Rh 20 mg.kg^{-1} Metal	
	w	T	*w*	T	*w*	T
Pt	M	M	8.04	5.56	6.12	2.50
Pd	66.44	1.46	M	M	5.28	5.50
Rh	4.81	0.10	7.24	4.24	M	M
Ir	7.50	0.25	7.56	6.45	3.22	5.00
Ru	0.85	0.35	5.31	3.05	35.91	36.50
Os	0.98	0.52	8.86	7.43	6.61	8.75
Au	0.12	0.07	0.44	0.18	1.82	0.75
Ag	8.90	0.27	0.64	0.47	0.61	0.25
Cu	2.45	1.39	5.50	3.13	0.58	0.25
Ni	5.28	0.26	0.58	0.46	18.13	19.75
Fe	6.88	0.14	1.82	1.31	2.59	2.00
Pb	3.42	0.12	1.01	0.58	1.18	0.50
Mg	0.08	0.06	0.27	0.27	0.74	0.50
Mn	2.78	0.01	0.13	0.13	0.46	0.25
Si	5.57	2.95	36.49	42.47	21.44	17.75
Al	0.20	0.17	0.75	1.07	1.30	0.75
Sb	0.83	0.51	0.97	0.53	1.17	1.00
Cr	0.03	0.02	0.48	0.38	1.07	0.50
Sn	0.92	0.38	1.10	0.82	0.85	0.50
Ti	0.13	0.06	0.41	0.35	0.93	0.50
Zr	33.40	0.29	0.16	0.09	0.73	0.50
Ca	3.96	0.13	0.74	0.67	5.11	3.75
Zn	11.96	1.34	5.74	3.52	N/A	N/A
B	1.59	0.05	0.60	0.39	0.71	0.50
Co	4.33	0.08	10.37	9.28	5.11	0.50
V	0.22	0.12	0.75	0.66	1.10	1.00
Mo	1.04	0.33	0.87	0.45	1.12	0.75
Bi	0.26	0.21	0.75	0.64	0.58	0.25
As	0.50	0.27	N/A	0.00	1.46	1.25
Se	0.21	0.07	N/A	0.00	1.35	1.25
Te	0.43	0.09	1.25	0.76	1.26	1.25
Cd	0.09	0.03	1.25	0.95	3.41	2.25

Table 5.7: Pair wise evaluation of heterogeneity across surface for silicon in palladium

t	7.00
b	6.00
n	30.00
q	4.46
SSt	12174.52
SSb	1564.91
SST	25789.49
s	20.04168
w	36.49164

Absolute mean differences

Position	1	2	3	4	5	6	7
1							
2	2.22						
3	2.35	4.58					
4	35.38	33.16	37.74				
5	40.11	37.89	42.47	4.73			
6	3.69	1.47	6.05	31.69	36.42		
7	1.55	3.77	0.81	36.93	41.66	5.24	

Table 5.8: Pair wise evaluation of heterogeneity across surface for aluminium in palladium

t	7.00
b	6.00
n	30.00
q	4.46
SSt	7.92
SSb	27.79
SST	40.74
s	0.409332
w	0.75

Absolute mean differences

Position	1	2	3	4	5	6	7
1							
2	0.02						
3	0.65	0.66					
4	0.92	0.94	0.28				
5	1.05	1.07	0.41	0.13			
6	0.02	0.01	0.67	0.94	1.07		
7	0.17	0.18	0.48	0.75	0.88	0.19	

From Table 5.6 it can be concluded that the heterogeneity of silicon in the metal was dependent on position. Position 5 appears not to be identical to any of the other positions. For aluminium, position 4 and position 5 were

both unidentical to the other positions. For some elements the same value was obtained for each burn regardless of position, and for which no critical value could not be quantified (as a root of zero cannot be defined). Elements for which only non-numeric figures (intensities lower than the background) were obtained or the same value was obtained for all the samples, no calculations could be done and the critical value was described as N/A in the table.

Evaluation of platinum matrix

Osmium, magnesium, silicon and bismuth showed heterogeneity across the bottom surface, face in contact with the mould. This heterogeneity was observed at different positions in the two standards. Magnesium, in the same position (position 5), lead to heterogeneity in both the standards. Position 5 was placed at the first contact point of the metal to the crucible upon casting. This could either be due to the reaction of the metal with the mould material, or from segregating during rapid cooling of the metal before the mould was completely filled.

Evaluation of palladium matrix

Silicon showed heterogeneity across the surface (between positions) in the two spiked metals. It was homogeneous along the depth of the standard. This suggested that upon cooling, the Si segregated along the depth of the metal, and not across the face.

For the analysis of heterogeneity across depth (heterogeneity of the position at different layers), the data obtained from the two sides of the metal disks were combined to produce one matrix table and row-wise data analysis carried out on the extended table. A critical value was calculated and the difference between the highest and lowest mean (called T) compared against this value. Elements for which $T \leq w$, the standards were considered homogeneous. For those elements were $T > w$, the metal

was considered heterogeneous for that element. For the heterogeneous elements, differences between the means were then calculated for each pair to determine the positions on the face of the metal which were not homogenous.

Boron was heterogeneous along the depth of the metal in palladium, where values at the top surface are constantly higher than the bottom surface (surface in contact with the mould). The difference was about 1 $mg.kg^{-1}$. This difference was too small to be significant and does not indicate heterogeneity in the platinum metal.

Evaluation of rhodium matrix

Due to the limitation in the height of the metal, and the difficulty in preparing the surface of the metal, only four analyses were carried out for each surface of the metal. This resulted in outliers being included in the statistics. Excluding them would make the data insufficient for statistical analysis. Outliers were excluded for the comparison across the two surfaces, as enough data points existed.

On the top surface, only iridium and osmium showed heterogeneity. Positions 6 and 1, respectively were different from the other positions. The elements which failed the test showed heterogeneity to have resulted from the difference between just two positions being greater than w. This is a direct result of the inclusion of outliers in the statistic evaluation.

The inhomogeneous nature of the PGMs (ruthenium, iridium and osmium), across both surfaces and depth were of concern. Positions 1 and 6 were heterogeneous for all the elements. Position 6 had the lowest average of all the positions on the bottom surface, and position 1 the second lowest. However, on the top surface position 1 had the lowest average of all the positions. The results indicated that once the first cooling had occurred

when the molten metal contacted the mould, ruthenium, iridium, osmium, iron, boron and molybdenum migrated from the centre to the edges.

From this data it was decided that only the top surface of the calibration standards would be used and that it would be milled four times only before new standards are prepared.

5.2.4 ASSIGNMENT OF CONSENSUS VALUES

Due to the potential loss of analyte during melting it was decided that the impurities would be determined empirically in the calibration standards. This meant that the values were determined and assigned by chemical analysis, and not by calculation. The standards were analysed at Anglo American Platinum's Final Metals Laboratory (FML) and was also sent to two independent laboratories which routinely analyse for impurities in ultra-pure PGMs (Final Metals Laboratories at Impala and Lonmin Platinum). The samples were also sent to a third laboratory, Anglo American Research, which analyzes monthly check samples for FML. These laboratories are referred to as LAB A, LAB B, LAB C and LAB D (in no specific order) for data evaluation purposes. Of these four laboratories, one used both ICP-MS and ICP-OES for the analysis, another used just ICP-OES. The other two laboratories analysed by Spark-OES, using a SAFT Spectro instrument. The results obtained from the different laboratories were evaluated statistically for the assignment of consensus values using the ISO 13528:2005 standard procedure (ISO Committee, 2005).

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The analytical surfaces of the samples that were submitted to the laboratories using Spark-OES were milled prior to submission. No further sample treatment was done at these laboratories. The quality control

measures in the respective laboratories were followed, and each standard was sparked 10 times on the same day.

For the third laboratory, three different solutions of palladium standards were prepared. It was transferred into 25 ml sample vials and submitted for analysis. Each solution was analysed by ICP-OES over a time. It was diluted 50 times and analysed in duplicate by ICP-MS over three different days. Due to the challenges experienced with the transportation of solutions and the extra work at the laboratory to adjust calibrations to fit the range of the samples, solid samples of the other metals (platinum and rhodium) were submitted.

Platinum and rhodium standards were ground, acid washed and ~1 g of each standard was submitted to the laboratory. The samples were dissolved at the various laboratories analysed using ICP-OES and ICP-MS. For the analysis of platinum standards, two portions of 0.25 g of each standard were dissolved and made to 25 ml in a volumetric flask and analysed once by ICP-OES. The same samples were diluted ten times and each portion analysed four times by ICP-MS.

Three portions of ~0.25 g of rhodium standards were dissolved and analysed once by ICP-OES. The sample solutions were then diluted 10 times and each solution analysed three times by ICP-MS.

Prior to the statistical analysis of the data all non-numerical values, i.e. those below detection limit, were changed to a value that corresponds to half that of the detection limit. The substitution values were used for the determination of the consensus value. The results from the laboratories where the results obtained were greater than the LOD, were used for the calculation. The results from each laboratory were evaluated for outliers

using the Grub's test. The outliers were excluded from further data analysis and calculations.

The consensus values of the standards were determined from the values reported by the participants, in accordance to ISO 13528:2005. This approach was used as the measurement and sample preparation methods were defined, even though two different techniques were used for measurement. The consensus values were determined with robust statistical analysis, which uses the median of the averages. The median is a more robust statistical consensus value as opposed to the mean, and should suffer less from skewed results that might result from single gross outliers. However, if results are obtained from only three laboratories, then one laboratory's results may be used as the average. The calculation of the new robust average, which is the average assigned the standards, minimizes the chances of the results from one laboratory being assigned the consensus value. The results from all the laboratories were used for the determination of the consensus value to afford an aspect of "fairness" to the evaluation of each participant's results. The initial robust average (x^*) and robust standard deviation (s^*) were calculated as follows (ASTM International, 2003):

$$x^* = median\ of\ x_i \tag{5.7}$$

$$s^* = 1.483\ median\ of\ |x_i - x^*| \tag{5.8}$$

Where:

i = 1, 2, 3 …., p

The x^* and s^* values were then updated as follows*(ASTM International, 2003)*:

$$\delta = 1.5s^* \tag{5.9}$$

For each x_i, the following was calculated *(ASTM International, 2003)*:

$$x_i^* = \begin{cases} x^* - \delta, & if\ x_i < x^* - \delta \\ x^* + \delta, & if\ x_i < x^* + \delta \\ x_i, & otherwise \end{cases} \quad (5.10)$$

The new *x** and *s** values were calculated from:

$$x^* = \sum x_i^*/p \quad (5.11)$$

$$s^* = 1.134\sqrt{\sum (x_i^* - x^*)^2/(p-1)} \quad (5.12)$$

Where:
p = number of participating laboratories

The new x* was used as the consensus value for the calibration standards, and the new s* used as the standard deviation of the consensus value. The consensus values for all standards are reported in Annexure A1.1, A2.1 and A3.1.

The standard deviation (a robust standard deviation of the averages from all the laboratories) was high for all elements. The values were particular high for the high concentrations of the PGMs in the palladium and rhodium matrices. These were greater than 100. Osmium had standard deviations greater than 100 (%RSD of 65 in platinum and 89 in rhodium) for all matrices. These high standard deviations were possibly due to the concentrations in the standards being higher than the highest calibration standard and therefore had to be determined by extrapolation. Since two of the laboratories used Spark-OES analysis, with factory calibrations, the calibration range could not be extended. The other laboratory carried out

the analysis using an ICP-MS where the sample was greatly diluted to reduce the matrix element. To avoid using one laboratory's results, the results from all the laboratories was used for the assignment of consensus values.

Statistical values with a %RSD greater than 50% or an expanded uncertainty of 100% should not be reported. However, since no average from any of the laboratories was excluded (to avoid biased consensus values) these values were used as a guide to exclude standards in the calibration. Since the results are converted to a percentage before the determination of the purity of metal, the other standard deviations were accepted. These were tabulated separately for each matrix and reported in Annexure A1.2, A2.2 and A3.2.

The uncertainties of the consensus values for the calibration standards were estimated as:

$$u_x = 1{,}25 \times s^* / \sqrt{p} \qquad (5.13)$$

The uncertainties of the results remain just as high as the standard deviation of the results resulting in the small number of laboratories used. The uncertainty was calculated in $mg.kg^{-1}$, even though the results were converted to percentage for the determination of the purity of the metal. This final value is the value engraved on the metal before it is sold. Elements where a value of zero was reported for the uncertainty are those where either only one laboratory reported the result (i.e. boron and silicon in rhodium matrix) or where the "new robust average" of all the laboratories was the same value (i.e. calcium in platinum and palladium matrices).

The uncertainties for most of the elements in all the matrices increased with the increase in concentration of the standards. This was unexpected as uncertainty is expected to increase closer to the detection limit. The low values for the lower standards were due to the laboratories, except for FML, that reported values below the detection limit as smaller than values. Thus, half the detection limit was used in the calculations. The uncertainties for these standards are therefore an indication of how closely the detection limits of the laboratories agreed.

The larger uncertainty in the higher standards was mainly observed for the PGMs, as a result of the high standard deviations. The measurement of the standards by extrapolation of the calibration curves greatly increased the error, especially for non-linear curves used in Spark-OES. The uncertainties for the different matrices were tabulated and reported in Annexure A1.3, A2.3 and A3.3.

Each laboratory was evaluated for accuracy (z-scores, also known as h-statistics) and precision (k-statistics). z-Score is the difference between an individual laboratory's mean and the assigned value in units of standard deviation. The new robust average and robust standard deviation were used as the assigned value and standard deviation for all laboratories. For the purpose of this evaluation, a laboratory which reported results that gave a z-score above 3.0 or below -3.0 would have been considered to have poor accuracy. A laboratory with a z-score between 2.0 and 3.0, and -2.0 and -3.0 would have been considered to have satisfactory accuracy. A laboratory with a z-score below 2.0 and above -2.0 will be considered to have good accuracy (Table 5.9).

Table 5.9: Accuracy rating based on z-scores

z-Score	Rating
z-score < 2.0	Good
2.0 < z-score < 3.0	Satisfactory
z-score > 3.0	Poor

The precision of each laboratory was determined using k-statistics (as described in ASTM E1601-98 (ASTM International, 2003). The k-statistic value is the ratio between the individual laboratory's standard deviation and the standard deviation of all laboratories. This measure the variance of a laboratory's replicate data (repeatability) compared to the common variability of all other laboratories (Anderson, 2012). The k-statistics for each laboratory were compared using the critical values calculated from the published values for two-tailed student's test at 99.5%. k_{crit} and was calculated as follows:

$$k_{crit} = \sqrt{p/\big(1 + (p-1)\big)/F} \qquad (5.14)$$

Where:

F = 99.5% confidence limit (two-tailed) and has (n-1) and (p-1)(n-1) degrees of freedom.

For the purpose of this evaluation, a laboratory with a k-statistic value higher than the critical value at the 99.5% confidence limit, was considered to have poor precision. A laboratory with a k-statistic value below the confidence limit would be considered to have satisfactory precision. A laboratory with a k-statistic value outside the confidence limit shall be considered to have poor precision. A laboratory with a k-statistics value below 0.9 would be considered to have good precision, and below 0.5 to have excellent precision.

Table 5.10: Precision rating based on k-statistics

k-statistic	Rating
k > critical value	Poor
k < critical value	Satisfactory
k < 0.9	Good
k < 0.5	Excellent

The number of replicates used for the analysis for each laboratory was four. Laboratories that obtained fewer data points were not evaluated.
The accuracy and precision of each laboratory was evaluated for each calibration standards to establish whether a trend was visible from the data. None of the analytes showed a trend between the grades (concentration in the standard) of the analyte and the precision. For some of the laboratories, however, the evaluation was skewed by the same value being obtained for all the replicates i.e. less than detection limits. A graphical illustration of the accuracy and precision for the four laboratories for platinum in palladium matrix is presented in Figure 5.8 and Figure 5.9 respectively. This sample was selected as all of the standards had concentrations higher than the LOQs of all the laboratories. For most impurities standards 1 to 7 gave the same value for all replicates in most of the laboratories. This makes it impossible to determine the k-statistics as the standard deviation for the laboratories was zero.

LAB C has satisfactory accuracy for standard 1 and 5, and poor accuracy for Standard 3. The k-statistical values of the standards which failed in LAB C is zero (Figure 5.9), which shows that the laboratory had reported the same value for all replicates. LAB D showed poor accuracy on standard 10, while it had excellent precision for the same standard. This suggested that the average value reported by the laboratory was not of satisfactory accuracy. Since the laboratory had good accuracy for the

other standards the poor accuracy of standard 10 cannot be assigned to the method or the laboratory environment. An investigation is required to establish the cause.

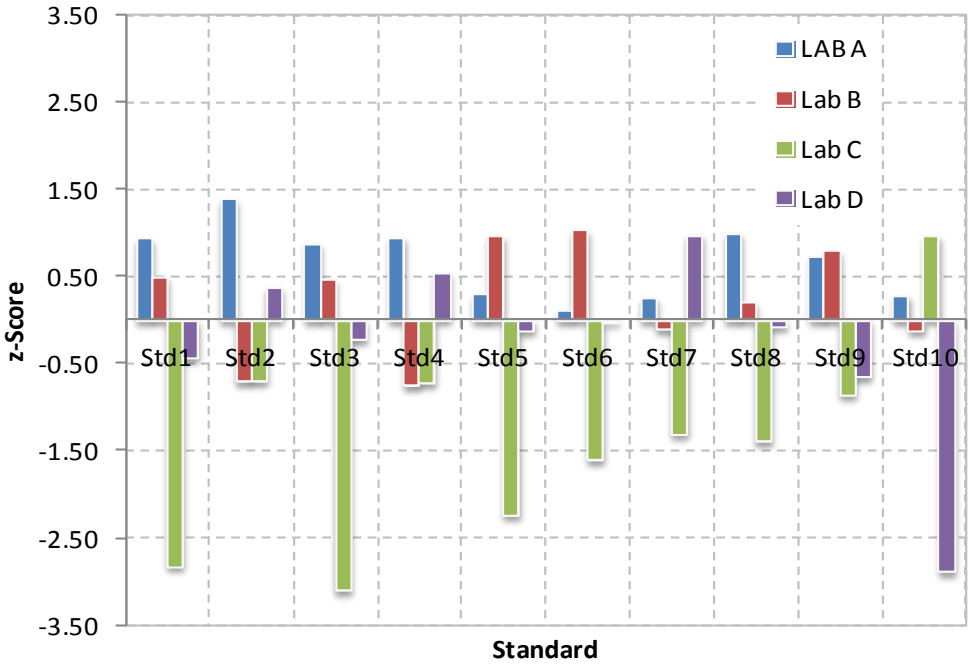


Figure 5.8: z-Scores of platinum in palladium metal for Standards 1-10

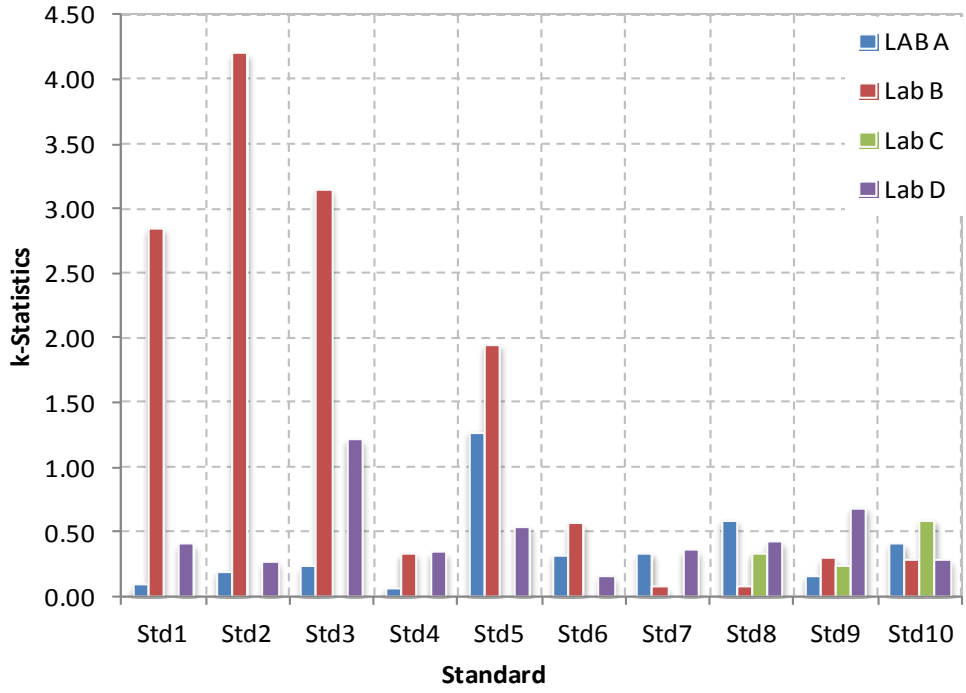


Figure 5.9: k-Statistics values for platinum in palladium metal for Standards 1-10

A summary of the z-score and k-statistics values appears in Annexure B.1-B.6 in a table. Each matrix is reported separately. The z-scores and k-statistics values of standards 1 and 10 are represented. The different standards are included to show the performance of the laboratories at the lowest and highest analyte concentrations.

5.3 CALIBRATION OF SPARK-OES

The calibration of the instrument forms the heart of instrumental analysis. The results reported from an analytical instrument are only as good as the calibration. This calibration process is defined in different ways. The NCSL international defines calibration as the operation that establishes, under specific conditions, the relationship between measurement values from an instrument (or measuring system) and the corresponding values of the

measurand (NCSL International, 2010). The determined relationship is usually represented graphically.

In the study The Thermo ARL4460 metals analyzer was selected for the analysis. Although the other two laboratories in the study used alternative instrumentation, the selection of the Thermo instrumemt was motivated by the extensive use of the instrument within the Anglo Platinum group. It is used after Fire Assay collection of the PGMs in a lead button. The Thermo instrument was preferred over the Spectro system (McIntosh, 2004). The in-house developed expertise on the instrument was an added incentive in the selection of the instrument.

5.3.1 INSTRUMENT CALIBRATION

The calibration was done with standards prepared in-house with the assigned values. The same instrument conditions were used for all matrices even though they have different Mohr hardness's. Platinum has a mineral hardness of 3.5, palladium 4.75 and rhodium 6.0 on the Mohr scale. The conditions used for the spark are tabulated in Table 5.11 where the following are stated:

- Argon flush time: the time that the stand is flushed with argon before analysis.
- Pre-integration time: the time in seconds of pre-integration (high energy spark).
- Integration time: time in seconds for analytical spark.
- Pre-integration delay time: time lapse between the pre-integration spark and integration spark. It allows the sample to cool before analysis to ensure repeatable sparking.
- Pre-integration source condition: a value is defined to select the source condition during pre-integration.

- Integration source condition: a value is defined to select the source condition during integration.

Table 5.11: Analytical conditions on the Spark-OES

Parameter	Platinum	Palladium	Rhodium
Argon flush time (s)	3	3	3
Pre-integration time (s)	10	10	10
Integration time (s)	5.00	5.00	5.00
Integration delay time (s)	0	0	0
Pre-integration source condition	25	25	25
Integration source condition	25	25	25

A longer pre-integration time allows for formation of a homogeneous area adequately devoid of localized inclusions. This time needs to be long enough to create an area, where the distribution of all elements is constant and the matrix effects on the analysis are eliminated. The elements for which a calibration was done, and their respective selected channels on the Spark-OES appear in Annexure C.

The software allows for automatic three adjustments regarding the calibration data; line overlap, background corrections, and inter-element corrections. Background corrections and line overlaps are achieved with one equation.

The elements were evaluated for inter-element interference.
Line overlap corrections are done within user defined limits and may be implemented for up to three channels. The adjustments have to be defined independently for each channel after the calibration standards have been sparked. The following formula (RTh, 2002) pertains:

$$I_{corrected} = \{I_{uncorrected} - \Sigma [K_0 + (K_1 * I) + (K_2 * I_2)]\} * f \qquad (5.15)$$

Where:

$I_{corrected}$ =Intensity (absolute or ratio) of the channel corrected by overlap or background correction.

