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Development of Selective Pre-concentration Methodology of some of the Platinum-Group Metals in acidic solutions, followed by their direct Determination by ICP-OES

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Abstract

The trace analysis of the platinum-group metals in complex, severely interfering matrices, such as industrial effluent, has been the focus of much research in the past forty years. However, despite the greater availability of much improved instrumentation, such as ICP-OES, NAA and XRF, most analytical techniques currently employed for the determination of the platinum-group metals require selective sample preparation that ensures enrichment of the individual platinum-group metals at the trace and ultra trace level, along with simultaneous matrix removal, prior to determination.

N-benzoyl-N', N'-dialkylthioureas act as selective complexing agents for the enrichment of platinum-group metals from strongly interfering matrices. This study describes the development of selective pre-concentration methodology for some of the platinum-group metals in post-processing effluents (using this class of ligands) followed by their direct determination by ICP-OES, in an effort to recover the residual platinum-group metals present in real waste effluents that are currently unable to be recovered, representing a substantial loss of income to the South African platinum-group metal producers.

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For Shane,
with all my love

"He who is certain he knows the ending of things when he is only beginning them is either extremely wise or extremely foolish; no matter which is true, he is certainly an unhappy man, for he has put a knife in the heart of wonder."

- Tad Williams, 1988 -

Chapter 1

Objectives of Research

1.1 Introduction

The platinum-group metals include platinum, palladium, rhodium, ruthenium, iridium and osmium and are among the 90 or so elements that comprise less than 2% by weight of the earth's crust. Their relative abundances are estimated to be [1]:

Pt	0.005 $\mu g.cm^{-3}$	Rh	0.0004 $\mu g.cm^{-3}$	Ru	0.0004 $\mu g.cm^{-3}$
Pd	0.001 $\mu g.cm^{-3}$	Ir	0.0004 $\mu g.cm^{-3}$	Os	0.0004 $\mu g.cm^{-3}$

In the past thirty years, the range and demand (Figure 1.1.1) of the platinum-group metals has dramatically increased. The principal applications of the platinum-group metals depend on either their nobility or their catalytic properties. The principal uses of platinum are shown in Figure 1.1.2. The largest single use of platinum is in autocatalysts as an oxidative catalyst, followed by jewellery, by Japan and the USA. Platinum oxidative catalysts are used outside the automotive industry in numerous air pollution reduction processes to remove carbon monoxide and toxic organic vapours. The chemical industry exploits the efficient catalytic properties of platinum in the production of various chemicals. Examples of this would be the oxidation of ammonia to nitric acid (platinum-rhodium alloy gauze as catalyst), platforming of low octane naphthas to high quality petroleum products (platinum gauze as catalyst) and platinum-catalysed hydrogenation, dehydrogenation, isomerisation and oligomerisation reactions in organic syntheses.

The electrical industry uses the nobility of platinum and its low, but temperature dependent resistance in temperature measurement (platinum and platinum/rhodium thermocouples), fuel cells (platinum electrodes) and gas detection (platinum sensors). Platinum is widely used in the glass making industry for the production of special glass such as camera and spectacle lens glasses, glass fibres used for insulating and reinforcing and optical fibres for telecommunications. Platinum also finds application in the jewellery industry in the production of platinum and platinum-alloy jewellery.

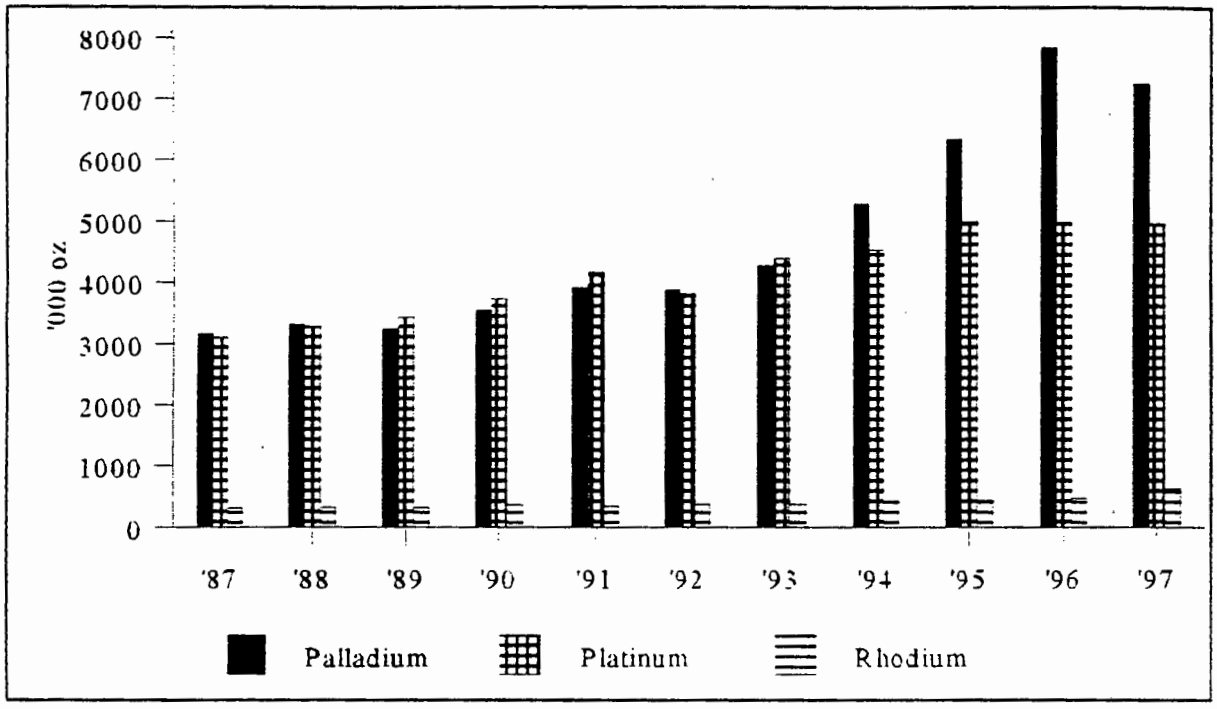

Figure 1.1.1: Annual growth in world demand of platinum, palladium and rhodium

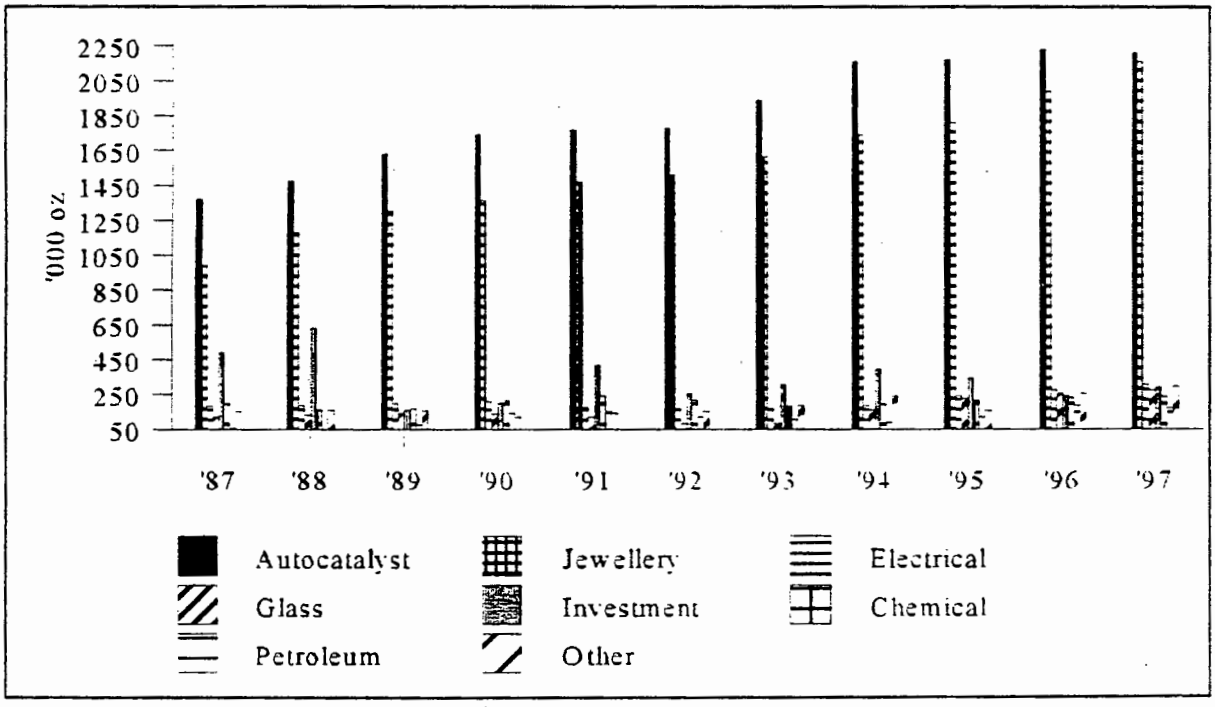

Figure 1.1.2: Annual world demand of platinum by application

Until 1995, the largest industrial use of palladium was in the electrical industry in the production of multi layer ceramic capacitors (for use in microcomputers, televisions, video recorders etc.), electrical contacts, conducting materials and thick film conductive track on hybrid integrated circuits.

The principal uses of palladium are shown in Figure 1.1.3 However, since the introduction of a palladium-rich catalyst in 1996, the automotive industry has become the prime consumer of palladium in the production of oxidative catalysts for automobile exhaust-gas emission control. The lower cost of palladium, compared with gold, has led to its increasing use in dentistry particularly in the USA and Japan. Gold-free alloys (containing 80+% palladium) bonded to porcelain jackets and low-gold alloys (containing ~20% palladium) are now widely used. Jewellery remains a significant application of palladium and the remaining use of palladium is mainly in the chemical industry as a constituent of platinum/rhodium gauzes in nitric acid production, hydrogen purification (palladium diffusion cells), high temperature brazing materials and selective catalysts for the hydrogenation and dehydrogenation of intermediates in the plastics, rubber and pharmaceutical industries.

The major applications of rhodium (Figure 1.1.4) are dominated by the automotive industry, in the production of three way autocatalysts for automobile exhaust-gas emission control (in 1997, 90% of all rhodium produced was used in this industry). In recent years, rhodium has found applications in the glass making industry and significantly as a catalyst in the chemical industry, in the hydroformylation of olefins and the carbonylation of methanol to yield acetic acid. Rhodium has also found a limited application in the electrical industry in the production of thermocouples. However, these three industries together used only 10% of all rhodium produced in 1997 [2].

Ruthenium is used mainly by the electrical industry in the production of resistor tracks of hybrid integrator circuits, chip resistors and resistor networks. Other applications of ruthenium are as chemical catalysts in applications ranging from gas purification to pharmaceuticals production. Small quantities of ruthenium are used in alloys in jewellery, dental alloys and electrical contacts. Applications for iridium have risen in recent years, mainly in the electrochemical industry in the production of electro galvanised steel and the electrolytic production of chlorates and hypochlorites. A small, but growing market exists for radioactive ^{192}Ir in cancer research and for the radiographic inspection of pipelines and oil rigs. Osmium is both the scarcest and least useful of the platinum-group metals, with few obvious uses aside from the use of osmium tetroxide in

organic oxidations and as a staining reagent for the microscopic examination of tissues [3].

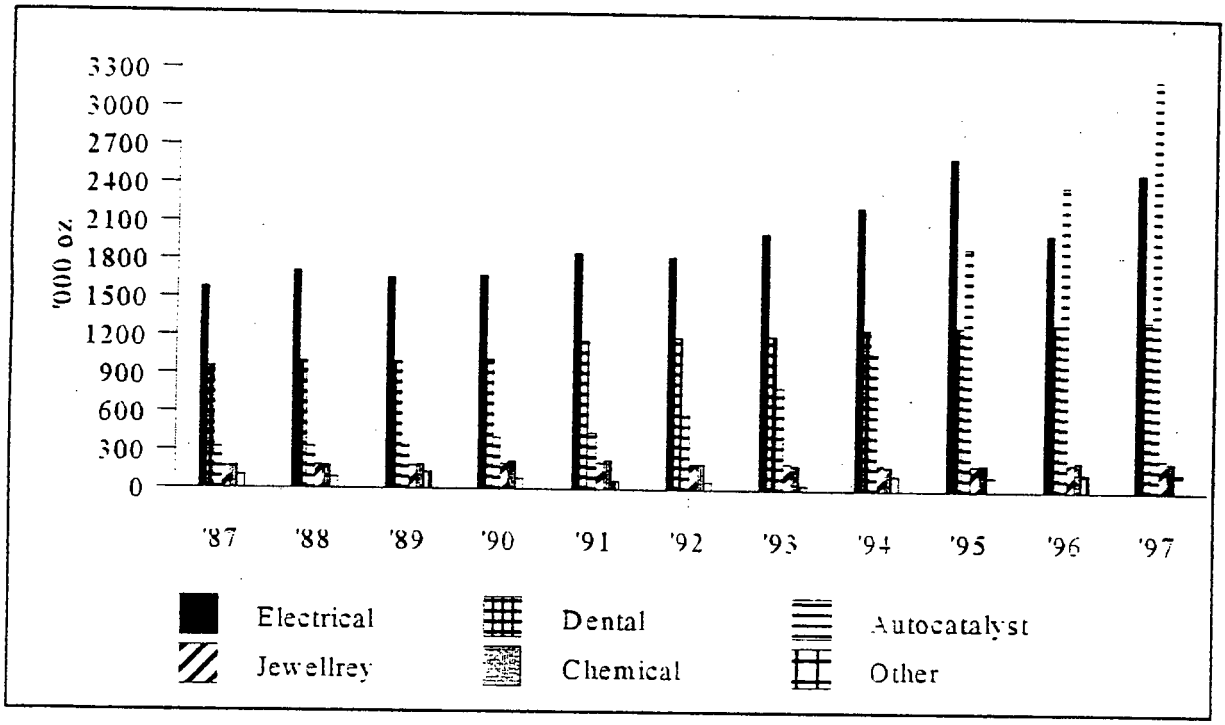

Figure 1.1.3: Annual world palladium demand by application

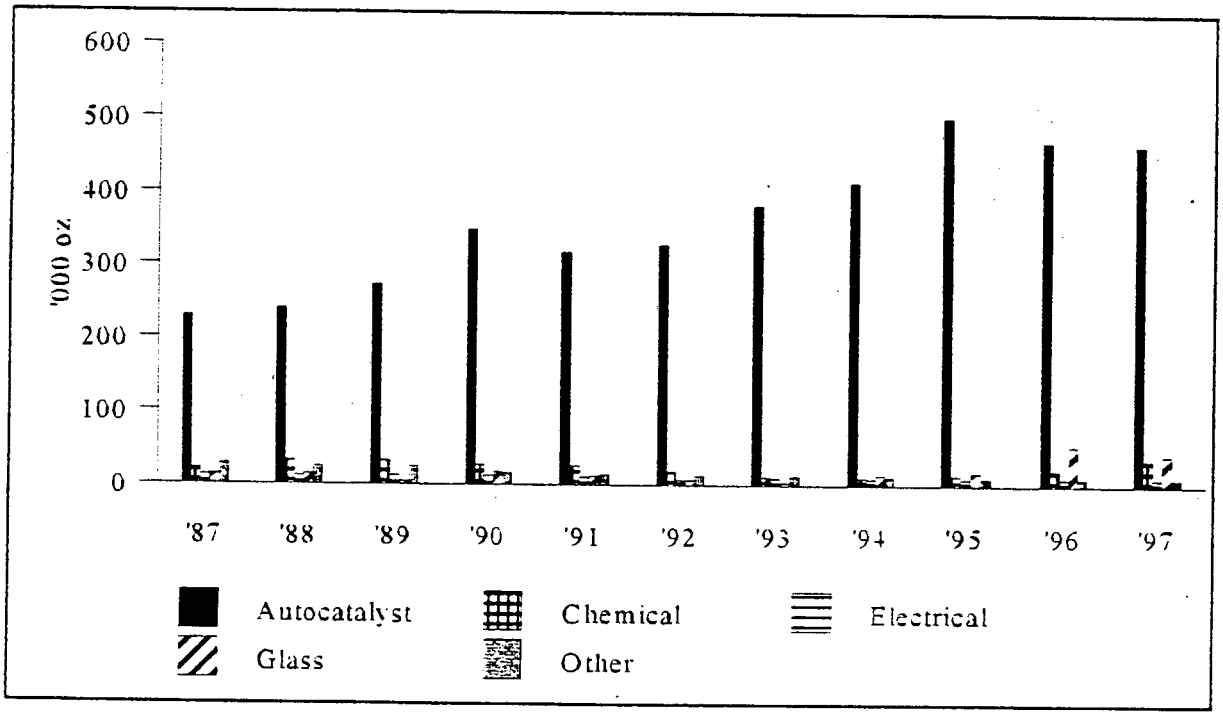

Figure 1.1.4: Annual world rhodium demand by application

1.2 Sources of Platinum-Group Metals

There are two principal sources of platinum-group metals. The primary source is from mining of ore deposits containing the platinum-group metals. Platinum-group metals obtained in this way are known as primary platinum-group metals and the industry as a primary production source of platinum-group metals. The smaller source is the reprocessing industry that recovers and refines platinum-group metal scrap and spent catalysts. Platinum-group metals obtained in this way are known as secondary platinum-group metals and the industry as a secondary production source of platinum-group metals.

From about 1960 onwards, the increase in the range and amount of usage of the platinum-group metals was accompanied by the dominance of the total world production (~98%) of primary platinum-group metals from only three sources - the Cu-Ni sulphide deposits in Canada, Russia and South Africa. These three sources have in common a low platinum-group metal grade, typically 2 to 10 $\mu g.cm^{-3}$, and usually a very close association between the platinum-group metal minerals and the 1st-row transition metal sulphide minerals.

Of these three sources, two - Canada and Russia - are mined in essence for their 1st-row transition metal content, the platinum-group metals being essentially byproducts. In South Africa, the reverse is true, with roughly 60% of the revenue being obtained from the platinum-group metals, and ~40% from the 1st-row transition metals [4]. Additionally, platinum is the major metal found in South African ores, whereas palladium is the major metal found in Russian and Canadian deposits. South Africa therefore dominates the world platinum market whereas Russia dominates the palladium market (Figures 1.2.1 - 1.2.3) [5].

The South African deposits lie in the Bushveld Igneous Complex (BIC), which is a saucer shaped area of about 24 000 km^2 with Pretoria on its southern central edge. It is a large igneous ore body, of layered intrusions, containing mafic and ultramafic rocks that are the largest sources of platinum-group metals. The BIC encompasses three reefs - the Merensky Reef, UG2 Reef and the Platreef. The Merensky Reef, the most actively worked, is only about 20 inches thick and below it at depths of 36 to 330 metres lies the UG2 Reef. The Platreef lies on the northern side of the BIC and was mined for a brief period in the 1920's. These three reefs contain almost 90% of the World's known reserves of platinum-group metals [6].

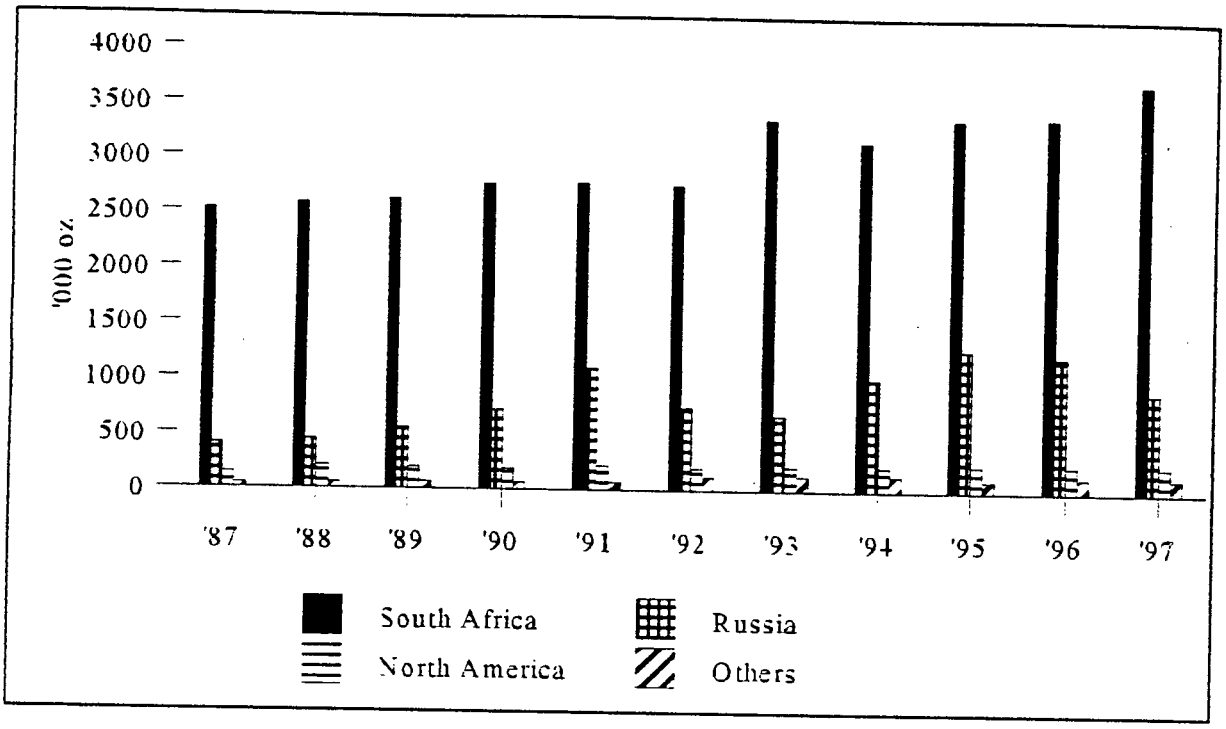

Figure 1.2.1: Annual world platinum supply by country

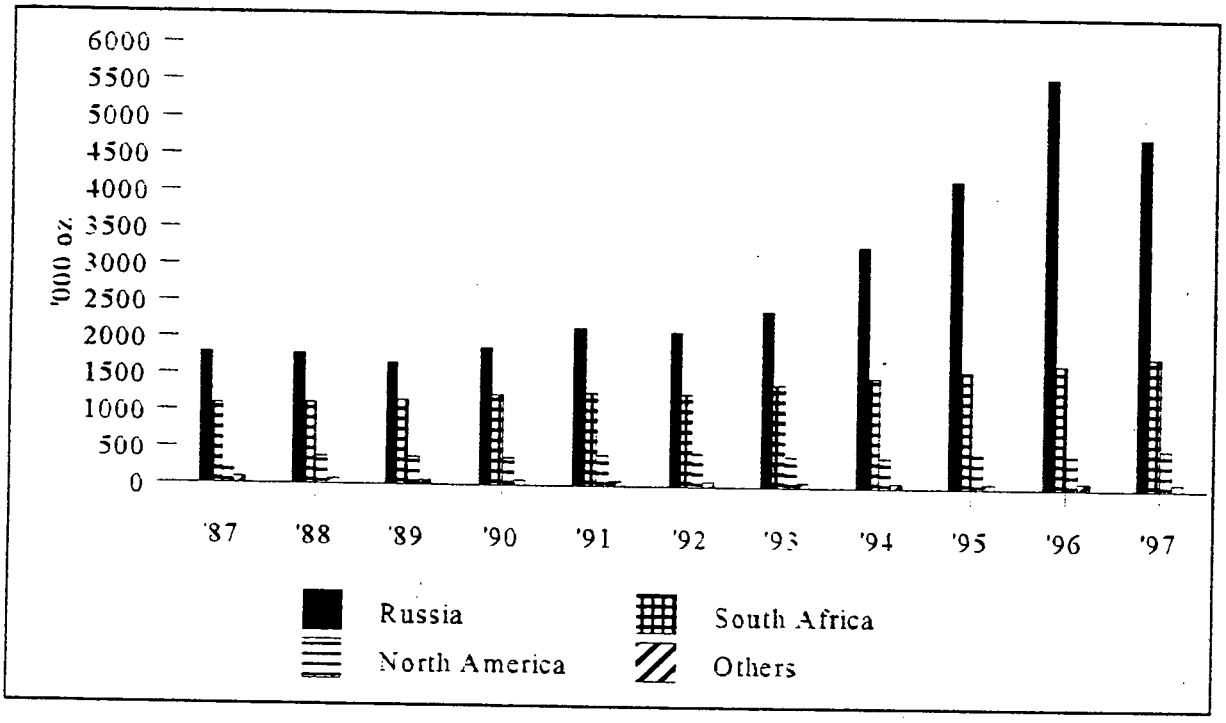

Figure 1.2.2: Annual world palladium supply by country

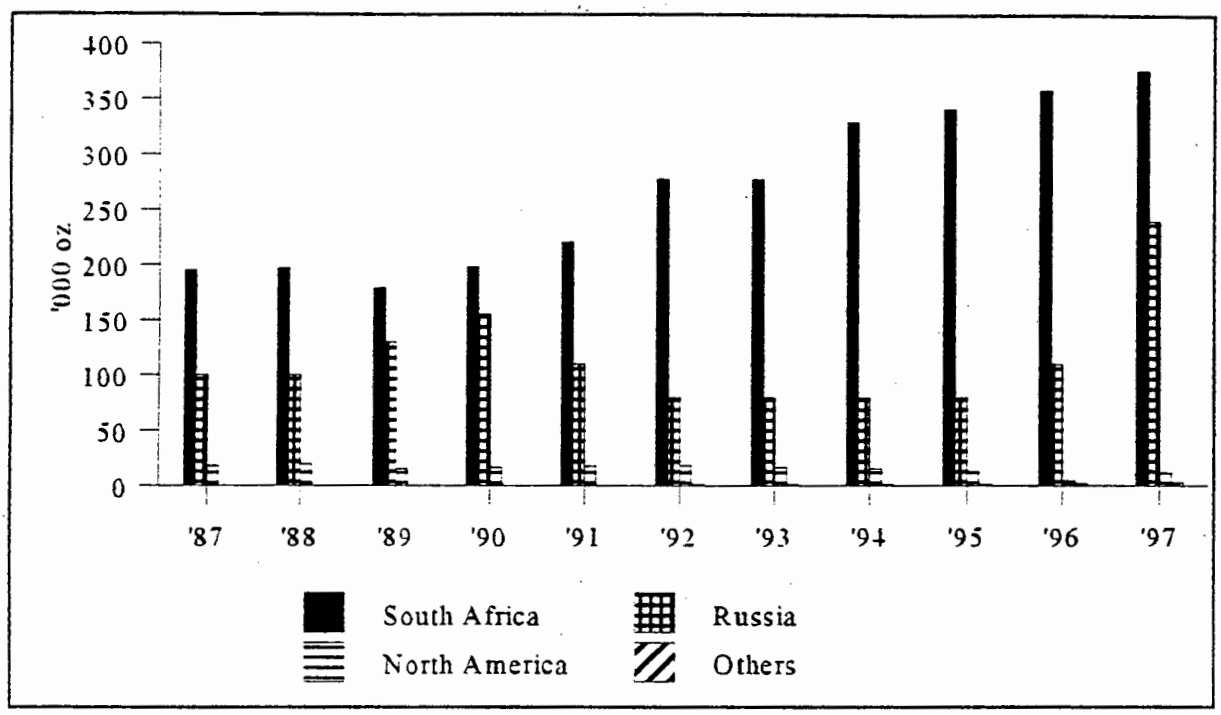

Figure 1.2.3: Annual world rhodium supply by country

The typical composition of platinum-group metals in the Merensky Reef is approximately ~60% platinum, 25% palladium, 4% rhodium and 11% ruthenium, iridium and osmium. The platinum bearing sulphide minerals, cooperite (PtS), braggite ((Pt, Pd, Ni)S) and the arsenide mineral sperrylite ($PtAs_2$) are all present in the Merensky Reef. Other sulphides, such as copper, nickel, iron, and chromite are also associated with the platinum-group metal minerals. The UG2 Reef has a lower copper and nickel content but higher chromite content. Although the concentration of platinum-group metals are not consistent throughout this reef, it does have some significant advantages over the mining of the Merensky Reef: improved tonnage to volume ratios due to its higher density; reduced treatment costs because of the lower 1st-row transition metal content and a higher relative proportion of rhodium present (12% compared to 4% present in the Merensky Reef) [7].

1.3 Platinum-Group Metal Recovery

The scarcity and high demand for the platinum-group metals has resulted in a correspondingly high commercial value (Figures 1.3.1 - 1.3.3) [8]. The high financial value attached to the platinum-group metals has demanded efficient and economical metallurgical recovery of the platinum-group metals from the geological deposits.