$I_{uncorrected}$=Intensity (absolute or ratio) of the uncorrected channel.

I =Intensity (absolute or ratio) of the overlapping or background channel.

f =Scaling factor applied to the intensity to produce convenient values. It is set during the development of the method

K_0, K_1&K_2 =Correction coefficients

By selecting the time resolved spectroscopy (TRS) windows for each channel line overlap and background can be minimized or eliminated all together. The TRS windows selected for all elements are listed in Annexure C. Background subtraction was activated for elements with high background equivalent concentrations (BEC) values.

All calibration curves were linear, with curve splitting where necessary.

5.3.2 EVALUATION OF INTER-ELEMENT INTERFERENCES

Due to the concentration of the analytes, particularly in comparison to the matrix element itself, inter-element interferences should not be significant (Slickers, 1993). Potential inter-element interferences were, however, considered. Inter-element effects, an effect of the chemical nature of the sample as well the interactions in the plasma, were investigated. For element-specific inter-element effects, the following equation can be used to linearly correct for the interference (Slickers, 1993):

$$M_{corr} = M_{meas}(1 + k \cdot \%b) = M_{meas} + M_{meas} \cdot k \cdot \%b \quad (5.16)$$

$$M_{corr} - M_{meas} / M_{meas} = k \cdot \%b$$

$$\Delta M / M_{meas} = k \cdot \%b$$

The influencing factor can be determined by plotting the $\Delta M/M_{meas}$ value of the analyte against the concentration of the interfering element. If the resultant plot is linear, then the corrections can be directly applied to the concentration. This is done using the WinOE software on the instrument. The background and spectral interference correction for elements that share analytical lines, and that are known from experience to suffer from interference, were verified using Microsoft Excel.

In Figure 5.10 – 5.11 the evaluation of the interferences in the different matrices are given. The palladium and rhodium matrices show the evaluation of adjacent elements, while the platinum matrix shows the common interference of nickel and copper on iridium. The three plots show that there is no interference for the range of concentrations analyzed as none of the plots are linear.

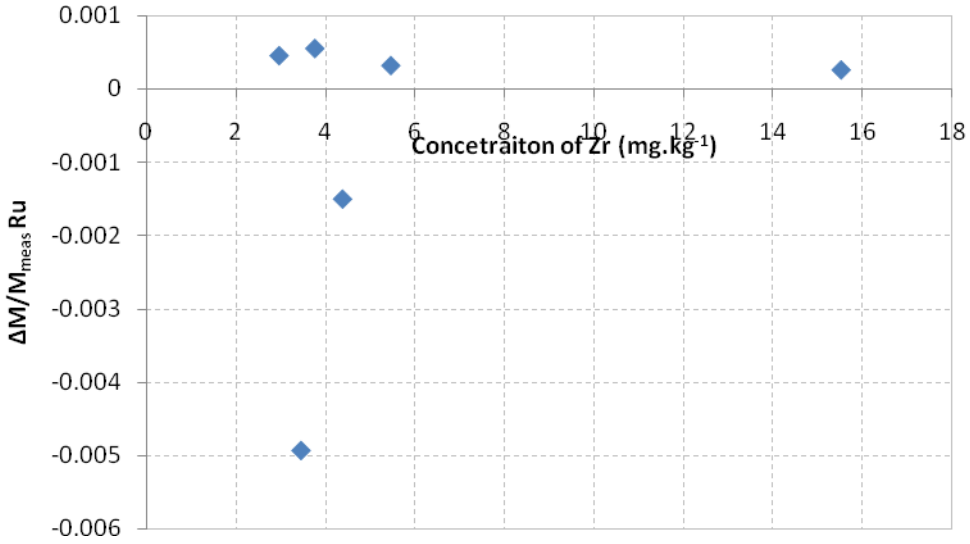


Figure 5.10: Interference of zirconium (349.62 nm) on ruthenium (349.89 nm) in palladium matrix

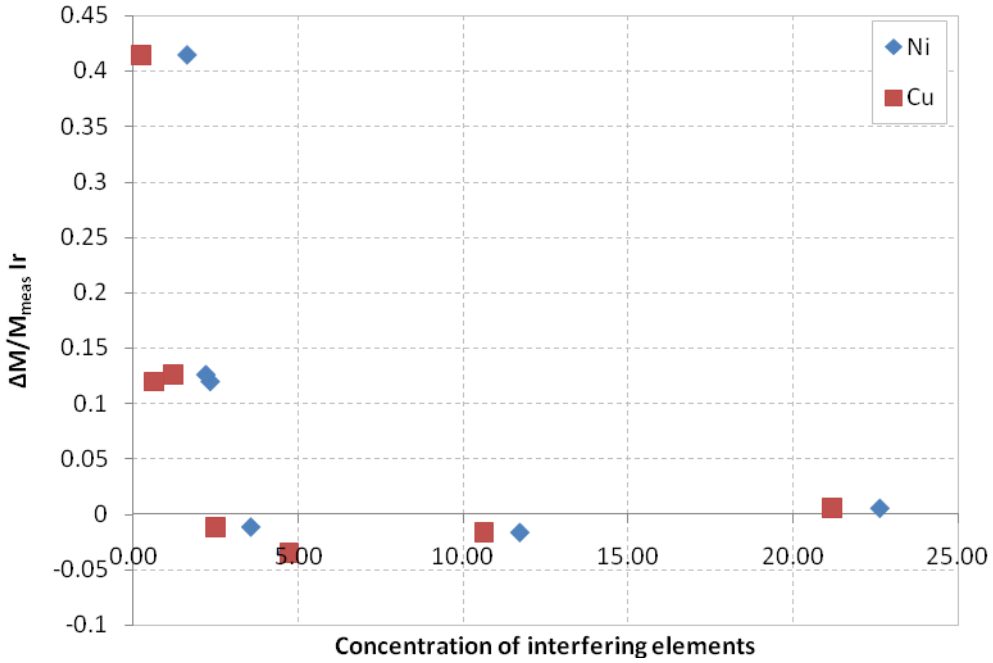


Figure 5.11: Interference of nickel and copper on iridium in platinum matrix

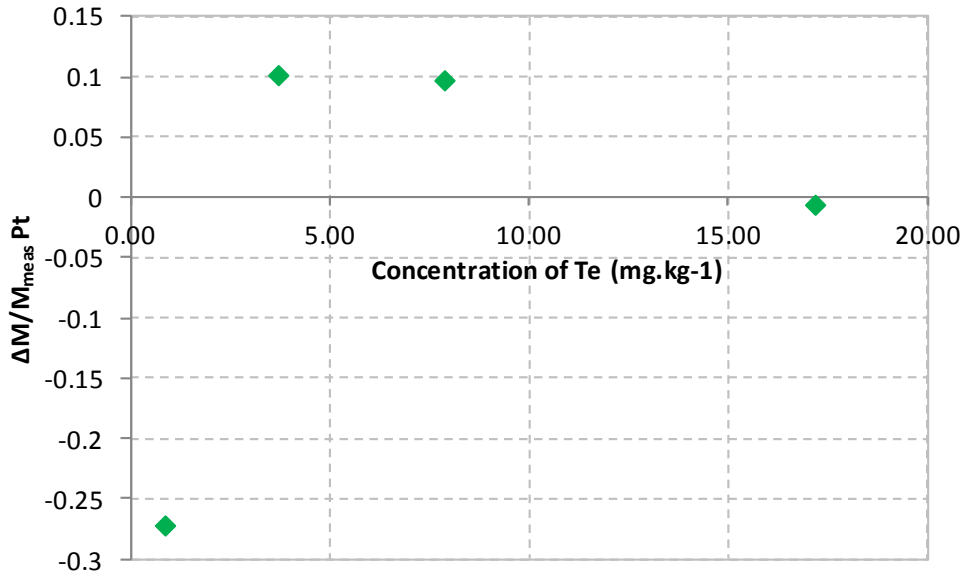


Figure 5.12: Interference of tellurium (214.27 nm) on platinum (214.42) in rhodium matrix

The relative differences of the measured value of the element were all high for the low standard. This was expected. Although the differences for all the concentrations were similar, division a smaller number (closer to zero) results in the ratio being amplified. None of the potential inter-element interferences proved to be significant enough to require correction.

5.3.3 EVALUATION OF CALIBRATION

The ARL 4460 software (WinOE) stores the relevant data for all calibrations. This includes calibration coefficients, limit of detection (LOD) and background equivalent concentration (BEC). The calibration coefficients, referred to in the software as base curves, can either be manually entered or be calculated by the software. The LOD and BEC are automatically calculated when a calibration is saved. The software uses

the following equation for the determination of the concentration of the analyte for linear plots (RTh, 2002):

$$Concentration = A_0 + A_1 * Intensity \quad (5.17)$$

Where:
A_0 = intercept
A_1 = slope of curve

The BEC is automatically calculated with the following equation (RTh, 2002):

$$BEC = A_0 + A_1 * 2 * Int_0 + A_2 * 4 * Int_0^2 + A_3 * 8 * Int_0^3 \quad (5.18)$$

Where:
Int_0 = intensity at 0% concentration
A_2 = coefficient for x^2 in second degree curves
A_3 = coefficient for x^3 in second degree curves

The LOD is automatically calculated with the following equation for a first degree curve (RTh, 2002):

$$DL = 3 * \sigma_{absolute} * Slope \quad (5.19)$$

Where:
$\sigma_{absolute}$ = absolute standard deviation stored for 10 runs of the pure matrix sample
Slope = the slope at 0% concentration

Since the calibration in this investigation did not involve a blank (0% concentration) for all elements the equations that the software used was

not suitable for our purposes. The calibration data, intensities and assigned consensus values of the standards, were therefore copied into an excel workbook. The data was re-processed with the Excel regression analysis tools. The calibrations were evaluated for linearity, sensitivity, limits of detection and limit of quantification.

5.3.3.1 LINEARITY

Linearity refers to the extent to which the measurement intensity is proportional to the concentration (CIPAC, 2006). Although ten calibration standards were prepared for each matrix, the number of standards included in each calibration curve varied for the elements. This was because some of the elements required more than one calibration for the different concentration surges, as well as the poor recoveries for analytes after melting for example silicon in rhodium matrix. For the purpose of this project, 3 calibration standards were considered adequate.

Linearity was visually inspected. Based on the linearity observed some elements required multiple linear curves according to a selected range. The WINOE software allowed for multiple calibration ranges of up to ten sections. However, were confined to two sections. Only curves for the lower ranges are given in Table 5.12. This is because the samples we would analyse only correspond to this concentration range.

Regression analysis was done on the calibration data and the correlation coefficient (r) was determined. The coefficient r is defined as:

$$r = \frac{\sum(Xi-X)(Yi-Y)}{\sqrt{(\sum(Yi-Y)^2(\sum(Y_i-Y)^2}} \qquad (5.20)$$

Where:

X_i = Concentration of standards

Yi = Corresponding instrument signals

$X = \sum X_i/n$

$Y = \sum Y_i/n$

n = number of standards

For perfect linearity r = 1 and a value of r = 0 implies that the concentration of the standards and the corresponding instrument response are not proportional at all. The acceptable coefficient is dependent on the method used and its purpose. Values of $r \geq 0.9980$ were regarded as acceptable linearity in this study. A summary of the correlation coefficients and the number of standards is presented in Table 5.12 for each impurity in the different metals.

Multiple sections of calibration for impurities in the chosen metals were used more extensively for palladium. The method for the analysis of impurities in palladium gave acceptable linearity coefficients for all the elements with perfect linearity obtained for 28 of the 31 elements determined. The lowest r value in platinum was antimony which was 0.9927. The lowest correlation coefficient obtained for rhodium was 0.9528 for the silicon calibration. The lowest number of standards used for a calibration section was 3.

A paired t-test on the significance of the r value was carried out. A paired t-test was done on all r values:

Hypothesis:

H_0: r = 0 there is no linear relation between x and y

H_1: $r \neq 0$ there is a significant linear relation between x and y

The t_{calc} and the critical value for t were calculated with the following equation:

$$t_{calc} = |r| \sqrt{n-2}/\sqrt{1-r^2} \quad (5.21)$$

$$t_{crit} = t_{DF;0.05} \quad (5.22)$$

Where:
DF = n – 2

If $t_{calc}>t_{crit}$, then the $\mathbf{H_0}$ is rejected and there is a significant linear correlation between x and y. If $t_{calc}<t_{crit}$, then the $\mathbf{H_0}$ is not rejected and there is no linear relation between x and y. A summary of the evaluation of the significance of the r coefficient for of all impurity elements in the different metals is presented in Table 5.13.

$t_{calc}>t_{crit}$ for all the elements determined, thus the null hypothesis is rejected and there is significant linearity between the concentration of the standards and the intensities obtained. This implies that all the elements met the minimum calibration requirements for validity.

Table 5.12: Summary of correlation coefficients

Elements	Pt		Pd		Rh	
	No Stds	r	No Stds	r	No Stds	r
Pt	**M**	**M**	5	0.9999	4	0.9983
Pd	8	0.9995	**M**	**M**	**4**	0.9998
Rh	6	0.9991	7	1.0000	**M**	**M**
Ir	7	0.9998	5	1.0000	3	0.9999
Ru	6	0.9997	7	1.0000	3	0.9964
Os	4	0.9999	6	1.0000	4	0.9989
Au	10	0.9999	8	1.0000	5	0.9990
Ag	6	0.9997	4	1.0000	8	0.9985
Cu	8	0.9996	4	1.0000	6	0.9978
Ni	8	0.9999	5	1.0000	7	0.9980
Fe	8	0.9993	5	1.0000	3	0.9995
Pb	6	0.9972	6	1.0000	6	0.9986
Mg	8	0.9993	5	1.0000	6	0.9878
Mn	10	0.9996	4	1.0000	5	0.9992
Si	9	0.9994	5	1.0000	6	0.9528
Al	3	1.0000	4	1.0000	4	0.9989
Sb	4	0.9927	6	1.0000	6	0.9992
Cr	8	0.9997	5	1.0000	6	0.9985
Sn	8	0.9995	5	1.0000	3	0.9987
Ti	6	0.9997	5	1.0000	6	0.9987
Zr	3	1.0000	6	1.0000	5	0.9971
Ca	6	0.9928	6	1.0000	4	0.9803
Zn	8	0.9996	6	0.9999	7	0.9992
B	5	0.9967	4	1.0000	9	0.9997
Co	7	0.9995	4	1.0000	5	0.9996
V	7	0.9997	6	1.0000	7	0.9989
Mo	6	0.9997	5	1.0000	7	0.9992
Bi	4	0.9997	6	1.0000	4	0.9999
As	6	0.9998	4	1.0000	7	0.9998
Se	9	0.9998	4	0.9999	5	0.9996
Te	5	0.9976	5	1.0000	4	0.9995
Cd	7	0.9999	5	1.0000	5	0.9995

Table 5.13: Summary of paired t-test results

Elements	Pt		Pd		Rh	
	t_{calc}	t_{crit}	t_{calc}	t_{crit}	t_{calc}	t_{crit}
Pt	**M**	**M**	109	2.57	24.47	2.78
Pd	80.73	2.31	**M**	**M**	80.75	2.78
Rh	45.99	2.45	12479	2.36	**M**	**M**
Ir	128.8	2.36	598	2.57	78.80	3.18
Ru	86.75	2.45	8179	2.36	11.71	3.18
Os	129.6	2.78	7100	2.45	30.76	2.78
Au	166.2	2.23	4848	2.31	37.98	2.57
Ag	80.91	2.45	1379	2.78	44.12	2.31
Cu	84.68	2.31	3242	2.78	29.88	2.45
Ni	144.2	2.31	1838	2.57	34.92	2.36
Fe	66.90	2.31	1355	2.57	30.49	3.18
Pb	26.61	2.45	2227	2.45	37.40	2.45
Mg	66.55	2.31	1730	2.57	12.71	2.45
Mn	102.1	2.23	1113	2.78	43.41	2.57
Si	77.16	2.26	7879	2.57	6.27	2.45
Al	136.3	3.18	3552	2.78	30.68	2.78
Sb	11.62	2.78	1836	2.45	49.62	2.45
Cr	95.08	2.31	4569	2.57	36.03	2.45
Sn	77.19	2.31	2276	2.57	19.70	3.18
Ti	76.09	2.45	1533	2.57	38.74	2.45
Zr	109.8	3.18	1785	2.45	22.68	2.57
Ca	16.53	2.45	1273	2.45	7.02	2.78
Zn	90.43	2.31	176.2	2.45	54.99	2.36
B	21.37	2.57	3626	2.78	116.69	2.26
Co	67.67	2.36	582.5	2.78	58.71	2.57
V	87.22	2.36	377.0	2.45	48.17	2.36
Mo	85.95	2.45	3797	2.57	56.94	2.36
Bi	56.79	2.78	2486	2.45	108.14	2.78
As	98.82	2.45	1378	2.78	103.97	2.36
Se	132.1	2.26	138.6	2.78	65.43	2.57
Te	24.84	2.57	810.0	2.57	44.45	2.78
Cd	162.7	2.36	709.4	2.57	57.40	2.57

M: the matrix (requires no calibration)

5.3.3.2 CALIBRATION SENSITIVITY

The calibration sensitivity is not necessarily the same as the method sensitivity, but is one of the factors which affect the sensitivity of the method. The sensitivity of the method is also affected by the precision of the method (the analytical sensitivity). Calibration sensitivity is defined as the slope of the calibration curve. It is independent of the grade (concentration of the analyte) (De Beer, 2006). For good sensitivity, the value of the slope must be greater than zero ($b \neq 0$). The slopes for elements, in matrices, were less than 1. To improve the calibration sensitivity a scaling factor of 1000 was applied to all elements. From Table 5.14 it can be seen that platinum in rhodium did not have satisfactory calibration sensitivity, and arsenic and selenium in palladium did not have satisfactory calibration sensitivity. The low sensitivity in these elements was due to the high background observed for these analytes in the low concentration range where the counts were measured. An increase in the counts was observed at very high intensities.

Table 5.14: Calibration sensitivity (cps.(mg.kg^{-1})$^{-1}$)

Elements	Pt	Pd	Rh
Pt	**M**	1	0
Pd	16	**M**	3
Rh	28	70	**M**
Ir	1	2	1
Ru	4	11	3
Os	2	5	1
Au	10	39	16
Ag	72	58	162
Cu	34	254	31
Ni	7	24	36
Fe	5	13	2
Pb	4	13	2
Mg	50	918	159
Mn	34	83	11
Si	9	32	16
Al	5	34	8
Sb	7	12	11
Cr	34	98	9
Sn	3	26	8
Ti	11	31	6
Zr	31	13	10
Ca	202	340	62
Zn	4	5	7
B	21	21	27
Co	10	70	10
V	9	7	5
Mo	13	14	31
Bi	4	15	25
As	4	0	11
Se	2	0	4
Te	2	3	5
Cd	14	2	1

M: the matrix (requires no calibration)

5.3.3.3 CALIBRATION UNCERTAINTIES

When evaluating the integrity of the calibration, three uncertainties are considered: uncertainty in the slope (S_b), uncertainty in the intercept (S_a) and the random calibration uncertainty ($S_{y/x}$). A random calibration uncertainty that is higher than uncertainties of both the slope and the intercept indicates a good calibration. The ratio of S_b to S_a is indicative of the suitability of the range of the calibration standards. A ratio greater than one would indicate that the range is not wide enough, and that more calibration standards need to be added at the lower range of the curve to improve the uncertainty in the slope. The S_b to S_a ratio therefore has to be kept less than one, with the smallest ratio optimum.

Only the lower range calibration curve, for multiple curves, is shown in Table 5.15. From the table it can be seen that the S_b to S_a ratios for all analytes in all matrices are less than one, indicating that the range of the calibration standards was sufficient.

Although the S_b is smaller than $S_{y/x}$ for all analytes in all matrices, the uncertainty in the intercept is larger than the random uncertainty of the elements. These elements include: lead and zirconium in the platinum matrix; platinum, copper, magnesium, cobalt, arsenic and selenium in the palladium matrix; lead, tin and calcium in the rhodium matrix. This indicated a greater uncertainty at the intercept. Since the range of the calibration met the criteria and the LOD for all these analytes (Table 5.15) were all relatively low (< 2 $mg.kg^{-1}$) the calibrations of these analytes was deemed satisfactory.

Table 5.15: Calibration uncertainties (mg.kg^{-1})

Elements	Pt		Pd		Rh	
	$S_{y/x}$	S_b/S_a	$S_{y/x}$	S_b/S_a	$S_{y/x}$	S_b/S_a
Pt	**M**	**M**	0.25	0.04	0.43	0.05
Pd	2.68	0.02	**M**	M	0.86	0.07
Rh	3.75	0.03	0.37	0.03	**M**	**M**
Ir	3.75	0.03	0.04	0.13	0.36	0.03
Ru	0.21	0.01	0.09	0.03	3.22	0.07
Os	0.03	0.05	0.04	0.04	0.76	0.05
Au	0.35	0.04	0.19	0.09	2.98	0.19
Ag	2.48	0.06	0.23	0.20	91.86	0.08
Cu	1.49	0.06	0.54	0.11	19.03	0.09
Ni	0.18	0.06	0.09	0.22	35.82	0.06
Fe	0.27	0.05	0.33	0.04	0.65	0.08
Pb	0.06	0.24	0.10	0.08	2.05	0.06
Mg	1.01	0.12	2.34	0.21	131.19	0.15
Mn	0.98	0.08	0.39	0.21	4.40	0.09
Si	4.76	0.00	1.19	0.00	505.00	0.01
Al	0.06	0.08	0.06	0.15	11.05	0.04
Sb	0.17	0.17	0.33	0.03	11.32	0.04
Cr	1.21	0.06	0.13	0.21	2.44	0.14
Sn	0.08	0.09	0.15	0.12	1.50	0.22
Ti	0.43	0.06	0.12	0.24	4.34	0.06
Zr	0.30	0.07	0.08	0.14	12.18	0.06
Ca	12.38	0.12	1.86	0.16	37.52	0.20
Zn	0.13	0.08	0.15	0.32	3.66	0.08
B	2.73	0.06	0.07	0.10	11.15	0.05
Co	0.48	0.06	0.25	0.36	1.55	0.15
V	0.41	0.05	0.37	0.09	2.20	0.09
Mo	0.68	0.04	0.04	0.15	26.54	0.04
Bi	0.03	0.36	0.18	0.06	6.46	0.05
As	0.11	0.05	0.00	0.12	6.53	0.04
Se	0.07	0.06	0.01	0.29	1.42	0.07
Te	0.05	0.26	0.04	0.13	1.49	0.10
Cd	0.20	0.08	0.05	0.08	0.35	0.12

M: the matrix (requires no calibration)

5.3.3.4 LIMIT OF DETECTION (LOD) AND QUATITATION (LOQ)

The LOD of the method is the lowest concentration of analyte that produces a response detectable above the background noise level of the instrument. The LOD is defined as three times the background noise, and could be theoretically calculated using the regression data. The limit of detection can be represented as follows:

$$Y_{LOD} = a + (3*S_a) \quad (5.23)$$

Where:
a = intercept

$$S_a = S_{y/x}\sqrt{\sum x_i^2 / n\sum(x_i - x)^2} \quad (5.24)$$

The limit of detection is defined as follows:

$$Y_{LOD} = bX_{LOD} + a \quad (5.25)$$

Thus:

$$X_{LOD} = 3 \times {}^{S_a}/_{b} \quad (5.26)$$

Where:

b = slope of the curve

The LOQ is the lowest concentration that can be quantitative determined with reasonable precision. It is defined as ten times the background noise. It was calculated theoretically using the regression data by the following equation:

$$X_{LOD} = 10 \times S_{a/b} \quad (5.27)$$

The LOD of all the impurities were determined from the regression data and are summarised in Table 5.16. The LODs and LOQs are rounded off to the nearest integer as the impurities in the samples are reported as integers when calculating the percentage purity of the product.