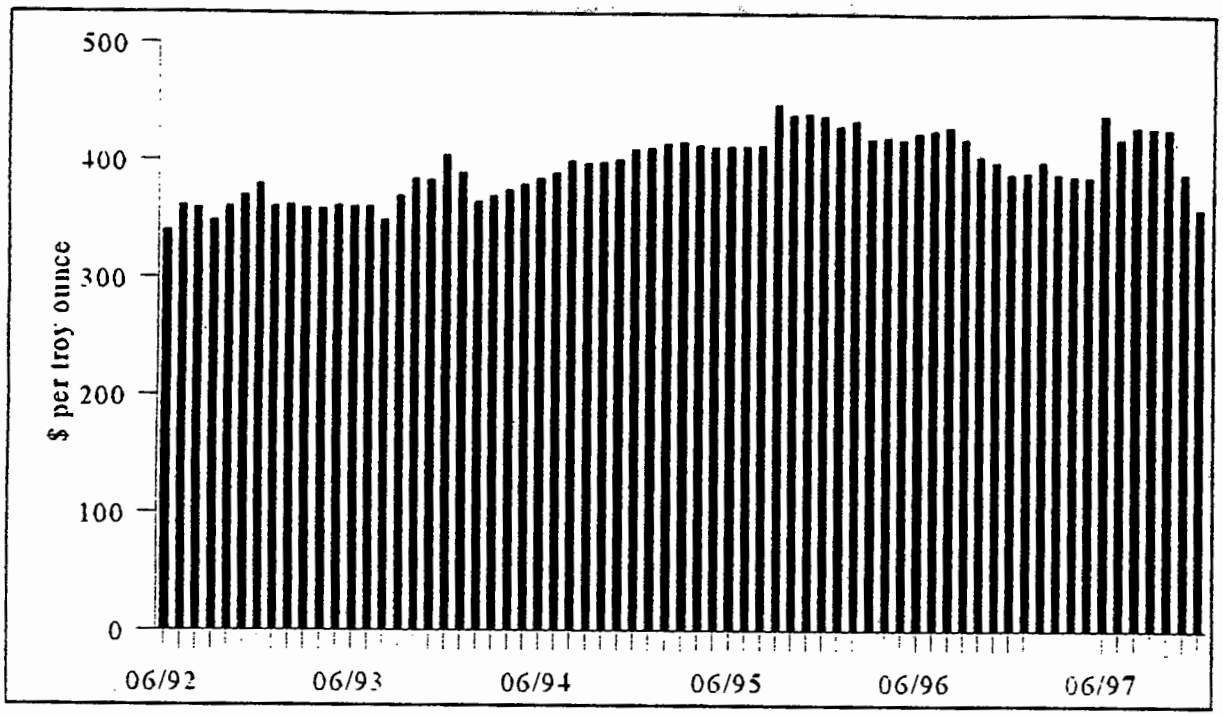

Figure 1.3.1: Average monthly price of platinum 1992 - 1997

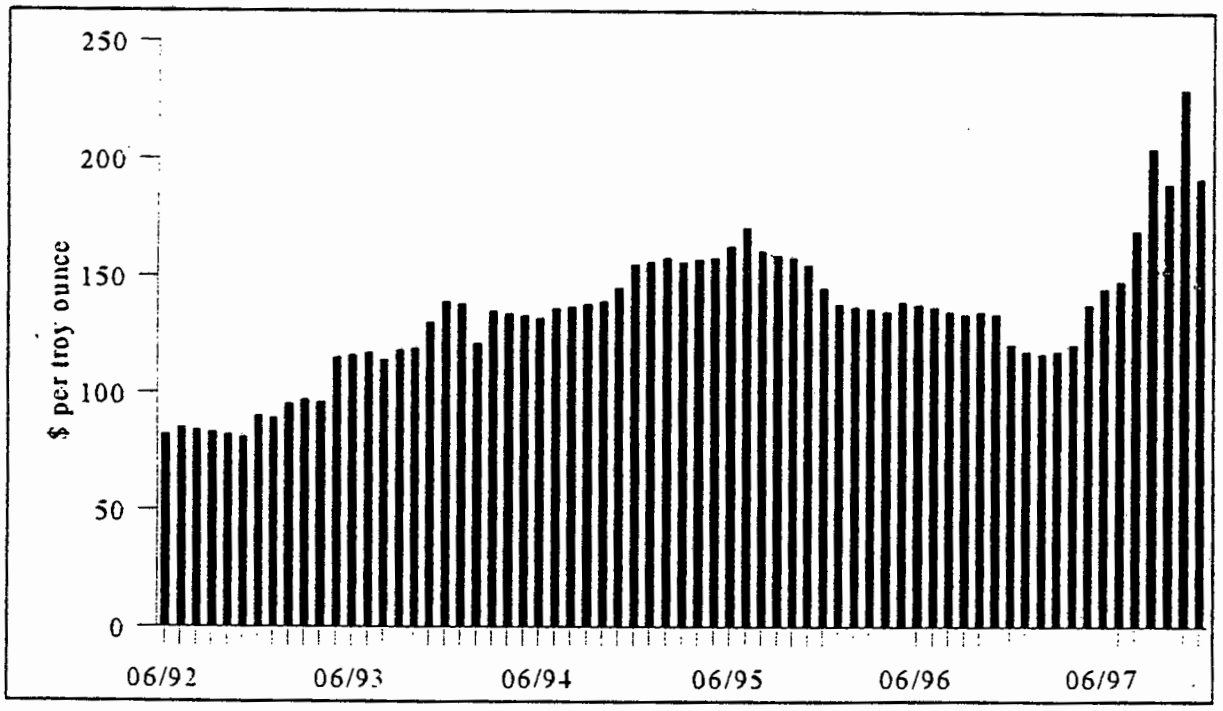

Figure 1.3.2: Average monthly price of palladium 1992 - 1997

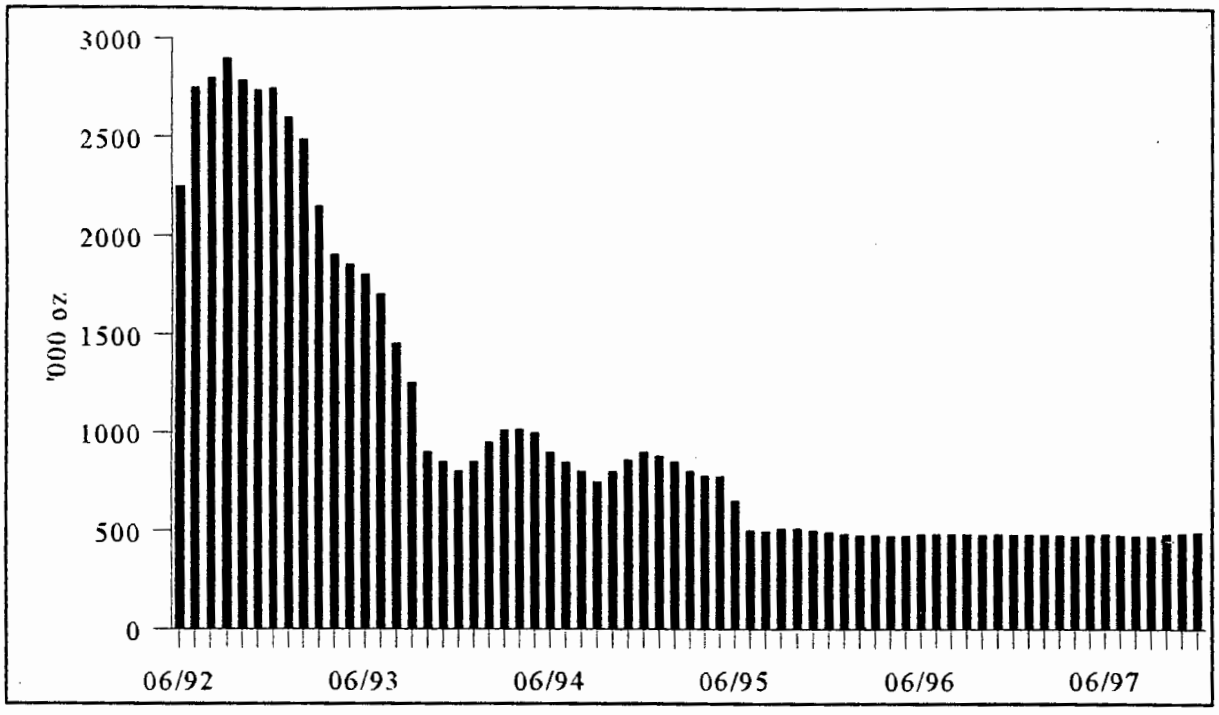

Figure 1.3.3: Average monthly price of rhodium 1992 - 1997

Most ores treated today contain trace quantities of platinum-group metals in the presence of relatively large amounts of copper, nickel and iron sulphides. Thus, the initial steps in the recovery of the platinum-group metals from the mined ore are very closely related to the recovery of the associated 1st-row transition metals, and the processing only becomes distinct once a concentrate containing the platinum-group metals can be separated from the 1st-row transition metals (Figure 1.3.4).

The mined ore is crushed and ground to a suitable size, and mixed with water. The sulphide minerals are then recovered from the ore by froth floatation (bulk sulphide floatation) with hydrophobic organic reagents (xanthates with $CuSO_4$ as activator) that coat the platinum-group metals and sulphides, and float them to the surface on bubbles introduced into this slurry as a froth. The froth is skimmed from the surface of the floatation vats and the concentrate obtained either first treated by a gravity separation technique to remove some of the platinum-group metals (~20%) or directly smelted in an arc furnace, at 1250 to 1350°C, to produce a matte. The composition of the matte produced ('green matte') is dependent on the nickel and copper content of the concentrate. In South Africa a typical composition would be 40% Fe, 20% Ni, 10% Cu, 30% S and platinum-group metals 500 to 1000 $\mu g.cm^{-3}$.

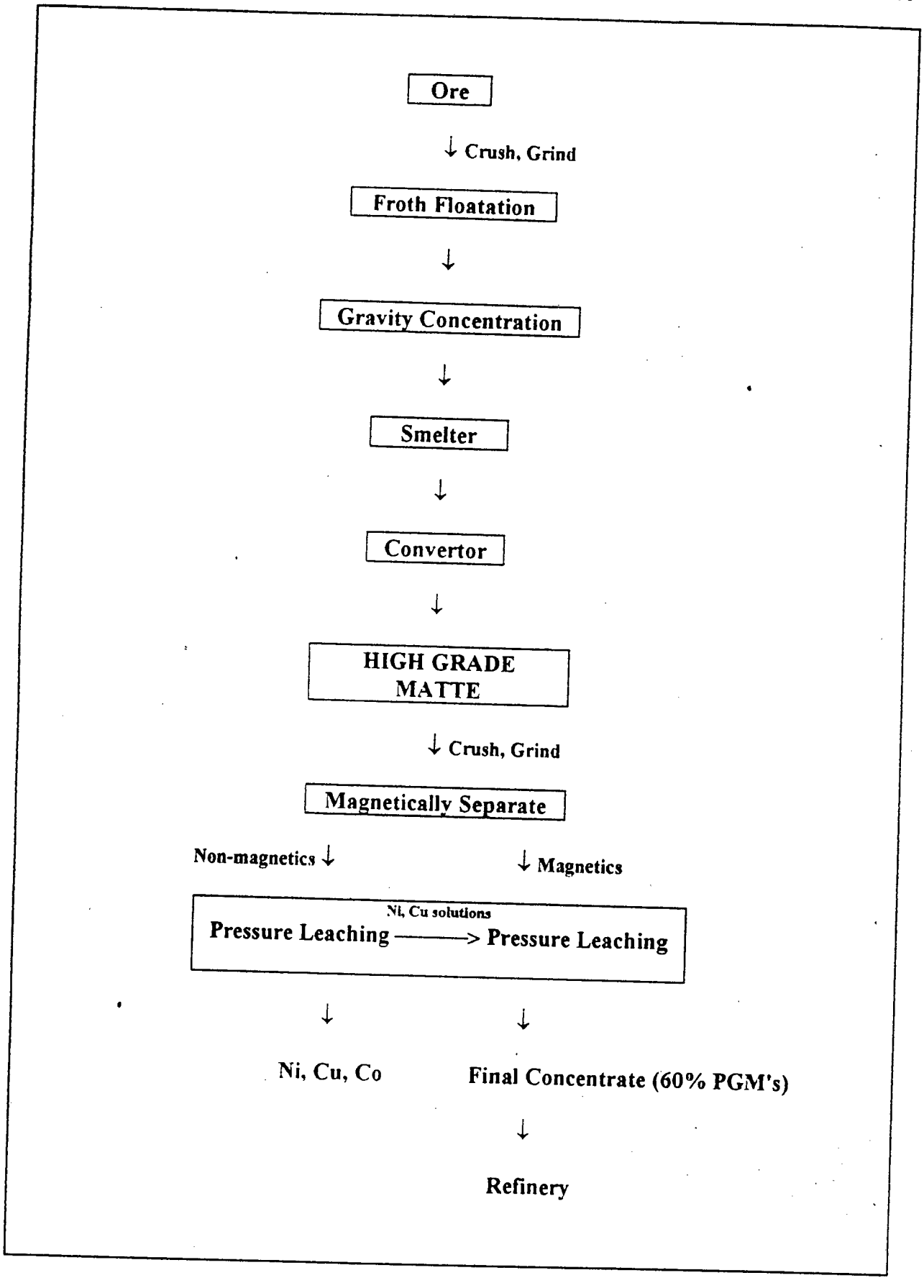

Figure 1.3.4: Typical recovery process of the platinum-group metals from mined ore

Recovery of the platinum-group metals in the matte is very high, usually > 98%. Losses of the platinum-group metals, discarded with the slag, are almost entirely due to mechanical causes. The matte phase produced is also an excellent collector of various minor constituents of the ore, such as Se, Te, As, Sb, Pb, Co, Bi, etc., and these are thus concentrated along with the platinum-group metals. The next step is the converting operation in which the sulphur in the green matte is partly oxidised to SO_2, and Fe oxidised in the presence of SiO_2 to form a fayalite slag.

After conversion the high grade matte produced, on South African plants, has a typical composition of 50% Ni, 25% Cu, 22% S, 1 - 2% Fe and platinum-group metals 2000 to 4000 $\mu g.cm^{-3}$. This high grade matte is then crushed and ground and treated by magnetic separation to remove the residual iron sulphide. Pressure leaching, using sulphuric acid, removes the bulk of the Cu, Ni, and Co to yield a final concentrate with a ~60% platinum-group metal content, the remainder being largely Cu and Ni. Typically, the matte-leach residue or platinum-group metal concentrates produced are complex materials containing besides platinum-group metals, substantial quantities of other metals. These include trace amounts of Se, Te, As, Sb, Bi, Sn, etc. The platinum-group metals content of the material can vary widely, depending on the efficiency of the leach and the actual leach process used. Normally, a concentrate grade of 60% is achieved and this is suitable for further treatment in the refinery.

1.4 Refining

The recovery of the platinum-group metals from the platinum-group mineral ore (**1.3**) is a highly efficient and optimised procedure, with minimal losses of the platinum-group metals. The final concentrate produced is then subjected to refining processes to produce the desired finished product - high purity platinum-group metals.

Treatment of the final concentrate in the refinery, varies depending upon the impurities and ratios of the platinum-group metals present and the final use. The most widespread refining process in processing plants today is the separation of the platinum-group metals from one another by precipitation and solvent extraction. Most platinum-group metal separations are based on the properties of the chloro-complex anions formed by the platinum-group metals in chloride solutions. The classical process has been developed over several years and is performed with little variation for platinum and palladium, but for the other metals a greater variety of methods are still used. The

final concentrate is leached in aqua regia, resulting in the ready solubility of gold, platinum and palladium.

The other minor metals are insoluble in aqua regia. Gold is precipitated by reduction to metal with sulphur dioxide and following this iron(II) sulphate, and removed. Platinum is then precipitated as $(NH_4)_2PtCl_6$ by addition of ammonium chloride to the pregnant liquor and removed. The remaining solution contains palladium, traces of platinum, most of the minor platinum-group metals and substantial quantities of 1st-row transition metal chlorides. This solution is neutralised while hot with aqueous ammonia and the palladium in solution is converted to $[Pd(NH_3)_4]^{2-}$. Hydrochloric acid is added and palladium precipitated as $Pd(NH_3)Cl_2$. All these above reactions produce a high purity salt that is readily converted to the corresponding metal on heating.

The undissolved material, containing the minor platinum-group metals, is fused with sodium carbonate and sodium peroxide at elevated temperatures, cooled, solidified and leached with water. Ruthenium and osmium are dissolved as RuO_4^{2-} and OsO_4^{2-} respectively, while rhodium and iridium are precipitated as oxides. Ruthenium and osmium are removed from solution by oxidation to their volatile tetroxides with Cl_2. The hydroxide residue, containing rhodium and iridium is dissolved in hydrochloric acid and iridium precipitated as $(NH_4)IrCl_6$ by addition of ammonium chloride to the solution.

Finally, rhodium is recovered by heating of the solution and addition of aqueous ammonia, in the presence of alcohol as catalyst, followed by addition of hydrochloric acid to precipitate $[Rh(NH_3)_5H_2O]^{3+}$.

All effluent solutions produced by refining processes are further treated in a variety of ways; including zinc in cementation vats, to recover the residual platinum-group metals they contain (Figure 1.4.1) [9]. This reduction procedure recovers most of the platinum and palladium. However, the minor platinum-group metals are slow to be reduced, and significant quantities of these metals are discarded with the final post-processing effluent cycled from the plant to waste dams. This waste effluent is a complex chemical matrix (Table 1.4.1), which limits accurate and reproducible platinum-group metal analysis at trace and ultra trace concentrations.

This is of concern considering the volumes of effluent produced, as even trace levels of platinum-group metals accumulate to represent a substantial loss of income for the platinum-group metal industry. Industry in South Africa is also presently moving towards the design of zero effluent plants to comply with the introduction of stricter environmetal legislation regarding the production, management and disposal of industrial effluent.

1.5 Objectives of Research

Matte leach residues and post-processing effluents contain approximately 0 - 200 and <0.5 $\mu g.cm^{-3}$ platinum-group metals, respectively. Platinum-group metals present in the matte leach residue are subjected to further treatment in the recovery plant to recover the platinum-group metals. Post-processing effluents undergo no further treatment and are cycled to waste and collected in outside dams, where losses are incurred by for example, seepage into the soil etc. The platinum-group metals in these effluents, although at low levels, accumulate in the dams and represent a substantial loss of income when the volumes of effluent produced are considered and are a significant source of error in process control and management thereof.

These unrecovered platinum-group metals could be recovered, if a suitable pre-concentration and detection system was available and used, before the post-processing effluent is cycled to waste. However, a review of the literature of platinum-group metal pre-concentration (**2.1**) and determination (**3.1**) methods illustrate that there is neither one technique currently available that achieves pre-concentration of all the platinum-group metals, from a complex matrix such as post-processing effluent, nor a determination technique that is without limitations.

As such, this forms an important field for investigation and improvement.

The objectives of research were thus:

1. Identification of a suitable preconcentration system for the platinum-group metals present in industrial effluent - **non-polar platinum-group metal chelates pre-concentrated on a reverse-phase column**

2. Identification of a suitable detection system for the platinum-group metals, subsequent to pre-concentration from the industrial effluent - **ICP-OES**

3. Synthesis of chosen pre-concentration chelating agent - ***N*** **- benzoyl -** ***N, N'*** **- dialkylthioureas**

4. Development of suitable pre-concentration system using synthetic effluent solutions containing platinum-group metals - **identification of all system variables**

5. Optimisation of developed pre-concentration system variables - **recovery experiments**

6. Development of suitable detection sytem using synthetic effluent solutions containing platinum-group metals - **identification of all system variables**

7. Optimisation of developed detection system variables - **optimisation experiments**

8. Pre-concentration and determination of platinum-group metals present in real industrial effluent with developed system - **recovery experiments**

9. Validation of developed system for the pre-concentration and determination of platinum-group metals present in real industrial effluent - **standard addition, spiking and mass balance recovery experiments**

1.6 Approach

An experimental pre-concentration system was devised. The factors influencing pre-concentration of the most commercially valuable platinum-group metals (Pt, Pd, Rh) with the devised system were studied, using synthetic post-processing effluents. Subsequent refinements were developed and incorporated into the system. The analytical merit of the pre-concentration system was evaluated by means of ICP-OES determination.

The matter of the determination technique was then approached. Factors influencing ICP-OES determination of the platinum-group metals, with the devised pre-concentration system, were studied. After evaluation of the results, refinements were developed and employed. Finally, a procedure using the developed pre-concentration system with subsequent ICP-OES determination.

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Chapter 2

Review of Analytical Techniques for the Pre-concentration of the Platinum-groupMetals

2.1 Introduction

The trace analysis of the platinum-group metals in complex, severely interfering matrices, such as industrial effluent, has been the focus of much research in the past forty years. Two main factors have stimulated interest. Firstly, the annual growth in demand for platinum-group metals due to their ever increasing application in many commercial and industrial fields. Secondly, the development of highly sophisticated and sensitive instrumentation with increasingly greater trace and ultra trace analysis capabilities, such as inductively-coupled plasma spectroscopy (ICP) and inductively-coupled plasma - mass spectrometry (ICP-MS), neutron-activation analysis (NAA), and X-ray Fluorescence spectroscopy (XRF).

Despite the greater availability of much improved instrumentation, most analytical techniques currently employed for the determination of the platinum-group metals require selective sample preparation that ensures enrichment of the individual platinum-group metals at the trace and ultra trace ($<1\ \mu g.cm^{-3}$) level, along with simultaneous matrix removal, prior to determination. Several procedures have been developed to achieve pre-concentration of the platinum-group metals prior to trace analysis and these procedures can be divided into six diverse categories: fire assay (**2.2**), solvent extraction (**2.3**), ion-exchange (**2.4**), chromatography (**2.5**), solid sorbents (**2.6**) and co-precipitation (**2.7**). For each category a generalised description of the methodology involved will be given, followed by some specific examples that possess some ideal pre-concentration characteristics described below.

An ideal pre-concentration technique should encompass the following characteristics

1. Analyte Selectivity
2. Accuracy
3. Reproducibility
4. High Percentage Recovery
5. Low Pre-concentration Complexity
6. Time Efficiency
7. Cost Efficiency

8. Simplicity of Use

9. On-line Capabilities

2.2 Fire Assay and Cupellation

Fire Assay is universally considered the classical analytical technique for the pre-concentration of gold, platinum, palladium and rhodium. Ruthenium, osmium and iridium are also pre-concentrated by fire assay, but fire assay is not always the technique of choice for pre-concentration. Several metals, in the molten state, effectively preconcentrate the platinum-group metals, of which lead is the most effective. Classical lead collection fire assay of the above noble metals involves their extraction with a flux containing lead oxide (litharge) and varying quantities of sodium carbonate, potassium carbonate, borax, silica, potassium nitrate and starch or flour. This mixture is fused with the ore (or other matrix) and the precious metals are collected in the 'button' of lead formed when the litharge is reduced by flux and sample components. The 1st-row transition metal constituents (e.g. Cu, Ni, Fe) of the sample usually end up in the slag. The lead 'button' obtained in the fusion step still contains interfering impurities which can be removed by scorification. Scorification, unlike fusion, is carried out in an oxidising environment, in which the lead is oxidised to form a slag that further extracts impurities. After scorification, cupellation results in the lead being reoxidised to litharge (absorbed into the cupel), leaving the platinum-group metals behind, collected in the silver cupellation button [1,2].

The collection of the noble metals is critically dependant on the cupellation button composition and assay conditions (furnace temperature being the most important). Rhodium is relatively insoluble in lead and low recoveries for rhodium have been reported [3]. Along with the mechanical losses of rhodium during fire assay, the elevated temperatures of assay conditions prevent the collection of osmium and ruthenium, due to their evolution as volatile tetroxides [4]. Despite the above disadvantages as well as being a time-intensive method, classical lead collection fire assay is a highly selective and effective technique that is readily adaptable to routine operations, and is widely used in the platinum-group metal industry to this day.

Neoclassical fire assay [5,6] also concentrates precious metals by a fusion process, as in classical lead collection fire assay, but various sulphide systems or 1st-row transition metals other than lead are used as collectors. Examples include SnO_2, NiO, Cu_2O, NiS, Cu_2S. The neoclassical nickel sulphide fire assay is the most commonly utilised and involves extraction of the precious metals with a flux containing nickel carbonate and sulphur, which combine to form nickel sulphide when heated gradually to 1100°C. Upon cooling, the nickel matte separates cleanly from the slag, which is discarded. The nickel "button" is parted with concentrated hydrochloric acid dissolving the

nickel sulphide, while the precious metal sulphides remain insoluble. This neoclassical fire assay overcomes many problems associated with the classical lead collection fire assay. Rhodium is soluble in the nickel sulphide matrix, thereby avoiding mechanical losses of the metal. The collection of the precious metals is also less significantly affected by the assay conditions. However, prevention of losses of the volatile platinum-group metals (Os, Ru) requires special precautions to be taken during the collection of the noble metals. The disadvantages of this method are two-fold: the method is time-consuming, and acid dissolution of the nickel sulphide matrix is tedious and complex - if losses of the pre-concentrated noble metals are to be avoided.

2.3 Solvent Extraction

Fire assay/cupellation techniques are applicable to ores and floatation concentrates in which the platinum-group metals are in mineral form. In contrast, solvent extraction works only once the platinum-group metals are concentrated or dissolved in some acid matrix.

Solvent extraction methods rely on the desired platinum-group metal ions being selectively extracted from an aqueous phase by an immiscible organic solvent. It is of equal importance that the metal be able to be back-extracted with another suitable aqueous phase. The organic and aqueous phases used must also be compatible with process control, health and safety, and cost considerations [7] and thus only cost-effective, non-hazardous solvents can be used.

The ability of the solvent to extract the metal is defined by a distribution coefficient [8], **D**, where

$$\mathbf{D} = \frac{\text{Concentration of element in the organic solvent phase}}{\text{Concentration of the element in the aqueous phase}}$$

The value of D applies at a given set of conditions for the system (temperature, ionic strength and pH) and is a complex conditional equilibrium relationship, which is usually constant for dilute solutions. However, commercial system process solutions are often not dilute and organic solvents only possess a limited capacity for extracting metal, known as the maximum solvent loading capacity.

One of the most effective solvent extraction media for the platinum-group metals, is the chloride system and it is widely used since the platinum-group metals are routinely dissolved by chlorine gas and/or hydrochloric acid leading to the formation of platinum-group metal chloro species. The solvent extraction chemistry considered here is therefore based on the chloride system. The normal platinum-group metals species encountered, in hydrochloric acid media, are shown in Table 2.3.1.

Table 2.3.1: Common Platinum-Group Metal Chloro Species

Element	Oxidation state	Major chloro species
Platinum	Pt(II) d^8	$(PtCl_4)^{2-}$
	Pt(IV) d^6	$(PtCl_6)^{2-}$
Palladium	Pd(II) d^8	$(PdCl_4)^{2-}$
	Pd(IV) d^6	$(PdCl_6)^{2-}$
Rhodium	Rh(III) d^6	$(RhCl_6)^{3-}$
		$RhCl_5(H_2O)^{2-}$
		$RhCl_4(H_2O)_2^-$

These species slowly aquate in chloride solutions of low concentration and water, but this equilibrium is inhibited at higher chloride concentrations. Platinum-group metal chloro complexes are generally much more stable than the concomitant 1st-row transition metal complexes (e.g. Cu^{2+}, Ni^{2+}, Fe^{3+}, $Co^{2+/4+}$) and this allows platinum-group metals/1st-row transition metals separation based on the stability of the corresponding anionic chloro complexes. Complexes containing heavier donor atoms are more stable and generally the following overall order applies:

$$S \sim C > I > Br > Cl > N > O$$

Reaction mechanisms for solvent extraction processes fall into three categories: compound formation, solvation and ion-pair formation. Complex formation extractants can be chelating agents, carboxylic or sulphonic acids, or organophosphorous compounds. Substitution kinetics for the platinum-group metals are relatively slow compared to the kinetics of the 1st-row transition metals [9, 10]. A generalised form of this reaction is:

$$[MCl_x]^{n-} + yS \rightleftharpoons (MCl_{x-y}Sy)^{y-n} + yCl^-$$

Solvating extractants are either carbon or phosphorous bonded oxygen bearing extractants, and react as follows:

$$(MCl_x)^{n-} + yS \rightleftharpoons (MCl_x)^{n-}.yS$$

The Lewis basicity of such solvents is low, with the equilibrium lying more to the left.

Ion-pair formation includes the high molecular weight amines and quaternary ammonium compounds. In general the reaction is:

$$[MCl_y]^{n-} + nR^+X^- \rightleftharpoons (R^+)_n[MCl_y]^{n-} + nX^-$$

Equilibrium depends on the basicity of R and where R = R_4N^+, R_3NH^+.

In the past decade, research has shifted from time-consuming and labour-intensive techniques, to more versatile methods that are not only more efficient, rapid and selective for the platinum-group metals, but also possess on-line capabilities. Solvent extraction satisfies these requirements and the many documented methods are based upon the great affinity of noble metals to form complexes with organic reagents, such as thiobenzanilide [11], tri-n-octylamine [12], ammonium pyrrolidine dithiocarbamate [13] and *N*-benzoyl-*N'*, *N'*-dialkylthioureas [14].

Shkil' and Zolotov" [15] investigated the extraction of platinum, as $PtCl_6^{2-}$, from hydrochloric acid media using thiobenzanilide (Figure 2.3.1) in the presence of tin(II) chloride and potassium iodide. Platinum was found to be extracted rapidly and quantitatively into methyl isobutyl ketone and chloroform, as $PtCl_4^{2-}$, under these conditions.

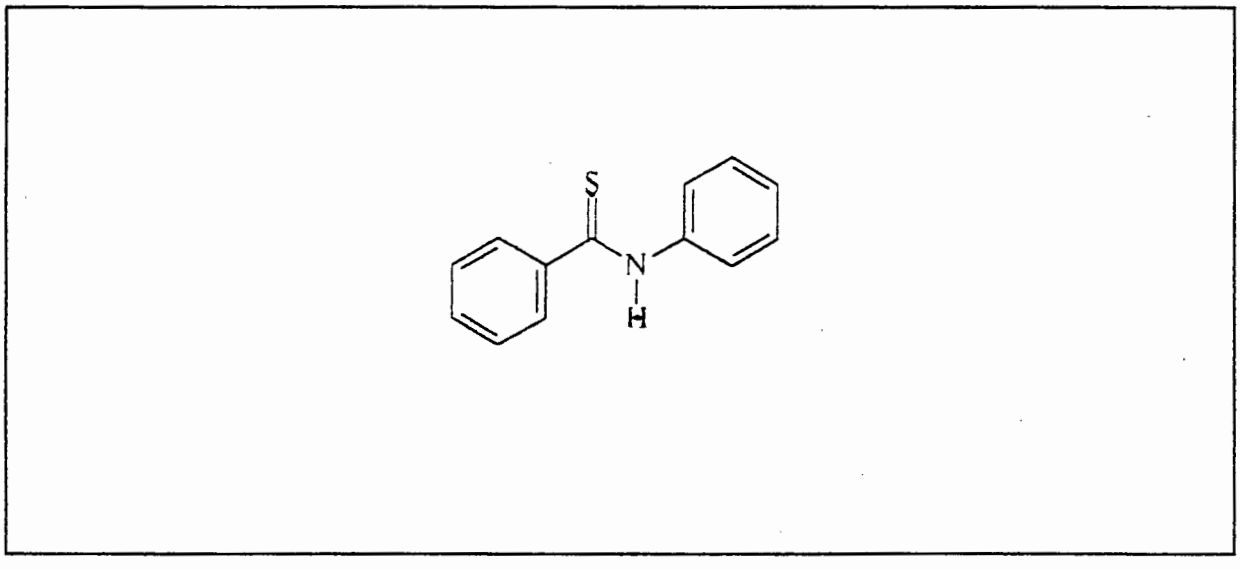
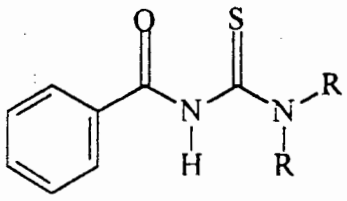


Figure 2.3.1: Thiobenzanilide

Thiopicolinamide and its derivatives were shown to have an extremely low affinity towards the platinum-group metals, except in the presence of a large excess of a labilising agent such as potassium iodide or tin(II) chloride [16, 17]. Consequently, this method has not resulted in further research because of the time-consuming nature of the pre-concentration step and also the impractability of adding $SnCl_2$ as a 'contaminant' to the sample matrix.

Complexation of the noble metals with ammonium pyrrolidine dithiocarbamate (APDC) was first described by Brooks *et al.* in 1989 [18]. The study was conducted on the formation of stable noble metal complexes in strongly acidic solutions. These resultant complexes were readily extracted into methyl isobutyl ketone, thus achieving pre-concentration of the platinum-group metals under study. A shortfall of this method was the necessity for precise adjustment and control of the pH for quantitative extraction to be achieved for palladium(II) and iridium(III). Platinum(II) and rhodium(III) failed to be extracted significantly by this method. This method has, however, been applied successfully to the pre-concentration of palladium(II) in standard ore.

More successful and selective complexing agents for the solvent extraction pre-concentration of the platinum-group metals are *N*-benzoyl-*N'*, *N'*-dialkylthioureas (Figure 2.3.2) [19 - 23].



where R = alkyl group

Figure 2.3.2: Generalised structure of *N*-benzoyl-*N'*, *N'*-dialkylthiourea

N-benzoyl-*N'*, *N'*-dialkylthioureas are a class of ligands (1, 3 - dichalcogen group) that enable complexation and enrichment of the platinum-group metals from strongly interfering matrices. The nature of the coordination chemistry and specific donor properties of this class of ligands enables selective complexation of the platinum-group metals, silver and mercury from acidic solutions containing other elements.

Complex formation between the platinum-group metals and *N*-benzoyl-*N'*, *N'*-dialkylthioureas involve the formation of neutral complexes in a bidentate configuration with coordination via the sulphur and oxygen atoms of the ligand [24]. The neutral complex is lipophilic and readily extractable into apolar, organic solvents (Figure 2.3.3).

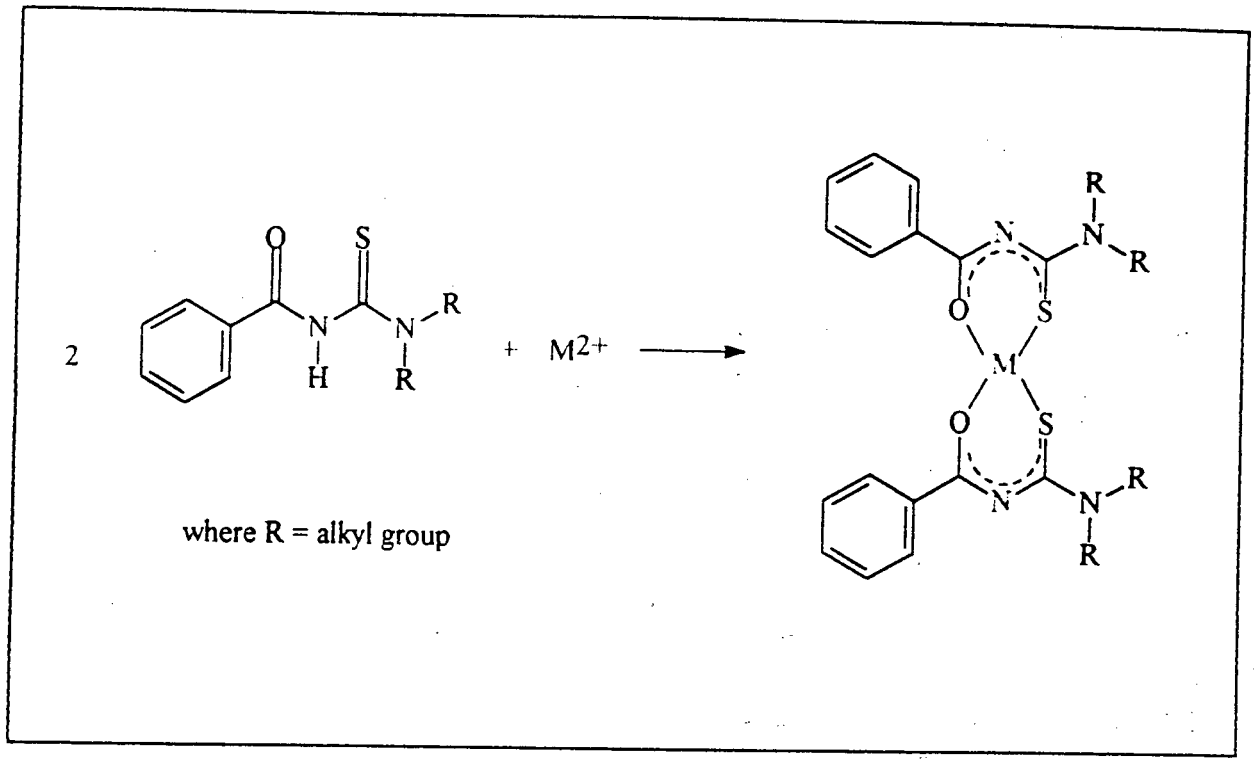


Figure 2.3.3: Schematic complexation of *N*-benzoyl-*N'*, *N'*-dialkylthioureas

Köning, Schuster and Vest [25, 26] reported successful solvent extraction of the platinum-group metals with *N*-benzoyl-*N'*, *N'*-dihexylthiourea (DHBT), resulting in efficient extraction of palladium(II), platinum(II) and ruthenium(III). These metals were quantitatively extracted and thereby pre-concentrated, from a hydrochloric acid medium into toluene within a few minutes - palladium(II), and one hour - platinum(II) and ruthenium(III). The presence of excess 1st-row transition metals such as iron, tin and copper did not interfere with the pre-concentration of the platinum-group metals.

The literature contains many more solvent extraction procedures, but these procedures do not possess many ideal pre-concentration characteristics and thus will not be described.

2.4 Ion-exchange

Ion-exchange is most commonly used as a separation procedure in which ions of like charge are separated by elution from a column packed with a finely divided resin. However, some methods have been devised to use ion-exchange as a pre-concentrating procedure for the platinum-group metals. Synthetic ion-exchange columns are high-molecular-weight polymeric materials containing many ionic functional groups per molecule and can be of two types: cation-exchange columns and anion-exchange columns [27].

Cation-exchange resins can be either a strong-acid type with sulphonic acid groups ($RSO_3^-H^-$) or a weak-acid type containing carboxylic acid groups (RCOOH). Anion-exchange resins contain basic amine functional groups attached to the polymer molecule. 'Strong-base' exchangers are quaternary amines [$RN(CH_3)_3^-OH^-$]; 'weak-base' types contain secondary or tertiary amines. An important property of all ion-exchange resins is that they are essentially insoluble in aqueous media and swell in the presence of water. Thus when a cation exchanger is immersed in an aqueous media containing the cation M^+, the following exchange equilibrium is quickly established:

$$xRSO_3^-H^+ + M^{x+} \rightleftharpoons (RSO_3^-)_xM^{x-} + xH^+$$

where M^{x+} is a cation and R represents that part of the resin molecule containing one sulphonic group. The analogous process involving a typical anion-exchange resin can be written as:

$$xRN(CH_3)_3^-OH^- + A^{x-} \rightleftharpoons [RN(CH_3)_3^-]_xA^{x-} + xOH^-$$

where A^{x-} is an anion.

The use of ion-exchange as a pre-concentration tool in the trace analysis of the platinum-group metals has not increased significantly in the past decade. Cation-exchange resins can be used to retain 1st-row transition metals from platinum-group metal containing solutions, while the platinum-group metals, owing to the stability of their chloro complexes are unretained as anions and pass into the effluent. Conversely, anion-exchange resins retain the platinum-group metal chloride complexes, while the cationic 1st-row transition metals pass into the effluent. However, ion-exchange can only be applied to relatively dilute solutions of platinum-group metals and invariably the ion-exchange resin is rarely selective to the noble metals [28]. Successful pre-concentration is often compromised by an inability to elute some of the pre-concentrated platinum-group metals from the resin, resulting in poor recoveries. An additional disadvantage of this method is that careful manipulation of separation conditions and solution pH are required to obtain quantitative pre-concentration of the platinum-group metals [29].

Palladium, iridium and rhodium are effectively the only platinum-group metals that could commercially be pre-concentrated by means of ion-exchange. The following functional group-modified resins have been used with some degree of success: sulphur-bonded dehydrodithiozone [30], δ-aminopropyl-triethoxysilane [31], 2, 2'-dipyridyl-3-[(4-amino-5-mercapto)-1, 2, 4-triazolyl]hydrazone [32], Cellex T [33], 2-amino-1-cyclopentene-1-dithio-carboxylic acid [34] and poly(aniline) [35].

Although these modified resins possess commercial potential with respect to palladium pre-concentration, these resins all require careful manipulation of solution pH and suffer from an inability to recover the pre-concentrated metal without subsequent burning of the resin. This leads to undesirable time-consuming and costly pre-concentration methods.

2.5 Chromatography

Chromatography is a technique in which the components of a mixture are separated based upon the rates at which they are carried through a stationary phase by a gaseous or liquid mobile phase. Chromatographic methods are of two types: Column chromatography, in which the stationary phase is held in a narrow tube and the mobile phase is forced through the tube under pressure or by gravity, such as normal phase-HPLC (NP-HPLC) and reverse phase-HPLC (RP-HPLC); and planar chromatography, in which the stationary phase is supported on a flat plate or in the pores of a paper and the mobile phase moves through the stationary phase by capillary action or under the influence of gravity, such as TLC.

Stationary phases suitable for the chromatographic separation of the platinum-group metals have only recently been used for pre-concentration of the platinum-group metals. These methods use one of two systems: either chemically derivatised columns containing silica gel bonded organic ligands that complex and preconcentrate the platinum-group metals prior to their separation; or the pre-concentration of non-polar platinum-group metal chelates, introduced into the chromatographic system [36].

Two methods [37, 38] developed by the National Institute for Metallurgy in the 1970's were moderately successful. The principle used in both methods involved reversed-phase extraction chromatography. Tri-n-butyl phosphate (TBP), immobilised on silica gel, as stationary phase and hydrochloric/sulphuric acid as eluent were investigated. Excellent results were obtained for solutions in which the concentration of platinum-group metals was higher than coexisting 1st-row transition metals. However, 1st-row transition metals (e.g. Cu^{2+}, Ni^{2+}) at higher concentrations than coexisting platinum-group metals, were found to interfere significantly with the pre-concentration of the platinum-group metals by competitive complexation with the available TBP. Thus it was essential to ensure that in the case of elevated 1st-row transition metal concentrations, the 1st-row transition metals be removed prior to the pre-concentration of the platinum-group metals on the column. For this purpose, a cation-exchange resin (BIORAD AG 50W-X3) was used to remove the 1st-row transition metals. The addition of this 'clean up' column, prior to the introduction of the solution into the chromatographic column, eradicated 1st-row transition metal interference.

The above two methods successfully achieved pre-concentration and separation of the platinum-group metals. Time efficiency, like many techniques documented in the literature was the only limiting factor as pre-concentration utilising two columns markedly increased the analysis time.

One of the most exciting developments has been the increasing interest in the realm of 'molecular recognition' ligands [39] as pre-concentration agents for the platinum group metals. Bergeron *et al.* described the ability of a silica gel bonded 8-crown-ether ligand (Superlig 202: SL-202) to quantitatively and selectively preconcentrate platinum, palladium and rhodium in the presence of cobalt, copper, chromium, nickel, lead and zinc (Figure 2.5.1) by ion pair formation [40].

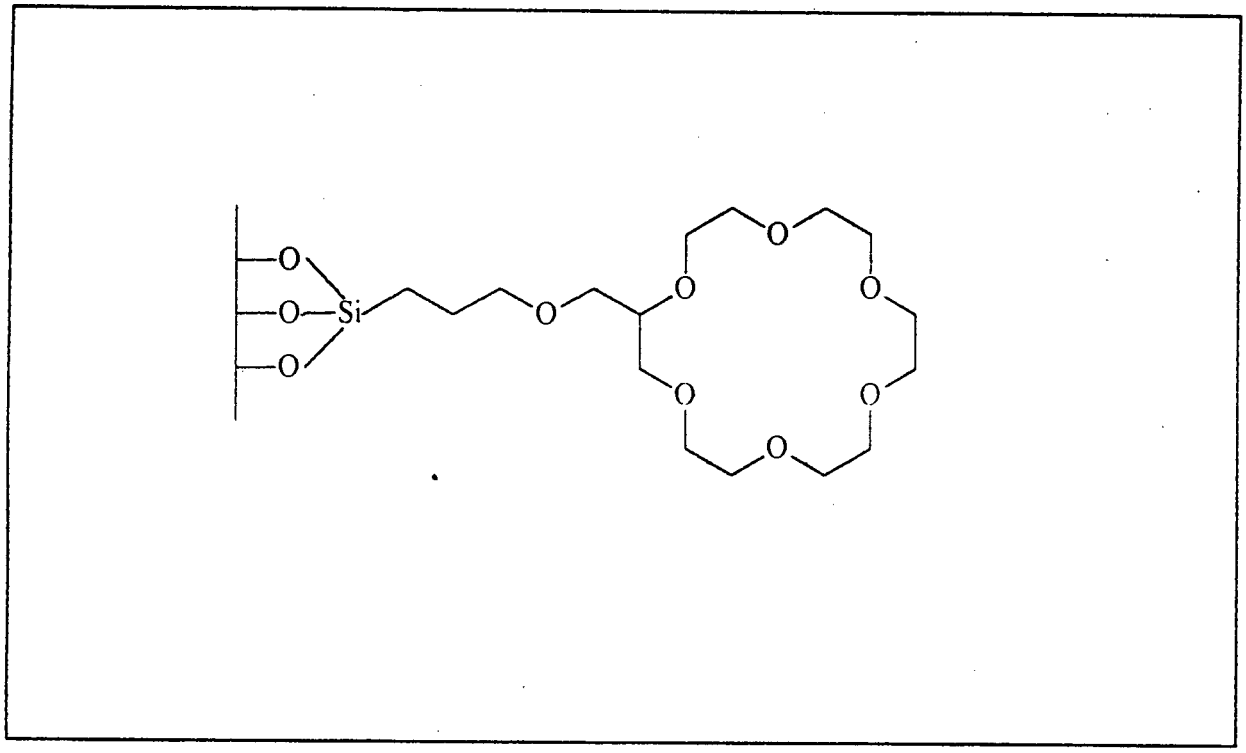


Figure 2.5.1: General structure of Superlig 202: SL-202

The main inhibiting factor to widespread use of this method is the cost of the ligand. The ligand is commercially manufactured and has been patented and and so commands a high purchase price.

Basova *et al.* [41] reported conditions for the pre-concentration of palladium, platinum and rhodium by extraction chromatography using 1-(2-pyridylazo)-2-naphtol (PAN) as the stationary phase, and chloroform or isopentanol as the mobile phase. Quantitative pre-concentration of palladium, platinum and rhodium was achieved in the presence of a 80 to 100-fold excesses of copper and cobalt.

2.6 Solid Sorbents

Solid sorbent pre-concentration techniques have developed into a procedure of choice for the trace analysis of the platinum-group metals, as these are the most effective and convenient methods for pre-concentration and separation of noble metal ions from aqueous solutions [42]. Many different solid sorbents have been used in this respect; which (defined by their interaction with the platinum-group metals) all belong to one of two types: chelating sorbents and co-ordinating sorbents. These two types are further classified into various physical forms: beads, powder, foam or fibres.

The selectivity of the sorbents is dependent on the complex-forming groups they contain. High selectivity for the noble metals is mainly achieved by using functional groups containing nitrogen and sulphur as donor atoms. Sorbents containing no sulphur atoms are the most selective in the presence of 1st-row transition metals eg. Cu, Ni, Co, etc. Additional selectivity with respect to 1st-row transition metals is achieved by varying the acidity [43] of the sample solution. Usually adsorption of noble metal ions onto solid sorbents takes place on prolonged shaking or heating, owing to the low rate of ligand exchange of the platinum-group metals. Mechanisms of adsorption are not well understood because of the difficulty of establishing the nature and type of complexes formed with the insoluble sorbent. Desorption of pre-concentrated platinum-group metals is also difficult for many solid sorbents and in general, solid sorbents have to be destroyed by ashing at high temperature or by parting with perchloric/sulphuric acid to recover the pre-concentrated platinum-group metals [44].

Sun and Yu [45] successfully pre-concentrated palladium, and Brackenbury *et al.* [46] pre-concentrated platinum onto polyurethane foam, in the presence of excess 1st-row transition metals. Khan *et al.* [47] studied a polythioether foam to pre-concentrate palladium in the presence of excess 1st-row transition metals. These methods achieve pre-concentration of palladium and platinum, but in all studies the polyurethane and polythioether foams were found to decompose at high acid concentrations and this precluded analysis of strongly acidic samples such as industrial effluent.

Chung and Barnes synthesised a poly(dithiocarbamate) sorbent that pre-concentrated platinum and palladium in the presence of 1st-row transition metals with an extremely high degree of accuracy and reproducibility [48]. Shortfalls of this method were that the uptake of platinum and palladium was highly pH dependant and the resulting chelated platinum/palladium complex was too strongly retained by the sorbent. A complicated method to remove the adsorbed platinum-group metals was required after pre-concentration had been achieved. Removal was achieved by hydrogen peroxide digestion of the platinum/palladium loaded sorbent, but this significantly increased mechanical losses of the sorbed platinum and palladium. Additionally, analysis time was prolonged

because of the need for these unwieldy operations.

Bis(carboxymethyl)dithiocarbamate (CMDTC) chelates supported on a XAD-4 resin (Figure 2.6.1) overcame many shortfalls of the poly(dithiocarbamate) sorbent [49]. This developed system differed from the preceding methods in that a separate platinum-group metal complex was formed which was then retained on the XAD-4 resin.

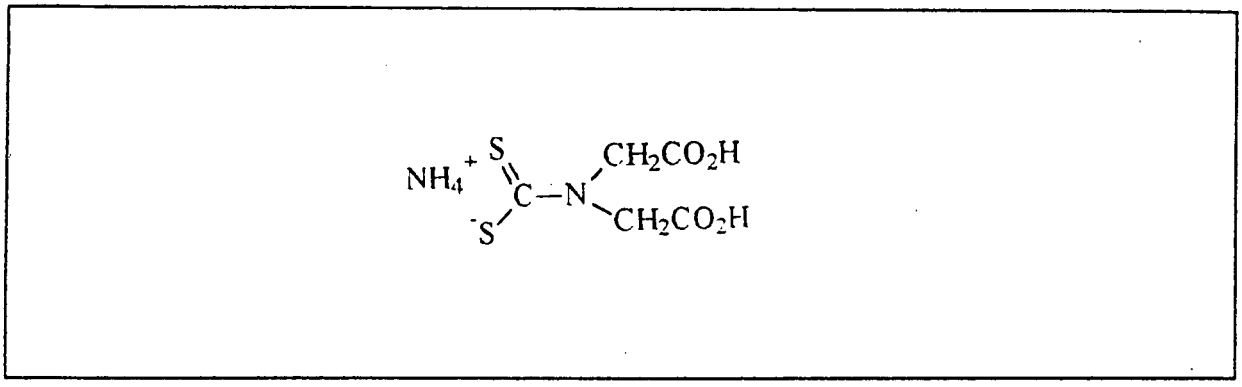


Figure 2.6.1: Structure of Bis(carboxymethyl)dithiocarbamate

Elution of the adsorbed platinum, palladium and rhodium CMDTC chelates from the resin was easily accomplished with ammonia, but pH was again critically important. Additionally, CMDTC dissociated readily upon exposure to air, which appeared to result in losses of the platinum-group metals as the CMDTC decomposed, resulting in poor recoveries.

Chang *et al.* [50] synthesised and investigated a polyacrylacylisothiourea chelating fibre (Figure 2.6.2) that offered many advantages compared to other available solid sorbents.

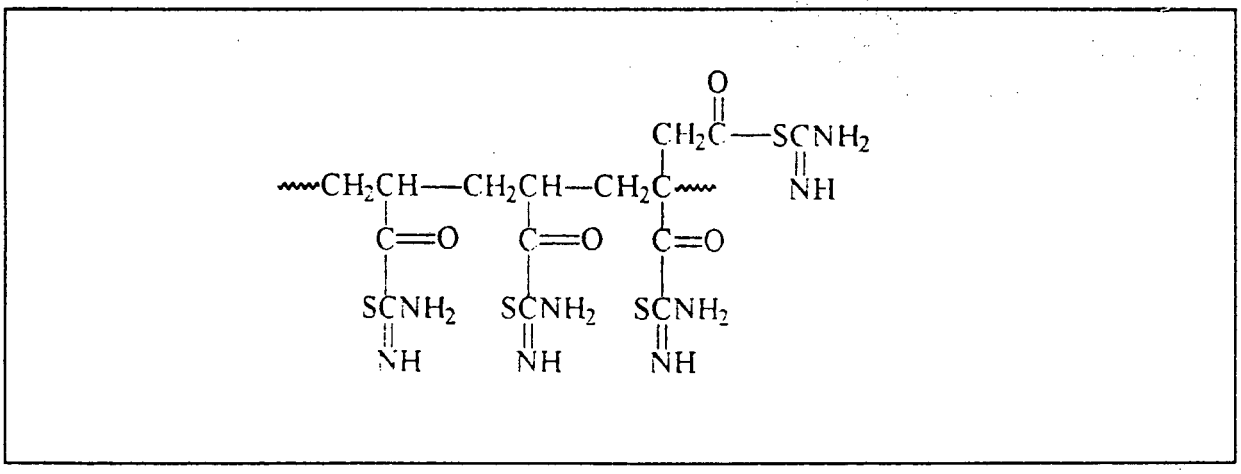


Figure 2.6.2: Structure of Polyacrylacylisothiourea chelating fibre

Quantitative pre-concentration of palladium(II) and ruthenium(III) was easily achieved with less critical dependence on pH control, in the presence of 1st-row transition metals. Elution of the resultant palladium(II)/ruthenium(III) complexes was readily accomplished with dilute nitric/hydrochloric acid. The drawback to the commercial use of this resin was the need to ensure a stable elution flow rate. The desorption of the platinum-group metal complexes was critically dependant on the flow rate of the eluent over the loaded sorbent. A slight decrease (<1%) in the flow rate of the eluent resulted in poor recoveries of the palladium and ruthenium. This disadvantage could be reduced to manageable levels by a skilled analyst.

To date, although a variety of solid sorbents used for pre-concentration of the platinum-group metals have been described, few methods meet all of the desirable analytical requirements of the ideal pre-concentration system (**2.1**).

2.7 Co-precipitation

Several co-precipitation techniques are documented in the literature and the five main methods utilise co-precipitation with: mercury [51], tellurium [52, 53], selenium [54], dithiozone [55] and thiourea [56] co-precipitation. The general technique is the addition of one of the above metals to a digested sample containing the platinum-group metals. Manipulation of the sample pH etc. results in the precipitation of the co-precipitation metal with the platinum-group metals present in the original sample. This technique is most often used in an intermediate stage during classical or neoclassical fire assay to improve analysis accuracy and reproducibility, by preventing some losses of the platinum-group metals that occur in a pure fire assay procedure (**2.2**). The nature of the method is time-consuming, labour-intensive and generally nonspecific. No significant advantage of co-precipitation over the previously documented pre-concentration categories is recorded in the literature. As a result this method will not be described in any detail for the purposes of this review.

2.8 Conclusion

The first stage in the accurate and precise trace analysis of the platinum-group metals is pre-concentration from the sample matrix, with the purpose of eliminating potential interferents or more simply to increase the platinum-group metal concentration to match the sensitivity of the analytical technique subsequently used to determine the concentration of the platinum-group metals present in the sample. As can be seen from a review of the literature, no documented pre-concentration technique achieves simultaneous pre-concentration of all of the platinum-group metals. Neither do any of the documented methods posseass all the desired characteristics of an ideal pre-concentration technique.

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Chapter 3

Review of Analytical Techniques for the Determination of the Platinum-group Metals

3.1 Introduction

The second stage in the trace analysis of the platinum-group metals is the choice of a suitable detection system following the preconcentration step as described in Chapter 2. The goal of determining the concentration of platinum-group metals in a sample, is to obtain an analytical result as rapidly as possible, as precisely and accurately as possible, with equipment that is as cost effective as possible. Thus, the choice of a suitable detection system involves reviewing problems associated with inadequate detection limits of available analytical techniques and the multiplicity of matrix effects which might be present in the sample.

The determination of the platinum-group metals can be achieved either by classical chemical methods or by spectroscopic methods. For the low to medium concentration range (1 - 10% PGM in sample) there are opportunities for a chemical method of determination. In the high range (10 - 100% PGM in sample) chemical methods are generally superior to instrumental methods, primarily because of their superior accuracy. For the trace to ultra trace range (0.01% or less PGM in sample) the platinum-group metals are preferably determined instrumentally. Since trace and ultra trace analysis is the focus of this research, only the spectroscopic methods of determination will be considered here [1]. The most important spectroscopic techniques used in the determination of the platinum-group metals, can be divided into seven diverse categories: spectrophotometry (**3.2**), flame atomic absorption spectroscopy (**3.3**), flame atomic emission spectroscopy (**3.4**), X-ray fluorescence spectroscopy (**3.5**), neutron-activation analysis (**3.6**), inductively-coupled plasma - optical emission spectroscopy (**3.7**) and inductively-coupled plasma - mass spectrometry (**3.8**).

For each category a brief description of the principle of the instrumental technique is given, followed by some specific examples in which the detection system possesses some ideal characteristics described below. An ideal detection system should encompass the following characteristics:

1. High sensitivity

2. Low detection limits
3. Large dynamic concentration range
4. Long and short term reproducibility
5. Accuracy
6. Minimal sample pretreatment
7. Few chemical interferences
8. Minimal inter-element interferences
9. On-line capabilities

3.2 Determination of the platinum-group metals by Spectrophotometry

Spectrophotometric techniques encompassing ultraviolet and visible light absorption are employed primarily for quantitative analysis and are often more widely used than any other single procedure. This is the case in the literature, as in the past decade the number of new or modified spectrophotometric methods reported have increased [2].

Every atomic/molecular species, according to quantum theory, has a unique set of energy states, the lowest of which is the ground state. At room temperature, most atomic/molecular species are in their ground state. When a photon of radiation passes near an atomic or molecular species, absorption becomes probable only if the energy of the photon exactly matches the energy difference between the ground state and one of the higher energy states of the particle. Under these circumstances, the energy of the photon is transferred to the atom, ion, or molecule, converting it to an excited state. Excitation of a species M to its excited state M* can be described by the equation:

$$M + h\nu \rightarrow M^*$$

where h = planck's constant and ν = frequency of electromagnetic radiation.

After a brief period (10^{-6} - 10^{-13} s), the excited species relaxes to its ground state, transferring its excess energy to other atoms or molecules in the medium (or by radiationless relaxation - fluorescence), which causes a small rise in temperature of the surroundings, and is described by

the equation:

$$M^* \rightarrow M + \text{heat}$$

The lifetime of M* is extremely short and so its concentration at any instant is ordinarily negligible. Additionally, the amount of thermal energy released during relaxation is usually so small as to be undetectable. Thus, absorption measurements have the advantage of creating minimal disturbance of the system under study. Ultraviolet and visible absorption spectra are usually obtained on a gaseous sample of an analyte or on a dilute solution of an analyte in a transparent solvent. The functional relationship between the quantity measured in an absorption method (A) and the quantity sought (the analyte concentration c) is known as Beer's Law, which can be written as:

$$A = \epsilon l c$$

where l is the path length of radiation, and ϵ is the molar absorptivity.

The absorbing characteristics of a species are conveniently described by means of an absorption spectrum, which is a plot of some function of the attenuation of a beam of radiation versus wavelength, frequency, or wave number. Absorption of ultraviolet and visible radiation by molecules occurs in one or more electronic absorption bands (vibrational and rotational lines), each of which is made up of numerous closely spaced but discrete lines. Thus the number of lines contained in a typical band is large and their separation from one another small. In solution, however, the atomic/molecular species freedom to rotate is largely lost, and lines due to differences in rotational energy levels are eradicated. Furthermore, in the presence of solvent molecules, energies of the various vibrational levels are modified in a complex way. Thus, the energy of a given state in an assemblage of molecules takes on a normal distribution and the resultant absorption spectrum consists of a continuous, smooth, Gaussian plot of absorbance versus wavelength [3, 4].

In summary, the most important characteristics of spectrophotometric methods are:

1. Wide applicability
2. High sensitivity

3. Moderate to high selectivity
4. Good accuracy
5. Ease and convenience of use
6. On-line capabilities

Haj-Hussein *et al.* [5] developed a flow injection analysis (FIA)-spectrophotometric method with simultaneous determination of palladium(II), copper(II) and nickel(II), based on the metals complexation with EDTA. Limitations to the use of EDTA as a developing agent were that pH control was essential, and the presence of excess metals caused spectral interferences, in addition to depletion of the EDTA reagent. This resulted in low recoveries of the desired analyte. This method was less sensitive than classical spectrophotometry, but was more rapid and less costly.

4-(5-chloro-2-pyridylazo)-1, 3-diaminobenzene (a chromogenic reagent) [6] (Figure 3.2.1), was used successfully by Xu *et al.* to selectively complex rhodium(III) and palladium(II) in the presence of excess 1st row transition metals with no significant reduction in recovery of the two platinum-group metals observed.