The criterion set for the LOD is that it must be smaller than 2 $mg.kg^{-1}$for all elements. Detection limits for silicon in all the metals was very high, particularly in rhodium. This was due to contamination incurred during melting, and the consequent high concentrations in the standards. The high temperature at which rhodium metal was melted resulted in rhodium standards containing very high concentrations of silicon, and consequently high limits of detection. Aluminium and platinum in rhodium also had LODs higher than the required 2 $mg.kg^{-1}$. All elements which had LODs of less than one (zero) were assigned an LOD of < 1 $mg.kg^{-1}$ for reporting purposes.

No criterion was set for the LOQs as less than the detection limits is used when reporting. It can be seen from the table that the limits of quantitation of most of the elements is less than 3 $mg.kg^{-1}$. For the platinum matrix only six of the thirty analytes had LOQs higher than 3 $mg.kg^{-1}$ and rhodium had 16 analytes. The palladium method had no analytes with LOQs higher than 3 $mg.kg^{-1}$. This is in general a good performance.

Table 5.16: Limits of detection and limits of quantitation in mg.kg^{-1}

Elements	Pt		Pd		Rh	
	LOD	LOQ	LOD	LOQ	LOD	LOQ
Pt	**M**	**M**	1	2	3	9
Pd	2	7	M	M	1	2
Rh	2	8	0	0	**M**	**M**
Ir	2	8	0	0	1	4
Ru	1	2	0	1	4	13
Os	0	2	0	0	2	7
Au	0	1	0	0	0	1
Ag	1	2	0	0	1	3
Cu	1	2	0	0	1	4
Ni	0	1	0	0	1	5
Fe	1	3	0	0	1	4
Pb	0	2	0	0	1	5
Mg	0	1	0	0	2	5
Mn	0	1	0	0	1	3
Si	10	33	0	0	88	293
Al	0	1	0	0	3	9
Sb	2	5	0	0	2	5
Cr	1	2	0	0	1	2
Sn	0	1	0	0	1	2
Ti	1	2	0	0	1	4
Zr	0	1	0	0	2	8
Ca	1	5	0	0	2	7
Zn	0	1	0	0	1	2
B	2	8	0	0	0	2
Co	1	3	0	0	0	1
V	1	2	0	0	1	2
Mo	1	3	0	0	1	4
Bi	0	0	0	0	1	2
As	1	2	0	0	1	3
Se	0	1	0	0	1	2
Te	0	2	0	0	1	2
Cd	0	1	0	0	0	1

M: the matrix (requires no calibration)

5.4 DISCUSSION

In this section the methods used for the preparation of the calibration standards for the Spark-OES are described and the calibration of each standard is evaluated.

The use of rapidly cooled moulds, facilitate almost instantaneous cooling of the metal. Therefore, it should eliminate the migration of elements in the metal during cooling. This should assist in the production of a homogenous of the metal. However, the testing showed that the bottom surface of rhodium metal was not homogenous. Care was taken to calibrate the instrument using only the top surface of the metal.

When assigning consensus values to the standard, Anglo American Platinum Final metals laboratory (FML) was considered as the primary laboratory. The preparation of the standards as well as their preparation for analysis was carried out at the FML. Some elements were analyzed only by FML, and these results were assigned the consensus values. Elements that were analyzed by only one laboratory (not FML) were not assigned values. Due to the difference in results from the laboratories used for the assignment of consensus values to the calibration standard, some values had high standard deviation and %RSD greater than 50%. This implied that there is no confidence in the accuracy of the assigned values.

The analytes that did not meet the required criteria for calibration analysis are presented in Table 5.17. The criteria that the element failed to meet are marked with an “X”. Only a few elements in each matrix failed more than one criterion. These elements are of great concern. It was observed that the elements that failed more than one criterion are those which had more than five standards with %RSD values higher than 50%. Silicon in

rhodium is not included as it was only reported by one laboratory which was not FML.

Table 5.17: Summary of calibration evaluation

Matrix	Analyte	Linearity	Calibration Sensitivity	Calibration Uncertainty	LOD
Pt	Pb	x		x	
	Sb	x			
	Ca	x			
	B	x			
	Te	x			
	Zr			x	
	Si				x
Palladium	As		x	x	
	Se		x	x	
	Pt			x	
	Cu			x	
	Mg			x	
	Co			x	
Rh	Ru	x			x
	Cu	x			
	Mg	x			
	Zr	x			
	Ca	x		x	
	Pt		x		x
	Pb			x	
	Sn			x	
	Al				x

Where “x” is a selection of the criterion not met

CHAPTER 6
METHOD EVALUATION

6.1 INTRODUCTION

According to the ISO/IEC 17025:2005 clause 5.4.5.1(ISO Committee, 2005), before any method can be used for chemical analysis a confirmation by examination has to be carried out to provide objective evidence that the particular requirements for a specific use are fulfilled. This implies that evidence has to be provided that the method, when applied correctly, is fit for its intended purpose. The ISO/IEC 17025:2005 also provides specific guidelines to be followed when evaluating an analytical procedure. The following should be obtained for the evaluation of a method for validity or "fitness-for-purpose (ISO Committee, 2005):

- Selectivity/ specificity of the method
- Linearity
- Limit of detection
- The uncertainty of the results
- Limit of repeatability and/or reproducibility
- Robustness

The Eurachem Guide to Quality in Analytical Chemistry (CITAC & EURACHEM, 2002) describes being "fit-for-purpose" as the method having "performance characteristics that are capable of producing results in line with the needs of the analytical problem". Thus, the performance characteristics of the method have to be proven to be scientifically sound under the conditions in which it is to be applied. These "performance characteristics" include (CITAC & EURACHEM, 2002):

- Selectivity & specificity (Description of the measurand),

- Measurement range,
- Calibration and traceability,
- Bias,
- Linearity,
- Limit of detection/ Limit of quantification,
- Ruggedness,
- Precision.

The Spark-OES method was thus evaluated for precision, robustness, traceability and bias. In this section, the evidence for these performance characteristics is presented. Each characteristic, as defined in the ISO/IEC 17025:2005 standard and CITAC/Eurachem guide is explained in detail in its own sub-section.

6.2 PRECISION

Precision refers to the proximity of a set of results. Precision is usually expressed in terms of standard deviation (CITAC & EURACHEM, 2002). There are two types of precisions, namely repeatability and reproducibility. Repeatability is when measurement results are obtained in the same laboratory, using the same method, material and operator within a short period of time. Reproducibility is when measurements are carried out by different operators, different laboratories, or different equipment using the same method, over a period of time.

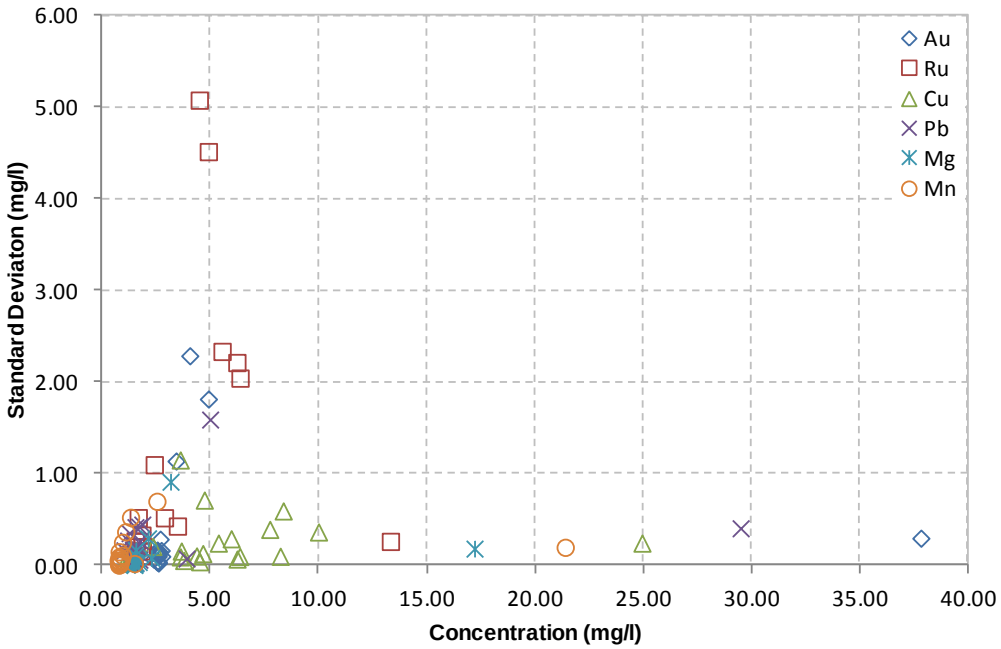
Precision is generally grade (concentration) dependent. As the concentration decrease, the precision deteriorates. Due the consistence of the samples produced by Anglo American Platinum, this phenomenon could not be adequately demonstrated. Two standards of 2 $mg.kg^{-1}$ and 20 $mg.kg^{-1}$ were prepared and evaluated for repeatability and reproducibility to evaluate the grade dependency of the precision. These metals were

evaluated together with the natural QC (NQC). The NQC was a typical sample with consensus values that was prepared with the sample to monitor deviations in sample preparation.

Evaluation of repeatability

The palladium matrix was carried evaluated first. Typical samples were sparked multiple times (between three and four times) and the standard deviation between the results was evaluated.

The standard deviation of the samples was plotted against the concentration of the sample, to establish if the repeatability precision is concentration dependant. The analytes plotted in Figure 6.1 were chosen randomly. To better illustrate this, the data for some of the elements (gold, ruthenium, copper and lead) are tabulated in Table 6.1 below. It can be seen that for most of the elements, the calibration range is limited; with most of the samples being less than 5 $mg.kg^{-1}$. This trend was observed for all the elements. The figure does not indicate a clear increase with an increase in the concentration, it can be concluded that the precision is not concentration dependant. The standard deviation was below one for most of the elements. Ruthenium and gold had standard deviations larger than 1. However, the concentration of the elements was high in these samples. The deviation might be from compromised pellets, which might have cracked or had visible inclusions.



*Standard deviations of other analytes not plotted. Trends of these are commented on in text.

Figure 6.1: Standard deviation (mg.kg^{-1}) of analytes in palladium matrix against the concentration in mg.kg^{-1} of the sample

The repeatability of ruthenium was poor. Six out of twenty standard deviations were larger than 1. This cannot be attributed to the ruthenium calibration, which were sensitive, and met all the requirements of a good calibration. The high standard deviation can be ascribed to sample preparation, or inclusions of high ruthenium in sample.

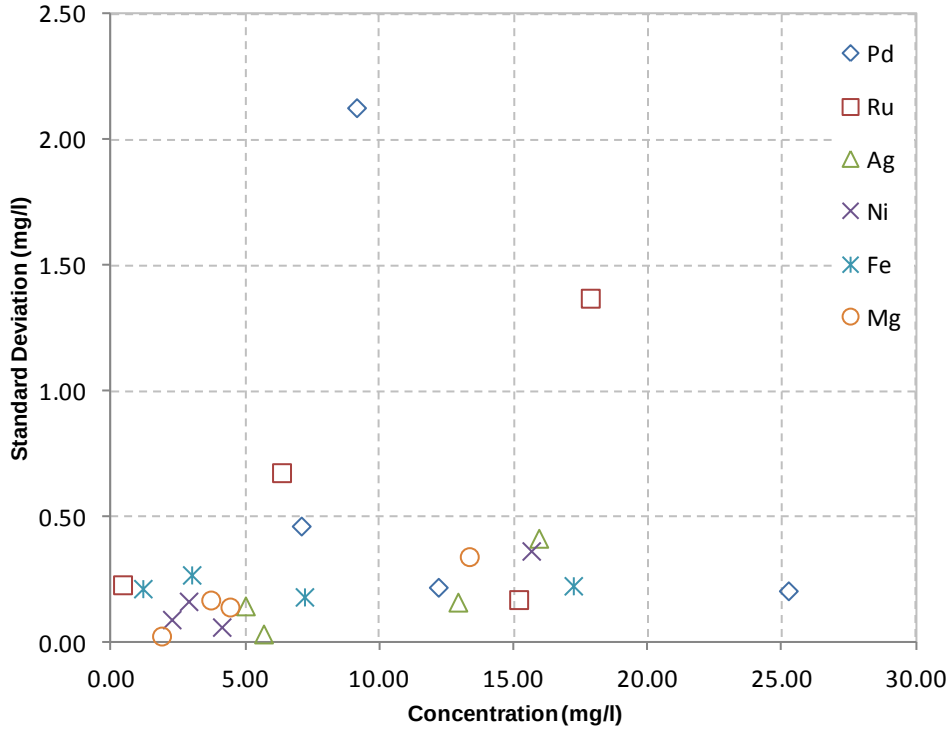
The repeatability of the analytes in the platinum and rhodium matrix was done on only three quality control materials: the NQC which was not spiked, the 2 mg.kg-1 QC and the 20 mg.kg-1QC. It was observed that the narrow concentration range of impurities in the typical samples did not offer a sufficiently wide range for a conclusive evaluation.

Table 6.1: Standard deviation ($mg.kg^{-1}$) of analytes in palladium matrix and their concentrations in $mg.kg^{-1}$

Sample ID	Au		Ru		Cu		Pb	
	Ave	Stdev	Ave	Stdev	Ave	Stdev	Ave	Stdev
2 mg/kg	2.36	0.07	1.39	0.05	1.13	0.09	1.02	0.17
20mg/kg	2.51	0.04	1.42	0.05	1.16	0.04	1.19	0.27
PPDS 1	2.53	0.16	1.46	0.09	2.33	0.21	1.22	0.03
PPDS 2	2.53	0.17	1.51	0.27	3.60	1.15	1.26	0.35
PPDS 3	2.55	0.14	1.53	0.20	3.60	0.10	1.30	0.15
PPDS 4	2.56	0.11	1.56	0.26	3.65	0.16	1.39	0.11
PPDS 5	2.58	0.10	1.66	0.52	3.76	0.06	1.41	0.17
PPDS 6	2.58	0.04	1.79	0.11	4.35	0.11	1.44	0.16
PPDS 7	2.58	0.03	1.79	0.16	4.50	0.04	1.52	0.03
PPDS 8	2.59	0.03	1.83	0.33	4.64	0.13	1.53	0.42
PPDS 9	2.60	0.13	1.85	0.21	4.71	0.71	1.53	0.22
PPDS 10	2.60	0.15	2.40	1.10	5.36	0.25	1.55	0.10
PPDS 11	2.62	0.15	2.87	0.52	5.95	0.29	1.61	0.15
PPDS 12	2.67	0.29	3.47	0.43	6.22	0.07	1.70	0.43
PPDS 13	2.72	0.16	4.48	5.08	6.35	0.10	1.71	0.06
PPDS 14	2.74	0.10	4.90	4.52	7.74	0.40	1.73	0.27
PPDS 15	3.40	1.14	5.53	2.34	8.22	0.10	1.84	0.45
PPDS 16	4.04	2.29	6.22	2.22	8.36	0.60	3.89	0.08
PPDS 17	4.90	1.82	6.36	2.05	9.99	0.37	4.98	1.59
PPDS 18	37.84	0.30	13.32	0.26	24.94	0.25	29.51	0.41

Ave: average

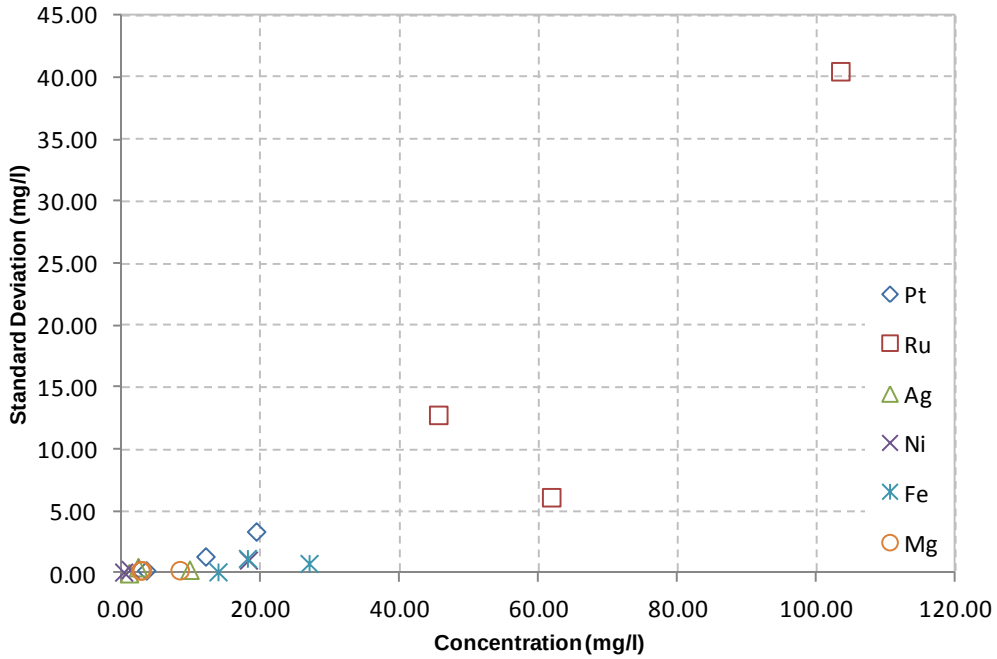
Stdev: standard deviation of the data



*Standard deviations of other analytes not plotted. Trends of these are commented on in text.

Figure 6.2: Standard deviation (mg.kg^{-1}) of analytes in platinum matrix against the concentration (grade) in mg.kg^{-1}of the sample

Figure 6.2 suggest that none of the elements showed a dependency on their concentration in the sample, as was the case with all the other analytes determined with this method. On average, a standard deviation of 0.5 for was achieved for all the elements. Some outliers were observed for palladium and ruthenium.



*Standard deviations of other analytes not plotted. Trends of these are commented on in text.

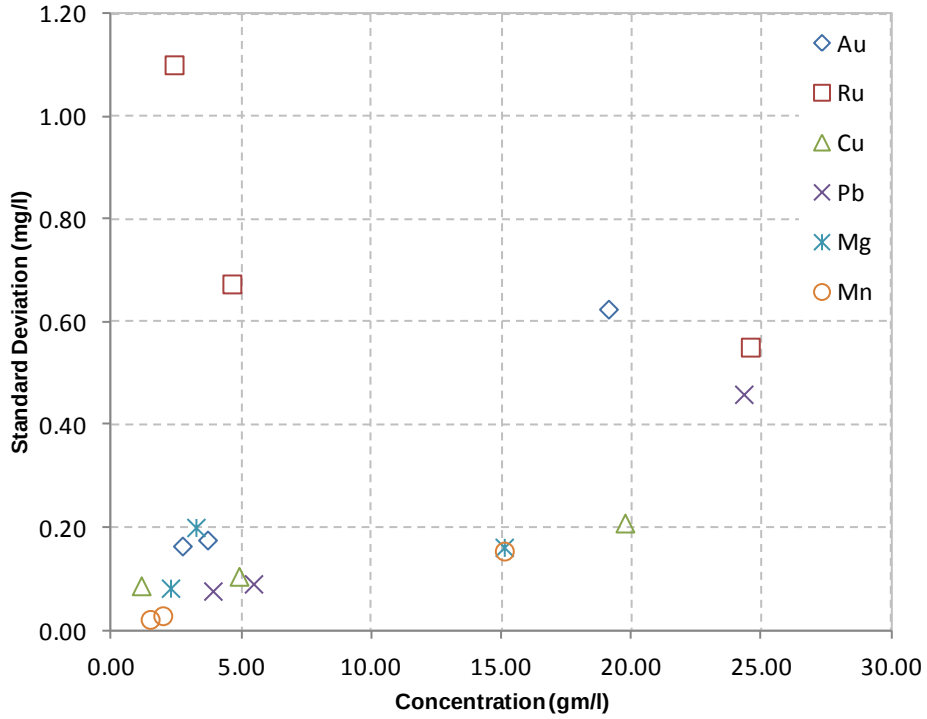
Figure 6.3: Standard deviation (mg.kg^{-1}) of analytes in rhodium matrix against the concentration (grade) in mg.kg^{-1} of the sample

The standards deviation for the analytes in rhodium metal appeared to be larger than for the other matrices. Ruthenium displayed exceptionally high standard deviation. It was observed that a single very high value in arm was responsible. The results of all the other elements in that run would differ only slightly. For the analysis of metal samples, this was attributed to the heterogeneity of ruthenium in rhodium also known as the 'raisin bread' effect. The high standard deviations in pressed pellets also have been a result of this effect.

Evaluation of reproducibility

The 2 mg.kg^{-1} metal disk and the 20 mg.kg^{-1} samples were milled with both the belt sander and the milling machine. This was done on different days. Since the effect of melting the samples is not expected to be

identical with every melt, different metals of the 2 $mg.kg^{-1}$ and 20 $mg.kg^{-1}$ were compared as different samples. NQC was also melted and analyzed over a number of days, after milling the sample. The standard deviations of the results were plotted against the concentrations of the impurity elements to establish if a trend exists between the concentration and the standard deviation (Figure 6.4).

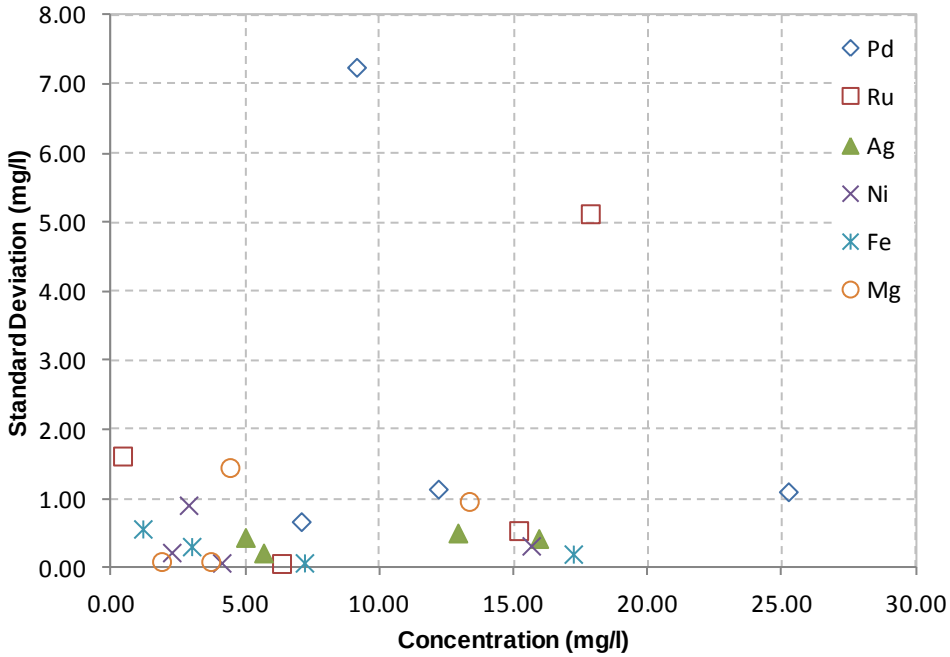


*Standard deviations of other analytes not plotted. Trends of these are commented on in text.

Figure 6.4: Standard deviation ($mg.kg^{-1}$) vs the concetration ($mg.kg^{-1}$) of analytes in palladium matrix.

Ruthenium was the only element in the palladium matrix that showed a correlation between reproducibility precision and concentration. No trend was evident for any of the other elements. The reproducibility standard deviation appeared to be higher than the repeatability standard deviation. Although unexpected, it was due to the number of data points used for the

calculation. Since the repeatability was measured over a short period, the average used fewer data points than those used for the determination of reproducibility.