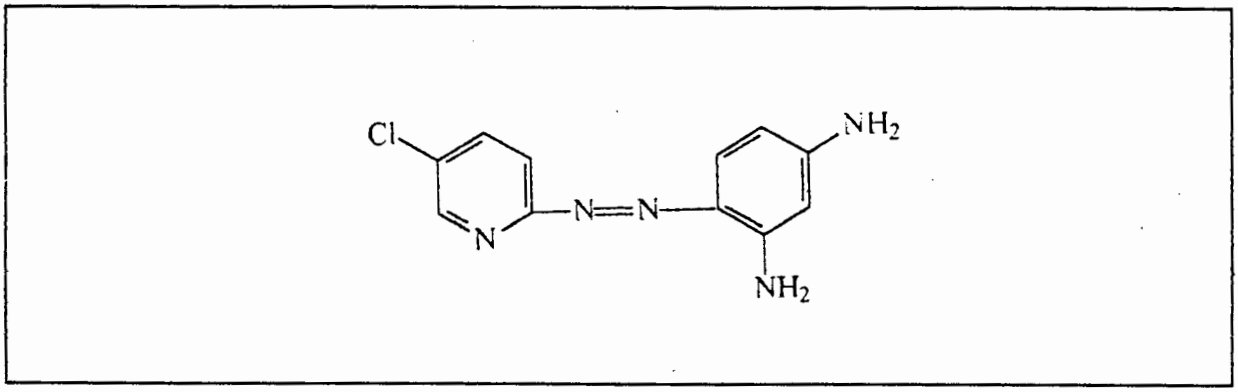

Figure 3.2.1: Structure of 4-(5-chloro-2-pyridylazo)-1, 3-diaminobenzene

Platinum(IV/II) failed to complex significantly with this reagent, and rhodium(III) was found to react slowly at room temperature. Microwave heating of the solution accelerated complexation of rhodium(III), but did not result in platinum(IV/II) complexation. An additional problem was the critical dependence of rhodium(III) determination on the concentration of palladium(II) present in the solution; at palladium(II) concentrations greater then 5 $\mu g.cm^{-3}$, the spectrophotometric determination of rhodium was severely affected.

A more successful method, involved the reaction between sulphochlorophenolazorhodanine (SCPAR) (Figure 3.2.2) and palladium(II), in the presence of nineteen other metal ions, e.g. iron, lead, aluminium, copper and zinc and was investigated by Shiundu *et al.* [7]. Selectivity to palladium(II) was high in acidic media with no 1st row transition metal interferences reported, but under these conditions other platinum-group metals interfered appreciably with the spectrophotometric determination of palladium(II).

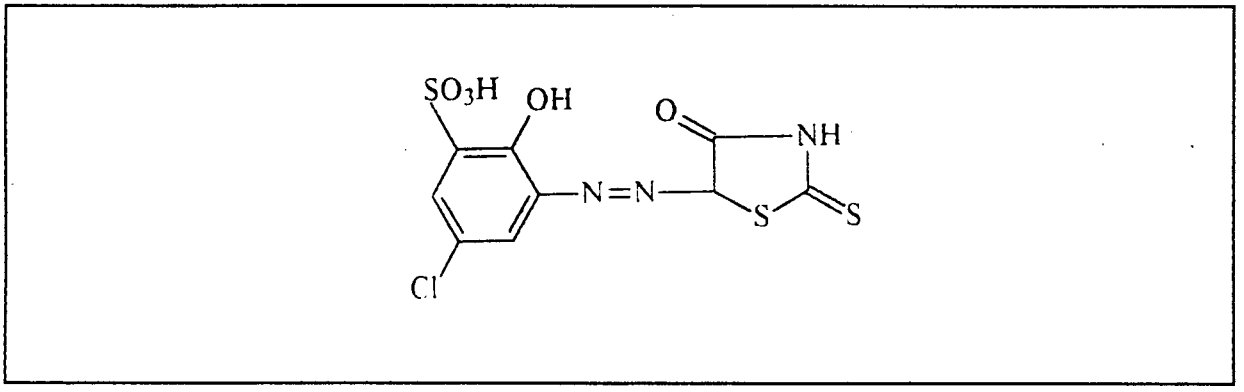

Figure 3.2.2: Sulphochlorophenolazorhodanine

Advantages of this method included: relatively inexpensive equipment, high precision, high sample throughput and low sample and reagent consumption.

The use of chromogenic reagents 1, 8-dihydroxy-2-(4-chloro-2-phosphonophenyl-azo)-7-(6, 8-disulphononaphthylazo)napthalene (RI) and its derivatives (Figure 3.2.3) was further investigated by Xu *et al.* [8].

The proposed method selectively complexed palladium(II) in the presence of other metal ions and was applicable to a variety of palladium(II) determinations. Analysis in acidic media eliminated 1st row transition metal and platinum-group metal interferences. Limitations of this method were its low linear dynamic range (1 - 5 $\mu g.cm^{-3}$ Pd(II)) and the need to heat the reaction, as complexation of palladium(II) by RI (and its derivatives, RII and RIII) was slow at room temperature.

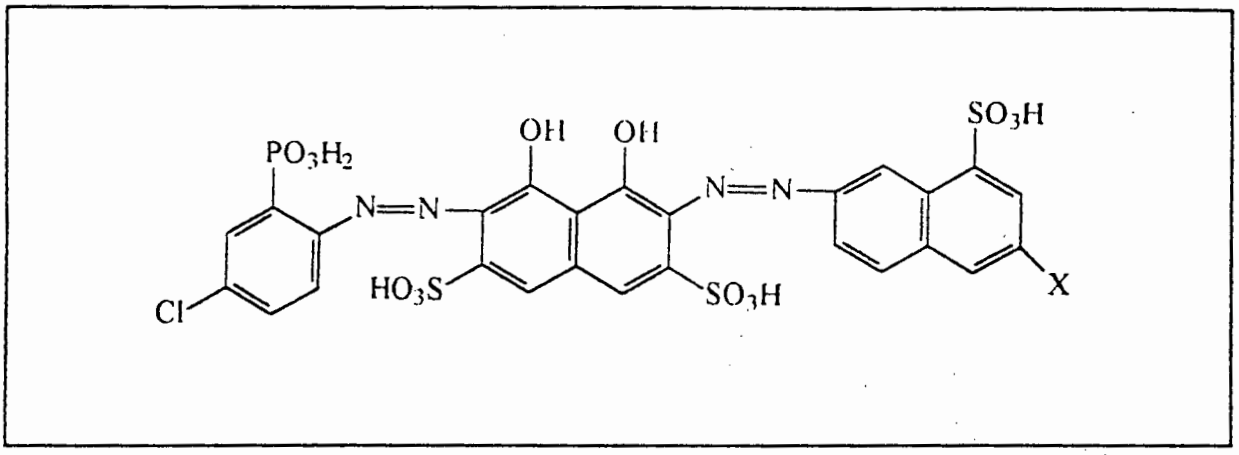

Figure 3.2.3: Structure of RI, X = SO_3H; RII, X = SO_2NH_2 and RIII, X = $CONHCH_2CO_2H$

He *et al.* [9] reported complexation of DCS-asenazo (2-(2-arsenephenylazo)-7-(2,6-di-chloro-4-sulphophenylazo)-1,8-dihydroxynapthalene-3,6-disulphonic acid) with palladium(II). This ligand was found to be relatively selective for the determination of palladium(II) in the presence of other metals. However, the reported method had a low linear range and a poor tolerance of a 20 - 100 fold excess of other metals. Above this 20 - 100 fold excess, interferences by coexisting metal ions were significant in the determination of palladium(II) in the sample.

The major limiting factors with respect to spectrophotometric determination of the platinum-group metals are the often poor selectivity towards the platinum-group metals, common inter-element interferences and the often tedious and complex sample manipulations required to obtain an accurate and precise determination.

3.3 Determination of the platinum-group metals by Flame Atomic Absorption Spectroscopy

Flame atomic absorption spectroscopy can be applied to atoms that absorb ultraviolet or visible light radiation. It is a comparative method of analysis, sample concentration being obtained by comparison of the analyte absorption signal to a prepared calibration curve.

Atomic absorption is a process in which a cloud of atoms, selectively absorb certain frequencies of electromagnetic radiation emitted by a light source of that particular element. Atoms absorb the light by the promotion of electrons out of their ground state levels into higher excited states. Only

light of the energy that is equal to the difference in energy levels between the ground state (M) and excited state (M*) will be absorbed by the atom. After a brief period (10^{-6} - 10^{-9} s), the excited species relaxes to its ground state, generally with losses of its excess energy by thermal means. The lifetime of M* is extremely short and so its concentration at any instant is ordinarily negligible. The functional relationship between the quantity measured in an absorption method (A) and the quantity sought (the analyte concentration c) is known as Beer's Law (**3.2**) [10].

Atoms are relatively simple compared to molecules and so the number of energy levels they possess is relatively small and the interactions between them relatively infrequent. Thus it follows that one can isolate and measure independently, many more narrow atomic bands or lines than broad molecular bands. In the technique of atomic absorption spectrometry, it is necessary to produce a 'dilute solution' of atoms in just the same way as one produces a 'dilute solution' of molecules for spectrophotometry. However, free atomic species cannot be produced in solution, so to overcome this problem, a solution of a compound of the element (organic or inorganic) is introduced into a flame. Upon introduction of the compound into the flame, the following four processes occur [11, 12].

(1) Desolvation

eg. $RhCl_3 \cdot xH_2O$ (aq.) → $RhCl_3$ (s)

(2) Vaporisation

eg. $RhCl_3$ (s) → $RhCl_3$ (g)

(3) Atomisation/Ionisation

eg. $RhCl_3$ (g) → Rh^0 (g) + $3Cl^0$ (g)

(4) Absorption of radiation

eg. Rh^0 (g) → Rh*(g)

These processes take place within the flame and at a steady state, with a fixed number of atoms produced in the flame proportional to the analyte concentration. The flame therefore acts as an atom-resevoir within which measurements are made. Commonly used flames are shown in Table 3.3.1 [13].

Table 3.3.1: Maximum flame temperatures and their fuels

Flame type	Fuel gas	Maximum flame temperature (°C)
Cool	Propane / Air	1930
Cool	Butane / Air	1930
Moderate	Acetylene / Air	2300
Hot	Acetylene / Nitrous oxide	2900

Typically, the absorption of radiation from an external source by an atomic species in a flame takes the form of a series of narrow lines that are the result of transitions of an electron from the ground state to one of several higher energy levels. The natural width of an atomic absorption line is of the order of 10^{-3} nm. However, no ordinary monochromator can yield a band of radiation as narrow as the peak width of an atomic absorption line. Consequently, the use of radiation isolated from a continuous source by a monochromator inevitably causes instrumental departures from Beer's Law. In addition, since the fraction of radiation absorbed from such a beam is small, the detector receives a signal that is only slightly attenuated and the resultant sensitivity of the measurement is low.

Two temperature dependant effects, however, cause observed line widths to be broadened by a factor of 100 (or more): Doppler broadening (rapid motion of atoms as they absorb radiation) and pressure broadening (collisions among atoms, causing variations in their ground state energies) [14]. Even allowing for these broadening effects, the band of radiation from a monochromator, is still not as narrow as the observed atomic line width.

This problem has been surmounted by using radiation from a source that not only emits a line of the same wavelength as the one selected for absorption measurements but also one that is narrower. Thus the most commonly employed line source in flame atomic absorption

spectroscopy, is the hollow-cathode lamp, which emits radiation much narrower in band width than the resultant atomic absorption band. In this lamp the cathode is fabricated from the analyte metal and the anode from tungsten metal. When a potential is applied across the electrodes, the inert gas contained within the lamp is ionised and as the inert gas migrates towards the cathode, the ionised gas strikes the cathode and dislodges the analyte metal producing an atomic cloud. Some dislodged analyte atoms are in excited states and emit their characteristic wavelengths as they return to the ground state. Such lamps enable absorption measurements to be made with radiation that is fully monochromatic with respect to several atomic absorption bands. The development of the hollow-cathode lamp as a radiation source, made atomic absorption spectroscopy practical [15].

In summary, the most important characteristics of flame atomic absorption spectroscopy are [16, 17]:

1. Virtually element specific
2. High precision
3. Good accuracy
4. Low sample manipulation
5. Few spectral interferences
6. Rapid analysis
7. Ease and convenience of use
8. Cheap instrumentation
9. On-line capabilities

Arpadjan *et al.* [18] studied atomisation of the platinum-group metals, in the presence of ist row transition metals, in high purity platinum and palladium samples. Relatively low platinum concentrations caused a strong depression of the signal observed for iridium, rhodium and ruthenium. The signal depression for rhodium and ruthenium was found to increase with a rise in the platinum concentration of the sample. Aneva studied the atomisation of palladium, in the presence of Ag, Bi, Ca, Co, and Zn, in high purity platinum. A depression of the signal for palladium (by platinum) was observed that remained constant for platinum concentrations higher than 3 $\mu g.cm^{-3}$. The depressive effects of platinum, on palladium absorption, were corrected mathematically using predetermined inter-element correction

factors; therefore, the use of standard addition or matrix matching was not required [19].

A review of the documented methods in the literature using flame atomic absorption spectroscopy for the determination of the platinum-group metals, leads to the conclusion that flame atomic absorption spectroscopy is an unsatisfactory tool for the determination of the platinum-group metals in aqueous solution resulting from poor sensitivity and strong interferences from many elements. The presence of Cu, Pb, Zn, Ni, Cr, Fe, Te, Mn, Ba, Sr, and Al in concentrations equal to or lower than the platinum-group metal content leads to a suppression of the analytical signal. Mutual interferences between the individual platinum-group metals, was also a severe problem. Releasing agents (e.g. La^{3+}) reduced mutual interference between the platinum-group metals, within the flame, but were not completely satisfactory in this regard.

The use of a nitrous oxide/acetylene flame reduced interferences but at the cost of an increase in the detection limit. The overall reduction in sensitivity occurring with this flame, ruled out this approach as a simple means of determination of all the noble metals in one solution [20, 21]. Improvement in the selectivity and sensitivity of flame atomic absorption spectroscopy measurements were obtained by an initial solvent extraction of the platinum-group metals, followed by direct aspiration of the organic extract [22].

A study by Pilipenko *et al.* [23] focused on the selection of solvents that would provide the maximum sensitivity in the determination of platinum, by direct aspiration, and elimination of interfering elements. Among the reagents tested were dithiozone and 8-hydroxyquinoline. Solvents studied were: ethyl acetate, butyl acetate, n-butanol, acetone, chloroform and methyl isobutyl ketone. The study indicated that Cu, Ni, Co, Fe, Sn and Pb did not influence the sensitivity of the determination of platinum in chloroform, methyl isobutyl ketone and n-butanol over a wide range of concentrations.

3.3.1 Electrothermal Atomic Absorption Spectroscopy

The fundamental difference between electrothermal atomic absorption and flame atomic absorption spectroscopy is in the production of the atom cloud. In flame atomic absorption spectroscopy (**3.3**), the free atomic species are produced by means of flame atomisation. In electrothermal

absorption spectroscopy, the free atomic species are produced in a graphite furnace atomiser. Here the sample (2 - 100 µl) is deposited in a graphite furnace and subjected to an electrical heating programme in an inert atmosphere. Drying of the sample is followed by charring (to remove the organic matter present in the sample) and finally thermal atomisation is achieved by the passing of a large current through the furnace, resulting in a transient absorption signal (2000 - 3000°C).

This technique supplements flame atomic absorption methods, as it offers greatly enhanced sensitivity in some cases. In flame atomic absorption methods, the sample passes through the observation zone so rapidly that the effective lifetime of the absorbing atom is very brief - 10^{-3} to 10^{-4} s. In electrothermal atomic absorption methods, the residence time of the absorbing atoms in the light beam is 100 - 1000 times longer (0.1 s), thus providing correspondingly greater sensitivity [24, 25, 26].

An investigation by Cantarero *et al.* [27] used an alumina micro column for preconcentration, followed by electrothermal atomic absorption determination. The determination of platinum at sub-µg.dm^3 levels was achieved, with almost no interference from other metal ions.

Lin *et al.* reported pre-concentration of palladium, on an activated carbon fibre, followed by electrothermal atomic absorption determination. The detection limit of this method was 0.3 ng.cm^{-3} palladium, with reproducible and accurate analysis easily achieved [28].

Schuster *et al.* described the selective determination of palladium(II) by on-line column pre-concentration and electrothermal atomic absorption spectroscopy [29]. Palladium(II) was pre-concentrated on a micro column loaded with *N*-benzoyl-*N'*, *N'*-diethylthiourea (NEBT) (**2.3**), after which the palladium complex was eluted with ethanol directly into the graphite furnace. Alkaline, alkaline-earth and 1st row transition metal ions such as Cu, Fe, Co and Ni and precious metals were tolerated up to concentrations of 10 g.dm^3 or higher.

The disadvantages of electrothermal atomic absorption spectroscopy are that precision is significantly poorer, compared to flame atomic absorption spectroscopy, because of the small volume of the sample solution (2 - 100 µl) used in analysis. The control of atomisation conditions and reproducible sampling is also often difficult. Spectral and chemical interferences are also more

severe with graphite atomisers than flame atomisers.

3.4 Determination of the platinum-group metals by Flame Atomic Emission Spectroscopy

Atomic emission spectra are produced when the electrons in an atom or ion are excited by thermal energy in a hot source, with subsequent relaxation to the ground state by emission of a photon of radiation. This can be described as follows:

$$M + \text{thermal energy} \rightarrow M^*$$

$$M^* \rightarrow M + h\nu$$

Thus, in atomic emission spectroscopy, the excited analyte atoms or ions serve as the source of radiation and no external source of radiation is required. Atomic emission is induced in an atom cloud by thermal energy (flame atomic emission spectroscopy) or electrical discharges (sparks, arcs and plasmas). Flame temperature determines the number of excited and unexcited atoms in a flame or plasma. As flame temperature increases, atomisation efficiency increases and the total atom population in the flame increases [30]. However, the increase in atom population is offset by the number of atoms lost to ionisation (as all elements ionise partially in a flame), described by the equilibrium:

$$M \rightleftharpoons M^{x+} + xe^-$$

Flame atomic emission spectroscopy, based as it is on the population of excited atoms, requires much closer control of flame temperature than flame atomic absorption spectroscopy, in which the analytical signal depends upon the population of unexcited atoms. The number of unexcited atoms, in a typical flame, exceeds the number of excited atoms by a factor of 10^3 - 10^{10}. Thus flame atomic emission methods are less sensitive than flame atomic absorption methods.

Spectra are recorded by placing the inner cone of the flame (the hottest region), in front of the entrance slit of a monochromator. The output from the exit slit of the monochromator is monitored as the spectrum is scanned by rotating the grating or prism and subsequently obtaining the flame emission spectrum of the sample [31].

A review of the documented methods in the literature using flame atomic emission spectroscopy in the determination of the platinum-group metals, leads to the conclusion that flame atomic emission spectroscopy cannot be applied to the determination of the platinum-group metals, since the maximum temperature of the flame at 2900°C, is insufficient for the adequate excitation of atoms of the platinum-group metals [32].

Spark and direct current (DC) arc emission sources, overcome the energy threshold for excitation of the platinum-group metals, due to the increased temperature these emission sources achieve: 4000 - 5000°C (DC arc), 40 000°C (spark).

Several methods have been developed for high purity platinum and palladium determination [33] but they will not be described here as spark and DC arc emission sources are difficult to reproduce, leading to a decrease in the accuracy and precision of analysis [34]. The instrumentation required for these two alternative emission sources is also a limiting factor, due to the high cost involved in production of these emission sources. The third alternative emission source, plasma, has widespread application in the determination of the platinum-group metals and as a result is described in its own category for the purposes of this review (**3.7**).

3.5 Determination of the platinum-group metals by X-ray Fluorescence Spectroscopy

X-ray fluorescence spectroscopy is an atomic emission technique, in which a sample is directly exposed to radiation, with an energy greater than the excitation threshold of the element(s) under study. The method is based on measurement of the secondary X-rays emitted by the constituents of a sample excited by primary X-rays. The intensity of the secondary X-rays emitted, by the constituents of a sample, depends on the intensity of the sufficiently energetic primary X-rays [35]. Inner shell electrons of heavier atoms have binding energies greater than those of lighter atoms and X-rays of shorter wavelength (higher energy) are required for their ejection.

The excited atom is unstable and relaxes to a more stable electronic state. This relaxation involves the replacement of the excited inner shell electron, by an outer shell electron. However, the outer shell electron replacing the inner shell electron vacancy is of higher energy, and during relaxation the excess energy is released as a X-ray photon. This energy emitted is equivalent to the energy

difference between the two electron shells involved.

This energy difference, and therefore the wavelength of the photon emitted, is characteristic of the element initially irradiated with primary X-rays. Since several energy levels may be involved in such transitions, each element emits a characteristic spectrum of secondary (fluorescent) X-rays. Secondary or fluorescent X-rays are always of a longer wavelength (lower energy) than the primary excitation X-rays. Also, heavier atoms have greater energy differences between shells than lighter atoms, so the X-ray spectra of heavier atoms are of a shorter wavelength (higher energy) than those of lighter atoms. From this excitation mechanism, three series of X-ray lines are expected, resulting from the ionisation of the K, L, and M electron shells.

Primary excitation X-rays are produced in a sealed X-ray tube containing an anodic target. This target can be made from W, Cr. Au, Rh, Mo, or Sc. A heated tungsten filament generates high energy - electrons that accelerate towards the anodic target by the application of a 10 - 100 kV potential difference across the electrodes. The accelerated electrons bombade the anodic target resulting in the emission of a continuum of primary excitation X-rays, with the characteristic X-ray line spectrum of the target element superimposed. It should be noted that heavier element anodic targets are used to produce more intense, shorter wavelength primary excitation X-rays.

The primary excitation X-ray continuum produced, is directed onto the sample surface resulting in the production of a beam of secondary X-rays from the sample constituents. This beam of secondary X-rays strikes the surface of an analysing crystal and the individual sample constituent wavelengths are reflected from the lattice planes only when the path difference between two X-rays is an integral number of wavelengths (constructive interference does occur).

Detection of the separated secondary X-rays, involves conversion of the X-ray photons into light pulses, which are passed between a series of anodes in a photo multiplier tube. The anodic pulses due to each photon are then detected and counted. Quantitative analysis by X-ray fluorescence spectroscopy is based on the principle that at a given intensity of the primary excitation X-rays, the intensity of the separated secondary X-rays, produced by the sample constituents, will be proportional to the amount of each constituent present in the sample [36, 37].

Modern X-ray fluorescent spectrometers facilitate highly reproducible results with random and

systematic instrumental errors below 0.1 %. The main advantages over the various competitive determination techniques (atomic emission or atomic absorption) are that it is nondestructive, thus allowing recovery of the original sample after the determination and its simplicity. It is a very useful technique in the determination of major elements in materials such as slag and industrial residues. Regarding sensitivity of the platinum-group metals, the radiation of the K-lines of Ru, Rh, and Pd, are 2 - 3 times more intense than that of the L-lines of Os, Ir and Pt [38].

Platinum, palladium and ruthenium in corrosion-resistant steels were analysed by Eddy [39], using X-ray fluorescence spectroscopy. The three platinum-group metals, Fe and Cr, were determined successfully in the solid samples with high precision (1%), and good accuracy (<2%). However, inter-element correction was necessary to compensate for the positive and negative effects of other platinum-group metals and 1st row transition metals, on the analyte signals for the platinum-group metals being determined.

Zmievskaya *et al.* [40] adsorbed rhodium onto chemically modified silica, followed by direct X-ray fluorescent determination of the adsorbent phase. The determination by X-ray fluorescent spectroscopy was compared with a spectrophotometric, atomic absorption and DC arc emission determination of the rhodium in the adsorbent phase. The X-ray fluorescent determination detection limit was 10 μg.g, compared to 2.0, 3.0 and 0.05 $\mu g.cm^{-3}$ for the spectrophotometric, AAS and DC arc determinations respectively. The X-ray fluorescent determination was slower than the AAS and DC arc determinations, but faster than the spectrophotometric determination.

The mutual interactions of the platinum-group metals were investigated by Dement'ev *et al.* [41], in the X-ray fluorescent determination of Au, Ir, Pd, Pt, Rh and Ru, after preconcentration of the platinum-group metals with a chelating ligand (Polyorgs XI-H). It was found that in the noble metal concentration range of 7 to 300 μg PGM per g of sorbent, the positive and negative interactions on the analyte signals for the platinum-group metals being determined, could be ignored [42].

3.6 Neutron Activation Analysis

Gamma rays, charged particles (protons, deuterons, tritons and helions), and particularly neutrons can react with stable or unstable isotopes of various elements present in a sample, producing radioactive nuclides. These radioactive nuclides can be identified by the properties of the radiation

they emit [43, 44].

The optimum nuclear reaction is chosen with four considerations in mind: (1) Production of a large activity should be achieved within a reasonable irradiation time; (2) the radioisotope produced should have a reasonable half-life (T>min); (3) the energy and type of radiation produced by the radioisotope should not present counting difficulties and (4) few interfering reactions should be involved. If the composition of the sample is known then the best reaction for the identification of the isotope of interest is used, but if the sample composition is completely unknown, neutron irradiation is used as neutrons are absorbed by most isotopes. Neutrons are produced artificially, except in the case of californium which undergoes spontaneous fission. Neutrons are defined as thermal neutrons when they are in equilibrium with matter at room temperature and have a velocity of approximately 2200 $m.s^{-1}$, and energies of about 0.025 eV. Neutron sources include reactors, accelerators and isotopic sources. Nuclear reactors are, by far, the most frequently used irradiation sources as they provide an abundant flux of thermal neutrons.

When a radioactive isotope (X^*) decays, it produces another stable or radioactive nucleus with a significant release of energy emitted as radiation, the measurement of which represents a value proportional to the quantity of irradiated element. A γ-ray is energy released during nuclear stabilisation. The emission of γ-rays does not alter either the atomic mass or the atomic number of the elements. This radiation is absorbed by matter, which becomes ionised in the process. γ-Rays are the most penetrating form of radiation with energies from a few keV to a few MeV. More generally, a nuclear reaction produced by a flux of neutrons occurs only if the kinetic energy of the neutrons is higher than the excitation threshold of the target element [45, 46].

After irradiation is completed, the sample is counted using an appropriate system. For γ-radiation, scintillation counters or solid semiconductor detectors are used. The most common substance for scintillation γ-counting, is sodium iodide crystals containing traces of thallium (NaI/Tl). Scintillation detectors have good counting efficiency but poor resolution. Consequently, solid semiconductor detectors are used increasingly. The most common of which is Ge(Li), which has a very good resolution. The output signals of the scintillation counters and semiconductor detectors are proportional to the incident γ-photon energy. Scanning γ-spectrometers and multichannel spectrometer exist, allowing a simultaneous count of the different photons of the studied spectrum, from the mixture of radioisotopes produced in the sample, during irradiation [47].

The counts of the different photons are compared to a calibration curve (to obtain a concentration value for the isotopes present) measured with a primary standard, the matrix of which is similar to that of the sample. This primary standard is placed side by side with the samples during irradiation to receive exactly the same neutron flux.

Hoffman [48] investigated neutron activation analysis for the determination of gold and the platinum-group metals, in rocks, soils and drill cores. The study found that for the platinum-group metals some separation or preconcentration was necessary, either before or after neutron irradiation. Neoclassical nickel sulphide fire assay (**2.2**) was the preferred preconcentration method prior to irradiation. A neutron activation method developed by Shazali *et al.* [49] for the noble metals involved preconcentration by co-precipitation with tellurium (**2.7**), followed by irradiation with reactor neutrons and analysis by γ-ray spectrometry. This method achieved high precision and good accuracy in the determination of the noble metals. Rhodium determination by fire assay preconcentration (Bi as collector) prior to irradiation, was reported by Artem'ev *et al.* [50]. A detection limit of 10 $ng.cm^{-3}$ rhodium(III) was achieved with bismuth as collector. Lead as collector was initially used, but the detection limit was found to be two orders of magnitude higher, owing to the formation of ^{204m}Pb upon activation of the matrix. Flerov *et al.* [51] described a neutron activation analysis method for the determination of iridium(IV) using a dual scintillation (NaI/Tl) counter and Ge(Li) detector. The sensitivity of the method was 5 $ng.cm^{-3}$ Ir(IV) in relatively unfavourable matrices. The use of a dual detection system improved the quality of the γ-spectra by a factor of 4 - 6 in the regions of interest.

The disadvantages of neutron activation analysis in the determination of the platinum-group metals are: the requirement of expensive equipment, non trivial analysis of results, interference reactions produced by 1st row transition metals in the samples and the preparation of a primary standard, which in the case of the complex matrices in which the platinum-group metals reside, is never a simple task.

3.7 Determination of the platinum-group metals by Inductively-Coupled Plasma - Optical Emission Spectroscopy

Inductively-coupled plasma - optical emission spectroscopy (ICP-OES) is a variant of DC arc emission spectroscopy (**3.4**), based on the use of a plasma, for excitation of analyte atoms. ICP-

OES is based on the principle that in high-intensity electromagnetic fields, gases become conductors and complex electric charge-transfer phenomena, called gas discharges, occur [52]. The result of a gas discharge is the production of an ionised gas, or plasma, at very high temperature (6000 - 8000°C, in the case of Ar), containing electrons, positive ions, neutral atoms and molecules. Some properties of ideal gases, such as the relationship between pressure and volume, still apply, although the presence of charged particles (ions, electrons) leads to plasmas exhibiting different properties from those of ideal gases in terms of viscosity and thermal conductivity. Ignition of a plasma requires the supply of a source of external energy to the electrons in order to ionise the gas, and to maintain a plasma a high frequency magnetic field is required (Figure 3.7.1). The provision of an external energy source represents a significant constraint, but through the external source it is possible to maintain a certain degree of control over the properties of the plasma. In practice, the plasma acts as an energy reservoir [53]. One common way to induce/sustain a plasma is the use of a radiofrequency magnetic field that consists of a water- or air-cooled copper coil looped around a piezoelectric quartz tube. The radiofrequency magnetic field oscillates at 27.12 or 40.68 MHz, at incident powers varying from 0.5 to 2.5kW. Higher powers are usually applied when organic solvents are aspirated, to overcome the problem of electron scavenging within the plasma by the carbon atoms of the organic solvent, leading to the extinction of the plasma.

In general the plasma is generated by a system in which argon gas flows through a torch (Figure 3.7.2), consisting of three concentric tubes usually constructed from fused silica. The outer tube delivers gas to cool the plasma and 'feeds' the toroid. The intermediate tube serves to accelerate the gas passing between the outer and the intermediate tubes, reducing gas consumption. The inner tube, or injector, introduces the sample into the plasma. The torch serves three purposes: it electrically insulates the plasma from the induction coil, stabilises the plasma, and injects the sample to be analysed. The energy is mostly contained in the external layer of the plasma, because of the 'skin' effect resulting from the high-frequency field [54].

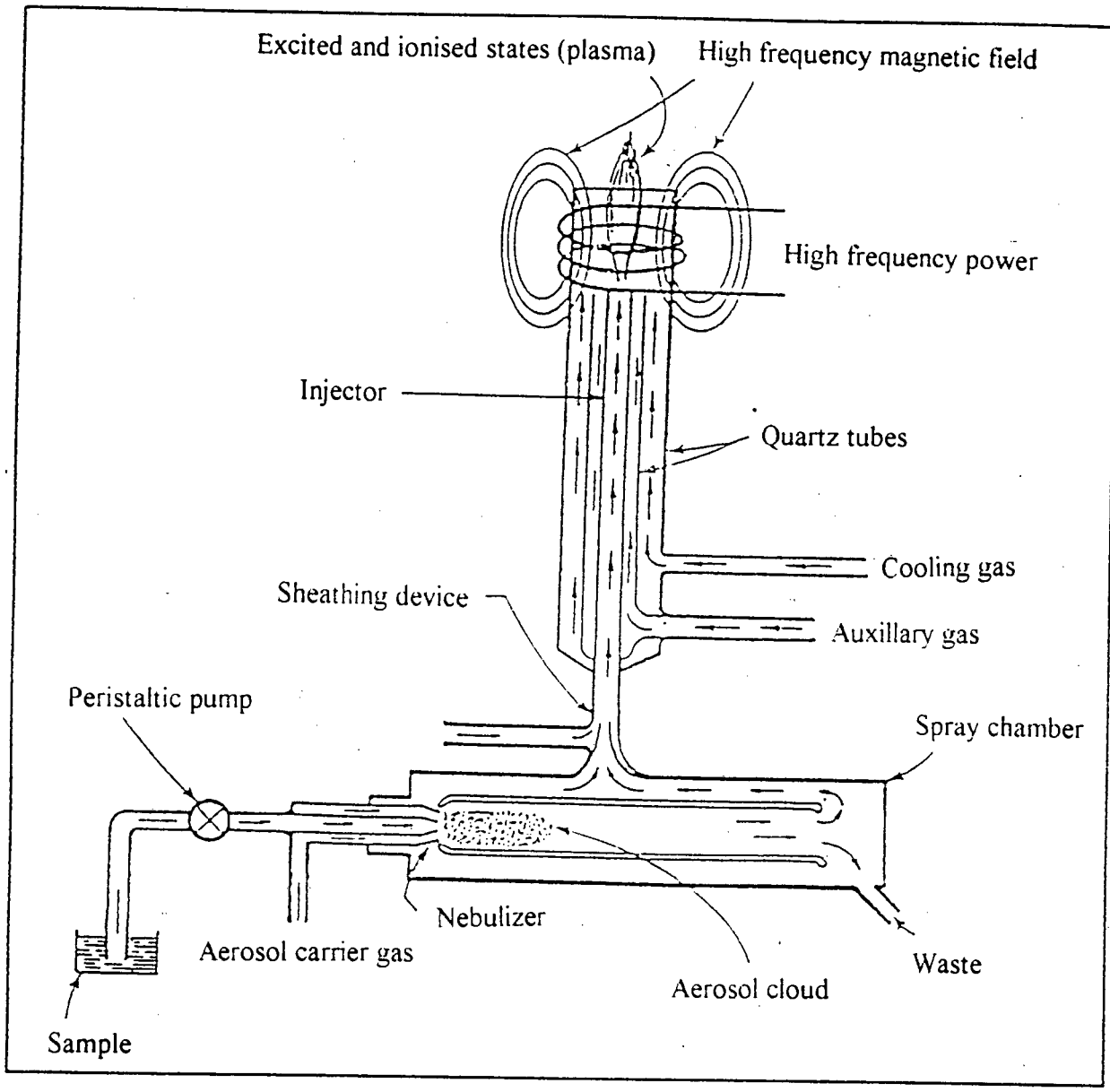

Figure 3.7.1: ICP system operating principle

The plasma is initiated by seeding the argon stream with electrons provided by a Tesla coil. The electrons, detached from ionised argon atoms, collide with other argon atoms and populate the coil region with positive and negative charges. As a result of the magnetic field the particles flow in a closed annular path.

Owing to the conductance of the gases in the coil region the charged particles are heated by inductive coupling to a temperature equalling the ionisation temperature of the support gases. A chain reaction of collisional ionisation of the argon gas occurs, resulting in the formation of the inductively-coupled plasma [55].

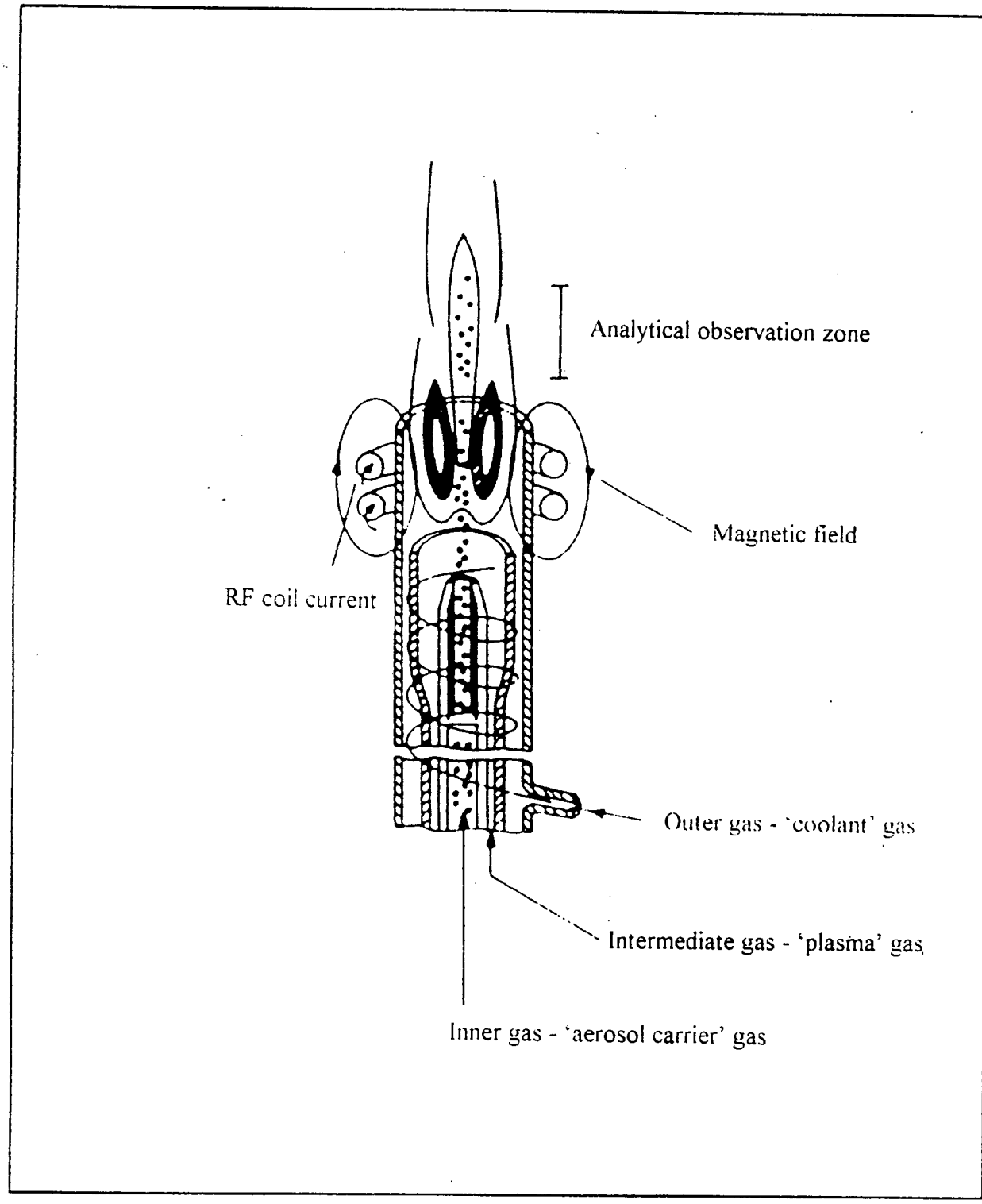

Figure 3.7.2: An inductively-coupled plasma torch assembly

Argon is used for several reasons: the high excitation temperatures obtained provide efficient atomisation and reduce chemical interferences; its high ionisation potential allows for the determination of most elements of the periodic table and finally, the emission spectrum of argon

is very simple and the potential for spectral line interference is reduced.

The structure of the inductively-coupled plasma (Figure 3.7.3) consists of five regions, each having unique spectroscopic, thermal and chemical characteristics.

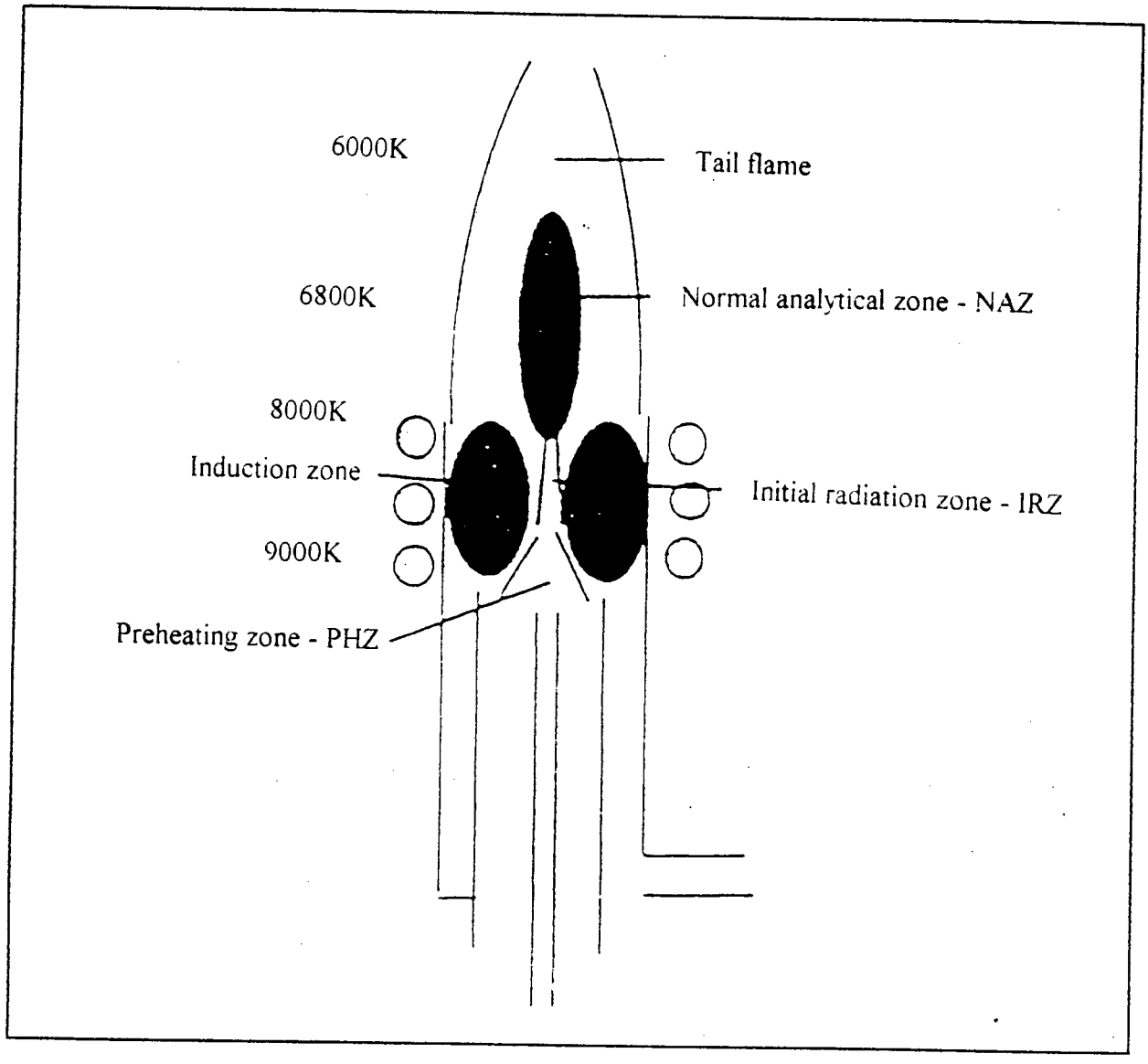

Figure 3.7.3: The structure of the inductively-coupled plasma

The main body of the plasma is called the 'induction region' (IR), where inductive energy transfer from the load coil takes place. The temperature of the plasma is at its maximum in this region. This region contains the highest population of excited argon ions and atoms. When argon carrier gas is injected into this region, the plasma forms an annular, doughnut-shaped area. The analytical benefits of this region are limited due to the high-intensity argon emission and continuum.

However, the injection of the sample and its interaction with this energetic region is the basis for the analytical performance of the inductively-coupled plasma.

The second region is the 'preheating zone' (PHZ). Particles traversing this region are subjected to very high temperatures by conduction, convection and radiation. Liquid aerosols undergo desolvation when transported into this region, with the formation of solid particles of a size below 1μm. Following desolvation, the particles undergo vaporisation to form a molecular gas which is then atomised. During passage of the molecular gas through the axial region of the plasma, the gas is exposed to the elevated temperature of the surrounding plasma in the third region of the inductively-coupled plasma - the 'initial radiation zone' (IRZ). This is the region where the sample atoms are excited and ionised through collisions with energetic electrons. Usually the residence time of the particles is sufficient for atomisation to take place without the influence of the sample matrix. The 'normal analytical zone' (NAZ) is the fourth region. As in the IRZ, excitation and ionisation occur in this region but the NAZ is characterised by a relatively high signal-to-background ratio. The height of observation for multi-element analysis varies from 10 to 18 mm above the IRZ apex [56]. The fifth and final region is the tail flame characterised by a low continuum emission and low spectral background.

The first stage in the ICP analysis of any sample is its introduction into the ICP torch. Liquid sampling is the normal method of sample introduction, and is generally introduced as a solution into a nebulizer to form a fine aerosol. The most commonly used device for sample introduction is the pneumatic nebulizer and this may be of two design types: concentric or crossflow. In both types efficient aerosol production requires very high gas velocities and consequently the use of fine capillary tubes. Ideally, the nebulizer should generate droplets of less than 10 μm diameter for efficient transport to the plasma. In practice many larger droplets are simultaneously generated, and have to be removed. In addition to the nebulizer itself, the function of the spray chamber (Figure 3.7.4) is critical. The primary purpose of the spray chamber is to remove the larger droplets from the aerosol before it enters the ICP torch. Very small changes in pressure within the spray chamber have serious effects on the emission signal, and it is important that the drainage system is arranged so that minimum pressure fluctuations occur [57].

For most nebulizer/spray chamber systems now in use, the proportion of solution going to waste is large. The transport efficiency (analyte mass reaching the plasma compared to analyte mass

aspirated) of a standard nebulizer is usually below 3% and often less than 1%. Pumps are frequently used to control the flow rate of liquid entering the nebulizer. Pumps help to control pressure fluctuations in the spray chamber, and also reduce variations in viscosity from one solution to another.

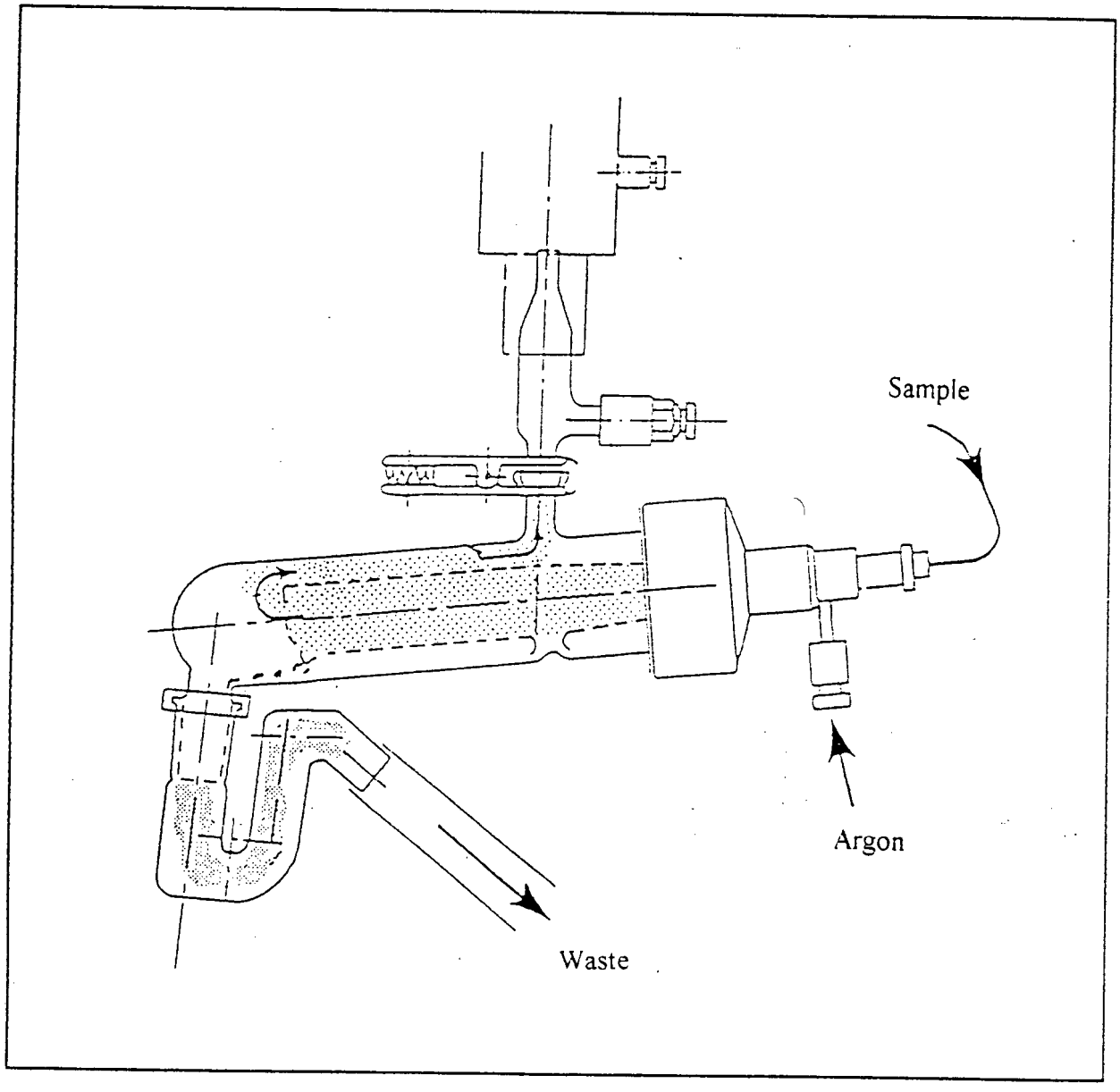

Figure 3.7.4: Spray Chamber

Since the basis for all emission spectroscopy is that atoms or ions in an energised state spontaneously revert to a lower energy state by photon emission, and that the emitted energy is proportional to the concentration of atoms or ions for quantitative emission spectroscopy. However, it is possible that some emitted photons will be absorbed by the same emitting atoms

or ions, and in consequence the observed radiation will be reduced. This will destroy the proportionality between element concentration and light emitted. ICP-OES succeeds to some extent, as a result of the highly energised plasma, in avoiding self-absorption in the very wide range of concentrations for which linear calibration curves can be obtained.

In addition to the wide dynamic range of ICP-OES, is the inherently good sensitivity and widely reported absence of interference effects. The good sensitivity stems from the efficiency of the high temperature inductively-coupled plasma in exciting the atomic or ionic lines, together with low background radiation [58].

The light emitted by the atoms of an element in the ICP must be converted to an electrical signal that can be measured quantitatively. This is done by resolving the light into its component radiation, by means of a diffraction grating, and finally measurement of the emitted light intensity by a photo multiplier tube at the specific wavelength for each element line. Two types of spectrometers are in widespread use: the polychromator and the scanning monochromator. The polychromator is a simultaneous instrument - all lines (channels) are measured at the same time. The scanning monochromator measures one element after another, giving an unrestricted choice of wavelengths to be measured, but requires much more time for the analysis. The resolution of the spectrometer determines the success of the system in separating adjacent spectral lines and thus avoiding inter-element effects. In all spectrometers stray light and scattered light is found to occur. However good the grating used, the intense emission from some strong lines causes stray light signals to be recorded on other channels [59].

The measured light intensities of specific wavelengths are compared to a calibration curve to obtain concentrations of each constituent of the measured sample. The standards for the calibration curve are measured under the same plasma conditions as the sample, to obtain the highest possible accuracy for the analysis.

Advantages of inductively-coupled plasma - optical emission spectroscopy, over other competitive techniques, can be summarised as [60]:

1. High sensitivity
2. Multi-element analysis

3. High precision
4. Good accuracy
5. High reproducibility
6. Rapid analysis
7. Large linear dynamic range
8. Few chemical interferences
9. On-line capabilities

Spectral interferences originating from matrix elements in samples of metallurgical and ore processing products, were investigated by Markova [61]. The noble metals determined in the samples were Au (242.79 nm, 267.59 nm), Ag, Pt (214.42 nm, 265.94 nm) and Pd (340.458 nm, 229.651 nm), in the presence of 1000 $\mu g.cm^{-3}$ or more of Fe, Mn, Cr, Ni and Cu. Significant spectral interferences from these 1st row transition elements were observed. The Pd (340.45nm) line was relatively free of spectral interferences. A separation of Au, Pt and Pd by solvent extraction with isoamyl alcohol improved the determination of the noble metals by reducing spectral interferences to manageable levels.

The determination of palladium, platinum and rhodium in silica-alumina based catalysts by ICP-OES, was studied by Etoh [62]. Aluminium interfered significantly with the determination, consequently the platinum-group metals were separated with 2-mercaptobenzothiazole prior to determination by ICP-OES. Yttrium was added as an internal standard to obtain the ratio of the analyte signal to the internal standard signal to be used to determine the analyte concentration of the sample. The remaining Cu and Sn present in the sample after separation, were found not to interfere with the analysis of the platinum-group metals in concentrations up to 100-times higher than those of the platinum-group metals.

A method for determination of rhodium in catalyst samples by ICP-OES was reported by Watananbe *et al.* by preconcentration of the rhodium with potassium xanthate prior to determination [63]. A 10-fold amount of K, Ca, Cu, Pd, Au, Ce and Pt, a 50-fold amount of Mg, a 200-fold amount of Al and a 6000-fold amount of Na were tolerated in the determination. However, a 50-fold excess of Ni interfered significantly with the determination. Removing the Ni by extraction with butyl xanthate at room temperature before determination, was necessary.

Baucells *et al.* [64] determined trace amounts of palladium in pure gold by ICP-OES. The study found that the most sensitive line for palladium (340.458 nm) suffered from interferences by Au lines nearby. However, the spectrum obtained showed that the Au (340.49 nm) line had low intensity and thus, did not interfere significantly with the palladium determination.

The pre-concentration of palladium in the presence of 1st row transition elements (Ca, Cd, Co, etc.) by complexation with sulphonated azo-dyes was investigated by Abollino *et al.* [65] prior to determination by ICP-OES. An anion-exchange resin was used for pre-concentration which resulted in an increase in the palladium detection limit of the inductively-coupled plasma atomic emission spectrometer by two orders of magnitude.

Van Staden *et al.* [66] studied the pre-concentration of trace quantities of platinum on an alumina column followed by determination by ICP-OES. This system achieved an enrichment factor of 25.5 (compared to the original sample) and a precision of better than 5% was obtainable at the 0.72 $mg.dm^{-3}$ Pt level.

The disadvantages of ICP-OES spectroscopic determination of the platinum-group metals are based primarily on the use of solutions. The number of elements soluble in the same solution is limited; sample preparation is time consuming and there is a risk of loss or contamination of the sample at trace concentrations. As mentioned previously, the dissolution of samples containing platinum-group metals is not a simple procedure. Use of a pneumatic nebulizer is another limitation of the technique. Besides the risk of blocking, most system instabilities arise from the nebulizer. However, the main disadvantage to this technique is the possibility of spectral interference. Although the most sensitive lines can be used frequently, it is often necessary to verify that the lines are free from spectral interferences when a new matrix is analysed.

3.8 Determination of the platinum-group metals by Inductively-Coupled Plasma - Mass Spectrometry

The first published paper describing the coupling of an argon plasma and a mass spectrometer was in 1980 [67]. The principle of ICP-MS determination is the extraction of ions from a plasma and subsequent introduction into a quadrupole mass spectrometer for mass resolution, detection and quantification. ICP-MS is a multi element technique with sub-$ng.dm^3$ detection limits for many

elements. However, its suitability for platinum-group metal determinations has only recently been examined.

Sample solutions are nebulized into an ICP where ions are formed at the plasma temperature of 6000 - 8000°C [68]. Part of the plasma, extracted through the cool 'boundary layer', is sampled via a circular orifice (nickel or copper, 0.5 - 1.0 mm in diameter), into a differentially pumped region at approximately 1 Torr. From this pumped region the sampled ions pass into a second vacuum chamber (10^{-5} Torr) where the ion optics are situated. Ions of selected *m z* range leave the mass analyser and are deflected into a channel electron multiplier for detection in a pulse-counting mode. Element sensitivity achievable by ICP-MS depends upon five parameters: isotopic abundances, degree of ionisation of the element in the ICP, the ion lens voltages, sample introduction and plasma operation. The spectrometer scans through the chosen masses in a discontinuous manner in one of two possible scanning modes, termed 'sequential' and 'multichannel'. In sequential analysis, the spectrometer is tuned into each mass for the specified measurement time only once. In multichannel mode, the spectrometer scans the selected range repeatedly until the dwell times on each mass accumulate to total the measurement time [69].

The determination of precious metals in geological samples by ICP-MS, was reviewed by Denoyer *et al.* [70]. The performance characteristics of ICP-MS were compared with other commonly employed techniques and several typical ICP-MS methods were described. ICP-MS was found to compare very favourably with other competitive techniques, combining high precision analysis with low detection limits for the platinum-group metals.

Wood *et al.* [71] investigated the ICP-MS determination of trace levels of gold and platinum in natural aqueous solutions (brine, seawater, etc.) with high contents of total dissolved solids. ICP-MS was found to be particularly well suited for analysis of sulphide-containing solutions without preconcentration or pretreatment, provided that standard addition was employed. Platinum and gold recovery was greater than 89% with high precision (RSD less than 10%). The presence of sulphide(S^{2-}) and fulvic acid increased the sensitivity for platinum and gold by a factor of 4. However, the sensitivity for platinum decreased with increasing sulphate concentration.

Platinum in airborne particulate matter was determined by ICP-MS [72] combined with a flow injection system. It was found that hafnium caused suppression of the observed signal intensity of

platinum and a spectral interference by hafnium oxide. Thus it was necessary that a cation-exchange resin be incorporated into the flow injection system for trapping hafnium and major matrix elements, prior to determination of the platinum content. The detection limit was found to be 5 ng.cm^3 Pt in airborne particulate matter.

Sen Gupta *et al.* [73] determined palladium, iridium and ruthenium using isotope dilution ICP-MS. The platinum-group metals were co-precipitated with tellurium (**1.7**) prior to determination by ICP-MS. The presence of nickel nitrate was found to yield up to a ten-fold enhancement in the platinum-group metal analyte ion count rate. Copper nitrate was also found to cause this enhancement but to a smaller degree.

Methods were developed by Colodner *et al.* [74] to determine Re, Ir, and Pt in natural waters and sediments by isotope dilution inductively coupled plasma mass spectrometry. A stable isotope-enriched spike was added to the sample before processing. Anion-exchange of the chloro complexes of iridium, platinum and perrhenate ion was used to pre-concentrate the elements and separate them from the concomitant 1st row transition metals prior to determination, to prevent the formation of molecular ions in the argon plasma resulting in isobaric interferences. Overall recoveries were 90% for all three elements with detection limits of 5 pg of Re, 6 pg of Ir and 14 pg of Pt.

Limitations of inductively-coupled plasma-mass spectrometry in the determination of the platinum-group metals are few but serious. Spectral interferences are common and occur from mass overlaps of isotopes of other elements (e.g. hafnium overlapping platinum), and matrix-induced interference is frequently encountered during analysis. Matrix-induced interference can be broken down into three effects: 'ionisation' interference (due to high concentrations of matrix elements), 'ion-sampling' interference (a change in the ion population during sampling) and 'mass-dependent signal drift' (due to deposition of salt on the ion optics).

Careful selection of isotope lines can reduce these interferences but never eliminate them. An additional shortfall of the technique is the expensive equipment required for analysis. Long-term stability is also decidedly inferior to other competitive techniques but will no doubt improve as the technique becomes more widespread.

3.9 Conclusion

The second stage in the trace analysis of the platinum-group metals is their determination in the sample matrix, with or without preconcentration prior to determination. A summary of the available analytical techniques described is presented below (Table 3.9.1) [75].

Table 3.9.1: Comparison of characteristics of the described analytical techniques

Methods	Precision	Detection limit	Sample size	Nondestructive analysis	Multi-element analysis	Analysis time
Spectroph.	4-8%	10^{-5}-10^{-7}g	mg - g	no	no	hrs
NAA	2-10%	>10^{-12}g	mg - g	yes	yes	min-wks
XRF	1-2%	10^{-3}-10^{-5}g	g	yes	yes	hrs
FAAS	2-5%	10^{-6}-10^{-7}g	g	no	no	hrs
FAES	2-5%	10^{-6}-10^{-7}g	g	no	no	hrs
GFAAS	8-12%	10^{-11}-10^{-12}g	mg	no	no	hrs
ICP-OES	5-20%	10^{-5}-10^{-6}g	mg	no	yes	hrs
ICP-MS	20-30%	10^{-3}-10^{-9}g	mg	no	yes	hrs

As seen from a review of the literature, no documented determination technique is without limitations regarding the determination of the platinum-group metals. Neither do the techniques fulfill all of the desired characteristics of an ideal determination technique.

Twenty years ago, the chemical repertoire for the analysis of the platinum-group metals was largely limited to gravimetric methods (including fire assay), enhanced to a limited extent by various spectrophotometric methods. The introduction of instrumental methods of analysis has reduced the need for extensive chemical separations. However, only a few platinum-group metal materials can be analysed by purely instrumental techniques.

Random errors in instrumental methods can often be limited to 1% (relative), but systematic errors are significantly greater unless standard samples of the same composition (both chemical and physical) are available and used, and the instrumental method is properly calibrated. Where a

higher degree of precision is required (in the case of trace amounts of platinum-group metals), pre-concentration before instrumental determination is often required.