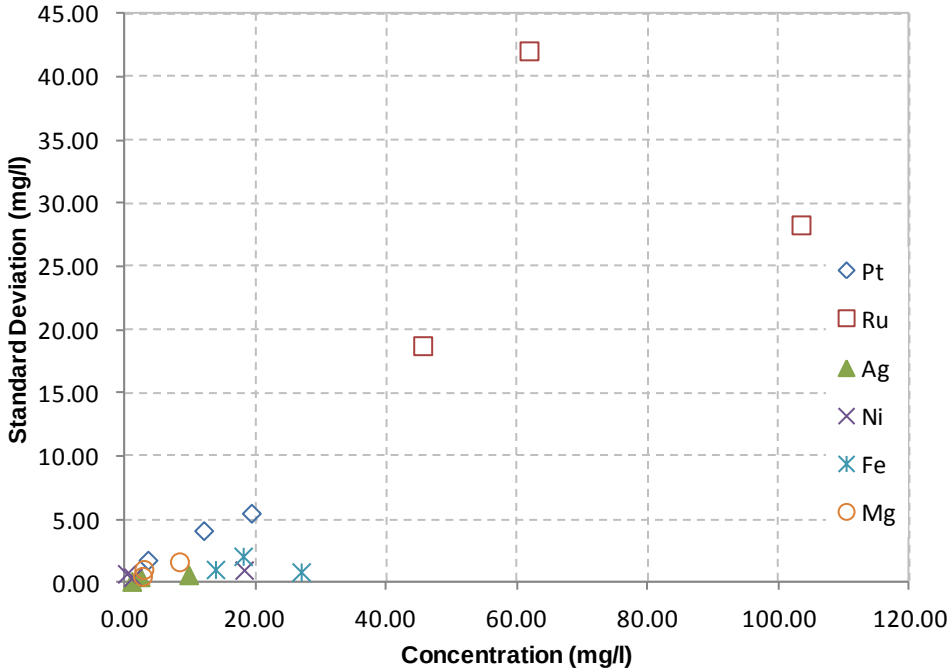
*Standard deviations of other analytes not plotted. Trends of these are commented on in text.

Figure 6.5: Standard deviation (mg.kg^{-1}) vs the grade (mg.kg^{-1}) of analytes in platinum matrix.

No dependence between the standard deviation and the concentration of the sample could be seen (Figure 6.5). This was true for all the elements determined in the platinum matrix. On average, the standard deviation was less than one, except the two outliers in ruthenium and palladium.

The reproducibility of analytes in rhodium matrix is illustrated in Figure 6.6. It can be seen that ruthenium has an exceptionally high standard deviation, and therefore very poor reproducibility. Although iridium, which also displayed heterogeneity on both surfaces, it did not suffer such high

standard deviations. Os was not considered as one of the samples was below the LOD and no standard deviation value could be determined. The poor reproducibility of ruthenium in rhodium emphasized the heterogeneity of ruthenium in rhodium.



*Standard deviations of other analytes not plotted. Trends of these are commented on in text.

Figure 6.6: Standard deviation (mg.kg^{-1}) vs. the concentration (mg.kg^{-1}) of analytes in rhodium matrix.

6.3 ROBUSTNESS

Robustness, also known as ruggedness, measures the effect of small variations on the analysis procedure within the same method. It can either be expressed as standard deviation or relative standard deviation (%RSD). A large number of the variations that can be done on the analysis have little effect on the results. It is therefore possible to vary more than one factor at a time.

Samples preparation was limited to either compacting the powdered sample or milling the analytical surface of the metal sample. Not much variation existed in sample preparation. Changing the tonnages to press the samples could results in pellets that are not compact enough. The sample would then break before or during analysis. If the sample flakes-off onto the spark stand during the analysis, it would make the analysis difficult. Variation in the melting conditions will also change the sample matrix. Oxidation and/or formation of an uneven surface with holes could result, as observed in section 5.2.1. Variations in the sample preparation would hamper analysis, and result in incorrect conclusions. No variations on the sample preparation methods were done.

The temperature of the instrument room was not regulated but monitored within set limits. The spectrometer temperature was used as a measure and not the room temperature. Therefore, the effect of slight changes in temperature would be included in the precision analysis (reproducibility). Another factor that was changed to evaluate the robustness of the method was the sample preparation technique. Samples were sparked as pressed pellets and then melted and analyzed using the same calibration as metal samples. This was to evaluate if melting the sample prior to analysis would compromise the results.

The routine samples were relatively consistent. The data did not cover a wide enough range for it to be evaluated with regression analysis. A paired t-test was conducted on the data to determine the significance of the difference between the results obtained from the sponge and the melt:

Hypothesis:

H_0: there is no statistically significant difference between the results

H_1: there is statistically significant difference between the results

The t_{calc} and the critical value for t were determined as before.

If $t_{calc}>t_{crit}$, then the $\mathbf{H_0}$ is rejected and there is statistically significant difference between the results of the sponge and of the metal. If $t_{calc}<t_{crit}$, then the $\mathbf{H_0}$ is not rejected and there is no statistically significant difference between the two results.

A summary of the t-test results can be seen on Table 6.1. The elements for which the null hypothesis was rejected is printed in red. Most of the analytes, particularly in the platinum and rhodium matrices are printed in red. These elements have statistically different values for the sponge and metal disk.

The t-test really measures the bias between the mean of two sets. It determines if one set is consistently higher than the other. The difference between the two sets of result ($mg.kg^{-1}$) was determined to evaluate if the difference in concentration was tolerable. The difference was obtained by subtracting the sponge results from the metal results. Negative differences indicate that the sponge results were larger than those obtained for the metal sample.

Table 6.2: Paired t-test of sponge results vs. metal results of the same sample

Element	Pt		Pd		Rh	
	t-Stat	t-crit	t-Stat	t-crit	t-Stat	t-crit
Pt	**M**	**M**	-0.25	2.26	-21.42	2.23
Pd	-3.26	2.26	**M**	**M**	1.14	2.23
Rh	0.00	2.26	-3.27	2.26	**M**	**M**
Ir	-7.18	2.26	-2.10	2.26	-0.68	2.23
Ru	-0.98	2.26	-1.63	2.26	-22.81	2.23
Os	3.75	2.26	2.61	2.26	2.92	2.23
Au	-15.47	2.26	-7.31	2.26	6.89	2.23
Ag	4.82	2.26	-1.76	2.26	-6.46	2.23
Cu	-2.1E+08	2.26	-4.18	2.26	-8.15	2.23
Ni	4.58	2.26	-0.89	2.26	-2.78	2.23
Fe	-5.80	2.26	-5.14	2.26	-6.44	2.23
Pb	-3.16	2.26	-1.82	2.26	-18.83	2.23
Mg	-31.18	2.26	-9.08	2.26	-2.98	2.23
Mn	-9.56	2.26	0.36	2.26	-4.03	2.23
Si	-16.80	2.26	-11.93	2.26	7.54	2.23
Al	-26.48	2.26	-3.98	2.26	2.47	2.23
Sb	2.72	2.26	-0.67	2.26	-19.10	2.23
Cr	-6.22	2.26	-0.97	2.26	-3.54	2.23
Sn	-16.30	2.26	1.00	2.26	2.44	2.23
Ti	-1.85	2.26	-5.64	2.26	-3.55	2.23
Zr	-3.23	2.26	-3.52	2.26	2.69	2.23
Ca	-13.23	2.26	-7.06	2.26	3.54	2.23
Zn	3.97	2.26	0.00	2.26	-21.36	2.23
B	-14.85	2.26	-4.92	2.26	4.62	2.23
Co	-2.93	2.26	0.00	2.26	-1.58	2.23
V	-4.22	2.26	1.50	2.26	-39.65	2.23
Mo	2.60	2.26	4.79	2.26	-1.85	2.23
Bi	0.91	2.26	-7.26	2.26	-28.22	2.23
As	-8.89	2.26	2.36	2.26	9.40	2.23
Se	-6.15	2.26	1.80	2.26	0.00	2.23
Te	-13.26	2.26	-6.59	2.26	-33.72	2.23
Cd	-13.07	2.26	1.96	2.26	3.72	2.23

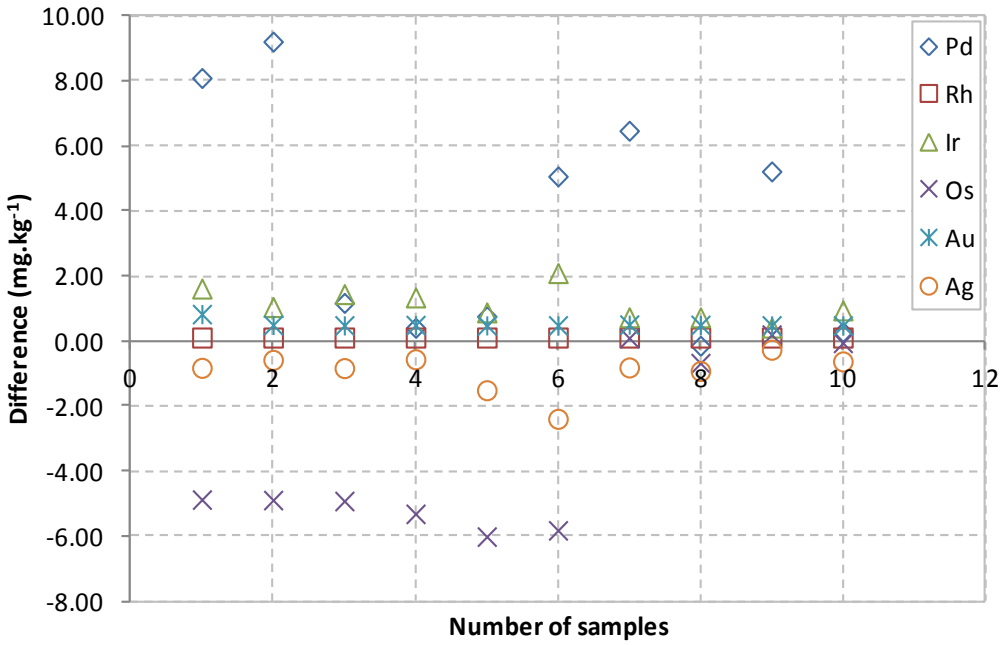


Figure 6.7: Difference in the concentrations obtained from metal samples and sponge sample in platinum matrix.

Results that were different by more than 3 $mg.kg^{-1}$ were considered to be significantly different. Results different by less than 3 $mg.kg^{-1}$ were considered to have insignificant differences in concentration and the results were accepted. However, most elements were significantly different and it was evident that the sample changed during the melting. Samples should not be prior the analysis.

6.4 TRACEABILITY AND ACCURACY

The calibration and analysis has to be done traceable with regards to measurement standard, preferably a certified reference material (CRM). The CRM can also used for the validation of the accuracy of the method. z-Score analysis are used for the determination of the accuracy and traceability. Due to the lack of PGM CRMs, establishing method traceability can be cumbersome. The method could, therefore, not be

traced to a CRM. An internal QC material was prepared instead as described in section 7.1.2.

The values for the internal QC material were, validated with results from two other laboratories. The concentration of impurities in the material could not be certified due to a number of limitations. A limited number of laboratories in the country use the analysis and between them they did not use a standard method. For certification, the standards would need to be sent abroad and returned to the country. Due to the high value of the metals and the level of security associated with their transportation, this was impractical. Spiked metal sponges, to be used for melting, could also not be submitted internationally for certification as there will be losses experienced during the melting of the metal.

The capacity of the induction furnace (maximum of 250 g platinum) was another limitation to the number of laboratories that could analyze the reference material. 250 g of the reference material would not allow a large number of analyses, assuming that not all laboratories use the Spark-OES technique.

The materials were thus measured and evaluated against specified limits. Each analysis had to agree within the specified limits. These were calculated at twice the standard deviation (sd) of the FML results (warning limit) and at three times the sd the action limits. The QC data with the respective limits and the values obtained on the Spark-OES are presented in Annexure D1.1 – D3.2. Each QC from the different matrices is tabulated separately.

Each of the QC materials was measured with the Spark-OES and the results were compared to the limits determined by the FML results. It was observed that analytes that failed the lower QC standard (2 $mg.kg^{-1}$) did

not always fail the high QC standard (20 $mg.kg^{-1}$). The platinum matrix had many more failures than for the other two matrices. 68% of the analytes in the platinum matrix failed. The elements that failed both standards in the Pd matrix: gold, silver, arsenic and selenium. Selenium and arsenic results were lower than the detection limit for both QCs. The same channels are used in all three matrices. It performed well with the platinum and rhodium matrices. So the lower results were ascribed to the palladium matrix. This can only be verified at the factory with specialized instruments.

6.5 BIAS

The bias or systematic error of the method was evaluated by comparing results obtained by Spark-OES to those obtained by ICP-OES (the method routinely used in the FML). Routine samples were analyzed using both methods, over a short period, to establish the bias. Data is being collected to determine a more “long-term” bias. Both sponge and metal samples of platinum and palladium matrices were submitted for analysis. The two sets of results for the different samples were evaluated for bias. Rhodium samples were only submitted as sponge samples.

The standard deviations between the two sets of data were evaluated. This was done to decide whether the variance between the two instruments was greater than the variance obtained using Spark-OES analysis. An analysis of variance (ANOVA) could not be done since different samples of different concentrations were used. The variance within and between laboratories would seem higher than they actually were. The standard deviations were plotted against the concentration of the samples to establish if the error was dependent on concentration.

Elements with poor precision (high standard deviations for reproducibility) were plotted, for the platinum matrix (Figure 6.8). It shows that there was

no trend between the bias standard deviation and the concentration of the sample. The standard deviation obtained for the bias analysis was lower than that obtained for the reproducibility analysis for elements in the plot. This suggested that the acceptable limits between the two instruments and the limits acceptable for replicate analysis should not be very different. It was repeated for palladium and rhodium matrices. Only the elements with a high standard deviation for reproducibility were used.

The bias standard deviation for palladium metal increased for a very short range, suggesting a correlation between concentration and standard deviation. Since most of the samples were of similar concentration, there was insufficient data to make a conclusion. Because of the increasing trend of the standard deviation, the bias standard deviation was larger than the reproducibility standard deviation.

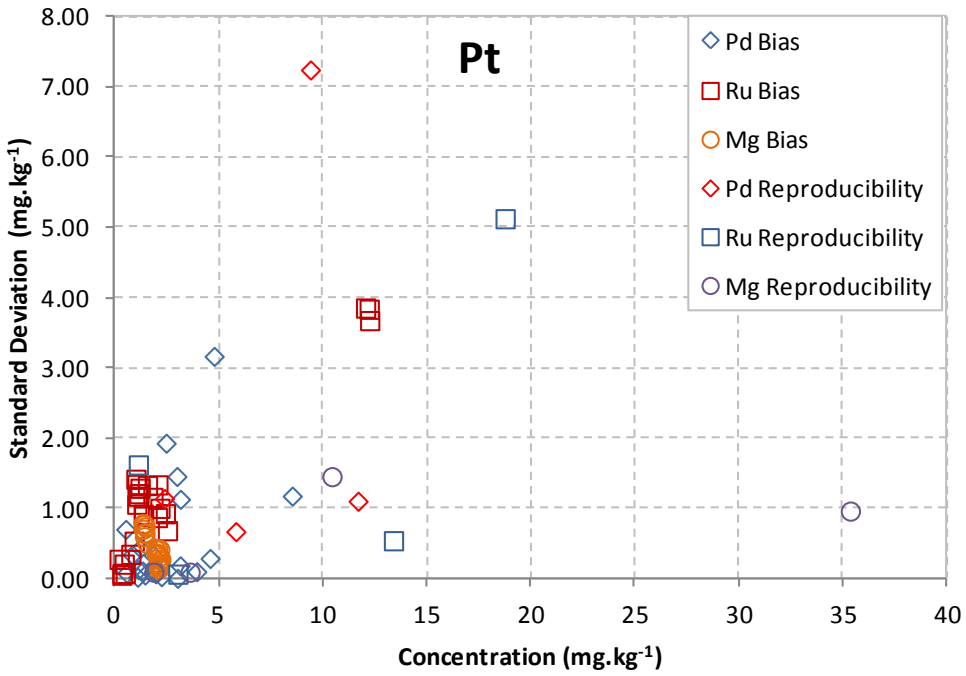


Figure 6.8: Standard deviation between ICP-OES and Spark-OES (bias) and the reproducibility standard deviation against grade for platinum metal

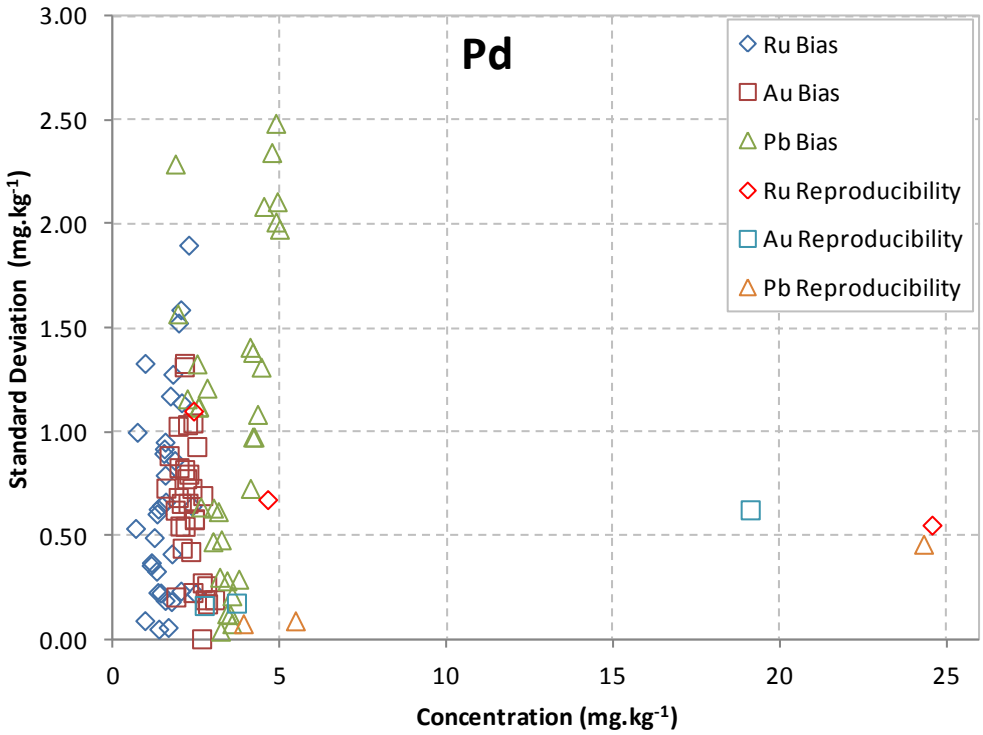


Figure 6.9: Standard deviation between ICP-OES and Spark-OES (bias) and the reproducibility standard deviation against grade for palladium metal

The standard deviation between different instruments and standard deviations of the same samples over a long period (using different conditions) are depicted in Figure 6.10. The standard deviations obtained for the rhodium matrix were generally very high. It suggests very poor agreement between the two methods. It can be seen that ruthenium still showed excessively high standard deviations. None of the analytes exhibited dependency of the standard deviation on the concentration of the sample. Platinum and iridium bias standard deviations are higher than the standard deviation for reproducibility. Although expected, it was not ideal. The standard deviations obtained between the two methods for ruthenium and platinum did not follow the expected trend. It suggests that one of the calibrations may not be fit for the analyses.

Since the calibration of ruthenium in rhodium failed to meet the calibration evaluation criteria, the Spark-OES method was not deemed fit for purpose for the determination of Ru in rhodium. Of all the analytes in rhodium, only 17 of the 30 elements had standard deviations of less than 5 for the samples analyzed, showing poor comparison between the two methods.

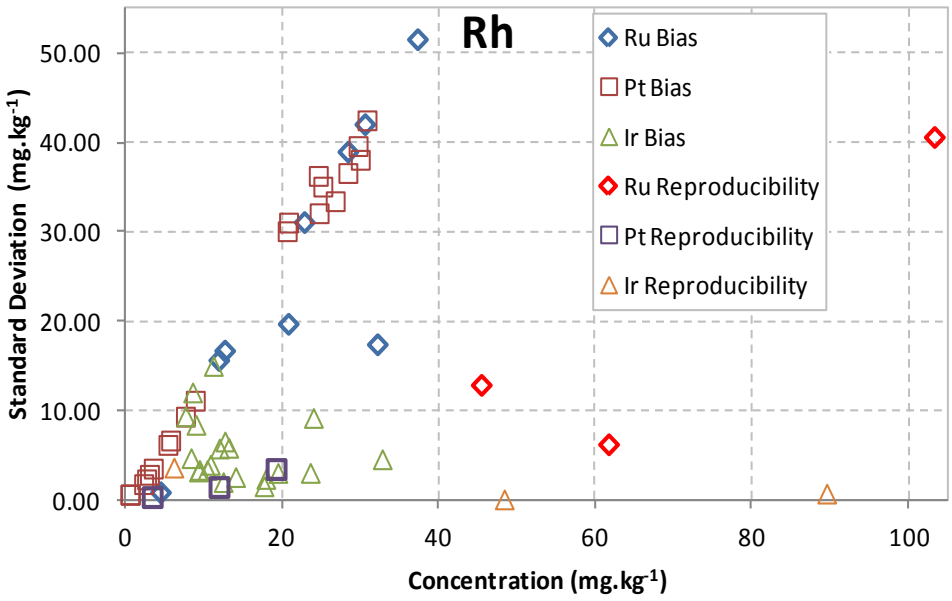


Figure 6.10: Standard deviation between ICP-OES and Spark-OES (bias) and the reproducibility standard deviation against grade for rhodium metal

6.6 MEASUREMENT UNCERTAINTY

The measurement uncertainty of the method was estimated using the following equation:

$$U = \sqrt{\%RSD^2 + \%RBias^2} \qquad (6.1)$$

The %RSD is the error in measurement obtained from the precision, repeatability and reproducibility of the method. The %RBias is the relative

percentage bias of the analysis. This was used to incorporate all factors that might affect the uncertainty in measurement in the estimate of reproducibility of the method. Using this method, all possible uncertainties are included. No trend was seen on any of the uncertainty data so uncertainty was calculated using all elements.

The bias term was calculated using the difference between the ICP-OES and Spark-OES results from the FML laboratory. Production samples, with concentrations of the analytes typically less than the detection limit, were originally used for this calculation. However, the bias values were considered too high because of the possible error. A better indication of the bias was obtained from the calibration standards. These were analyzed as unknowns and the results from the Spark-OES were compared with the FML ICP-OES results. The calibration standards cover a wider range than the production samples. The ICP-OES results used were averages taken over a period of time. It was believed to give a better indication of the bias between the two methods. The results are presented in Table 6.2.

Analytes not determined by ICP-OES at FML are reported as “na” on the table, “not analysed”. Analytes where the uncertainty were greater than 50% and had expanded uncertainties greater than 100% are written in red. Statistically, these analytes should be reported as 100% error which would imply there is no confidence in the results.

Analytes which had expanded uncertainties over 100% in the platinum matrix were the following: ruthenium, vanadium and molybdenum. In the palladium matrix it was: rhodium, aluminium, zirconium and selenium while in the rhodium matrix was: tin, cobalt, selenium and cadmium.

Table 6.3: Measurement uncertainty in relative percentage difference

Analyte	Pt		Pd		Rh	
	Unexpanded	Expanded	Unexpanded	Expanded	Unexpanded	Expanded
Pt	M	M	20.8	41.6	17.5	34.9
Pd	42.9	85.9	M	M	16.6	33.3
Rh	27.3	54.6	61.4	122.7	M	M
Ir	35.8	71.6	19.3	38.5	1.8	3.5
Ru	54.4	108.7	21.9	43.7	26.3	52.5
Os	14.1	28.2	20.0	39.9	9.9	19.8
Au	11.3	22.6	7.0	14.0	7.5	15.0
Ag	7.4	14.9	10.6	21.3	13.0	25.9
Cu	14.1	28.1	4.2	8.4	15.1	30.2
Ni	34.9	69.9	13.6	27.1	30.5	61.1
Fe	13.7	27.5	11.5	22.9	3.9	7.7
Pb	7.4	14.8	4.3	8.6	23.5	46.9
Mg	6.8	13.6	8.4	16.9	19.5	39.0
Mn	4.0	8.0	13.7	27.5	14.4	28.8
Si	8.6	17.1	2.4	4.7	na	na
Al	21.3	42.6	58.2	116.4	19.6	39.3
Sb	17.9	35.7	9.7	19.3	16.0	32.0
Cr	6.6	13.2	3.6	7.3	5.6	11.3
Sn	19.9	39.9	20.1	40.2	69.3	138.6
Ti	29.7	59.3	32.8	65.5	15.1	30.2
Zr	20.9	41.8	56.9	113.8	26.7	53.4
Ca2	17.0	33.9	20.7	41.4	14.0	28.1
Zn	43.0	85.9	6.6	13.2	27.2	54.4
B	18.9	37.7	9.2	18.4	na	na
Co	17.5	35.0	24.1	48.1	144.0	288.1
V	55.9	111.9	9.0	18.1	11.7	23.3
Mo	50.5	101.0	18.6	37.2	10.6	21.2
Bi	20.1	40.1	7.4	14.8	19.9	39.8
As	12.1	24.1	23.9	47.8	6.5	13.1
Se	22.4	44.7	101.8	203.6	183.2	366.5
Te	29.1	58.3	12.4	24.9	18.5	37.1
Cd	11.7	23.4	44.2	88.5	126.5	253.0

It was observed that the greatest contributor to a high uncertainty in the platinum and palladium matrix was the reproducibility term. The exception was selenium in the palladium matrix. The bias term here was the greatest contributor to uncertainty. The repeatability term may be improved by using a longer term reproducibility of the methods or by evaluating the reproducibility of more samples, particularly those with high concentrations. For rhodium matrix analytes, the high uncertainties resulted mainly from the bias term. The bias term, which is a comparison of the two techniques, is a reflection of the analytical programme used for the analysis. This can only be improved upon by using better calibration standards.

The uncertainties are reported as relative percentage difference in Table 6.2. Although the values appear high, for the low concentrations of the analytes, the absolute values of the uncertainty of the measurement were relatively low. To illustrate this, the uncertainties associated with 5 $mg.kg^{-1}$ are tabulated in Table 6.3.

Table 6.4: Uncertainty of results for 5 mg.kg^{-1}

Analyte	Pt		Pd		Rh	
	Unexpanded	Expanded	Unexpanded	Expanded	Unexpanded	Expanded
Pt	M	M	1.04	2.08	0.87	1.75
Pd	2.15	4.29	M	M	0.83	1.66
Rh	1.36	2.73	3.07	6.14	M	M
Ir	1.79	3.58	0.96	1.93	0.09	0.18
Ru	2.72	5.44	1.09	2.19	1.31	2.63
Os	0.70	1.41	1.00	2.00	0.49	0.99
Au	0.57	1.13	0.35	0.70	0.38	0.75
Ag	0.37	0.74	0.53	1.06	0.65	1.30
Cu	0.70	1.41	0.21	0.42	0.76	1.51
Ni	1.75	3.49	0.68	1.36	1.53	3.05
Fe	0.69	1.37	0.57	1.15	0.19	0.39
Pb	0.37	0.74	0.21	0.43	1.17	2.35
Mg	0.34	0.68	0.42	0.84	0.98	1.95
Mn	0.20	0.40	0.69	1.37	0.72	1.44
Si	0.43	0.86	0.12	0.24	na	na
Al	1.07	2.13	2.91	5.82	0.98	1.96
Sb	0.89	1.79	0.48	0.97	0.80	1.60
Cr	0.33	0.66	0.18	0.36	0.28	0.56
Sn	1.00	1.99	1.00	2.01	3.47	6.93
Ti	1.48	2.97	1.64	3.28	0.76	1.51
Zr	1.05	2.09	2.84	5.69	1.34	2.67
Ca2	0.85	1.70	1.04	2.07	0.70	1.40
Zn	2.15	4.30	0.33	0.66	1.36	2.72
B	0.94	1.89	0.46	0.92	na	na
Co	0.88	1.75	1.20	2.41	7.20	14.40
V	2.80	5.59	0.45	0.90	0.58	1.17
Mo	2.53	5.05	0.93	1.86	0.53	1.06
Bi	1.00	2.01	0.37	0.74	1.00	1.99
As	0.60	1.21	1.20	2.39	0.33	0.65
Se	1.12	2.24	5.09	10.18	9.16	18.32
Te	1.46	2.91	0.62	1.24	0.93	1.85
Cd	0.58	1.17	2.21	4.42	6.32	12.65

6.7 DISCUSSION

The precision of the method was assessed for both repeatability and reproducibility using the standard deviations of the samples. The precision of the method is an important performance characteristic. It affects both the sensitivity of the method and the uncertainty of the result.

The precision of the three methods (analysis of platinum, palladium and rhodium) was satisfactory. However it was observed that ruthenium had poor precision in all the matrices. The extremely poor precision (both repeatability and reproducibility) for the determination of ruthenium in rhodium meant that there is little confidence in the results. The uncertainty of the results will be very high. Statistically, values with a %RSD (uncertainty) greater than 50% should not be reported. The %RSD for precision for ruthenium in rhodium was less than 50% for all samples. For the reproducibility of analysis; only the sponge sample had a %RSD of less than 50%. Thus, the results for ruthenium in rhodium metal samples should not be reported. The uncertainty of these results would be too large.

The results indicated that the method was not robust towards the different sample preparation techniques. There was insufficient data to establish whether or not the method can be used for analysis of melted samples. Thus, sponge samples are to be analyzed as pressed pellets for all matrices. From the large difference in results of sample preparation techniques, it can be deduced that the melting procedure was inconsistent (between melts). The effect of minor changes in the method (which were incorporated in the reproducibility determination) can have an insignificant effect on the results. The exceptions are mentioned in the evaluation of the reproducibility of the method.

The bias between the two methods showed a poor comparison between the methods particularly for rhodium. Despite this, tolerance limits between the two methods was kept the same as the tolerance limits between replicates. This could be achieved with the platinum matrix and further optimization of the Spark-OES method should result in better comparisons between the two methods.

From the measurement uncertainty there were a few elements (5 elements in platinum, 4 elements in palladium and 4 elements in rhodium) that had uncertainties of over 50% and expanded uncertainty of 100%. Although some elements might not have met other validation parameters, the uncertainty and accuracy of the results of are greater importance. The accuracy was evaluated using an in-house prepared standard material, not a CRM, which is not traceable to an SI unit. This was done using averages and limits obtained by ICP-OES. It was validated by other laboratories. The achieved accuracy was considered satisfactory, taking into account the difference between the two techniques. The low-range QC, where the typical samples are analyzed, performed well in all metals. The high QC had more values outside the limits. This was particularly true for platinum where 68% of the analytes failed. The use of segmented calibration curve should be considered to improve the accuracy of the platinum determination at higher levels.

CHAPTER 7
QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

7.1 INTRODUCTION

The integrity of any chemical measurement depends on the level of confidence in the results. Clause 4.2.1 of ISO/IEC 17025:2005 states that "any test laboratory shall establish, implement and maintain a quality system appropriate to the scope of its activity" (ISO Committee, 2005).

The Quality Assurance (QA) principle has been adopted with increased frequency as a concerted measure to ensure that data produced in the laboratory is fit for its intended purpose. These procedures do not actually guarantee the quality of the data produced (CITAC/ EURACHEM GUIDE to Quality in Analytical Chemistry, 2002). While QA refers to the overall measures taken to ensure the quality of the results, Quality Control (QC) is used to describe individual measures taken. An internal quality control system (IQC) is therefore, the final check of the correct execution of all procedures prescribed in the analytical protocol (Thompson & Wood, 1995).

An IQC traditionally depends on two strategies; the analysis of reference material (preferably CRM) to monitor accuracy, and duplication to monitor precision. Quality control procedures typically include the analysis of (Simonet, 2005):

- reference/materials measurement standards (CRM);
- " blind" samples;
- QC samples and control charts;
- blanks;
- spiked samples;
- duplicates; and,

- proficiency.

This chapter details the quality system to be followed to ensure the accuracy of the results during the Spark-OES analysis. The quality control material, their preparation and validation are also discussed.

7.2 INTERNAL QUALITY CONTROL PROCEDURES

The CITAC/EURACHEM guide to quality in analytical chemistry states that each laboratory must operate an appropriate level of IQC checks and participate, wherever possible, in appropriate proficiency testing schemes. The IQC checks and the quality principles followed in this study were developed to achieve the following objectives:

- To quantify accuracy through the determination of bias and precision.
- To put systems in place that maximizes the quality of results.

The IQC checks employed in this study included:

- Instrument monitors,
- Matrix-matched reference materials and control charts,
- Replicate analysis.
- Twin-stream analysis.
- 10% checks.
- Proficiency testing.

7.2.1 INSTRUMENT MONITORING

To ensure accurate analysis from the instrument, there are parameters which need to be monitored and controlled. The limits for these are obtained from the manufacturer and ensure the optimum working

conditions of the instrument. The parameters to be monitors on the ARL 4460 are given in Table 7.1. The status of the instrument, with regards to these parameters, is to be recorded at the beginning of every shift. WinOE software checks these parameters before the analysis of every sample but does not display the values for anyone to see. Only warning or fatal alarms are displayed in the event of any of the parameters being out of limits (Freed, 2009). The vacuum level and spectrometer temperatures are the two parameters that will substantially affect the results.

Table 7.1: Description of the parameters to be monitored on the ARL 4460

Parameter	Description
Mains	The main power supply to the instrument. Instrument will not start if outside limits.
Neg 1kV	Power supply to attenuators and PMTs. It converts light to electrical signal at the PMTs.
CTemp	Cabinet and electronics temperature.
STemp	Temperature of the spectrometer. Measures the mechanical stability of the instrument. Would move entrance and exit slits off peak.
Vacuum	Vacuum in spectrometer, used to evacuate air.
Pos volts	Power supply to electronics
Neg 100V	Reference voltage for PMTs. The first dynode of PMT is kept at -100 V.
CCS	Current control source to stand. Does not affect operation of instrument

Another factor that could affect the measurement is the height of the electrode. An electrode that is too far from the sample can cause reduction of plasma temperature and the degree of ablation of the sample, resulting in lower intensities. An electrode height adjustment tool is supplied with the instrument. The height of the electrode needs to be adjusted after changing the spark stand and as the electrode becomes worn. The tip of the electrode needs to be assessed continually and renewed when blunt.

7.2.2 MATRIX-MATCHED REFERENCE MATERIALS AND CONTROL CHARTS

The accuracy of measurements is evaluated by the use of quality control standards (QC) with certified values for all the elements of interest. The QC match the matrix and grade of the material being analyzed. Due to the commercial unavailability of such material, in-house QC standards were manufactured. Two QC materials were used: one for monitoring the preparation procedure (natural QC or NQC) and the other for monitoring the instrument (instrument QC or IQC).

The IQC materials were prepared by spiking and melting a bulk sample (250 g). The standards were analyzed by Spark-OES and ICP-OES at the FML and sent to two other laboratories using Spark-OES for the assignment of consensus values.

Preparation of QC material

The preparation of QC material consisted of two vital components: preparation and its certification. According to ISO/IEC 17025:2005 (ISO Committee, 2005), the preparation should be carried out by a Competent Person or Organization, provided procedures for preparation exist. Sufficient proof of homogeneity and that the QCs are appropriate can be provided. The standard also states that certification should be done by an

independent, competent, professional person or organization, preferably accredited to the ISO Guide 43. Since such an Organization is not currently present in South Africa, quality control materials were prepared in-house and were validated but not certified.

A base metal (m-mix), separate from that prepared for calibration standards, was prepared for the making of quality control (QC) standards. This was prepared by weighing each base metal oxide composite group separately in accordance to their certified mass percentages. A QC with a m-mix of analytes with concentrations in the same order of magnitude resulted. 1 g of Group A composite, 1 g of Group B composite, 0.65 g of Group C composite, 0.26 g of SiO_2 and 0.7 g analytical grade graphite were accurately weighed (to four decimals) into a separate sample bottle. The graphite was added as a diluent as the m-mix was used for all matrices. These were mixed for 15 min using a Retsch MM301 mixer mill at 25 Hz using 7 mm polyamide mixing balls.

Preparation

A typical test material with known levels of impurities was selected from in-house prepared material as the matrix (blank). The matrix was spiked with both base metals and PGM m-mixes. The same m-mix used for the preparation of calibration standards. Two IQCs (2 ppm and 20 ppm) were prepared to cover the analytical range of the calibration. 0.014 ± 0.0005 g of the PGM master mix and 0.08271 ± 0.0005 g of the base metal was added to 100 g of matrix for the 20 ppm QC, while 0.0014 ± 0.0005g and 0.0083 ± 0.0005 g of the two matrices, respectively, were added to 100 g matrix for the 2 ppm QC material. The melting was done using the ICON IRM, according to the optimum melting conditions for each matrix.

Assignment of true values

The quality control materials were assigned true values for analysis for all elements of interest (Thompson and Wood, 1995). The first sets of QC material prepared were analyzed by the FML and sent to two of the laboratories used for the assignment of the consensus values for calibration standards (Impala and Lonmin final metal's laboratory). The results obtained were evaluated for outliers using the Grubb's test. Since Spark-OES has a high LOD and poor sensitivity compared to the ICP-OES, most of the analytes determined were below the detection limits for the two laboratories used. To also avoid validating Spark-OES by Spark-OES, the results obtained by ICP-OES at FML were assigned the standard values and the results from the other laboratories were used to validate the results.

The results were validated by conducting a paired t-test of each laboratory's result against the FML results. To evaluate if there is a statistically significant difference between the two laboratories, each laboratory's results were compared separately to the results from FML. The following hypothesis was done:

> **H_0**: $t_{calc}<t_{crit}$: there is no statistically significant difference between the results
>
> **H_1**:$t_{calc}<t_{crit}$:there is statistically significant difference between the results

A paired t-test uses ratio of the average difference between the two results and the standard deviation of the difference and compares that to a critical value. The t_{calc} is calculated as follows (De Beer, 2006):

$$t_{calc} = {|\bar{x}_d|\sqrt{n}}/{s_d} \qquad (7.1)$$

From the equation it can be seen that if the standard deviation of the differences is small or the mean of the difference between the samples is large, the sample might still fail the t-test.

The t-test results are summarized in Tables 7.2 – 7.2. Analytes which have "0" for the t_{calc} value were not analysed by the laboratory with which the FML results were compared. Silicon in rhodium was not reported by FML, thus no could be done between Lab A and Lab B.

For most of the elements in all matrices $t_{calc}>t_{crit}$, therefore the null hypothesis is rejected. This implies that there is a statistically significant difference between the results obtained at FML and the other laboratories. It was taken into consideration that, particularly for the 2 $mg.kg^{-1}$, most of the analytes were below the LOD and therefore, had a standard deviation of zero. Due to the limitation of the t-test, a second method was used to determine if the difference was statistically significant.

The overlap between confidence intervals, (either using confidence intervals or standard errors) of all the laboratories was used for the determination of the statistical significance of the difference between the results. This method is based on the Student t-test method which compares the data ratio to the standard error. This method is widely used. However, it has limitations. Schenker and Gentleman (2001) argue that the method of overlap of confidence intervals should not be used for "formal significance testing" unless the analyst is aware of its deficiencies. The major deficiency of this method is that the 95% confidence intervals used are often too wide (Payton et al., 2003). Thus, it fails to reject the null hypothesis more frequently. However, the rejection of the null hypothesis implies rejection by the "standard method" (Schenker & Gentleman, 2001).

Table 7.2: Paired t-test results for platinum QC materials

Analyte	2 mg.kg^{-1}				20 mg.kg^{-1}			
	LAB A		LAB B		LAB A		LAB B	
	t_{calc}	t_{crit}	t_{calc}	t_{crit}	t_{calc}	t_{crit}	t_{calc}	t_{crit}
Pd	14.0	2.2	17.9	2.3	3.9	2.2	1.1	2.3
Rh	1.7	2.2	5.3	2.3	6.1	2.2	4.4	2.3
Ir	2.5	2.2	1.0	2.3	4.2	2.2	8.0	2.3
Ru	2.3	2.2	8.4	2.3	8.2	2.2	7.7	2.3
Os	11.3	2.2	2.2	2.3	29.1	2.2	8.5	2.3
Au	13.4	2.2	11.2	2.3	11.5	2.2	0.9	2.3
Ag	12.8	2.2	10.8	2.3	25.7	2.2	7.3	2.3
Cu	14.3	2.2	47.1	2.3	46.4	2.2	7.0	2.3
Ni	3.0	2.2	3.0	2.3	51.2	2.2	0.9	2.3
Fe	1.9	2.2	2.2	2.3	2.4	2.2	5.7	2.3
Pb	8.1	2.2	1.9	2.3	28.8	2.2	1.5	2.3
Mg	1.1	2.2	2.3	2.3	4.1	2.2	20.8	2.3
Mn	5.8	2.2	8.6	2.3	56.2	2.2	12.2	2.3
Si	17.8	2.2	12.9	2.3	12.9	2.2	8.2	2.3
Al	0.7	2.2	1.5	2.3	2.7	2.2	16.3	2.3
Sb	45.1	2.2	36.2	2.3	27.8	2.2	21.4	2.3
Cr	19.1	2.2	16.3	2.3	27.9	2.2	14.5	2.3
Sn	3.2	2.2	0.1	2.3	16.0	2.2	16.7	2.3
Ti	17.6	2.2	9.0	2.3	51.2	2.2	40.9	2.3
Zr	4.1	2.2	6.5	2.3	4.9	2.2	13.7	2.3
Ca	1.2	2.2	0.9	2.3	1.3	2.2	1.8	2.3
Zn	2.7	2.2	17.8	2.3	6.3	2.2	3.0	2.3
B	4.6	2.2	1.6	2.3	7.7	2.2	14.1	2.3
Co	9.0	2.2	19.1	2.3	13.0	2.2	5.6	2.3
V	25.8	2.2	0.0	2.3	11.4	2.2	0.0	2.3
Mo	6.4	2.2	2.0	2.3	23.2	2.2	18.7	2.3
Bi	0.6	2.2	7.6	2.3	3.5	2.2	8.0	2.3
As	6.8	2.2	4.1	2.3	4.4	2.2	16.7	2.3
Se	0.0	2.2	0.0	2.3	0.0	2.2	0.0	2.3
Te	5.1	2.2	0.0	2.3	10.2	2.2	13.4	2.3
Cd	5.9	2.2	5.9	2.3	87.4	2.2	10.6	2.3

Table 7.3: Paired t-test results for palladium QC materials

Analyte	2 mg.kg^{-1}				20 mg.kg^{-1}			
	LAB A		LAB B		LAB A		LAB B	
	t_{calc}	t_{crit}	t_{calc}	t_{crit}	t_{calc}	t_{crit}	t_{calc}	t_{crit}
Pt	3.8	2.2	3.3	2.3	6.4	2.2	2.0	2.3
Rh	27.7	2.2	23.0	2.3	31.2	2.2	81.5	2.3
Ir	16.3	2.2	8.1	2.3	9.4	2.2	13.1	2.3
Ru	9.5	2.2	19.9	2.3	3.7	2.2	8.0	2.3
Os	14.5	2.2	0.3	2.3	12.9	2.2	3.9	2.3
Au	15.9	2.2	13.8	2.3	6.8	2.2	28.8	2.3
Ag	33.3	2.2	28.6	2.3	22.4	2.2	19.7	2.3
Cu	16.7	2.2	150.9	2.3	10.6	2.2	65.2	2.3
Ni	20.5	2.2	15.6	2.3	0.8	2.2	8.5	2.3
Fe	27.1	2.2	20.6	2.3	12.5	2.2	15.2	2.3
Pb	7.9	2.2	6.2	2.3	5.1	2.2	5.2	2.3
Mg	13.6	2.2	12.4	2.3	21.1	2.2	31.8	2.3
Mn	13.1	2.2	9.1	2.3	7.1	2.2	16.1	2.3
Si	0.4	2.2	1.8	2.3	1.1	2.2	0.5	2.3
Al	2.4	2.2	32.0	2.3	11.3	2.2	21.6	2.3
Sb	15.4	2.2	13.1	2.3	31.1	2.2	11.1	2.3
Cr	1.7	2.2	5.0	2.3	2.5	2.2	4.9	2.3
Sn	3.2	2.2	1.4	2.3	1.4	2.2	21.5	2.3
Ti	29.8	2.2	11.7	2.3	21.0	2.2	8.3	2.3
Zr	14.9	2.2	0.0	2.3	18.3	2.2	0.0	2.3
Ca	2.3	2.2	2.4	2.3	10.1	2.2	12.6	2.3
Zn	6.1	2.2	6.5	2.3	9.7	2.2	7.4	2.3
B	8.1	2.2	0.0	2.3	11.6	2.2	0.0	2.3
Co	9.8	2.2	2.8	2.3	7.0	2.2	9.3	2.3
V	6.7	2.2	0.0	2.3	3.3	2.2	0.0	2.3
Mo	1.6	2.2	4.4	2.3	0.4	2.2	8.3	2.3
Bi	6.2	2.2	3.4	2.3	5.7	2.2	7.0	2.3
As	5.1	2.2	3.0	2.3	11.9	2.2	2.0	2.3
Se	0.0	2.2	0.0	2.3	0.0	2.2	0.0	2.3
Te	10.0	2.2	1.1	2.3	21.6	2.2	0.0	2.3
Cd	15.5	2.2	5.9	2.3	16.6	2.2	0.5	2.3

Table 7.4: Paired t-test results for rhodium QC materials

Analyte	2 mg.kg^{-1}				20 mg.kg^{-1}			
	LAB A		LAB B		LAB A		LAB B	
	t_{calc}	t_{crit}	t_{calc}	t_{crit}	t_{calc}	t_{crit}	t_{calc}	t_{crit}
Pt	4.2	2.2	4.1	2.3	3.8	2.2	2.7	2.3
Pd	0.0	2.2	12.5	2.3	27.7	2.2	10.0	2.3
Ir	67.9	2.2	65.6	2.3	16.3	2.2	51.6	2.3
Ru	1.7	2.2	0.9	2.3	9.5	2.2	5.0	2.3
Os	17.9	2.2	0.0	2.3	14.5	2.2	8.3	2.3
Au	0.9	2.2	1.6	2.3	15.9	2.2	20.4	2.3
Ag	2.3	2.2	24.6	2.3	33.3	2.2	11.9	2.3
Cu	8.3	2.2	12.6	2.3	16.7	2.2	65.1	2.3
Ni	12.9	2.2	0.2	2.3	20.5	2.2	60.6	2.3
Fe	7.1	2.2	3.0	2.3	27.1	2.2	45.0	2.3
Pb	31.2	2.2	6.1	2.3	7.9	2.2	20.7	2.3
Mg	2.4	2.2	2.1	2.3	13.6	2.2	14.3	2.3
Mn	5.4	2.2	4.5	2.3	13.1	2.2	0.4	2.3
Si	0.0	2.2	0.0	2.3	0.0	2.2	0.0	2.3
Al	2.8	2.2	16.5	2.3	2.4	2.2	87.0	2.3
Sb	1.4	2.2	3.0	2.3	15.4	2.2	14.6	2.3
Cr	4.0	2.2	21.5	2.3	1.7	2.2	20.6	2.3
Sn	5.5	2.2	2.5	2.3	3.2	2.2	13.0	2.3
Ti	3.2	2.2	19.0	2.3	29.8	2.2	8.7	2.3
Zr	2.3	2.2	0.0	2.3	14.9	2.2	1.4	2.3
Ca	0.8	2.2	0.6	2.3	2.3	2.2	2.4	2.3
Zn	3.3	2.2	0.0	2.3	6.1	2.2	6.5	2.3
B	0.0	2.2	0.0	2.3	8.1	2.2	0.0	2.3
Co	20.5	2.2	8.5	2.3	9.8	2.2	2.8	2.3
V	10.5	2.2	0.0	2.3	6.7	2.2	0.0	2.3
Mo	4.6	2.2	39.7	2.3	1.6	2.2	4.4	2.3
Bi	6.2	2.2	1.7	2.3	6.2	2.2	3.4	2.3
As	2.1	2.2	3.9	2.3	5.1	2.2	3.0	2.3
Se	0.0	2.2	0.0	2.3	0.0	2.2	0.0	2.3
Te	3.6	2.2	3.6	2.3	10.0	2.2	1.1	2.3
Cd	6.0	2.2	0.0	2.3	15.5	2.2	5.9	2.3

Payton *et al*. recommend that for a method has to be used a probability of generally around α = 0.15 to 0.17 should be used for the calculation of the confidence interval.