Presented below is the result of a survey conducted in 1973 to determine the principal analytical techniques applied to the determination of the platinum-group metals by American laboratories (Table 3.9.2) [76].

Table 3.9.2: Percentage of each analytical technique used by laboratories, in the trace analysis of platinum-group metal materials

Method	Percentage
Spectrophotometry	41.5
FAAS / FAES	48.5
ICP-OES	23
XRF	13
NAA	14
ICP-MS	9
Other (polarography etc.)	38.5

The results of this survey, though of interest, correspond to the situation in 1973. Since then in the trace analysis of the platinum-group metals, there has been a significant shift away from spectrophotometric and flame atomic absorption techniques towards inductively-coupled plasma emission, X-ray fluorescence and neutron activation analysis methods of determination,. In the past twenty years, the interdependence of chemical and instrumental methods in the determination of trace amounts of platinum-group metals has been clearly shown.

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Chapter 4

Optimisation of Palladium(II), Platinum(IV) and Platinum(II) Pre-concentration

4.1 Introduction

The ideal pre-concentration technique characteristics were discussed in Chapter 2 and after reviewing the literature, *N*-benzoyl-*N'*, *N'*-dialkylthioureas [1-5] were seen as one of the most promising of the documented pre-concentration agents for the platinum-group metals. *N*-benzoyl-*N'*, *N'*-dialkylthioureas fulfilled many of the characteristics of the envisaged ideal pre-concentration technique. *N*-benzoyl-*N'*, *N'*-dialkylthioureas rapidly (time efficiency) complexed platinum-group metals quantitatively (accuracy, high percentage recovery and reproducibility), into apolar, organic solvents (simplicity of use and low pre-concentration complexity), in the presence of other elements without interference (selectivity, **2.3**). Additionally, ligand synthesis was uncostly and straightforward (cost efficiency). As a result of these promising characteristics this class of ligands was selected as the pre-concentration agent for this study.

In previous studies *N*-benzoyl-*N'*, *N'*-dialkylthioureas were used as pre-concentration agents for platinum-group metals in solvent extraction type systems. However, the method of pre-concentration chosen for this work was the pre-concentration of the non-polar platinum-group metal-*N*-benzoyl-*N'*, *N'*-dialkylthiourea chelates onto a reverse-phase column, followed by elution off the column prior to determination by ICP-OES. This also allowed pre-concentration of the platinum-group metals directly from the effluent solutions, further reducing the pre-concentration complexity of the system. To achieve pre-concentration directly in the aqueous effluent, a more water-soluble (hydrophilic) *N*-benzoyl-*N'*, *N'*-dialkylthiourea was synthesised namely, *N*-benzoyl-*N'*, *N'*-di-(2-hydroxyethyl)thiourea (Figure 4.1.1).

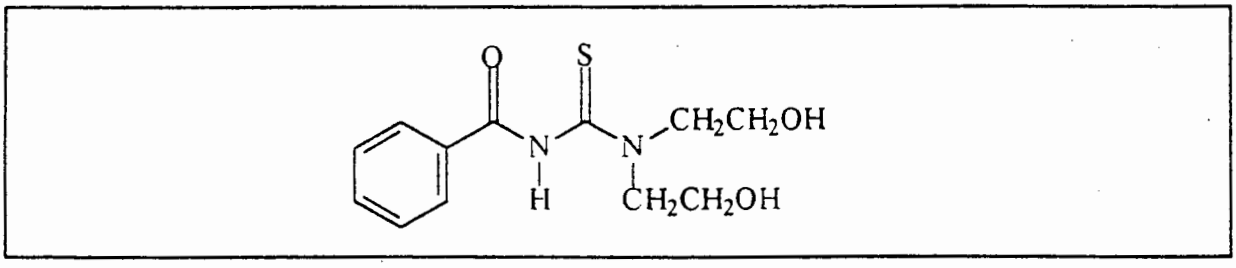

Figure 4.1.1: *N*-benzoyl-*N'*, *N'*-di-(2-hydroxyethyl)thiourea

N-benzoyl-*N'*, *N'*-di-(2-hydroxyethyl)thiourea being more hydrophilic than other ligands of its class was expected to complex the platinum-group metals directly from the industrial effluent, thus negating the use of a solvent extraction-type system of pre-concentration. The neutral, non-polar platinum-group metal chelates thus formed, would be inherently more hydrophobic than the free ligand and as a result enable pre-concentration of the platinum-group metal chelates onto a reverse-phase C_{18} column.

The initial pre-concentration system designed, optimisation of all system variables was necessary to ensure that the best set of conditions to solve the analytical problem under study, were determined. As expected, various chemical and physical parameters were critical to optimisation of the pre-concentration step. The effects of the following parameters were studied and optimised:

1. Maximum column loading capacity of *N*-benzoyl-*N'*, *N'*-di-(2-hydroxyethyl)thiourea
2. Ligand concentration
3. Eluent concentration
4. Effect of sample and eluent pump-flow rate
5. Effect of pH
6. Column lifetime
7. Maximum column loading capacity of palladium(II) and platinum(IV/II)
8. Pre-concentration factors for palladium(II)

Parameters 1 - 6 and 8 above, were determined using palladium(II) solutions only, as palladium(II) complexation with the ligand occured quantitatively and rapidly, resulting in a much simplified determination of the optimised parameters necessary for quantitative pre-concentration of the platinum-group metals.

4.2 *N*-benzoyl-*N'*, *N'*-di-(2-hydroxyethyl)thiourea (Ligand) Breakthrough on Column

The maximum amount of ligand that could be loaded onto the column before breakthrough occured, was determined by pumping aliquots (5 cm^3) of 0.002 M *N*-benzoyl-*N'*, *N'*-di-(2-hydroxyethyl)thiourea over the reverse-phase column at 1 cm^3min^{-1}. Breakthrough was considered to have been achieved when the UV absorbance of the sample solution, after having been pumped over the column, equaled 1% of the maximum UV absorbance (at λ = 320 nm), of a freshly

prepared 0.002 M solution of ligand (Table 4.2.1).

Table 4.2.1: Absorbance vs volume readings at λ = 320 nm

Volume of ligand solution pumped (cm^3)	Absorbance at λ = 320 nm (AU)
Blank solution	0.002
5	0.003
10	0.003
12	0.003
13	0.003
14	0.003
15	0.041
22	0.067
27	1.003
Pure Ligand	3.029

A 1% absorbance reading (see Figure 4.2.1 for the experimental UV absorption spectra) was obtained after 15 cm^3 of ligand solution had been pumped over the column. This equated to a maximum of 8.04 mg ligand loaded onto the column before breakthrough was achieved. This also fixed the theoretical upper limits of the platinum-group metals that could be pre-concentrated on the column assuming a fixed metal:ligand ratio based on well-documented platinum-group metal-ligand species [6].

The theoretical upper limits were calculated to be 4.02 mg palladium(II) (1:2 metal:ligand ratio), 2:68 mg platinum(IV) (1:3 metal:ligand ratio), 4.02 mg platinum(II) (1:2 metal:ligand ratio) and 2.68 mg rhodium(III) (1:3 metal:ligand ratio). The molar absorptivity of the pure ligand was found to be 1.52×10^4 (ϵ = A/cl).

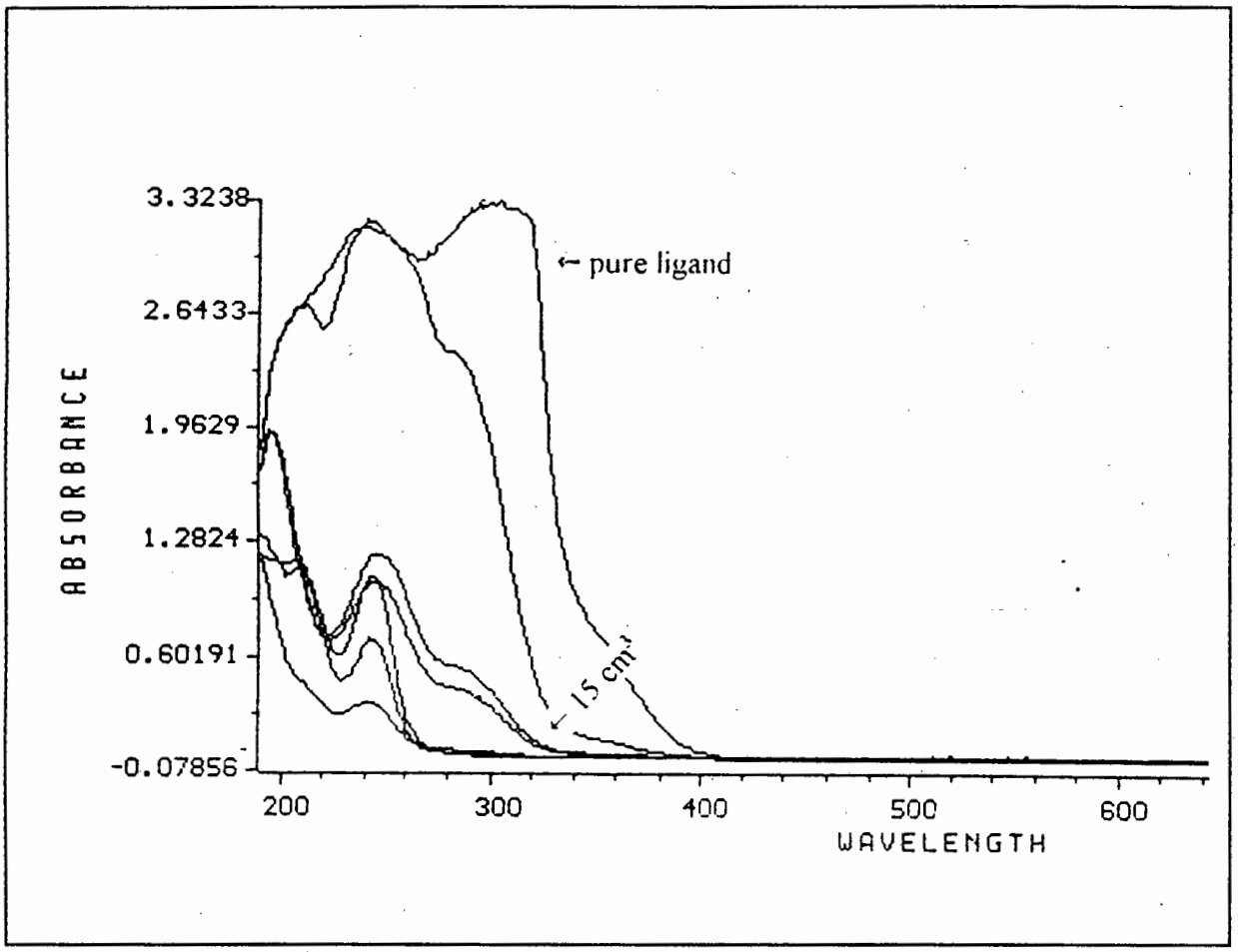

Figure 4.2.1: Experimental UV absorption spectra of the ligand

4.3 Ligand Concentration Optimisation

The optimum metal:ligand ratio required for complete pre-concentration of the platinum-group metal chelate was determined using (Table 4.3.1, 4.3.2), 2 $\mu g.cm^{-3}$ and 4 $\mu g.cm^{-3}$ palladium(II) solutions with varying amounts of ligand (1:0 - 1:20, metal:ligand ratio) pre-concentrated onto the reverse-phase column at a pump-flow rate of 1 cm^3 min^{-1}.

The pre-concentrated complex was eluted off the column with methanol and the eluate analysed by ICP-OES. Calibration standards utilised in this study were palladium(II) standards in 2 M perchloric acid. The use of standard solutions containing no ligand, enabled simultaneous evaluation of any enhancement or depression, by the ligand, on the ICP-OES detection signal.

Table 4.3.1: Palladium(I) atomic line intensity at 340.458 nm vs metal:ligand ratio

Metal:Ligand ratio (1:X)	Mean $I_{Pd(I)}$ at 340.458nm c_{Pd} = 2 μg.cm^{-3} (iu)	* Mean Pd(II) concentration determined c_{Pd} = 2 μg.cm^{-3} (μg.cm^{-3})	* 95% Confidence interval of mean Pd(II) determined c_{Pd} = 2 μg.cm^{-3} (μg.cm^{-3})	Mean $I_{Pd(I)}$ at 340.458nm c_{Pd} = 4 μg.cm^{-3} (iu)	* Mean Pd(II) concentration determined c_{Pd} = 4 μg.cm^{-3} (μg.cm^{-3})	* 95% Confidence interval of mean Pd(II) determined c_{Pd} = 4 μg.cm^{-3} (μg.cm^{-3})
1:0	346	2.00 +- 0.16	1.60 - 2.40	500	4.00 +- 0.09	3.78 - 4.22
1:1	353	2.15 +- 0.21	1.65 - 2.65	500	4.15 +- 0.10	3.90 - 4.40
1:2	350	2.11 +- 0.15	1.71 - 2.51	505	4.15 +- 0.10	3.90 - 4.40
1:4	352	2.13 +- 0.16	1.73 - 2.53	498	4.01 +- 0.13	3.69 - 4.33
1:6	321	1.75 (ppt.)#	-	274	1.20 (ppt.)#	-
1:8	349	2.10 +- 0.09	1.88 - 2.32	347	2.07 (ppt.)#	-
1:10	349	2.03 +- 0.09	1.81 - 2.25	550	4.23 +- 0.11	3.96 - 4.50
1:12	355	2.08 +- 0.10	1.83 - 2.33	560	4.18 +- 0.02	4.13 - 4.23
1:14	354	2.08 +- 0.09	1.86 - 2.30	561	4.15 +- 0.04	4.05 - 4.25
1:16	360	2.13 +- 0.05	2.01 - 2.25	555	4.07 +- 0.12	3.77 - 4.37
1:20	360	2.13 +- 0.06	1.98 - 2.28	565	4.06 +-0.05	3.94 - 4.18

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t =4.30 for N = 3

ppt. = precipitation of metal-ligand complex observed

Table 4.3.2: Palladium(II) ionic line intensity at 229.651 nm vs metal:ligand ratio

Metal:Ligand ratio (1:X)	Mean $I_{Pd(II)}$ at 229.651 nm c_{Pd} = 2 μg.cm^{-3} (iu)	* Mean Pd(II) concentration determined c_{Pd} = 2 μg.cm^{-3} (μg.cm^{-3})	* 95% Confidence interval of mean Pd(II) determined c_{Pd} = 2 μg.cm^{-3} (μg.cm^{-3})	Mean $I_{Pd(II)}$ at 229.651 nm c_{Pd} = 4 μg.cm^{-3} (iu)	* Mean Pd(II) concentration determined c_{Pd} = 4 μg.cm^{-3} (μg.cm^{-3})	* 95% Confidence interval of mean Pd(II) determined c_{Pd} = 4 μg.cm^{-3} (μg.cm^{-3})
1:0	222	2.00 +- 0.03	1.93 - 2.07	330	4.00 +- 0.09	3.78 - 4.22
1:1	228	2.08 +- 0.02	2.03 - 2.13	317	4.06 +- 0.03	3.99 - 4.13
1:2	226	2.08 +- 0.05	1.96 - 2.20	328	3.96 +- 0.09	3.74 - 4.18
1:4	230	2.10 +- 0.07	1.93 - 2.27	327	3.95 +- 0.06	3.80 - 4.10
1:6	211	1.76 (ppt.)#	-	202	1.22 (ppt.)#	-
1:8	230	2.11 +- 0.01	2.09 - 2.13	245	2.39 (ppt.)#	-
1:10	230	2.07 +- 0.15	1.70 - 2.44	370	4.18 +- 0.01	4.16 - 4.20
1:12	240	2.05 +- 0.07	1.88 - 2.22	395	4.17 +- 0.23	3.60 - 4.74

Metal:Ligand ratio (1:X)	Mean $I_{Pd(II)}$ at 229.651 nm c_{Pd} = 2 μg.cm^{-3} (iu)	* Mean Pd(II) concentration determined c_{Pd} = 2 μg.cm^{-3} (μg.cm^{-3})	* 95% Confidence interval of mean Pd(II) determined c_{Pd} = 2 μg.cm^{-3} (μg.cm^{-3})	Mean $I_{Pd(II)}$ at 229.651 nm c_{Pd} = 4 μg.cm^{-3} (iu)	* Mean Pd(II) concentration determined c_{Pd} = 4 μg.cm^{-3} (μg.cm^{-3})	* 95% Confidence interval of mean Pd(II) determined c_{Pd} = 4 μg.cm^{-3} (μg.cm^{-3})
1:14	241	2.07 +- 0.03	2.00 - 2.14	400	4.14 +- 0.10	3.89 - 4.39
1:16	249	2.16 +- 0.16	1.76 - 2.56	398	4.17 +- 0.08	3.97 - 4.37
1:20	253	2.20 +- 0.17	1.78 - 2.62	390	4.09 +- 0.06	3.94 - 4.24

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t =4.30 for N = 3

ppt. = precipitation of metal-ligand complex observed

Higher metal:ligand ratios (> 1:8) were found to be less susceptible to precipitation of the palladium(II) chelate into solution. This was attributed, by Le Chateliers principle, to the complexation equilibrium favouring the formation of a soluble palladium(II) chelate at higher ligand concentrations. A metal:ligand ratio of 1:20 was found to be the optimum ratio for preconcentration of a 2 μg.cm^{-3} and 4 μg.cm^{-3} palladium(II) solution. This ratio was also selected as it was found to yield the maximum intensity at both the atomic Pd(I) line 340.458 nm and ionic Pd(II) line 229.651 nm.

Additionally, the platinum-group metal content of the real effluent solutions were unknown and a sufficient excess of ligand was essential to ensure that all the platinum-group metals present in the effluent solution were pre-concentrated. For a ratio of 1:6 (2 and 4 μg.cm^{-3}) and a ratio of 1:8 (4 μg.cm^{-3}), the palladium-ligand chelate precipitated and poor palladium(II) recovery results were obtained for these solutions.

Stability of the platinum-group metal chelates, at the various ratios, were simultaneously investigated by re-analysing the eluate samples (used in the previous study) 24 and 96 hours later and comparing these results with the freshly analysed results initially obtained (see Table 4.3.3, 4.3.4, 4.3.5, 4.3.6).

Table 4.3.3: Analysis of the 2 $\mu g.cm^{-3}$ samples, 24 and 96 hours later, at palladium(I) 340.458 nm

Metal:Ligand ratio (1:X)	Initial mean palladium(II) concentration determined c_{Pd} = 2 $\mu g.cm^{-3}$ ($\mu g.cm^{-3}$)	* Mean Pd(II) concentration determined 24 hrs c_{Pd} = 2 $\mu g.cm^{-3}$ ($\mu g.cm^{-3}$)	* 95% Confidence interval of mean Pd(II) determined 24 hrs c_{Pd} = 2 $\mu g.cm^{-3}$ ($\mu g.cm^{-3}$)	* Mean Pd(II) concentration determined 96 hrs c_{Pd} = 2 $\mu g.cm^{-3}$ ($\mu g.cm^{-3}$)	* 95% Confidence interval of mean Pd(II) determined 96 hrs c_{Pd} = 2 $\mu g.cm^{-3}$ ($\mu g.cm^{-3}$)
1:1	2.15	-	-	2.09 +- 0.09	1.87 - 2.31
1:2	2.11	-	-	0.61 (ppt.)#	-
1:4	2.13	-	-	0.92 (ppt.)#	-
1:6	1.75 (ppt.)#	-	-	2.03 +- 0.10	1.78 - 2.28
1:8	2.10	-	-	2.34 +- 0.15	1.97 - 2.71
1:10	2.03	2.07 +- 0.02	2.02 - 2.13	-	-
1:12	2.08	2.04 +- 0.04	1.94 - 2.14	-	-
1:14	2.08	2.08 +- 0.08	1.88 - 2.28	-	-
1:16	2.13	2.15 +- 0.26	1.50 - 2.80	-	-
1:20	2.13	2.20 +- 0.13	1.88 - 2.52	-	-

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t =4.30 for N = 3

ppt. = precipitation of metal-ligand complex observed

Table 4.3.4: Analysis of the 2 $\mu g.cm^{-3}$ samples, 24 and 96 hours later, at palladium(I) 229.651 nm

Metal:Ligand ratio (1:X)	Initial mean palladium(II) concentration determined c_{Pd} = 2 $\mu g.cm^{-3}$ ($\mu g.cm^{-3}$)	* Mean Pd(II) concentration determined 24 hrs c_{Pd} = 2 $\mu g.cm^{-3}$ ($\mu g.cm^{-3}$)	* 95% Confidence interval of mean Pd(II) determined 24 hrs c_{Pd} = 2 $\mu g.cm^{-3}$ ($\mu g.cm^{-3}$)	* Mean Pd(II) concentration determined 96 hrs c_{Pd} = 2 $\mu g.cm^{-3}$ ($\mu g.cm^{-3}$)	* 95% Confidence interval of mean Pd(II) determined 96 hrs c_{Pd} = 2 $\mu g.cm^{-3}$ ($\mu g.cm^{-3}$)
1:1	2.08	-	-	2.13 +- 0.11	1.86 - 2.40
1:2	2.08	-	-	0.67 (ppt)#	-
1:4	2.10	-	-	1.00 (ppt)#	-
1:6	1.76 (ppt.)#	-	-	2.13 +- 0.06	1.98 - 2.28
1:8	2.11	-	-	2.45 +- 0.09	2.23 - 2.67
1:10	2.07	2.06 +- 0.01	2.04 - 2.08	-	-

Metal:Ligand ratio (1:X)	Initial mean palladium(II) concentration determined c_{Pd} = 2 μg.cm^{-3} (μg.cm^{-3})	* Mean Pd(II) concentration determined 24 hrs c_{Pd} = 2 μg.cm^{-3} (μg.cm^{-3})	* 95% Confidence interval of mean Pd(II) determined 24 hrs c_{Pd} = 2 μg.cm^{-3} (μg.cm^{-3})	* Mean Pd(II) concentration determined 96 hrs c_{Pd} = 2 μg.cm^{-3} (μg.cm^{-3})	* 95% Confidence interval of mean Pd(II) determined 96 hrs c_{Pd} = 2 μg.cm^{-3} (μg.cm^{-3})
1:12	2.05	2.07 +- 0.07	1.90 - 2.24	-	-
1:14	2.07	2.07 +- 0.05	1.95 - 2.19	-	-
1:16	2.16	2.14 +- 0.14	1.79 - 2.49	-	-
1:20	2.20	2.23 +- 0.08	2.03 - 2.43	-	-

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t =4.30 for N = 3

ppt. = precipitation of metal-ligand complex observed

Table 4.3.5: Analysis of the 4 μg.cm^{-3} samples, 24 and 96 hours later, at palladium(I) 340.458 nm

Metal:Ligand ratio (1:X)	Initial mean palladium(II) concentration determined c_{Pd} = 4 μg.cm^{-3} (μg.cm^{-3})	* Mean Pd(II) concentration determined 24 hrs c_{Pd} = 4 μg.cm^{-3} (μg.cm^{-3})	* 95% Confidence interval of mean Pd(II) determined 24 hrs c_{Pd} = 4 μg.cm^{-3} (μg.cm^{-3})	* Mean Pd(II) concentration determined 96 hrs c_{Pd} = 4 μg.cm^{-3} (μg.cm^{-3})	* 95% Confidence interval of mean Pd(II) determined 96 hrs c_{Pd} = 4 μg.cm^{-3} (μg.cm^{-3})
1:1	4.15	-	-	1.09 (ppt.)#	-
1:2	4.15	-	-	0.59 (ppt.)#	-
1:4	4.01	-	-	3.95 +- 0.12	3.65 - 4.25
1:6	1.20 (ppt.)#	-	-	0.92 (ppt.)#	-
1:8	2.07	-	-	1.82 (ppt)#	-
1:10	4.23	4.26 +- 0.07	4.09 - 4.43	-	-
1:12	4.18	4.12 +- 0.06	3.97 - 4.27	-	-
1:14	4.15	4.25 +- 0.08	4.05 - 4.45	-	-
1:16	4.07	4.11 +- 0.02	4.06 - 4.16	-	-
1:20	4.06	4.08 +- 0.08	3.88 - 4.28	-	-

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t =4.30 for N = 3

ppt. = precipitation of metal-ligand complex observed

Table 4.3.6: Analysis of the 4 $\mu g.cm^{-3}$ samples, 24 and 96 hours later, at palladium(II) 229.651 nm

Metal:Ligand ratio (1:X)	Initial mean palladium(II) concentration determined c_{Pd} = 4 $\mu g.cm^{-3}$ ($\mu g.cm^{-3}$)	* Mean Pd(II) concentration determined 24 hrs c_{Pd} = 4 $\mu g.cm^{-3}$ ($\mu g.cm^{-3}$)	* 95% Confidence interval of mean Pd(II) determined 24 hrs c_{Pd} = 4 $\mu g.cm^{-3}$ ($\mu g.cm^{-3}$)	* Mean Pd(II) concentration determined 96 hrs c_{Pd} = 4 $\mu g.cm^{-3}$ ($\mu g.cm^{-3}$)	* 95% Confidence interval of mean Pd(II) determined 96 hrs c_{Pd} = 4 $\mu g.cm^{-3}$ ($\mu g.cm^{-3}$)
1:1	4.06	-	-	1.11 (ppt.)#	-
1:2	3.96	-	-	0.57 (ppt.)#	-
1:4	3.95	-	-	3.99 +- 0.36	3.10 - 4.88
1:6	1.22 (ppt.)	-	-	0.93 (ppt.)#	-
1:8	2.39	-	-	1.86 (ppt.)#	-
1:10	4.18	4.25 +- 0.05	4.13 - 4.37	-	-
1:12	4.17	4.15 +- 0.06	4.00 - 4.30	-	-
1:14	4.14	4.15 +- 0.07	3.98 - 4.32	-	-
1:16	4.17	4.07 +- 0.06	3.92 - 4.22	-	-
1:20	4.09	3.92 +- 0.13	3.60 - 4.24	-	-

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t =4.30 for N = 3

ppt. = precipitation of metal-ligand complex observed

A metal:ligand ratio of 1:2, 1:4 (2 $\mu g.cm^{-3}$) and 1:1, 1:2, 1:6 and 1:8 (4 $\mu g.cm^{-3}$) resulted in precipitation of the palladium(II)-ligand chelate after 96 hours, and resulted in poor palladium(II) recovery. A metal:ligand ratio higher than 1:8 showed no precipitation of the palladium(II) chelate after 24 hours. Therefore, a 1:20 metal:ligand ratio was again deemed to be optimum, as the palladium(II)-ligand chelate was stable at both 2 and 4 $\mu g.cm^{-3}$.

An interesting observation was seen exclusively in the 1:6 (2 $\mu g.cm^{-3}$) solution, in which the initial addition of the ligand resulted in a 12.5% precipitation of the palladium(II) chelate, while 96 hours later no precipitation was evident and 100% palladium(II) recovery was recorded. This result indicated that the palladium(II)-ligand chelate in the 1:6 solution was present as at least two species in aqueous solution: an insoluble species and a soluble species. Initial precipitation of the insoluble palladium(II) chelate was observed upon addition of the ligand to the sample solution, whilst 96 hours later no precipitation was observed (soluble palladium(II) chelate). This was attributed to a slow equilibration of the initial insoluble palladium(II) chelate to the soluble

palladium(II) chelate species over time.

4.4 Eluent Optimisation

Prior to eluent optimisation, 2 cm^3 methanol was found to quantitatively elute the palladium(II) chelate off the reverse-phase column, allowing determination by ICP-OES. The use of a carbon-rich eluent, like methanol, caused significant problems in the ICP-OES determination step. High carbon content in the plasma often resulted in plasma instability (carbon atoms in the plasma 'scavenging' the electrons of the plasma, resulting in the loss of ionisation of the argon gas and finally plasma extinction) and a subsequent termination of the experiment. Thus it was essential that other possible eluents be investigated in addition to eluents containing various reagents to 'strip' the palladium(II) complex from the reverse-phase column material. Thiourea, potassium thiocyanate, methanol, ammonia solutions and mixtures of the above were all tested as possible eluents. Sample solutions containing fixed quantities of palladium(II) were pre-concentrated onto the reverse-phase column and subsequently eluted with the various eluents, at different elution volumes. The eluate solutions were analysed and the percentage recovery of the palladium(II) determined (Table 4.4.1).

Table 4.4.1: Percentage recovery of palladium(II) with alternative eluents

Eluent composition	Pd(II) pre-concentrated ($\mu g.cm^{-3}$)	Mean Pd(II) eluted ($\mu g.cm^{-3}$)	* Mean percentage recovery (%)	* 95% Confidence interval of mean percentage recovery (%)
15%(w/v) ammonia	40	20.9	52.3 +- 0.35	51.4 - 53.2
20%(w/v) methanol	40	24.0	60.0 +- 0.54	58.7 - 61.3
1.2% (w/v) thiocyanate	40	22.3	55.8 +- 0.83	53.7 - 57.9
0.003 M thiourea in 20 % methanol	40	29.4	73.5 +- 1.58	69.6 - 77.4
0.5 M thiourea in 20 % methanol	40	32.7	81.8 +- 0.22	81.3 - 82.3
1.0 M thiourea in 20 % methanol	40	39.2	98.0 +- 0.98	95.6 - 100.4
5% (w/v) thiourea in 20% methanol and 2 M $HClO_4$	40	39.0	97.5 +- 0.25	96.9 - 98.1
5% (w/v) thiourea in 20% methanol and 2 M $HClO_4$	40	39.8	99.4 +- 0.17	98.9 - 99.9

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t =4.30 for N = 3

A combination of eluents was needed to ensure the quantitative elution of the palladium(II) chelate off the column. The optimum eluent was found to be 10 cm^3 of 5% (w/v) thiourea in 20% methanol and 2 M $HClO_4$. Thiourea, in analogy with other sulphur donor ligands, readily forms stable compounds with the platinum-group metals. Thiourea has a strong trans ligand effect [7] and readily undergoes substitution with co-ordinated chloride atoms. An acidic solution was required to protonate the chelated ligands and result in the formation of a pendant ligand palladium(II) chelate species (Figure 4.4.1). This pendant ligand chelate species was vulnerable to substitution by thiourea, to form the hydrophilic palladium(II) thiourato species (Figure 4.4.2), simultaneously eluting the palladium(II) pre-concentrated by the ligand on the column.