The confidence interval for all samples with a probability of α = 0.15 were calculated and evaluated for overlap. The confidence interval was calculated as follows (De Beer, 2006):

$$CL\ of\ x: x = x \pm t_{DF;0.15} s_x \qquad (7.2)$$

Where:

$t_{DF;0.15}$ = t critical value

DF = degrees of freedom (n-1, where n is the number of replicates)

s_x is determined as follows:

$$s_{x0} = \frac{S_{y/x}}{b}\left\{\frac{1}{m} + \frac{1}{n} + \frac{(y_0 - \bar{y})^2}{b^2 \sum_i (x_i - \bar{x})^2}\right\}^{1/2} \qquad (7.3)$$

Where:

s_{x0} = uncertainty in unknown sample

$S_{y/x}$ = random calibration uncertainty

m = number of measurements of unknown

n = number of calibration standards

b = slope of calibration

y_0 = instrument response for unknown sample

$\bar{y}$ = average instrument response of calibration standards

x_i = intensity of calibration standards from 1, 2, …, i

$\bar{x}$ = average concentration of calibration standards

Payton et al. (2003) argued that the use of standard error should give the opposite effect of using 95% confidence intervals. That is, it leads to the rejection of the null hypothesis more often. Since the calibration data from the other laboratories could not be obtained. The results were only submitted with standard error and not the uncertainty, the comparison of standard error overlap was used. It was observed upon the evaluation of the overlap that most of the elements that failed were those with a standard error of zero.

The limits for the QC material were assigned as twice the sd of FML results for the warning limits and three times the sd as action limits. QC values outside of the action limits were not reported and the analysis was repeated, while values between the warning and action limits were to be investigated.

Because of the observed difference between the different laboratories and the techniques used at these laboratories, this method was selected to evaluate if the results obtained at FML agree with other laboratories.

Natural QC

A natural QC (NQC) (a quality control material used for the monitoring of the sample preparation process) was introduced to be used alongside the internal reference material. The existing FML method of preparation of this QC was not amended. The NQC's in use in the laboratory was adopted. This gave a better indication of the performance of the laboratory and the same QC was used for all methods in a laboratory. The NQC is a typical test material, distributed to different laboratories for analysis. The material was then analysed against ultra-pure certified materials and the results, together with those from the other laboratories was used for the assignment of average values and limits.

The NQC is prepared alongside test material, following the same process as the samples and using the same equipment. This is done to monitor if any changes that might occur during sample preparation had an effect on the results. Care had to be taken to ensure that the NQC was treated and prepared in exactly the same way as the test material.

The procedure to assign values for the NQCs was slightly different to that used for the QC material. Since the NQC is made from a typical sample, most of the analytes are reported below the LOD (typically 2 $mg.kg^{-1}$) for the laboratories participating in the validation. The consensus value was therefore, determined by analyzing the material against the certified ultra-pure material. The results from the other laboratories were used to validate the determined values by evaluating if they fell within the 95% confidence limit of the calculated values. The materials were assigned ±2 x sd warning limits and ±3 x sd action limits, where sd = intra-laboratory sd. The pooled standard deviation (inter-laboratory standard deviation) was not used as only results from one laboratory were applied for the determination of the actual limits.

7.2.3 REPLICATE ANALYSIS

Replicate analyses are employed to give an indication of the precision of the laboratory (intra-laboratory). Precision is the proximity of agreement between independent test results under specified conditions, and hence depends only on the distribution of random errors. It is measured as standard deviation (sd) and is expressed as % Relative Standard Deviation (%RSD).

For every batch of samples that is analysed, one sample should be analysed in duplicate. If the batch contains more than 12 samples, then a duplicate should be analysed after every 12 samples. This sample is to be

selected randomly. A separate pellet of the sample should be prepared. The relative percentage difference between the duplicates was plotted against the concentration (the average of the results) to establish if it was grade dependent.

If the relative percentage difference was not concentration dependent, the average of the relative percentage difference was to be used to determine the uncertainty (absolute ± values) of the determination. In the case where the relative percentage difference was concentration dependent, a curve was fitted to the data. The Thompson-Howarth approach which relates the error between the splits and the concentration of the material was used to determine uncertainty. The uncertainty is a factor of the instrument precision, and can be used to determine the allowable limits between replicates analysis.

7.2.4 TWIN STREAM ANALYSIS

Twin stream analysis is carried out to minimize the risk of handling errors. This analysis includes the preparation of samples by different analysts on the same day or different days. Therefore, each sample is to be analyzed by both ICP-OES and Spark-OES. The samples are to be prepared for Spark-OES by one analyst and the analysis carried out on the arrival of the samples. The same sample is to be prepared for ICP-OES by wet digestion, while the Spark-OES analysis is being carried out, and the sample analysed by ICP-OES.

The results are to be compared, and only reported if they pass the intra-lab limits (splitting limits). If the results pass the limits, an average of the two is to be reported. In the case where the results are outside the splitting limits, the sample should be re-analyzed. The splitting limits are calculated

in a similar manner as the replicate analysis splitting limits, but using the results from the two different instruments for the calculation instead.

7.2.5 TEN PERCENT CHECKS

The analysis of 10% of all the samples at a primary laboratory was used as a check. It was sent to an independent laboratory (secondary laboratory) for analysis. The percentage was determined by the site. The sampling manual suggests the use of 10% for a representative sample. Thus 10% was selected by Anglo Platinum Group Evaluation and Metal Accounting (Woollam, 2006). The performance of the method was evaluated by the extent of the bias between the two laboratories.

The relative percentage difference in results from the two laboratories is checked against the inter-lab limits. The inter-lab splitting limits are calculated with the same method as that for the intra-lab splitting limits, using the data that was collected over a substantial period.

The relative percentage differences were plotted on Shewhart charts to visually monitor the bias. To quantify the bias the average percentage bias between the labs was calculated as follows (Woollam, 2006):

$$PL - SL/(PL - SL/2) \times 100 \qquad (7.4)$$

Where
PL = average of primary laboratory
SL = average of sample for the secondary laboratory
To evaluate the significance of the bias, limits are determined as the intra-site limits divided by the square root of n, n being the number of paired results.

7.2.6 PROFICIENCY TESTING

A proficiency testing for the analysis of impurities in platinum, palladium and rhodium metal was implemented. The scheme was used to monitor the laboratory's performance through the statistical evaluation of the results obtained from all the laboratories involved.

Laboratories included in the scheme were those that are equipped to do the analyses of impurities in pure PGMs. These laboratories were required to demonstrate their ability to perform the analysis, by the presentation of either their certification (from a certifying body like ISO) or by presenting a validated method of analysis. The final metals laboratories of the other two leading PGM refining companies in the country, Impala and Western Platinum, were contracted.

Each laboratory sent one sample of their normal test material of each of the matrix (platinum, palladium and rhodium) to the participating laboratories. The proficiency testing was done on these. The test materials were collected on a quarterly basis. Each laboratory employed the method of analysis used for production purposes. The methods used, including sample preparation and sample pre-treatment, were distributed to the participating laboratories.

The results from the different laboratories are reported to a specific person, and a report is then compiled for discussion by delegates from all the laboratories involved. A meeting to evaluate and discuss the results is held every three months.

The laboratories were judged according to their accuracy and precision as described in ASTM 1601-98. The z-scores and k-statistics were used.

The results were also compared for accuracy using z-scores. The values obtained by the laboratory where the samples originated were considered as the accepted or true value. z-Scores larger than 3 would indicate poor precision and is registered as non-conformances. The cause for the failure is investigated and remedial action taken.

7.3 DISCUSSION

The QA/QC procedure described in the IQC of the laboratory has been implemented to ensure the quality of the results reported. The instrument monitors are to be checked at the beginning of each shift. The values are to be recorded and plotted in a Shewart chart on a daily basis. Any trends that develop from the data are to be investigated and the corrective action noted. Hard copies of these records are to be kept for 12 months. An electronic record of instrumental errors and any repairs done on the instruments are kept for three years.

Both the synthetic QC (IQC) and NQC materials are analysed with every batch of sample (i.e. twin stream leg). Both QC standards are analysed at the start of each batch, and the IQC is analysed after every six samples (if the batch has more than six samples) as well as at the end of the batch. The QC standard at the end of the batch is done irrespective of the amount of test materials between the last analysed QC and the last sample in the batch.

All replicate analysis samples are analysed with the batch. However the samples are placed at the end of the batch and not with the original sample. Replicate analysis is to be done for each stream, i.e. for both ICP-OES and Spark-OES separately. Samples analysed in duplicate may be different for the streams in each batch.

A batch is deemed unacceptable if two consecutive results for the QC falls outside the action limits of the QC. Failure of the IQC indicates a problem with the calibration and/or the instrument. The instrument should be checked and if no obvious faults are detected the ICP-OES should be recalibrated. The Spark-OES should be standardised. Failure of the NQC would indicate errors in the sample preparation procedure, and samples should be re-prepared.

If the QC results fall within the assigned control limits, the paired assays from that particular batch are checked against intra-site splitting limits. If the replicate pairs pass the intra-site splitting limits, results can be reported.

Due to high “short-term” bias between the PGM results from the Spark-OES and ICP-OES, the Spark-OES results are only to be used as an indication of the levels of acid-soluble salts and base metals. This is to allow for the timely return of the material to the plant for reprocessing as the turn-around time for Spark-OES is much shorter than that of the ICP-OES. The results from process control material, except for the PGMs in each matrix, can however be reported as final results as these are only used for the monitoring of the elements during processing.

If there are 8 consecutive QC failures, in any of the element, this is to be recorded and corrective actions taken and recorded. The QC bias for each element is to be calculated every month.

The 10% checks and the proficiency testing are to be used for laboratory performance monitoring. The 10% checks are to be used as more frequent analysis of the performance of the laboratory. The bias between the two laboratories is to be monitored continually as samples are reported. If any

of the results is outside of the limits, both labs have to investigate the cause. Corrective actions are to be taken to rectify the problem.

CHAPTER 8
OVERALL CONCLUSION

The method for the analysis of impurities in platinum, palladium and rhodium metal by Spark-OES, for the quantification of the percentage purity, was evaluated as an alternative method of analysis. From the data presented, it can be seen that the technique is capable of analysing impurities and relatively satisfactory limits of detection were obtained.

Calibration standards for the method were successfully prepared to the required ranges for most elements. This was despite the fact that good recoveries were not obtained for the standards. As this method develops, consensus values could be assigned from the small number of laboratories in the country that routinely do the analysis. The cost of analysis and the logistics of exporting standards outside the country made it difficult to include other laboratories in the determination of the consensus values for the calibration standards and quality control material. As a consequence, much uncertainty surrounds these assigned values.

The method showed great potential to be used as a primary method of analysis. Due to the unavailability of CRMs and laboratories that can be used for validation, the method can currently only be used as a secondary method (for validating the primary method's results). The method can also be used for the monitoring of the final stages of the production process, where the material is treated as sponges (metal powder).The greatest hindrances to the full validation of the method include:

- The lack of CRMs with all the elements of interest certified in the ranges of the sample:
    - It has prevented the reporting of traceable results for the calibration standards prepared as CRMs. Those that are commercially available are of 99.9% purity with very little

impurities. These could therefore not be used to validate the higher portion of the calibration curve where the calibration standards would be analysed. Therefore the values used for the calibration standards and the QC materials were not traceable.

- It not only makes it difficult to calibrate the instrument, but also made it impossible to validate the method for accuracy and traceability to an SI requirement. It rendered the method “inappropriate” for use as a primary method. The results of the primary standards are to be presented in a certificate of analysis and dispatched together with the product to customers internationally. Thus the method has to be traceable and accurate. Although it might be “fit for purpose” for the determination of the purity through the determination of impurities, without validation of its traceability and accuracy the method cannot be fully validated.

- The few laboratories that perform the analysis:
  - In the assignment of consensus values of the calibration standards and values to the QC material it became evident that the use of more laboratories would have been beneficial. Due to the small number of laboratories, it was difficult to exclude one during the assignment of consensus values. It is suspected that the large difference in the results between the laboratories is due to the difference in calibration. Another reason is that high standards were used for the calibration and the samples were determined by extrapolation of this calibration curves. These laboratories do the analysis on a routine basis, and each laboratory uses a calibration best suited for the refinery’s product. Since each refinery

produces impurities at different levels, their calibrations also mirror this.

The method presented in this report can be used for twin stream analysis in conjunction with a primary method. Because of its rapid turnaround time and the non-destructive nature, the method can also be used for plant control purposes where the level of accuracy required is not as stringent.

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ANNEXURE A

A1.1 CONSENSUS VALUES FOR PLATINUM MATRIX

Analyte	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7	Std 8	Std 9	Std 10
Pd	3.6	3.6	4.2	5.4	10.3	21.0	30.1	59.9	127	255
Rh	0.4	1.9	5.8	10.2	20.1	37.8	74.6	145	284	566
Ir	5.0	5.4	4.9	6.6	10.5	15.8	28.4	56.8	119	237
Ru	0.5	0.6	1.8	3.4	6.6	14.8	29.3	60.0	121	251
Os	0.6	1.9	3.1	5.9	11.1	27.9	45.4	84.7	168	332
Au	2.4	3.7	4.5	4.5	4.8	7.5	11.2	19.3	33.5	63.9
Ag	2.4	2.9	3.0	3.0	3.2	3.6	5.6	10.0	19.7	34.4
Cu	0.8	1.2	0.5	1.6	2.1	3.3	4.9	9.9	20.3	36.7
Ni	1.6	2.0	1.7	2.5	2.2	2.7	4.3	8.1	15.6	29.4
Fe	9.4	7.3	3.9	8.2	12.4	11.5	8.3	17.0	25.4	36.3
Pb	1.9	1.9	1.3	1.9	2.3	3.7	5.5	7.2	17.3	29.1
Mg	4.3	2.8	2.8	3.1	3.2	3.8	7.6	14.9	20.2	34.8
Mn	1.2	2.0	1.3	1.2	1.6	2.5	4.6	8.2	15.9	28.1
Si	81.1	110	78.9	162	116	124	106	118	200	447
Al	1.7	1.8	0.9	1.7	0.7	1.3	8.7	11.5	19.9	56.0
Sb	1.3	0.5	0.5	0.6	1.2	3.1	7.7	13.8	30.5	56.0
Cr	3.5	2.1	2.2	2.8	2.0	3.8	4.6	10.0	19.4	32.3
Sn	2.4	1.8	1.4	2.1	1.9	3.0	4.2	7.0	10.8	18.0
Ti	1.7	1.9	1.8	1.9	2.4	3.8	6.0	8.2	14.0	23.9
Zr	3.0	2.9	2.6	1.7	3.1	2.6	7.0	13.9	25.9	37.7
Ca	2.4	0.5	0.5	0.5	0.5	0.5	0.5	0.5	11.0	19.1
Zn	2.3	0.6	0.5	0.8	1.5	2.4	3.9	7.6	15.8	28.6
B	2.0	1.1	0.9	2.1	2.8	3.9	5.2	11.3	29.2	79.3
Co	2.4	2.2	2.1	2.3	1.2	4.3	6.8	12.5	23.5	30.0
V	2.3	0.5	0.5	0.6	0.7	1.6	3.9	8.0	17.1	48.2
Mo	0.6	0.8	0.8	0.9	1.4	1.9	4.1	7.2	15.3	45.3
Bi	1.1	0.6	0.7	1.0	1.0	2.3	4.9	9.0	19.3	31.5
As	3.4	3.0	2.3	3.3	3.7	4.9	12.2	20.0	38.6	59.9
Se	2.3	1.8	3.1	7.4	7.3	9.6	13.4	18.5	33.5	32.3
Te	0.6	0.5	0.8	0.5	1.8	2.2	4.5	8.5	19.9	36.3
Cd	1.1	0.7	0.9	1.7	1.3	1.4	4.4	7.1	15.8	24.1

A1.2ROBUST STANDARD DEVIATION OF CONSENSUS VALUES FOR PLATINUM MATRIX

Analyte	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7	Std 8	Std 9	Std 10
Pd	1.0	3.8	4.0	5.3	5.2	2.4	3.4	9.8	24.9	51.4
Rh	0.3	1.2	5.3	7.0	11.9	2.5	11.5	42.2	59.0	95.5
Ir	3.7	5.7	4.7	5.9	7.5	5.8	1.8	4.1	4.7	3.4
Ru	0.6	0.6	1.2	1.6	3.4	4.7	8.0	17.4	31.9	65.6
Os	0.9	1.9	3.3	6.9	11.7	27.4	37.7	61.8	111	226
Au	2.4	2.9	3.9	2.0	2.0	3.0	1.9	3.7	5.9	6.5
Ag	1.2	0.2	0.0	0.0	0.8	0.9	1.4	2.0	0.9	1.9
Cu	0.7	1.0	0.1	1.0	1.2	1.0	0.9	3.1	4.7	4.6
Ni	0.8	1.4	0.7	1.4	2.0	2.7	2.6	2.4	2.6	6.2
Fe	10.4	4.6	1.7	0.5	11.1	0.7	3.1	3.2	2.5	9.8
Pb	1.6	1.1	1.2	0.4	1.4	1.5	2.2	1.2	3.6	6.3
Mg	5.2	2.4	2.4	2.8	3.0	2.4	3.7	10.3	12.2	21.1
Mn	1.7	2.2	1.1	0.7	1.2	1.6	2.1	1.7	3.3	5.0
Si	22.1	45.2	34.9	62.3	47.7	54.1	45.4	45.6	75.4	135
Al	2.0	1.5	0.5	1.6	0.2	1.0	10.4	1.6	16.6	3.1
Sb	1.6	0.4	0.3	0.2	0.9	2.7	0.4	11.0	27.3	41.2
Cr	4.4	0.1	0.4	2.4	0.9	1.2	0.8	3.1	5.5	5.4
Sn	3.3	1.8	1.4	2.4	1.8	2.8	2.6	1.2	6.2	11.3
Ti	1.3	1.3	1.4	1.3	2.0	3.2	5.0	2.8	9.9	15.3
Zr	1.2	0.4	1.3	1.6	2.4	2.5	1.7	6.4	13.5	14.5
Ca	3.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.6	14.7
Zn	4.8	0.6	0.5	0.7	1.4	2.1	1.8	1.6	3.2	3.3
B	2.2	0.5	0.4	1.0	0.8	1.3	0.2	4.8	19.2	58.1
Co	1.0	2.4	2.0	2.4	1.2	2.7	2.9	4.3	7.9	17.8
V	2.2	0.5	0.6	0.7	1.0	1.8	1.3	0.0	1.5	1.5
Mo	0.5	0.4	0.3	0.3	0.5	0.4	1.1	3.1	6.5	13.1
Bi	1.1	0.8	0.7	0.8	1.0	1.3	1.2	0.9	0.9	4.3
As	3.7	3.3	2.7	3.1	4.6	6.1	2.6	3.9	3.0	1.1
Se	2.5	1.5	3.5	9.9	8.6	10.1	10.2	10.4	12.9	8.3
Te	0.30	0.11	0.37	0.49	1.2	2.0	4.6	6.6	14.0	20.7
Cd	1.5	0.69	0.92	1.8	0.99	1.1	3.7	5.0	5.1	1.8

A1.3 UNCERTAINTIES FOR CONSENSUS VALUES FOR PLATINUM MATRIX

Analyte	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7	Std 8	Std 9	Std 10
Pd	0.7	2.4	2.5	3.3	3.2	1.5	2.1	6.1	15.6	32.1
Rh	0.2	0.7	3.3	4.4	7.4	1.5	7.2	26.4	36.9	59.7
Ir	2.7	3.5	2.9	3.7	4.7	3.6	1.1	2.6	2.9	2.1
Ru	0.4	0.4	0.7	1.0	2.1	2.9	5.0	10.9	20.0	41.0
Os	0.6	1.2	2.0	4.3	7.3	17.1	23.6	38.6	69.4	141
Au	1.8	1.8	2.4	1.3	1.3	1.9	1.2	2.3	3.7	4.0
Ag	0.9	0.1	0.0	0.0	0.5	0.6	0.9	1.2	0.6	1.2
Cu	0.5	0.6	0.0	0.7	0.8	0.6	0.6	1.9	2.9	2.9
Ni	0.5	0.9	0.4	0.9	1.2	1.7	1.6	1.5	1.6	3.9
Fe	9.2	3.3	1.2	0.4	8.0	0.5	2.2	2.3	1.8	7.1
Pb	1.2	0.7	0.8	0.3	0.9	1.0	1.4	0.7	2.3	3.9
Mg	3.8	1.5	1.5	1.8	1.9	1.5	2.3	6.4	7.6	13.2
Mn	1.3	1.3	0.7	0.4	0.7	1.0	1.3	1.1	2.0	3.1
Si	19.6	32.6	25.2	44.9	34.4	39.0	32.8	32.9	54.4	97.7
Al	1.7	1.0	0.4	1.2	0.2	0.8	7.5	1.2	12.0	2.3
Sb	1.2	0.3	0.2	0.1	0.6	1.7	0.2	6.9	17.1	25.8
Cr	3.1	0.1	0.2	1.5	0.6	0.7	0.5	2.0	3.5	3.4
Sn	2.4	1.1	0.9	1.5	1.1	1.8	1.7	0.7	3.9	7.1
Ti	0.9	0.8	0.8	0.8	1.2	2.0	3.1	1.7	6.2	9.5
Zr	0.9	0.3	0.8	1.0	1.5	1.5	1.0	4.0	8.4	9.0
Ca	2.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.0	10.6
Zn	3.4	0.4	0.3	0.4	0.9	1.3	1.1	1.0	2.0	2.1
B	1.9	0.4	0.3	0.7	0.6	0.9	0.1	3.5	13.9	41.9
Co	0.7	1.5	1.3	1.5	0.7	1.7	1.8	2.7	4.9	11.1
V	2.0	0.4	0.4	0.5	0.7	1.3	0.9	0.0	1.1	1.1
Mo	0.3	0.2	0.2	0.2	0.3	0.3	0.7	2.0	4.0	8.2
Bi	0.8	0.5	0.4	0.5	0.6	0.8	0.7	0.6	0.6	2.7
As	2.7	2.1	1.7	2.0	2.9	3.8	1.7	2.4	1.9	0.7
Se	2.2	1.3	3.1	8.7	7.6	8.9	9.1	9.2	11.4	7.3
Te	0.2	0.1	0.2	0.3	0.8	1.3	2.9	4.1	8.8	12.9
Cd	1.1	0.4	0.6	1.1	0.6	0.7	2.3	3.1	3.2	1.1

A2.1 CONSENSUS VALUES FOR RHODIUM MATRIX

Analyte	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7	Std 8	Std 9	Std 10
Pt	17.0	10.2	26.8	13.1	33.4	38.3	49.0	71.5	149	393
Rh	1.8	0.1	0.6	0.5	8.1	26.2	65.7	125	259	540
Ir	0.5	0.8	1.4	2.6	5.2	12.6	28.1	64.7	140	281
Ru	1.4	1.7	4.6	6.2	10.8	21.2	40.6	74.5	154	310
Os	1.7	2.2	5.0	6.7	15.2	26.8	58.5	118	253	518
Au	2.0	2.1	2.4	2.9	3.5	4.5	8.8	13.4	29.8	88.2
Ag	2.6	1.7	0.7	0.9	1.3	4.0	6.8	11.5	21.2	34.0
Cu	3.1	3.6	3.6	4.0	4.5	5.7	9.9	11.1	19.4	35.0
Ni	0.8	0.7	0.9	1.2	1.2	1.4	5.9	5.9	13.7	27.0
Fe	2.2	1.4	1.2	1.2	2.0	1.2	2.0	1.2	1.3	21.5
Pb	1.9	2.3	2.2	2.6	2.8	3.1	7.4	8.7	17.8	33.4
Mg	1.2	1.6	0.7	0.8	1.1	1.4	2.7	7.5	23.7	48.8
Mn	0.7	1.4	0.9	1.0	1.6	2.4	4.3	7.9	15.6	30.0
Si	333	262	276	489	123	338	310	146	222	308
Al	4.8	2.1	2.5	3.6	2.1	14.9	12.3	14.3	16.2	27.0
Sb	0.8	0.7	1.0	0.9	1.5	1.9	4.2	8.1	16.2	30.7
Cr	1.6	2.0	2.0	2.0	2.0	2.6	5.0	8.3	16.2	31.3
Sn	0.9	0.7	0.9	1.0	1.2	1.8	2.8	6.2	13.7	29.3
Ti	0.8	0.4	0.8	1.0	1.2	2.5	5.9	7.9	14.4	26.5
Zr	4.0	2.7	2.8	2.3	4.0	3.4	4.5	7.8	13.0	24.8
Ca	1.4	0.7	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.8
Zn	0.8	0.4	0.5	0.5	0.6	1.2	2.3	4.2	9.1	21.4
B	2.0	1.7	2.1	2.0	2.4	2.7	3.2	5.1	13.5	32.9
Co	2.2	1.5	2.1	1.1	1.7	2.5	4.3	6.2	15.6	32.2
V	0.7	1.3	0.4	1.2	1.2	2.7	5.6	11.2	24.0	45.6
Mo	0.3	0.3	0.5	0.5	1.1	2.7	6.2	12.7	26.9	53.0
Bi	1.0	0.9	1.1	1.4	1.8	2.7	5.2	8.3	17.0	33.1
As	2.0	2.5	2.4	4.2	3.9	1.9	2.9	11.2	21.0	46.2
Te	2.2	0.5	1.1	1.1	3.4	2.9	6.9	14.7	30.6	59.8
Se	2.2	2.1	1.6	3.2	3.4	2.7	3.1	4.2	15.8	33.7
Cd	0.4	0.0	0.4	0.5	1.5	2.9	5.9	10.4	24.9	51.9

A2.2ROBUST STANDARD DEVIATION FOR RHODIUM MATRIX

Analyte	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7	Std 8	Std 9	Std 10
Pt	88.2	1.0	11.4	1.0	5.9	2.1	20.2	40.3	44.1	135
Pd	0.5	1.2	0.7	4.3	4.9	17.2	38.3	89.7	53.2	425
Ir	7.2	4.9	6.4	1.4	19.0	12.0	16.9	48.4	79.1	28.0
Ru	1.0	1.0	2.7	13.8	19.3	29.4	77.3	50.4	7.5	17.9
Os	1.4	3.1	4.3	8.7	11.1	20.4	43.5	87.3	172	337
Au	0.6	0.0	0.1	1.0	2.8	1.8	3.6	7.2	1.3	6.0
Ag	0.0	0.8	0.8	1.4	0.9	5.1	3.1	7.6	9.5	1.1
Cu	0.4	0.7	0.5	1.0	1.5	2.9	5.9	7.2	6.9	4.4
Ni	0.1	0.4	0.3	0.3	0.5	0.1	2.2	3.2	6.2	12.4
Fe	3.8	6.6	4.1	26.9	14.7	8.0	18.9	38.3	37.4	54.3
Pb	0.1	1.9	1.4	0.1	2.0	1.7	2.6	1.2	5.8	1.7
Mg	0.5	1.2	1.2	2.1	1.1	1.8	3.9	4.5	4.6	10.6
Mn	0.5	4.0	0.2	1.4	1.2	0.1	0.0	2.6	0.1	13.3
Si	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Al	5.0	0.7	0.3	1.0	0.9	3.5	1.0	3.6	12.2	13.4
Sb	0.0	0.3	1.9	1.9	1.4	5.4	14.4	10.5	47.4	114
Cr	1.6	2.9	2.0	2.0	3.0	2.9	2.7	6.7	4.6	0.2
Sn	1.8	1.7	0.1	0.7	6.8	3.3	2.5	1.4	6.5	13.8
Ti	1.0	1.0	1.0	1.0	1.0	1.0	3.0	4.8	9.5	0.5
Zr	4.7	4.4	10.8	12.7	29.0	20.9	132	18.3	94.9	80.3
Ca	2.8	4.2	3.1	4.7	3.5	2.2	8.5	7.8	1.6	1.2
Zn	0.5	0.4	0.2	0.8	0.0	0.2	0.1	3.9	0.0	8.5
B	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Co	16.3	7.9	2.5	8.1	2.3	7.0	5.9	6.2	12.4	15.8
V	3.7	2.7	0.3	0.7	0.4	1.9	2.8	3.9	5.8	7.2
Mo	0.2	0.1	0.6	0.8	0.4	0.3	1.5	0.9	7.0	15.0
Bi	0.9	0.5	0.2	0.5	0.7	3.5	3.5	3.7	7.1	1.4
As	3.0	7.1	3.8	4.0	5.8	6.1	10.3	26.8	36.3	56.6
Se	0.4	1.9	1.9	3.1	10.8	20.5	48.7	107	212	431
Te	1.6	1.7	2.7	2.4	1.0	0.3	2.1	4.4	1.0	7.9
Cd	1.8	2.8	2.0	3.1	1.1	1.5	0.5	2.4	0.9	0.9

A2.3UNCERTAINTIES FOR RHODIUM MATRIX

Analyte	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7	Std 8	Std 9	Std 10
Pt	63.6	0.7	8.2	0.7	4.2	1.5	14.5	29.1	31.8	97.6
Pd	0.4	0.8	0.5	3.1	3.5	12.4	27.6	64.7	38.4	307
Ir	5.2	3.5	4.6	1.0	13.7	8.7	12.2	34.9	57.1	20.2
Ru	0.7	0.7	2.0	9.9	14.0	21.2	55.8	36.4	5.4	13.0
Os	1.2	2.8	3.8	7.7	9.8	18.0	38.5	77.2	152	298
Au	0.5	0.0	0.0	0.7	2.0	1.3	2.6	5.2	0.9	4.4
Ag	0.0	0.7	0.7	1.2	0.8	4.5	2.7	6.7	8.4	1.0
Cu	0.4	0.6	0.4	0.9	1.3	2.6	5.3	6.3	6.1	3.9
Ni	0.1	0.3	0.2	0.2	0.4	0.1	1.6	2.3	4.5	9.0
Fe	3.4	5.8	3.6	23.8	13.0	7.1	16.7	33.9	33.0	48.0
Pb	0.1	1.3	1.0	0.1	1.5	1.2	1.8	0.9	4.2	1.2
Mg	0.4	1.0	1.0	1.9	0.9	1.6	3.4	4.0	4.1	9.4
Mn	0.4	2.9	0.1	1.0	0.8	0.1	0.0	1.9	0.1	9.6
Si	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Al	4.5	0.6	0.2	0.9	0.8	3.1	0.9	3.2	10.8	11.9
Sb	0.0	0.2	1.4	1.3	1.0	3.9	10.4	7.6	34.2	81.9
Cr	1.1	2.5	1.4	1.4	2.2	2.1	2.0	4.8	3.3	0.2
Sn	1.8	1.7	0.1	0.7	6.8	3.3	2.5	1.4	6.5	13.8
Ti	1.0	1.0	1.0	1.0	1.0	1.0	3.0	4.8	9.5	0.5
Zr	4.7	4.4	10.8	12.7	29.0	20.9	132	18.3	94.9	80.3
Ca	2.8	4.2	3.1	4.7	3.5	2.2	8.5	7.8	1.6	1.2
Zn	0.5	0.4	0.2	0.8	0.0	0.2	0.1	3.9	0.0	8.5
B	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Co	16.3	7.9	2.5	8.1	2.3	7.0	5.9	6.2	12.4	15.8
V	3.7	2.7	0.3	0.7	0.4	1.9	2.8	3.9	5.8	7.2
Mo	0.2	0.1	0.6	0.8	0.4	0.3	1.5	0.9	7.0	15.0
Bi	0.9	0.5	0.2	0.5	0.7	3.5	3.5	3.7	7.1	1.4
As	3.0	7.1	3.8	4.0	5.8	6.1	10.3	26.8	36.3	56.6
Se	0.4	1.9	1.9	3.1	10.8	20.5	48.7	107	212	431
Te	1.6	1.7	2.7	2.4	1.0	0.3	2.1	4.4	1.0	7.9
Cd	1.8	2.8	2.0	3.1	1.1	1.5	0.5	2.4	0.9	0.9

A3.1 CONSENSUS VALUES FOR PALLADIUM MATRIX

Analyte	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7	Std 8	Std 9	Std 10
Pt	64.0	0.7	8.7	0.7	4.7	7.4	15.5	50.4	73.0	234
Pd	3.9	2.8	2.2	5.7	7.3	17.1	34.9	140	128	365
Ir	13.0	4.0	7.3	14.6	18.0	10.9	12.7	35.5	57.5	78.4
Ru	0.7	0.7	3.0	13.3	14.6	23.8	56.2	47.4	180	318
Os	0.9	2.0	2.7	5.4	11.4	23.3	47.6	95.6	190	375
Au	1.1	1.0	1.0	1.9	3.0	2.7	4.8	8.4	26.4	49.8
Ag	0.5	1.0	1.0	1.3	1.0	3.2	2.0	8.2	10.9	27.7
Cu	0.7	0.8	0.7	0.9	1.1	1.8	3.1	8.8	19.0	37.7
Ni	0.1	0.4	0.3	0.7	0.5	1.6	3.9	7.4	14.6	29.9
Fe	2.2	3.4	2.3	12.4	7.0	4.0	8.8	17.4	17.0	24.5
Pb	2.9	1.9	3.0	3.8	2.0	3.8	5.7	9.9	19.3	32.6
Mg	0.8	1.2	1.2	1.8	1.2	1.6	2.9	3.3	3.4	7.1
Mn	0.6	3.4	1.0	1.8	1.6	3.8	5.4	10.1	22.1	28.9
Si	121	107	132	132	340	153	289	95.4	139	182
Al	4.6	0.9	2.4	3.1	4.7	2.7	9.1	12.9	19.6	43.7
Sb	0.0	0.6	1.9	1.8	1.5	4.4	10.8	8.0	34.7	82.2
Cr	1.4	2.5	1.6	1.4	2.5	2.7	5.2	9.0	19.4	41.0
Sn	1.5	1.5	0.6	2.1	6.4	3.1	5.1	11.4	19.4	39.2
Ti	0.7	0.7	0.7	0.7	0.7	0.7	3.3	9.5	19.9	33.2
Zr	3.9	4.2	7.7	8.7	20.0	16.4	86.8	22.7	77.0	84.1
Ca	3.7	4.6	4.0	4.9	4.2	3.3	7.3	6.8	3.0	1.9
Zn	0.4	0.8	0.8	0.8	0.5	0.5	2.2	6.4	12.1	19.2
B	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Co	15.9	27.4	21.3	39.1	11.8	17.7	13.6	38.0	35.4	50.1
V	2.4	2.1	0.2	1.3	1.1	1.6	4.6	10.3	21.8	44.2
Mo	0.3	0.5	0.5	0.8	1.1	2.2	5.1	10.4	20.8	41.8
Bi	0.7	0.6	0.5	0.8	1.0	3.0	4.2	10.1	17.9	31.0
As	2.3	5.0	2.9	3.0	4.1	4.3	6.9	17.2	23.2	35.8
Se	0.2	2.5	4.8	6.4	10.4	21.7	43.1	78.2	160	312
Te	1.1	1.2	3.5	1.7	3.1	6.8	7.9	15.1	32.9	56.5
Cd	1.1	1.9	1.2	2.1	0.9	1.2	0.9	1.9	1.5	1.8

A3.2ROBUST STANDARD DEVIATIONS FOR PALLADIUM MATRIX

Analyte	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7	Std 8	Std 9	Std 10
Pt	5.8	14.5	8.5	11.9	14.7	23.4	36.8	30.3	32.3	45.3
Rh	2.3	4.2	5.0	1.7	4.6	7.4	17.5	10.0	10.8	84.1
Ir	0.2	0.8	1.2	2.7	5.1	6.5	9.9	9.5	10.6	4.9
Ru	1.3	2.0	1.2	1.5	1.6	3.3	5.6	4.6	10.5	22.1
Os	2.0	2.0	2.2	5.0	2.7	11.1	5.6	7.0	67.4	92.8
Au	2.2	2.2	2.5	2.5	2.8	3.7	2.4	3.0	0.2	2.7
Ag	1.3	2.4	0.3	0.6	1.1	4.9	8.7	15.3	22.4	11.9
Cu	2.9	1.7	2.2	2.2	2.4	1.8	2.6	3.5	0.7	0.5
Ni	0.9	1.0	1.0	0.8	1.3	1.6	3.0	3.8	5.9	9.6
Fe	2.7	2.0	1.0	1.0	1.3	1.0	2.1	1.0	0.4	26.4
Pb	2.2	1.4	2.6	2.3	2.5	2.6	5.1	2.4	3.4	6.0
Mg	1.3	2.0	0.3	0.4	0.8	1.2	2.0	2.0	14.1	32.2
Mn	0.6	0.8	0.4	0.3	0.8	0.9	1.0	1.6	3.7	7.3
Si	77.0	37.9	41.7	99.7	0.1	34.9	29.1	6.5	26.9	7.1
Al	7.8	2.3	2.8	4.4	2.2	13.9	8.1	5.0	4.5	12.5
Sb	1.2	0.2	0.8	0.3	0.5	0.4	2.9	5.3	13.2	26.7
Cr	0.8	0.0	0.0	0.0	0.0	0.6	0.2	0.7	4.2	8.8
Sn	0.9	0.8	0.8	0.8	0.8	0.7	1.6	2.9	3.4	3.0
Ti	0.6	0.5	0.2	0.5	0.5	0.8	2.3	1.0	2.4	8.4
Zr	3.5	1.1	1.2	0.5	1.6	1.7	0.9	1.3	3.2	6.0
Ca	1.9	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4
Zn	1.2	0.5	0.4	0.2	0.2	1.0	2.5	4.6	7.9	9.9
B	2.3	2.6	2.6	2.4	3.1	3.5	4.4	7.4	8.5	5.5
Co	2.9	1.8	1.7	1.0	0.5	0.5	1.0	0.1	4.1	6.7
V	1.0	1.8	0.4	1.0	0.1	0.8	0.3	0.6	0.8	3.0
Mo	0.3	0.2	0.0	0.2	0.8	1.1	1.2	1.9	2.7	4.2
Bi	1.0	1.1	1.0	1.2	1.3	1.3	1.2	1.8	3.8	7.0
As	2.3	1.6	2.8	4.5	4.8	2.3	8.4	5.3	6.0	8.0
Te	8.3	14.8	17.2	16.0	16.0	17.5	10.6	0.4	20.4	8.4
Se	1.4	4.4	3.4	2.0	3.9	3.6	6.2	3.7	15.6	29.6
Cd	0.5	0.0	0.5	0.0	0.6	0.5	0.3	3.0	4.6	12.4

A3.3UNCERTAINTIES FOR PALLADIUM MATRIX

Analyte	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7	Std 8	Std 9	Std 10
Pt	3.6	9.0	5.3	7.4	9.2	14.6	23.0	18.9	20.2	28.3
Rh	1.4	2.6	3.1	1.1	2.9	4.6	10.9	6.2	6.7	52.6
Ir	0.1	0.5	0.8	1.7	3.2	4.0	6.2	5.9	6.6	3.0
Ru	0.8	1.2	0.8	0.9	1.0	2.0	3.5	2.9	6.6	13.8
Os	1.2	1.2	1.4	3.1	1.7	6.9	3.5	4.4	42.1	58.0
Au	1.4	1.4	1.6	1.6	1.7	2.3	1.5	1.9	0.1	1.7
Ag	0.8	1.7	0.2	0.4	0.8	3.5	6.3	11.0	16.1	8.6
Cu	2.1	1.2	1.6	1.6	1.7	1.3	1.9	2.5	0.5	0.3
Ni	0.5	0.6	0.6	0.5	0.8	1.0	1.9	2.4	3.7	6.0
Fe	2.4	1.4	0.7	0.7	1.0	0.7	1.5	0.7	0.3	19.0
Pb	1.4	0.9	1.6	1.5	1.6	1.6	3.2	1.5	2.1	3.8
Mg	0.8	1.3	0.2	0.2	0.5	0.8	1.2	1.2	8.8	20.1
Mn	0.4	0.5	0.2	0.2	0.5	0.5	0.6	1.0	2.3	4.5
Si	68.1	27.3	30.1	71.9	0.1	25.2	21.0	4.7	19.4	5.1
Al	6.9	1.6	2.0	3.2	1.6	10.0	5.8	3.6	3.2	9.0
Sb	0.8	0.2	0.7	0.2	0.4	0.3	2.6	4.7	11.7	23.6
Cr	0.6	0.0	0.0	0.0	0.0	0.4	0.1	0.5	3.0	6.4
Sn	0.6	0.5	0.5	0.5	0.5	0.4	1.0	1.8	2.1	1.9
Ti	0.4	0.3	0.1	0.3	0.3	0.5	1.4	0.6	1.5	5.2
Zr	3.1	1.0	1.1	0.5	1.4	1.5	0.8	1.1	2.9	5.3
Ca	1.7	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3
Zn	0.7	0.3	0.2	0.1	0.1	0.6	1.5	2.9	4.9	6.2
B	2.1	2.3	2.3	2.1	2.7	3.1	3.9	6.6	7.5	4.8
Co	1.8	1.1	1.1	0.6	0.3	0.3	0.7	0.1	2.6	4.2
V	0.7	1.3	0.3	0.7	0.1	0.6	0.2	0.4	0.5	2.2
Mo	0.2	0.1	0.0	0.1	0.5	0.7	0.8	1.2	1.7	2.6
Bi	0.6	0.7	0.6	0.8	0.8	0.8	0.7	1.1	2.4	4.4
As	1.5	1.0	1.7	2.8	3.0	1.4	5.2	3.3	3.7	5.0
Te	6.0	10.7	12.4	11.5	11.6	12.6	7.6	0.3	14.7	6.1
Se	0.9	2.8	2.1	1.2	2.4	2.3	3.9	2.3	9.7	18.5
Cd	0.3	0.0	0.3	0.0	0.5	0.4	0.2	2.2	3.3	9.0

ANNEXURE B

B.1 z-SCORES FOR PLATINUM MATRIX

Analyte	Standard 2				Standard 10			
	Lab A	Lab B	Lab C	Lab D	Lab A	Lab B	Lab C	Lab D
Pd	-0.29	-0.97	3.28	0.12	-0.69	0.93	-0.80	0.56
Rh	-0.10	0.01	-1.03	1.14	0.41	0.91	-1.74	-0.19
Ir	-0.52	1.33	-0.84	0.26	-0.73	0.87	0.64	-0.78
Ru	1.87	-1.04	-0.07	0.00	-1.18	0.92	-0.18	0.39
Os	-0.11	-1.03	23.78	0.02	1.08	-0.36	0.27	-0.98
Au	-1.06	1.05	0.24	-0.23	-0.26	0.52	-2.90	0.84
Ag	-0.38	-8.42	0.71	0.71	-0.30	0.58	-4.74	0.80
Cu	-0.94	-0.33	2.02	0.15	0.26	-0.11	-3.31	0.98
Ni	0.24	-1.40	-0.10	0.98	1.87	0.35	-0.75	-0.66
Fe	-0.21	na	0.93	-0.72	0.76	na	0.17	-0.93
Pb	0.70	-1.51	-0.37	0.71	1.01	0.34	-0.31	-1.04
Mg	0.15	3.56	-0.95	-0.33	-0.18	0.06	3.46	-1.01
Mn	0.38	1.88	-0.71	-0.71	0.88	0.48	-0.26	-1.10
Si	0.91	na	-0.84	-0.07	1.01	na	-0.72	-0.21
Al	0.84	na	0.07	-0.91	0.21	na	0.72	-14.66
Sb	8.51	-1.05	-0.03	-0.03	-0.32	0.15	-0.95	1.41
Cr	0.38	56.97	-0.71	-0.71	1.03	0.40	-0.92	-0.51
Sn	0.14	-0.95	-0.32	2.49	0.76	0.76	-0.73	-0.80
Ti	-0.01	2.12	-0.05	-1.04	0.63	0.88	-0.89	-0.62
Zr	-0.21	0.90	0.43	-2.01	-0.06	-0.01	3.52	-1.04
Ca	0.00	na	0.00	0.00	-0.21	na	2.50	-0.72
Zn	-1.01	22.39	0.05	-0.17	0.37	2.00	-0.70	-0.72
B	4.06	na	-0.21	-0.72	-0.72	na	-0.21	1.10
Co	0.38	1.04	-0.71	-0.71	0.46	0.88	-1.69	-0.23
V	0.84	-0.91	0.06	na	0.72	0.21	-2.49	na
Mo	1.00	-0.52	0.44	-0.93	0.77	0.63	-0.33	-2.21
Bi	-0.69	-0.72	0.36	2.90	0.89	0.48	-1.09	-0.27
As	0.76	-0.77	-0.76	0.77	8.47	-0.04	-1.05	-0.02
Se	-0.62	0.62	na	na	-0.62	0.62	na	na
Te	1.05	-4.69	0.03	0.03	0.66	0.74	-0.35	-1.30
Cd	0.12	-0.97	-0.27	7.71	0.39	-0.18	-6.32	0.92

Note:

na: Not analysed

nd: not determined

B.2 z-SCORES FOR PALLADIUM MATRIX

Analyte	Standard 1				Standard 10			
	Lab A	Lab B	Lab C	Lab D	Lab A	Lab B	Lab C	Lab D
Pd	0.94	0.50	-2.83	-0.43	0.29	-0.12	0.97	-2.89
Rh	0.24	-0.78	1.11	-0.56	-0.72	-0.35	0.26	-0.99
Ir	-0.83	1.20	-0.18	-0.18	6.35	0.10	-0.01	-53.53
Ru	0.89	-1.07	0.51	-0.32	0.21	1.06	-0.42	-0.96
Os	0.05	-0.86	1.17	-0.36	0.62	-3.58	0.55	-0.28
Au	0.33	-0.72	1.06	-0.68	0.72	1.01	-0.06	-23.66
Ag	-0.22	na	-1.64	9.46	0.44	na	-0.72	21.36
Cu	0.57	na	0.33	-0.90	0.62	na	-0.72	-0.21
Ni	0.13	-0.92	-0.35	1.14	0.72	0.32	-0.37	-1.00
Fe	0.44	na	na	-0.44	0.44	na	-0.18	-0.75
Pb	0.94	-0.86	-0.63	0.55	4.28	0.21	-0.43	-0.90
Mg	1.16	-0.09	-0.54	-0.54	0.62	-0.85	0.99	0.48
Mn	1.17	-0.91	0.01	-0.27	0.21	0.93	-0.18	-1.69
Si	0.44	na	0.58	-0.44	na	na	0.21	-7.87
Al	0.55	na	na	-0.55	0.62	na	0.96	-0.72
Sb	na	na	0.92	-0.25	-0.21	na	-0.62	0.62
Cr	-0.86	na	0.39	0.47	0.21	na	0.21	-1.99
Sn	-0.83	0.07	-0.40	1.21	-0.93	0.54	-0.27	-8.76
Ti	-0.21	1.17	-0.48	-0.48	-0.72	0.10	-0.05	-1.10
Zr	-0.24	na	-0.50	na	-0.62	na	-0.62	na
Ca	0.44	na	na	-0.44	-0.62	na	-0.21	-0.72
Zn	-0.67	1.21	-0.27	-0.27	0.72	0.54	-0.51	-0.95
B	0.62	na	-0.62	na	na	na	-0.62	na
Co	-0.49	-0.71	0.02	7.20	0.21	0.98	0.24	-1.58
V	-0.71	4.08	-0.21	na	0.62	0.12	-0.92	na
Mo	-0.39	-1.03	0.71	0.71	0.83	0.72	-0.37	-1.24
Bi	0.44	-0.93	-0.52	1.00	5.25	0.89	-0.58	-0.92
As	0.75	-0.87	-0.65	0.77	0.62	0.67	-2.20	-0.35
Se	-0.21	-0.72	3.01	na	0.62	-0.21	-0.72	na
Te	0.25	-0.86	-0.50	1.96	0.72	0.55	-0.63	-0.86
Cd	-0.53	na	0.18	1.13	0.62	na	0.72	-1.28