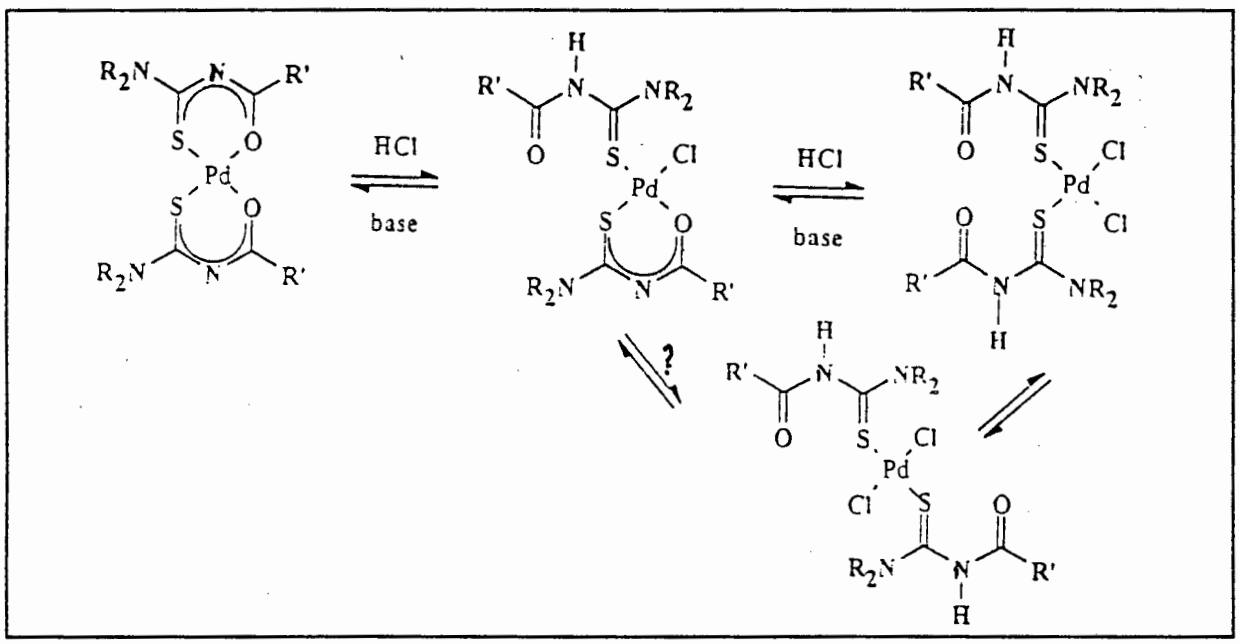

Figure 4.4.1: Palladium(II) chelate speciation in acidic solutions [8]

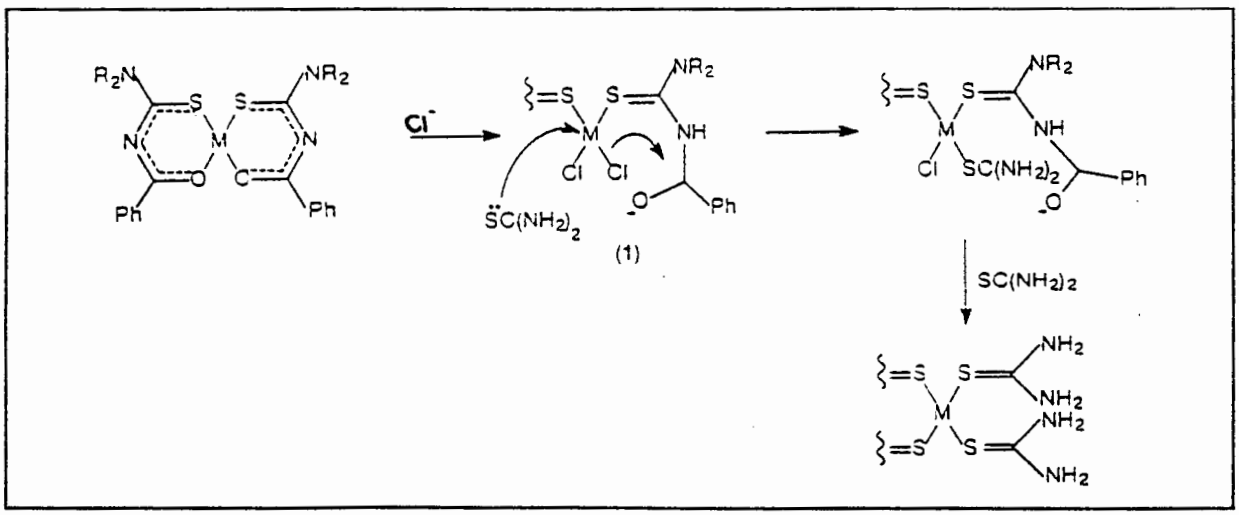

Figure 4.4.2: Formation of palladium(II) thiourato species

The addition of methanol to the eluent was required, as the acidity of the eluent solution resulted in the development of a significant back-pressure on the pre-concentration column. Using a 5% (w/v) thiourea solution in 2 M perchloric acid as eluent, resulted in the eluent flow rate dropping to below 0.25 $cm^3 min^{-1}$, and consequently a lengthy analysis time. The addition of 20% methanol to the eluent solution decreased the back-pressure of the column substantially and allowed for eluent flow rates from 0.25 - 2.5 $cm^3 min^{-1}$ to be studied, decreasing the analysis time significantly. The presence of methanol in the eluent solution required optimisation of the ICP-OES detection system (**6.1**) to tolerate a moderate quantity of carbon in the plasma, without affecting system accuracy, precision and reproducibilty.

4.5 Effect of sample and eluent flow rate on palladium(II) pre-concentration

The percentage recoveries of a 2 $\mu g.cm^{-3}$ palladium(II) solution were tested at different sample and eluent flow rates (0.25 - 2.5 $cm^3 min^{-1}$), to determine the optimum flow rates for the pre-concentration and the subsequent elution of the palladium(II) chelate (Figure 4.5.1, 4.5.2). The sample and eluent flow rates in this study were limited to a maximum of 2.5 $cm^3 min^{-1}$, by the back-pressure developed by the column packed with the fine C_{18} reverse-phase material at elevated flow rates.

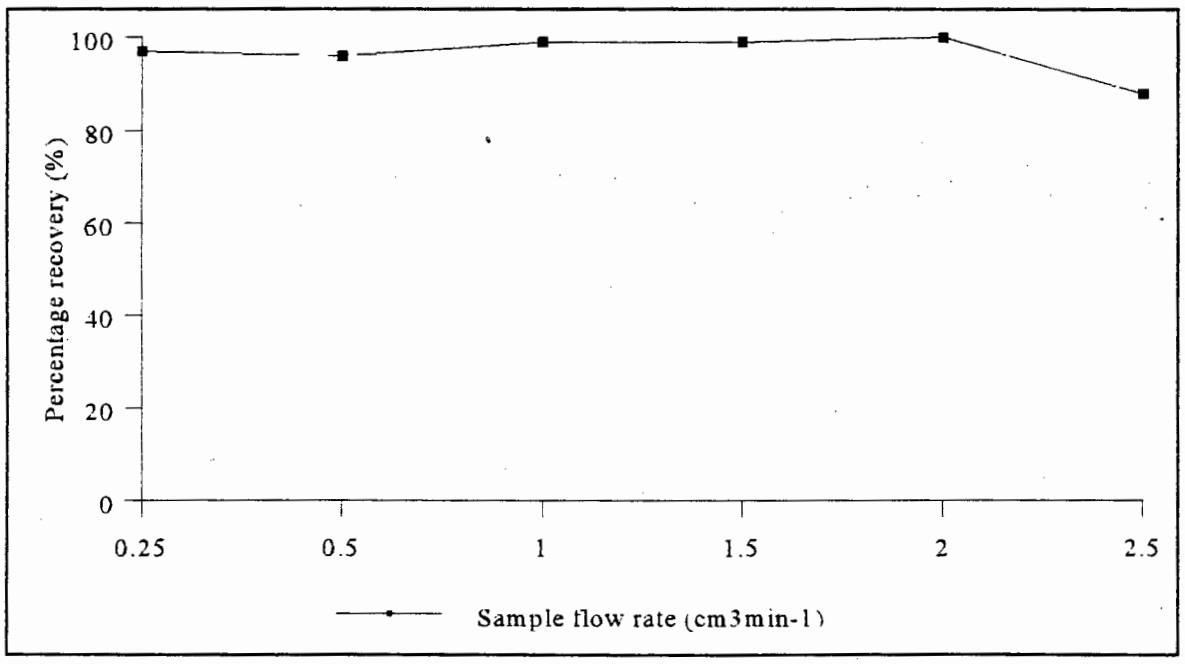

Figure 4.5.1: Effect of sample flow rate on percentage recovery of palladium(II)

The percentage recovery decreased slowly with increasing sample flow rate to 2.0 $cm^3 min^{-1}$ and

significantly decreased at 2.5 $cm^3 min^{-1}$. A higher sample flow rate was desirable, as this increased the time efficiency and sample throughput of the pre-concentration. However, a 1.8 $cm^3 min^{-1}$ sample flow rate was selected as optimum. This sample flow rate allowed a relatively high sample throughput without compromising the pre-concentration of the palladium(II) chelate, resulting in poor recoveries of the adsorbed palladium(II).

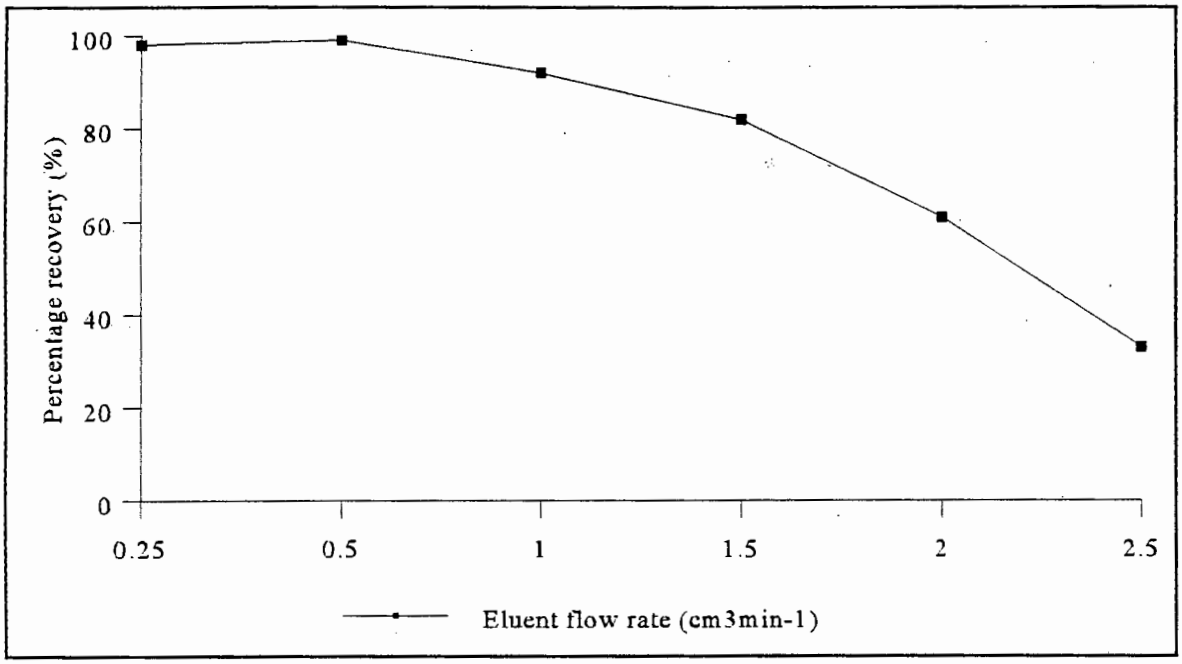

Figure 4.5.2: Effect of eluent flow rate on percentage recovery of palladium(II)

Elution flow rates were found to significantly effect percentage recovery of the pre-concentrated palladium(II) chelate. An elution flow rate higher than 0.5 $cm^3 min^{-1}$ resulted in decreased percentage recovery. Consequently an optimum elution flow rate of 0.5 $cm^3 min^{-1}$ was selected. The need for a low elution flow rate for quantitative percentage recovery was attributed to the stability of the palladium(II) chelate and the strong hydrophobic interaction between the neutral palladium(II) chelate and the C_{18} reverse-phase material, limiting formation of the elutable hydrophilic palladium(II)thiourato species.

4.6 Effect of pH on palladium(II) pre-concentration

C_{18} reverse-phase material is known to degrade in acidic media and thus it was essential to investigate the effect of pH on palladium(II) pre-concentration, to identify the optimum acidity for pre-concentration of the palladium(II) in the sample solutions (Figure 4.6.1).

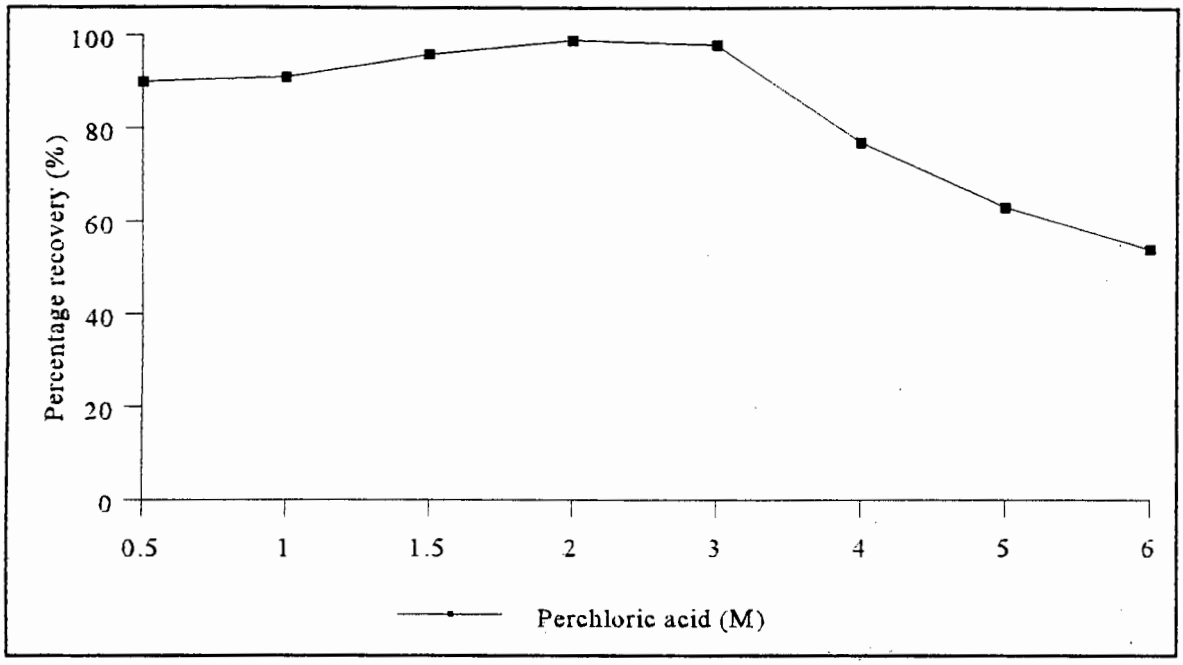

Figure 4.6.1: Effect of acidity of the synthetic sample solution on percentage recovery of Pd(II)

The results indicated that pre-concentration was quantitative in 1 - 3 M perchloric acid. Above a 3 M acid concentration, recovery decreased significantly, and was attributed to column degradation. Below 1 M acid concentration, percentage recovery decreased and was attributed to palladium(II) complexation being inhibited at higher pH. Consequently, 2 M perchloric acid was selected as the optimum acid concentration for this study. This acid concentration led to quantitative recovery of the palladium(II) and more importantly was acidic enough to limit complexation of 1st row transition metals present in the real effluent solutions, as this class of ligands preconcentrates 1st row transition metals readily above pH 4 [9].

4.7 Column lifetime

Column lifetime was evaluated by preconcentrating and eluting 4 cm^3 aliquots of a 10 $\mu g.cm^{-3}$ palladium(II) solution in 2 M perchloric acid and comparing the palladium(II) recovery obtained to the theoretical value expected (40 µg), until quantitative recovery results were no longer achieved. This decrease in quantitative recovery was then attributed to degradation of the reverse-phase material, by acid catalysed cleavage of the siloxane-dodecyl bond of the hydrophobic reverse-phase material, resulting in only partial retention of the hydrophobic palladium(II) chelate (Table 4.7.1) and a corresponding decrease in palladium(II) recovery.

Table 4.7.1: Percentage recovery of palladium(II) for a series of pre-concentrated samples

Sample no.	Mean palladium(II) eluted ($\mu g.cm^{-3}$)	* Mean percentage recovery (%)	* 95% Confidence interval of mean percentage recovery (%)
1	39.9	99.7 +- 0.20	99.2 - 100.2
10	39.9	99.7 +- 0.50	98.5 - 100.9
20	39.8	99.4 +- 0.61	97.9 - 100.9
50	39.7	99.2 +- 0.49	98.0 - 100.4
60	39.0	97.5 +- 0.73	95.7 - 99.3
80	38.9	97.2 +- 1.10	94.5 - 99.9
100	37.7	94.3 +- 0.41	93.3 - 95.3

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t =4.30 for N = 3

Initial column degradation was seen after 50 samples had been pre-concentrated and eluted off the column. A 1% loss in palladium(II) recovery was considered the maximum limit of acceptable column degradation, so 50 samples was selected as the optimum column lifetime. This necessitated careful repacking of the column with fresh C_{18} reverse-phase material, after each batch of 50 samples had been pre-concentrated and eluted, to prevent losses in the recovery of the pre-concentrated platinum-group metals.

4.8 Maximum column loading capacity of palladium(II) and platinum(IV/II)

The maximum palladium(II) and platinum(IV/II) chelate that could be loaded onto the column before breakthrough occured, was determined, to ensure that the maximum loading capacity was not exceeded during subsequent analyses. This prevented losses in the pre-concentrated platinum-group metals as a result of being unretained by the column and passing through as waste solution.

Aliquots of a 4 $\mu g.cm^{-3}$ palladium(II) and a 10 $\mu g.cm^{-3}$ platinum(IV/II) solution were pumped over the reverse-phase column at 1.8 cm^3min^{-1} (**4.5**). Breakthrough was considered to have been achieved when the waste solution (sample solution after platinum-group metal chelate was loaded on the column), analysed by ICP-OES contained 1% of the total palladium(II)/platinum(IV/II) content (0.04 $\mu g.cm^{-3}$ palladium(II) and 0.1 $\mu g.cm^{-3}$ platinum(IV/II)) initially pre-concentrated (Figure 4.8.1, 4.8.2, 4.8.3).

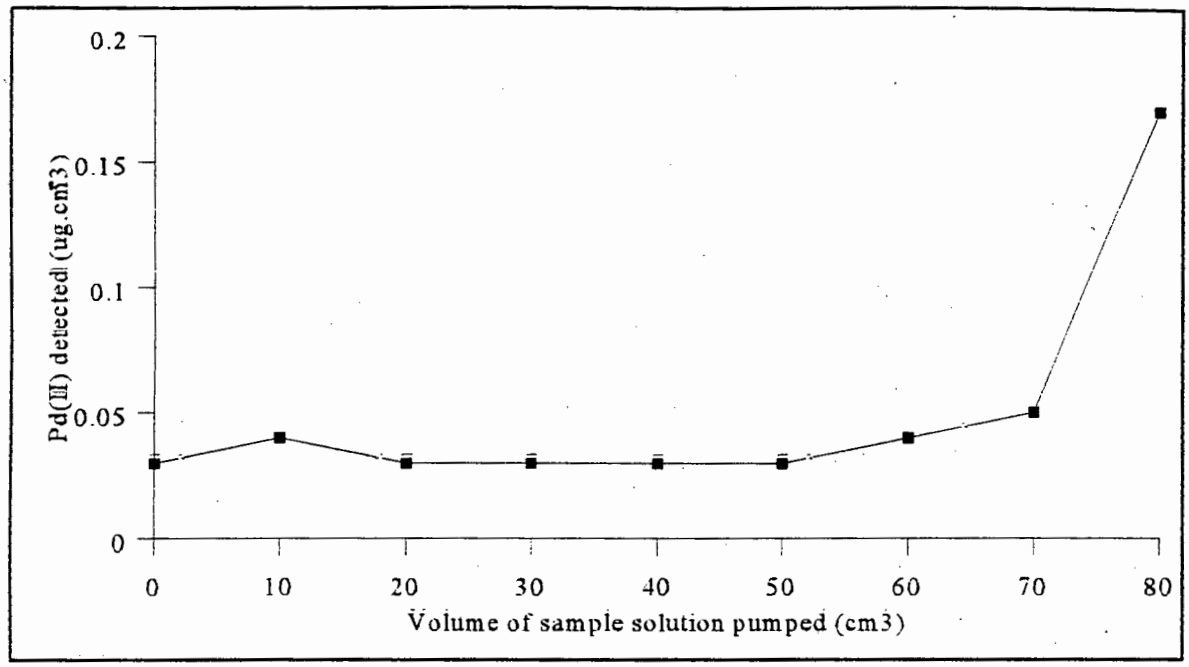

Figure 4.8.1: Volume of sample pumped vs palladium(II) detected

The maximum palladium(II) chelate that could be loaded onto the column was equal to 241 μg palladium(II) (60 cm^3 of a 4 $\mu g.cm^{-3}$ Pd(II) solution). This equated to a column capacity of 1.99 mg Pd(II) per gram of reverse-phase material. This is lower than the theoretical maximum of 4.02 mg Pd(II) loaded per gram of reverse-phase material, obtained in **4.3** as part of the study of the maximum achievable column capacity of ligand. The metal:ligand ratio of the chelate assumed in this calculation was 1:2. However, assuming a 1:4 metal:ligand ratio the theoretical maximum of Pd(II) loaded per gram of reverse-phase material was 2.01 mg and this was in agreement with the experimental column capacity of 1.99 mg. This result led to the possibility that the palladium(II) chelate was not forming as a 1:2 metal:ligand ratio, as expected from the literature [10], but as a 1:4 metal:ligand chelate, which could only hypothetically exist as a species with four pendant ligand molecules co-ordinating to the palladium(II) by the sulphur donor atoms only.

Pt(IV) breakthrough was achieved with a volume of 120 cm^3 of a 10 $\mu g.cm^3$ Pt(IV) solution. The maximum platinum(IV) chelate that could be loaded was equal to 1200 μg platinum(IV) and equated to a column capacity of 9.92 mg Pt(IV) per gram of reverse-phase material. This was significantly higher than the theoretical maximum of 2.06 mg Pt(IV) loaded per gram of reverse-phase material, obtained as part of the maximum column capacity of ligand study (**4.3**). The metal:ligand ratio assumed in this calculation was 1:3.

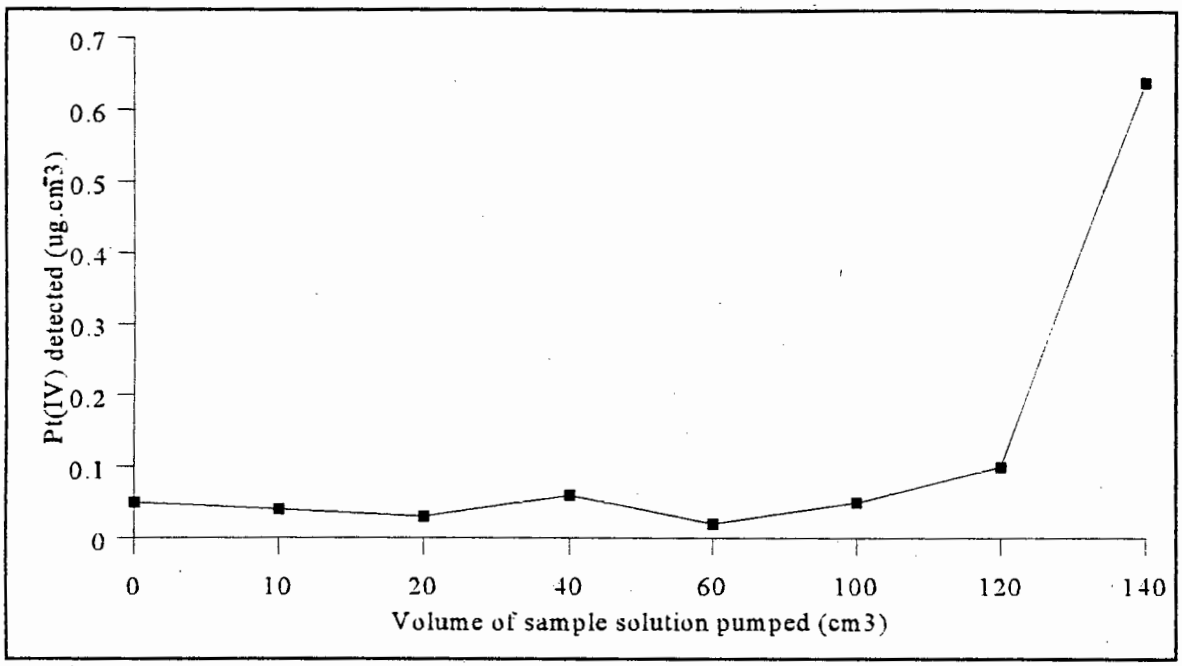

Figure 4.8.2: Volume of sample pumped vs platinum(IV) detected

However, assuming a 1:1 metal:ligand ratio the theoretical maximum of Pt(IV) loaded per gram of reverse-phase material was 8.04 mg, which was still significantly lower than the experimental column capacity of 9.92 mg. The higher experimental column capacity obtained was believed to be attributed to chemical or physical interaction between the unknown platinum(IV) chelate species and the reverse-phase material that allowed for greater loading of the platinum(IV) chelate than the expected theoretical maximum. Preliminary platinum(IV) chelate speciation was investigated later in this study (**9.1**) to obtain more detailed platinum(IV) speciation data to elucidate the exact nature of the unknown platinum(IV) chelate.

The maximum platinum(II) chelate that could be loaded was equal to 190 μg platinum(IV) (19 cm^3 of a 10 $\mu g.cm^{-3}$ platinum(II) solution) and equated to a column capacity of 1.57 mg Pt(II) per gram of reverse-phase material. This was significantly lower than the theoretical maximum of 4.02 mg Pt(II) loaded per gram of reverse-phase material, obtained in **4.3** as part of the maximum column capacity of ligand study. The metal:ligand ratio assumed in this calculation was 1:2. However, assuming a 1:4 metal:ligand ratio the theoretical maximum of Pt(II) loaded per gram of reverse-phase material was 2.01 mg and this was in closer agreement with the experimental column capacity of 1.57 mg.

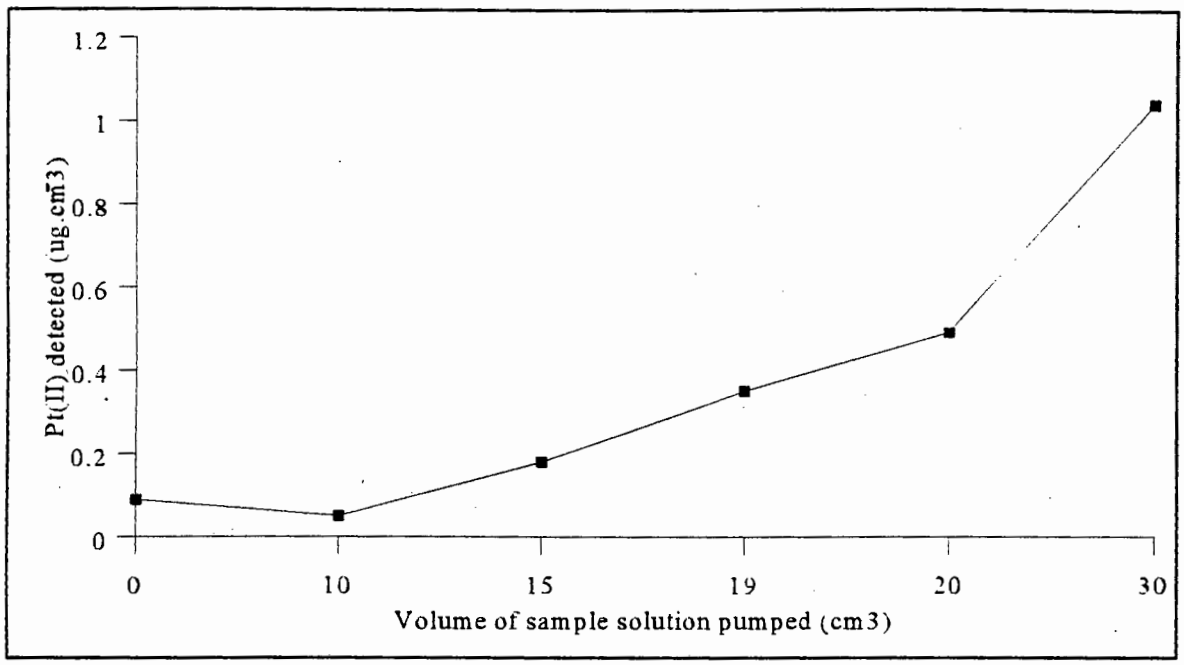

Figure 4.8.3: Volume of sample pumped vs platinum(II) detected

The disagreement between the theoretical and experimental column capacities in the case of platinum(II), was attributed to failure to quantitatively elute the platinum(II) chelate pre-concentrated on the column (percentage recovery: 94.7 compared to 99.34 Pd(II) and 96.3% Pt(IV)) and/or precipitation of the platinum(II) chelate onto the column, as formation of a brown discolouration was observed on the column, during Pt(II) pre-concentration. This brown discolouration was attributed to precipitation of an insoluble platinum(II) chelate species onto the column at elevated platinum(II) chelate concentrations.

4.9 Pre-concentration factors for palladium(II)

Analyte pre-concentration factors were considered a measure of pre-concentration system performance. Experimental pre-concentration factors indicate the maximum enrichment of an analyte achieveable on the column, without a loss in analyte percentage recovery. Real effluent solutions (**1.4**) were believed to contain approximately 0.5 $\mu g.cm^{-3}$ total platinum-group metal content, thus increasing sample volumes of 0.5 $\mu g.cm^{-3}$ palladium(II) synthetic effluent solutions, were pumped over the column at 1.8 cm^3min^{-1} and subsequently eluted of the column (10 cm^3) at 0.5 cm^3min^{-1} and percentage recovery determined (Table 4.9.1).