B.3 z-SCORES FOR RHODIUM MATRIX

Analyte	Standard 1			Standard 10		
	Lab A	Lab B	Lab D	Lab A	Lab B	Lab D
Pt	0.10	2.82	-0.72	-0.78	0.93	-0.14
Pd	1.54	-7.57	0.21	-0.72	1.07	-0.21
Ir	0.55	0.72	-1.72	6.35	-0.72	-0.21
Ru	3.60	-0.72	-0.21	0.21	0.72	-16
Os	1.17	-0.62	na	0.62	-0.62	na
Au	3.72	-0.74	-0.19	0.72	0.21	-4.6
Ag	515.14	-0.72	-0.21	0.44	na	-0.44
Cu	2.29	na	-0.44	0.62	na	-0.62
Ni	1.06	-0.72	8.87	0.72	0.21	-0.98
Fe	1.09	na	-0.44	0.44	na	-0.44
Pb	10.12	-41.31	0.72	4.28	-0.72	-0.21
Mg	1.84	na	-0.62	0.62	na	-0.62
Mn	5.71	-0.72	-0.21	0.21	0.72	-1.6
Si	na	na	nd	na	na	nd
Al	0.11	na	0.62	0.62	na	-0.62
Sb	3.09	-0.72	12.15	-0.21	1.81	-0.72
Cr	2.25	-0.91	0.06	0.21	-24.93	0.72
Sn	1.20	-0.72	2.43	-0.93	0.75	0.17
Ti	0.76	-0.72	-0.21	-0.72	45.07	-0.21
Zr	0.31	0.62	na	-0.62	0.62	na
Ca	2.18	na	-0.62	-0.62	na	0.62
Zn	3.04	-0.93	0.17	0.72	0.21	-2.2
B	na	na	nd	na	na	nd
Co	0.04	0.83	-0.92	0.21	0.72	-1.6
V	0.03	0.62	na	0.62	-0.62	na
Mo	0.00	0.21	0.72	0.83	-0.92	0.09
Bi	2.80	-0.72	-0.21	5.25	-0.72	-0.21
As	1.06	na	-0.62	0.62	na	-0.62
Se	2.36	-0.62	na	0.62	-0.62	na
Te	0.69	-0.72	4.75	0.72	0.21	-6.1
Cd	0.24	-0.62	na	0.62	-0.62	na

B.4 K-STATISTICS FOR PLATINUM MATRIX

Analyte	Standard 2				Standard 10			
	Lab A	Lab B	Lab C	Lab D	Lab A	Lab B	Lab C	Lab D
Pd	0.47	0.04	1.08	0.29	0.19	0.05	0.12	0.05
Rh	0.53	0.12	0.63	0.37	0.13	0.04	0.10	0.05
Ir	0.24	nd	0.00	0.33	1.90	nd	2.03	2.81
Ru	0.19	0.17	0.42	0.37	0.08	0.05	0.08	0.05
Os	1.01	0.04	3.27	0.41	0.23	0.01	0.02	0.02
Au	0.21	nd	0.00	0.00	0.19	nd	0.20	0.08
Ag	1.98	0.23	0.00	0.00	0.28	0.15	0.75	0.39
Cu	0.16	nd	0.51	0.49	0.17	nd	0.11	0.14
Ni	0.14	nd	0.35	0.36	0.10	nd	0.15	0.15
Fe	0.57	nd	0.21	0.27	0.15	nd	0.10	0.30
Pb	0.80	0.19	0.54	0.63	0.08	0.08	0.38	0.29
Mg	0.05	nd	0.00	0.00	0.04	nd	0.34	0.02
Mn	0.50	nd	0.00	0.00	0.16	nd	0.19	0.10
Si	0.18	na	0.07	0.08	0.21	na	0.35	0.09
Al	0.14	na	1.20	0.00	0.47	na	0.96	0.14
Sb	2.08	0.06	0.00	0.00	0.05	0.02	0.06	0.24
Cr	1.44	nd	0.00	0.00	0.14	nd	0.00	0.13
Sn	0.39	0.01	0.14	0.24	0.08	0.04	0.19	0.00
Ti	0.10	0.32	0.82	0.00	0.05	0.03	0.04	0.09
Zr	6.29	0.68	10.43	0.00	0.06	0.02	0.38	0.03
Ca	0.00	na	0.00	0.00	0.04	na	0.63	0.07
Zn	0.00	nd	0.00	0.00	0.23	nd	1.31	0.13
B	2.99	na	0.00	0.54	0.04	na	0.09	0.08
Co	0.38	0.04	0.12	0.00	0.05	0.03	0.05	0.00
V	1.09	nd	0.00	na	0.49	nd	0.55	na
Mo	1.01	0.57	0.00	0.00	0.20	0.07	0.00	0.04
Bi	0.13	0.12	0.35	0.00	0.22	0.09	0.69	0.31
As	1.19	nd	0.00	0.25	3.27	nd	8.18	3.79
Se	0.43	0.50	na	na	0.34	0.52	na	na
Te	5.71	3.40	0.00	0.00	0.10	0.13	0.19	0.15
Cd	0.72	0.33	0.00	1.19	0.24	0.55	3.51	1.12

B.5 K-STATISTICS FOR PALLADIUM MATRIX

Analyte	Standard 1				Standard 10			
	Lab A	Lab B	Lab C	Lab D	Lab A	Lab B	Lab C	Lab D
Pd	0.09	2.85	0.00	0.40	0.41	0.29	0.59	0.28
Rh	0.43	nd	0.25	0.00	0.21	nd	0.18	0.06
Ir	0.63	nd	0.00	0.00	2.15	nd	2.41	1.97
Ru	0.34	0.80	0.00	1.38	0.60	1.15	0.27	0.13
Os	0.53	0.10	1.05	0.13	0.16	0.10	0.15	0.10
Au	0.03	nd	0.26	0.00	0.27	nd	1.19	0.36
Ag	1.30	na	0.00	1.87	0.10	na	0.18	1.07
Cu	0.08	na	0.00	0.00	2.05	na	1.79	1.10
Ni	0.37	nd	0.00	0.57	0.16	nd	0.20	0.06
Fe	0.16	na	0.00	0.00	0.17	na	0.08	0.04
Pb	0.52	0.49	0.00	0.57	0.24	0.52	0.24	0.22
Mg	0.15	nd	0.00	0.00	0.00	nd	0.10	0.06
Mn	0.56	nd	0.48	0.00	0.04	nd	0.07	0.13
Si	0.43	na	0.10	0.06	4.21	na	1.84	0.38
Al	0.12	na	0.06	0.00	0.10	na	0.13	0.21
Sb	na	na	0.00	0.00	na	na	0.02	0.04
Cr	0.62	na	0.00	0.00	0.14	na	0.11	0.06
Sn	0.15	0.08	0.00	0.00	0.50	0.22	0.57	0.00
Ti	1.93	nd	0.00	0.00	0.14	nd	0.20	0.12
Zr	0.11	na	0.00	na	0.18	na	0.00	na
Ca	0.26	na	0.00	0.00	1.95	na	1.79	0.00
Zn	0.11	nd	0.00	0.00	0.15	nd	0.32	0.00
B	0.54	na	0.00	na	0.49	na	1.78	na
Co	0.49	0.01	1.29	4.41	0.42	0.30	0.26	0.07
V	0.00	nd	0.00	0.00	0.52	nd	0.16	0.00
Mo	1.27	1.11	0.00	0.00	0.24	0.13	0.14	0.20
Bi	0.04	0.02	0.00	0.51	0.18	0.43	0.23	0.31
As	0.75	nd	0.00	0.89	0.61	nd	0.93	0.10
Se	0.09	0.09	0.56	na	0.12	0.80	0.97	na
Te	0.84	nd	0.00	0.59	0.40	nd	0.20	0.04
Cd	0.32	na	0.00	0.00	0.08	na	0.25	0.00

B.6 K-STATISTICS FOR RHODIUM MATRIX

Analyte	Standard 1			Standard 10		
	Lab A	Lab B	Lab D	Lab A	Lab B	Lab D
Pt	0.10	0.30	nd	0.37	0.05	0.07
Pd	1.54	1.57	6.25	0.00	0.06	0.04
Ir	0.55	0.03	nd	0.49	0.04	0.35
Ru	3.60	0.11	nd	0.32	0.07	0.66
Os	1.17	0.01	na	0.04	0.00	na
Au	3.72	0.07	nd	0.62	0.04	0.29
Ag	515.14	6.25	nd	2.80	0.15	0.74
Cu	2.29	nd	nd	0.33	nd	0.67
Ni	1.06	nd	0.00	0.06	nd	0.12
Fe	1.09	nd	nd	0.03	nd	nd
Pb	10.12	1.46	nd	0.36	0.99	1.9
Mg	1.84	na	nd	0.04	na	nd
Mn	5.71	0.08	nd	0.14	0.09	0.04
Si	na	na	nd	na	na	nd
Al	0.11	na	1.57	0.10	na	0.81
Sb	3.09	nd	nd	0.04	nd	nd
Cr	2.25	nd	0.00	5.42	nd	8.6
Sn	1.20	0.01	0.28	0.93	0.01	0.29
Ti	0.76	nd	nd	2.24	nd	5.2
Zr	0.31	0.35	na	0.03	0.13	na
Ca	2.18	na	0.00	1.61	na	0.00
Zn	3.04	nd	nd	0.18	nd	nd
B	na	na	nd	na	na	nd
Co	0.04	0.04	nd	0.18	0.03	0.09
V	0.03	nd	na	0.11	nd	na
Mo	0.00	0.78	nd	0.11	0.04	0.06
Bi	2.80	0.04	nd	4.16	0.13	1.5
As	1.06	nd	nd	0.12	nd	nd
Se	2.36	3.84	na	0.01	0.01	na
Te	0.69	1.85	1.69	0.17	0.29	0.23
Cd	0.24	0.03	na	0.75	0.15	na

ANNEXURE C

7.4 CHANNELS AND WAVELENGTHS USED FOR CALIBRATION

Platinum		Palladium		Rhodium	
Channel	Wavelength	Channel	Wavelength	Channel	Wavelength
Pt6	**279.42x2**	Pt1	265.95x2	Pt5	214.42x2
Pd6	340.45x2	**Pd2**	**245.72x2**	Pd6	340.45x2
Rh1	343.48x2	Rh1	343.48x2	**Rh5**	**590.06x1**
Ir5	224.27x3	Ir2	313.33x2	Ir2	313.33x2
Ru1	349.89x1	Ru1	349.89x1	Ru1	349.89x1
Os	290.9x2	Os	290.9x2	Os	290.9x2
Au2	267.59x3	Au2	267.59x3	Au2	267.59x3
Ag4	328.07x2	Ag4	328.07x2	Ag5	338.29x2
Cu7	324.75x2	Cu7	324.75x2	Cu7	324.75x2
Ni9	316.94x2	Ni9	316.94x2	Ni9	316.94x2
Fe8	259.94x3	Fe8	259.94x3	Fe7	371.99x2
Pb6	405.78x2	Pb6	405.78x2	Pb6	405.78x2
Mg3	285.21x2	Mg3	285.21x2	Mg3	285.21x2
Mn1	257.61x3	Mn1	257.61x3	Mn1	257.61x3
Si3	288.15x2	Si3	288.15x2	Si3	288.15x2
Al8	396.15x1	Al8	396.15x1	Al8	396.15x1
Sb2	217.58x2	Sb2	217.58x2	Sb1	206.83x3
Cr4	425.43x1	Cr4	425.43x1	Cr4	425.43x1
Sn1	175.79x3	Sn6	303.41x2	Sn6	303.41x2
Ti6	368.51x1	Ti6	368.51x1	Ti6	368.51x1
Zr3	349.62x2	Zr3	349.62x2	Zr3	349.62x2
Ca2	393.37x1	Ca2	393.37x1	Ca2	393.37x1
Zn5	334.5x2	Zn5	334.5x2	Zn5	334.5x2
B1	182.64x3	B1	182.64x3	B1	182.64x3
Co4	345.35x2	Co4	345.35x2	Co4	345.35x2
V4	437.92x1	V4	437.92x1	V4	437.92x1
Mo5	379.83x2	Mo5	379.83x2	Mo6	386.41x1
Bi4	306.77x2	Bi4	306.77x2	Bi4	306.77x2
As2	197.26x3	As2	197.26x3	As1	189.04x3
Se1	196.06x3	Se1	196.06x3	Se1	196.06x3
Te2	214.27x3	Te2	214.27x3	Te2	214.27x3
Cd2	226.5x2	Cd2	226.5x2	Cd3	228.8x2

ANNEXURE D

D1.1 LIMITS FOR 2 $mg.kg^{-1}$ PLATINUM QC MATERIAL

Analyte	Lower limit	Average	Upper limit	Conc (mg.kg-1
Pd	1.7	4.9	8.0	10.6
Rh	1.9	3.6	5.4	2.1
Ir	3.2	8.0	12.7	5.3
Ru	2.6	3.7	4.8	3.6
Os	0.0	2.6	5.3	7.4
Au	0.0	2.4	7.9	4.0
Ag	2.7	3.2	3.7	5.3
Cu	1.6	2.0	2.4	1.3
Ni	2.0	2.8	3.6	1.0
Fe	1.6	12.0	22.4	4.6
Pb	0.0	3.7	7.4	3.9
Mg	0.0	4.7	10.3	4.2
Mn	2.1	2.3	2.6	3.5
Si	160	292	424	211
Al	3.5	5.5	7.6	5.4
Sb	106	171	236	4.0
Cr	1.6	2.2	2.7	2.9
Sn	1.5	2.9	4.4	2.1
Ti	2.1	3.8	5.4	2.7
Zr	0.0	2.2	4.8	3.9
Ca	0.0	2.7	7.1	4.4
Zn	0.0	0.9	2.0	8.9
B	0.0	4.7	11.1	2.6
Co	0.2	2.9	5.6	4.3
V	1.0	1.3	1.6	1.7
Mo	0.6	1.5	2.5	1.5
Bi	0.0	1.8	5.8	2.1
As	2.3	6.8	11.2	6.8
Se	0.0	2.0	5.5	4.2
Te	3.3	6.7	10.0	5.1
Cd	0.6	1.7	2.8	2.2

D1.2 LIMITS FOR 20 mg.kg^{-1} PLATINUM QC MATERIAL

Analyte	Lower limit	Average	Upper limit	Conc (mg.kg^{-1})
Pd	44.9	51.6	58.3	31.2
Rh	19.2	20.4	21.6	12.6
Ir	23.0	26.6	30.2	17.9
Ru	17.9	22.0	26.1	14.0
Os	15.2	21.8	28.4	32.6
Au	19.7	24.0	28.3	17.5
Ag	16.5	18.3	20.1	15.8
Cu	18.7	19.9	21.2	12.8
Ni	18.7	20.4	22.1	15.1
Fe	18.4	29.8	41.2	17.4
Pb	12.4	18.2	24.0	15.3
Mg	14.6	17.7	20.7	13.1
Mn	17.0	18.0	19.0	13.0
Si	93.1	191.3	289.6	202.8
Al	15.4	19.5	23.5	18.7
Sb	72.5	118.1	163.6	15.3
Cr	18.5	19.9	21.4	15.0
Sn	14.7	16.9	19.1	18.4
Ti	16.4	19.5	22.6	15.7
Zr	15.1	18.4	21.8	16.8
Ca	5.9	8.5	11.0	7.8
Zn	13.9	15.5	17.0	13.6
B	4.3	12.5	20.6	9.7
Co	18.3	21.5	24.6	15.2
V	15.2	16.0	16.9	11.3
Mo	14.6	16.1	17.6	11.0
Bi	6.8	15.1	23.4	13.6
As	20.4	27.0	33.6	19.4
Se	7.5	10.6	13.6	14.6
Te	18.3	20.9	23.5	14.4
Cd	10.2	11.2	12.2	10.9

D2.1 LIMITS FOR 2 mg.kg^{-1} PALLADIUM QC MATERIAL

Analyte	Lower limit	Average	Upper limit	Conc (mg.kg^{-1})
Pt	23.0	37.2	51.3	21.507
Rh	4.7	6.9	9.1	7.542
Ir	16.0	17.8	19.7	8.359
Ru	8.3	11.7	15.2	9.66
Os	1.4	2.6	3.7	!0.220
Au	2.1	3.1	4.1	5.289
Ag	2.4	3.1	3.8	2.179
Cu	5.1	5.5	5.8	4.303
Ni	3.0	3.6	4.2	2.397
Fe	4.1	8.4	12.7	!1.180
Pb	-1.2	7.7	16.6	5.492
Mg	1.5	3.7	5.8	3.703
Mn	2.4	2.6	2.9	2.683
Si	225.2	322.2	419.2	405.02
Al	3.8	4.4	4.9	3.978
Sb	2.7	3.9	5.1	3.685
Cr	1.1	3.4	5.7	3.074
Sn	0.0	1.9	4.9	2.061
Ti	6.7	8.0	9.2	6.196
Zr	2.6	4.3	6.1	4.733
Ca	2.9	6.6	10.4	2.931
Zn	0.6	1.9	3.1	!0.760
B	0.9	5.4	9.9	4.617
Co	3.5	5.0	6.5	1.499
V	0.2	1.2	2.2	2.143
Mo	0.7	1.4	2.1	1.938
Bi	1.8	3.5	5.3	3.433
As	1.6	6.3	10.9	!0.500
Se	2.2	4.5	6.9	!0.500
Te	0.6	2.6	4.7	2.624
Cd	1.4	1.9	2.4	0.586

D2.2 LIMITS FOR 20 mg.kg^{-1} PALLADIUM QC MATERIAL

Analyte	Lower limit	Average	Upper limit	Conc (mg.kg^{-1})
Pt	31.9	45.7	59.4	35.1
Rh	21.8	24.0	26.2	31.0
Ir	24.2	31.7	39.2	31.7
Ru	18.4	24.9	31.5	14.4
Os	12.3	19.1	25.9	16.3
Au	18.1	25.2	32.3	37.5
Ag	15.8	17.7	19.6	15.6
Cu	21.2	21.8	22.5	24.6
Ni	12.4	20.7	29.0	27.0
Fe	14.7	25.7	36.7	21.9
Pb	13.4	23.8	34.3	28.9
Mg	12.1	14.1	16.1	17.0
Mn	12.6	16.9	21.2	21.2
Si	319.1	476.6	634.1	573.3
Al	14.0	17.5	21.0	21.2
Sb	17.1	22.1	27.2	18.9
Cr	13.2	20.0	26.9	20.3
Sn	11.1	15.1	19.2	17.8
Ti	16.1	22.1	28.1	23.0
Zr	10.3	14.0	17.7	17.2
Ca	4.7	11.7	22.2	9.4
Zn	8.8	16.7	24.6	15.9
B	10.6	15.4	20.2	14.2
Co	16.6	22.3	28.0	17.5
V	11.1	14.9	18.6	15.3
Mo	8.2	13.7	19.1	21.0
Bi	11.0	21.6	32.1	21.7
As	5.6	25.4	45.2	!0.500
Se	10.4	20.2	30.0	!0.500
Te	14.0	19.2	24.5	24.6
Cd	15.5	18.0	20.5	11.1

D3.1 LIMITS FOR 2 mg.kg^{-1} RHODIUM QC MATERIAL

Analyte	Lower limit	Average	Upper limit	Conc (mg.kg-1)
Pt	9.9	20.8	31.7	7.5
Pd	2.4	4.7	7.1	!0.4
Ir	70.5	73.6	76.8	52.2
Ru	8.9	10.8	12.6	11.1
Os	3.8	4.5	5.3	4.6
Au	1.1	4.1	7.1	2.6
Ag	0.6	0.8	1.1	1.0
Cu	2.0	2.3	2.5	1.6
Ni	1.4	1.8	2.2	0.9
Fe	14.1	16.3	18.6	16.3
Pb	6.1	6.9	7.7	6.6
Mg	0.1	1.0	1.8	1.0
Mn	0.9	2.1	3.3	2.3
Si	na	n.a.	na	na
Al	5.4	7.0	8.5	7.2
Sb	-0.4	0.3	1.0	!0.2
Cr	2.4	2.8	3.2	6.1
Sn	6.4	11.0	15.7	4.1
Ti	1.8	3.2	4.6	3.4
Zr	1.1	3.0	5.0	3.3
Ca	-1.5	1.7	5.0	1.7
Zn	-0.2	0.4	0.9	!1.3
B	na	na	na	na
Co	18.6	22.0	25.4	3.2
V	1.2	1.7	2.2	1.9
Mo	0.4	1.1	1.8	1.1
Bi	4.9	6.9	8.9	5.7
As	0.8	2.4	4.0	2.2
Se	0.1	2.6	5.0	!0.7
Te	-0.2	0.6	1.4	2.4
Cd	0.1	2.3	4.6	2.0

D3.2 LIMITS FOR 20 $mg.kg^{-1}$ RHODIUM QC MATERIAL

Analyte	Lower limit	Average	Upper limit	Conc (mg.kg-1)
Pt	24.1	27.4	30.6	28.54
Pd	20.5	27.1	33.6	26.6
Ir	82.4	87.4	92.4	87.6
Ru	24.9	31.8	38.7	32.3
Os	16.5	23.7	30.9	25.0
Au	15.4	17.5	19.5	16.6
Ag	7.4	9.0	10.7	9.0
Cu	17.2	17.9	18.5	17.8
Ni	17.3	18.0	18.7	18.0
Fe	42.6	46.5	50.5	19.8
Pb	22.5	23.2	24.0	23.8
Mg	3.1	4.7	6.4	8.0
Mn	14.8	15.8	16.9	15.8
Si	na	na	na	na
Al	18.5	19.6	20.6	12.4
Sb	15.9	19.4	22.8	19.5
Cr	18.9	19.6	20.2	21.4
Sn	22.8	28.7	34.5	12.7
Ti	11.2	15.3	19.5	21.0
Zr	13.8	17.5	21.1	20.9
Ca	-1.2	2.9	7.0	na
Zn	6.8	7.5	8.1	7.6
B	na	na	na	na
Co	33.4	36.4	39.5	36.1
V	14.5	14.9	15.4	14.8
Mo	14.3	14.8	15.4	13.3
Bi	11.5	15.3	19.1	14.9
As	20.9	23.4	25.9	23.0
Se	14.4	18.6	22.8	17.9
Te	12.2	14.9	17.5	16.6
Cd	0.8	2.3	3.8	9.6