Table 4.9.1: Range of palladium(II) pre-concentration factors

Palladium(II) pre-concentrated (µg)	Mean Palladium(II) determined (µg)	* Mean percentage recovery (%)	* 95% Confidence interval of mean percentage recovery (%)	Pre-concentration factor
20	19.9	99.5 +- 0.07	99.3 - 99.7	4
40	39.8	99.5 +- 0.62	98.0 - 101.0	8
50	48.5	97.0 +- 0.23	96.4 - 97.6	10
100	97.4	97.4 +- 0.96	95.0 - 99.8	20

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t =4.30 for N = 3

For quantitative elution of the palladium(II) chelate a 10 cm^3 eluent volume was required. This automatically decreased the column pre-concentration factors for palladium(II) by a factor of 10. As a result, the pre-concentration factors were not comparable to those reported in the literature [11 - 13]. Above an 8-fold pre-concentration factor, palladium(II) percentage recovery was lowered and the precision of the analyses increased to an unacceptable level (> 5%). A pre-concentration factor of 4 was selected as the optimum pre-concentration factor, resulting in a maximum expected final palladium(II) effluent concentration of 2 $\mu g.cm^{-3}$, as this final concentration was considered to be adequate for accurate and precise ICP-OES determination of the platinum-group metal content of the real effluent solutions.

4.10 Conclusion

Optimisation usually involves consideration of the response of the pre-concentration system to changes in various parameters, in order to obtain experimental conditions that ensure selection of optimum values for all operating parameters. The selection of the optimum values required careful consideration of the sensitivity, accuracy and precision generated by the selected values, for the platinum-group metals under study.

It is evident from this chapter that critical consideration of several pre-concentration system parameters were necessary to yield a working system for pre-concentration of the platinum-group metals. An additional requirement was that the optimum conditions selected for single component analysis, not yield sub-optimum results when used in the simultaneous determination of mixtures of platinum(IV/II) and palladium(II), as in real effluent solutions. Thus optimum conditions (Table 4.10.1) were selected that would allow for simultaneous determinations (**6.1**) without a loss

in system sensitivity, precision or accuracy.

Table 4.10.1: Optimised conditions selected for quantitative pre-concentration

Pre-concentration parameter studied	Optimum value for quantitative pre-concentration
Ligand column loading capacity	8.04 mg per g reverse-phase material
Ligand concentration ratio	1:20 (metal:ligand)
Eluent	Thiourea (5% w/v in 20% methanol and 2 M perchloric acid)
Sample flow rate	1.8 cm^3 min^{-1}
Eluent flow rate	0.5 cm^3 min^{-1}
Sample solution acidity	2 M
Column lifetime	50 analyses
Palladium(II) column loading capacity	1.99 mg per g reverse-phase material
Platinum(IV) column loading capacity	9.92 mg per g reverse-phase material
Platinum(II) column loading capacity	1.57 mg per g reverse-phase material
Palladium(II) pre-concentration factor	4 times initial concentration

Initially, it was desired to pre-concentrate rhodium as well as platinum and palladium with the developed system, however, it was found that rhodium(III) pre-concentration could not be achieved with the developed system as the rhodium(III) chelate could not be eluted from the column after pre-concentration. This was believed to result from the relatively 'hard' rhodum(III) co-ordinating more strongly to the sulphur and in particular, oxygen atoms of the ligand compared to the 'softer' palladium(II) and platinum(IV/II). The stronger coordination of rhodium(III) prevented nucleophilic substitution by chloride ions in the acidic solutions, to form the pendant metal chelate described in Figure 5.4.1. This in turn, prevented formation of the pendant metal chelate that easily eluted off the column (in the case of palladium(II) and platinum(IV/II)), when the substituted chloride ion was displaced by the eluent, thiourea, as described in Figure 4.4.2.

4.11 References

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Chapter 5

Optimisation of ICP-OES Determination of Palladium(II), Platinum(IV) and Platinum(II)

5.1 Introduction

After reviewing the literature, inductively-coupled plasma-optical emission spectrometry [1-5] was expected to fulfill many of the characteristics of the ideal detection system described in Chapter 2.

The favourable analytical aspects of ICP-OES, such as precision, accuracy, multi-element capability, wide dynamic range and relatively few chemical interferences were seen as ideal for the determination of the eluent solutions containing pre-concentrated platinum-group metals. The detection system having been selected, optimisation of all system variables was necessary. This ensured that the best set of conditions, to solve the analytical problem under study, was determined. As expected, various chemical and physical parameters were critical to optimisation of the detection step. The effects of the following parameters on detection system performance were studied and optimised:

1. Effect of sample aspiration rate on emission intensities
2. Effect of attenuation voltage on emission intensities
3. Effect of aerosol gas flow rate on emission intensities
4. Effect of secondary argon feed pressure on emission intensities
5. Effect of observation height on emission intensities
6. Effect of methanol on emission intensities
7. Effect of thiourea on emission intensities
8. Effect of surfactant on emission intensities
9. Maximum linearity of concentration range
10. Platinum(IV/II) and palladium(II) ICP-OES detection limits

After examination of all the above parameters and their effects, compromise operating conditions were selected to yield optimum I_{PGM}/I_b signal ratios, the best plasma tolerance to organic material and the lowest detection limits for the atomic and ionic emission lines utilised in this work.

5.2 Effect of sample aspiration rate on signal intensity of palladium(II) and platinum(IV/II)

The effect of sample uptake rates from 0.5 to 3.5 cm^3 min^{-1} on the behaviour of the emission intensity of two palladium and platinum lines was studied, in order to demonstrate the effect of nebuliser uptake rate on analyte emission intensity. The emission lines used [6,7] are given in Table 5.2.1.

Table 5.2.1: The palladium and platinum emission lines used to study sample uptake rate changes

Element	λ (nm)	$V_{excitation}$ (eV)	Interfering elements
Pd(I)	340.458	4.46	Fe, Ti, V
Pd(II)	229.651	8.51	Fe, Ni
Pt(I)	265.945	4.66	Cr, Fe, Mg, Mn, V
Pt(II)	214.423	15.37	Al, Fe

The JY 70C simultaneous and sequential spectrometer was used under compromise operating conditions (Table 5.2.2) with the system variables fixed at standard (routinue) operating values. Sample aspiration rate (of a 2 $\mu g.cm^{-3}$ standard solution in 2 M perchloric acid) was determined using a Gilson Miniplus II (Gilson Medical Electronics, Inc., Wisconsin, USA) peristaltic pump, calibrated volumetrically.

At each aspiration rate, standard and blank intensity readings were recorded for 9 x 10 s integrations with deionised water used as a blank.

Table 5.2.2: Compromise operating conditions used for optimisation of the JY 70C spectrometer

Instrumental parameters	Compromise value
Gas:	
Argon feed pressure	600 kPa
Secondary regulator (in source box)	340 kPa
Inner (aerosol) gas flow	0.4 dm^3min^{-1}
Intermediate (plasma) gas flow	0.1 dm^3min^{-1}
Outer (coolant) gas flow	16 dm^3min^{-1}
Observation height	14 mm above coil
Sample uptake	2.0 cm^3min^{-1}
RF power:	
Incident	1000 watt
Reflected	< 5 watt
Integration:	
Time	10 s
Replicates	3

Operating parameters such as gas pressures and rf power readings were checked before and after each set of readings. No significant changes in instrumental parameters were observed during each set of readings.

The data obtained for the palladium(I) and platinum(I) lines are presented in Table 5.2.3 and 5.2.4, and in Figure 5.2.1 and 5.2.2 respectively. As seen in Table 5.2.3 the relative standard deviation of gross analyte intensity (I_{gross}) of the palladium(I) 340.458 nm line was lowest for aspiration rates between 1.51 and 2.50 cm^3min^{-1} with poorer precision at aspiration rates outside this range (mean gross analyte intensity = 3.2 %). The precision of gross analyte intensity for the platinum(I) 265.945 nm line (Table 5.2.4) was more uniform over the range of sample flow rates tested. The relative standard deviation lying between 2 and 5 %.

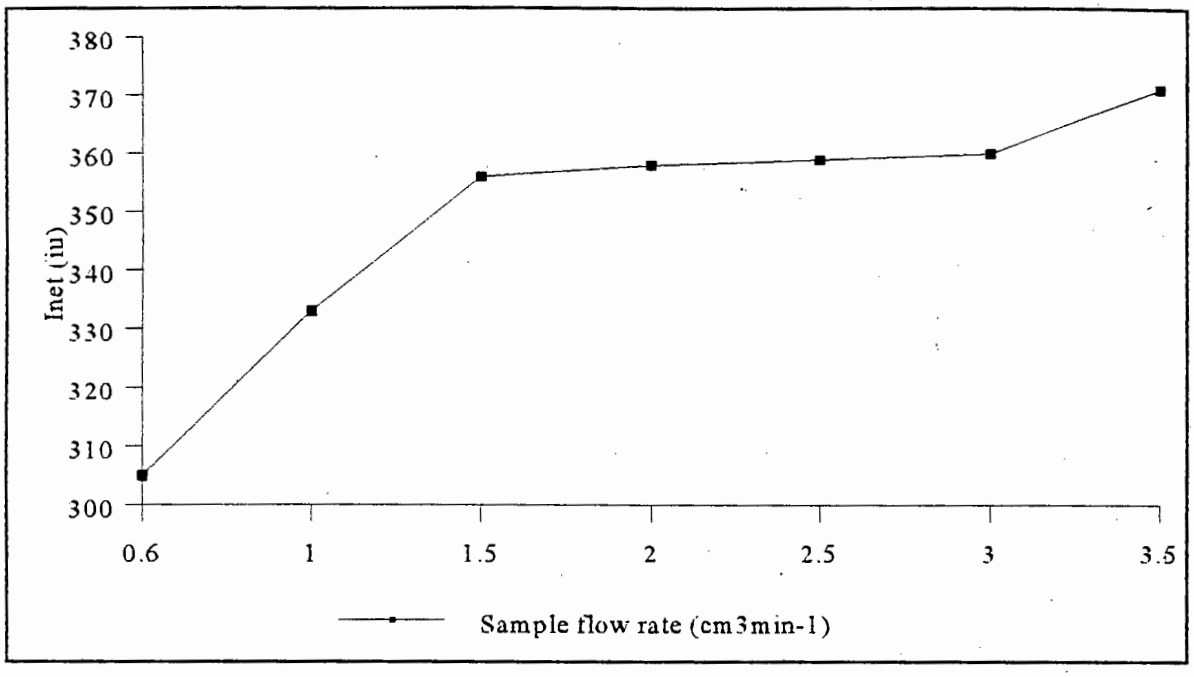

Figure 5.2.1: Effect of sample flow rate on net emission intensity (I_{net}) of Pd(I) 340.458 nm

Table 5.2.3: Emission intensity data for Pd(I) 340.458 nm

Aspiration rate ($cm^3.min^{-1}$)	* Mean I_{gross} (iu)	RSD (%)	* 95% Confidence interval of mean I_{gross}	* Mean I_{blank} (iu)	RSD (%)	* 95% Confidence interval of mean I_{blank}	I_{net} (iu)	Detection limit (2 σ) ($\mu g.cm^{-3}$)
0.6	458 +- 32	7	378 - 537	153 +- 1.2	0.5	150 - 156	305	0.02
0.98	474 +- 14	3	439 - 509	141 +- 1.7	0.6	137 - 145	333	0.02
1.51	479 +- 10	2	454 - 504	123 +- 1.6	0.6	116 - 130	356	0.02
2.00	545 +- 4	0.8	535 - 555	187 +- 1.2	0.6	184 - 190	358	0.01
2.50	550 +- 3	0.6	543 - 557	191 +- 1.0	0.8	189 - 194	359	0.01
3.02	615 +- 31	5	538 - 692	255 +- 0.9	0.8	253 - 257	360	0.01
3.47	628 +- 25	4	566 - 690	257 +- 0.9	1.0	255 - 259	371	0.01

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t = 4.30 for N = 3

The Pd(I) 340.458 nm line showed a linear dependence of net intensity for an aspiration rate between 1.5 and 3.0 cm^3min^{-1} with the net intensity showing the following dependence on aspiration rate (F_i) of: $I_{Pd(I)} = 2.6\ F_i + 352$ (correlation coefficient, r = 0.998).

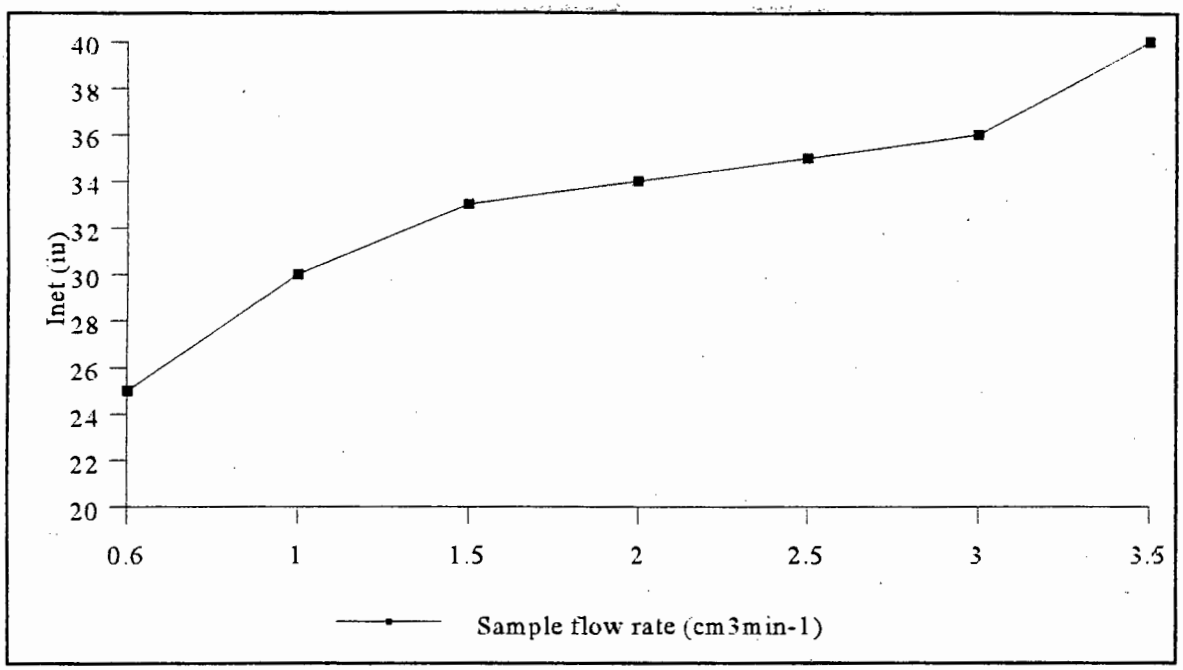

Figure 5.2.2: Effect of sample flow rate on net emission intensity (I_{net}) of Pt(I) 265.945 nm

Table 5.2.4: Emission intensity data for Pt(I) 265.945 nm

Aspiration rate ($cm^3.min^{-1}$)	* Mean I_{gross} (iu)	RSD (%)	* 95% Confidence interval of mean I_{gross}	* Mean I_{blank} (iu)	RSD (%)	* 95% Confidence interval of mean I_{blank}	I_{net} (iu)	Detection limit (2 σ) ($\mu g.cm^{-3}$)
0.6	26 +- 1	4	24 - 29	3 +- 0.2	7	2.5 - 3.5	25	0.03
0.98	34 +- 1	2	32 - 37	4 +- 0.3	8	3.3 - 4.7	30	0.04
1.51	36 +- 1	3	34 - 39	3 +- 0.2	7	2.5 - 3.5	33	0.02
2.00	43 +- 1	2	41 - 46	9 +- 0.7	8	7.3 - 10.7	34	0.08
2.50	40 +- 2	5	36 - 45	5 +- 0.4	8	4.0 - 6.0	35	0.05
3.02	43 +- 1	2	41 - 46	7 +- 0.1	1.4	6.7 - 7.3	36	0.01
3.47	46 +- 2	4	41 - 51	6 +- 0.7	11	4.3 - 7.7	40	0.07

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t = 4.30 for N = 3

The precision of the platinum(I) line was better than that of the platinum(II) 214.423 nm line, which is the emission line of platinum commonly used in routinue analysis of platinum solutions. The Pt(I) 265.945 nm line showed a lesser linear dependence (compared to the Pd(I) 340.458 nm line) of net intensity for an aspiration rate between 1.5 and 3.0 cm^3min^{-1} with the net intensity showing the following dependence on aspiration rate (F_1) of: $I_{Pt(I)} = 1.9\ F_1 + 30$ ($r = 0.994$).

The data for the two ionic lines of palladium and platinum viz., Pd(II) 229.651 nm and Pt(II) 214.423 nm is shown in Tables 5.2.5 and 5.2.6, and Figures 5.2.3 and 5.2.4 respectively.

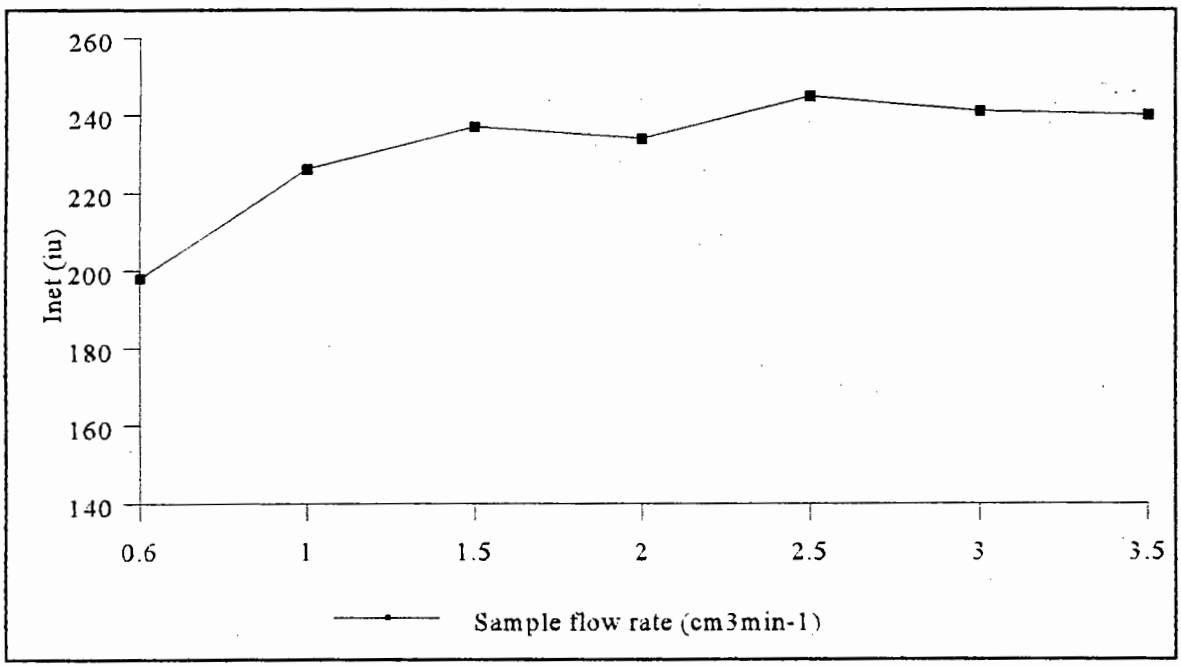

Figure 5.2.3: Effect of sample flow rate on net emission intensity (I_{net}) of Pd(II) 229.651 nm

Table 5.2.5: Emission intensity data for Pd(II) 229.651 nm

Aspiration rate ($cm^3.min^{-1}$)	* Mean I_{gross} (iu)	RSD (%)	* 95% Confidence interval of mean I_{gross}	* Mean I_{blank} (iu)	RSD (%)	* 95% Confidence interval of mean I_{blank}	I_{net} (iu)	Detection limit (2 σ) ($\mu g.cm^{-3}$)
0.6	342 +- 3	0.9	335 - 349	144 +- 1	0.7	142 - 147	198	0.03
0.98	387 +- 8	2	367 - 407	161 +- 2	1	156 - 166	226	0.04
1.51	368 +- 7	2	351 - 385	131 +- 1	0.8	129 - 134	237	0.02
2.00	364 +- 4	1	354 - 374	130 +- 5	4	118 - 142	234	0.08
2.50	371 +- 4	1	361 - 381	126 +- 1	0.8	124 - 129	245	0.05
3.02	372 +- 11	3	345 - 399	131 +- 1	0.8	129 - 134	241	0.01
3.47	372 +- 15	4	335 - 409	132 +- 2	2	127 - 137	240	0.07

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t = 4.30 for N = 3

The relative standard deviation of gross analyte intensity for the Pd(II) 229.651 nm line was between 1 and 4 %, with a mean precision of 2 %. This was an improvement over the mean precision, 3.2 %, obtained for the usual emission line of palladium employed for analytical determination of palladium (Pd(I) 340.458 nm). However, the mean relative standard deviation of the blank solution intensity increased to 2 % (compared to 0.7 %for Pd(I) 340.458 nm) leading to a worsening in the theoretical palladium detection limit achievable with this emission line.

The Pd(II) 229.651 nm line showed a linear dependence of net intensity for an aspiration rate between 2.5 and 3.5 cm^3min^{-1} with the net intensity showing the following dependence on aspiration rate (F_l) of: $I_{Pd(II)} = - 5.3\ F_l + 258$ (correlation coefficient, r = 0.999).

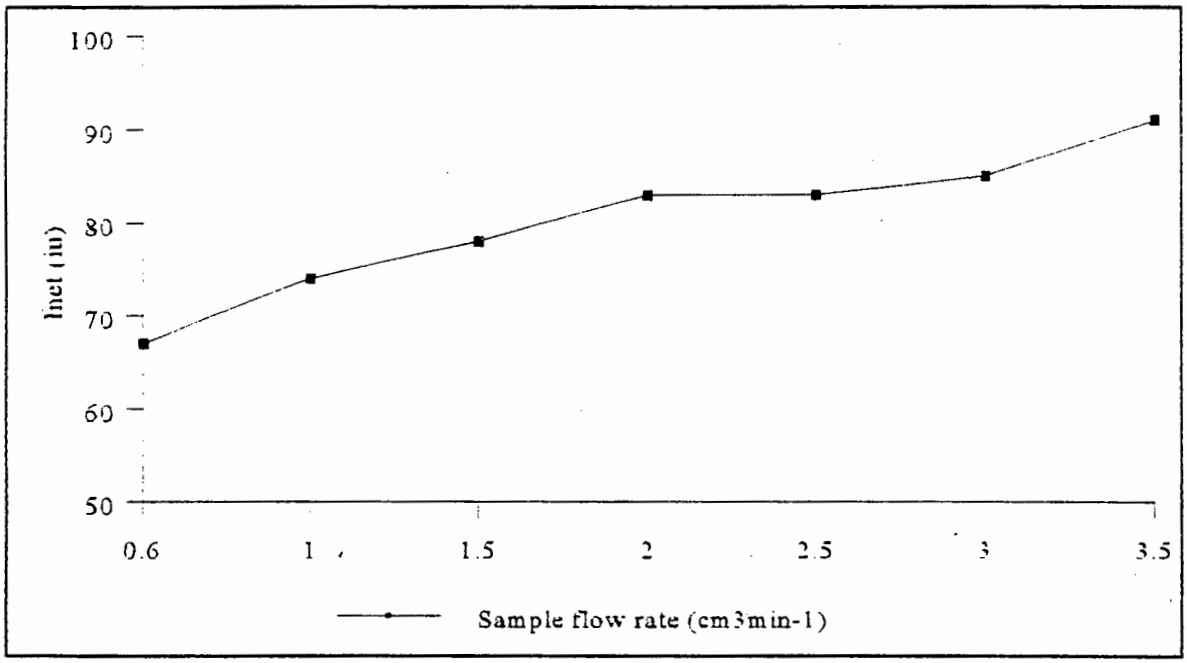

Figure 5.2.4: Effect of sample flow rate on net emission intensity (I_{net}) of Pt(II) 214.423 nm

As seen in Table 5.2.6 the relative standard deviation of gross analyte intensity (I_{gross}) of the platinum(II) 214.423 nm line was lowest for aspiration rates between 2.5 and 3.50 cm^3min^{-1} with poorer precision at aspiration rates outside this range (mean precision of gross analyte intensity = 3.3 %). The mean precision was marginally worse than that obtained for the Pt(I) 265.945 nm line (3.2 %).

Table 5.2.6: Emission intensity data for Pt(II) 214.423 nm

Aspiration rate ($cm^3.min^{-1}$)	* Mean I_{gross} (iu)	RSD (%)	* 95% Confidence interval of mean I_{gross}	* Mean I_{blank} (iu)	RSD (%)	* 95% Confidence interval of mean I_{blank}	I_{net} (iu)	Detection limit (2 σ) ($\mu g.cm^{-3}$)
0.6	119 +- 2	2	114 - 124	52 +- 3	6	45 - 59	67	0.20
0.98	124 +- 4	3	114 - 134	50 +- 2	4	45 - 55	74	0.10
1.51	129 +- 5	4	117 - 141	51 +- 2	4	46 - 56	78	0.10
2.00	104 +- 6	6	89 - 119	21 +- 2	10	16 - 26	83	0.10
2.50	131 +- 3	2	126 - 137	48 +- 2	4	43 - 53	83	0.10
3.02	135 +- 3	2	128 - 142	50 +- 2	4	45 - 55	85	0.09
3.47	134 +- 5	4	122 - 146	43 +- 3	7	36 - 50	91	0.10

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t = 4.30 for N = 3

The Pt(II) 214.423 nm line showed a lesser linear dependence (compared to the Pt(I) 265.945 nm line) of net intensity for an aspiration rate between 1.5 and 3.5 cm^3min^{-1} with the net intensity showing the following dependence on aspiration rate (F_l) of: $I_{Pt(II)} = 5.7\ F_l + 70$ ($r = 0.981$). The deviation from linearity of the Pt(II) 214.423 nm line implied that the associated transition excitation conditions for this line changed at different aspiration rates. Consequently, the theoretical platinum detection limit for this line was significantly worse than the detection limit calculated for the Pt(I) 265.945 nm.

The optimum sample flow rate was selected as 2.5 cm^3min^{-1}, as this aspiration rate resulted in the best precision and lowest detection limits for all four emission lines studied. Additionally, the two atomic lines studied were found to yield superior precision and detection limits compared to the two ionic lines and were chosen as the major analytical wavelengths in this work.

5.3 Effect of attenuation voltage on signal intensity of palladium(II) and platinum(IV/II)

In this experiment the attenuation voltage was set at values between 600 and 990 V, and the effect on the signal to noise ratio (I_{Pd}/I_b), of a 2 $\mu g.cm^{-3}$ standard solution for the two atomic emission lines, monitored and recorded (Figures 5.3.1 and 5.3.2).

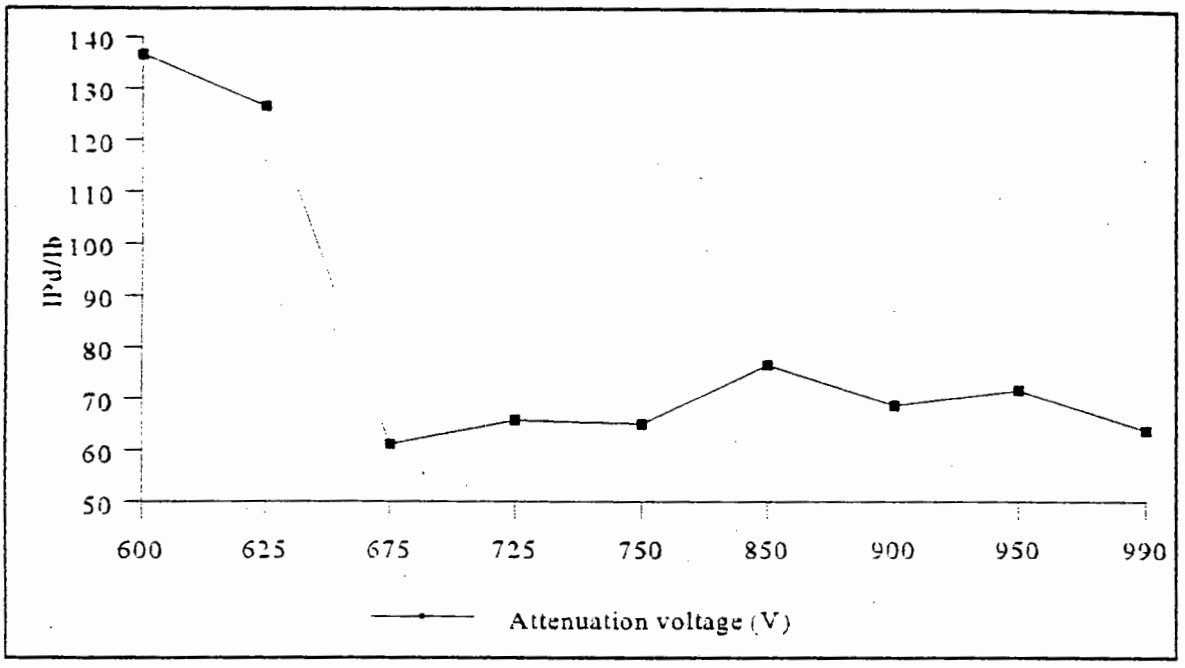

Figure 5.3.1: Effect of attenuation voltage on the signal to noise ratio of Pd(I) 340.458 nm

Increasing the attentuation voltage was expected to lead to an increase in net palladium signal intensity as excitation of elements with a relatively high excitation potential, like the platinum-group metals (> 4.0 eV), would be more easily accomplished at higher voltages than lower ones. However, it was believed that this would be offset to some degree, by the simultaneous increase in the blank signal intensity, resulting in an unfavourable signal to noise ratio. As expected an increase in attenuation voltage resulted in a marked decrease in the signal to noise ratio for voltages greater than 625 V. The net palladium signal intensity increased with increasing voltage (2577 % increase at 990 V compared to 600 V), but as the background noise increased appreciably more with increasing voltage (6410 % intensity increase compared to 600 V) the signal to noise ratio worsened with increasing voltage. Overall analysis precision also decreased with increasing voltages. An attenuation voltage of 625 V was selected as optimum, for the Pd(I) 340.458 nm line, as the precision obtained (3.7 %) at this voltage was superior to the precision recorded at 600V (9.4 %). This value determined experimentally, was subsequently checked through the use of the JY 70C 4.0 Quantitative and control software which computed an optimum attenuation voltage for the emission line in question. The computed value was 625 V and concurred with the value obtained experimentally.

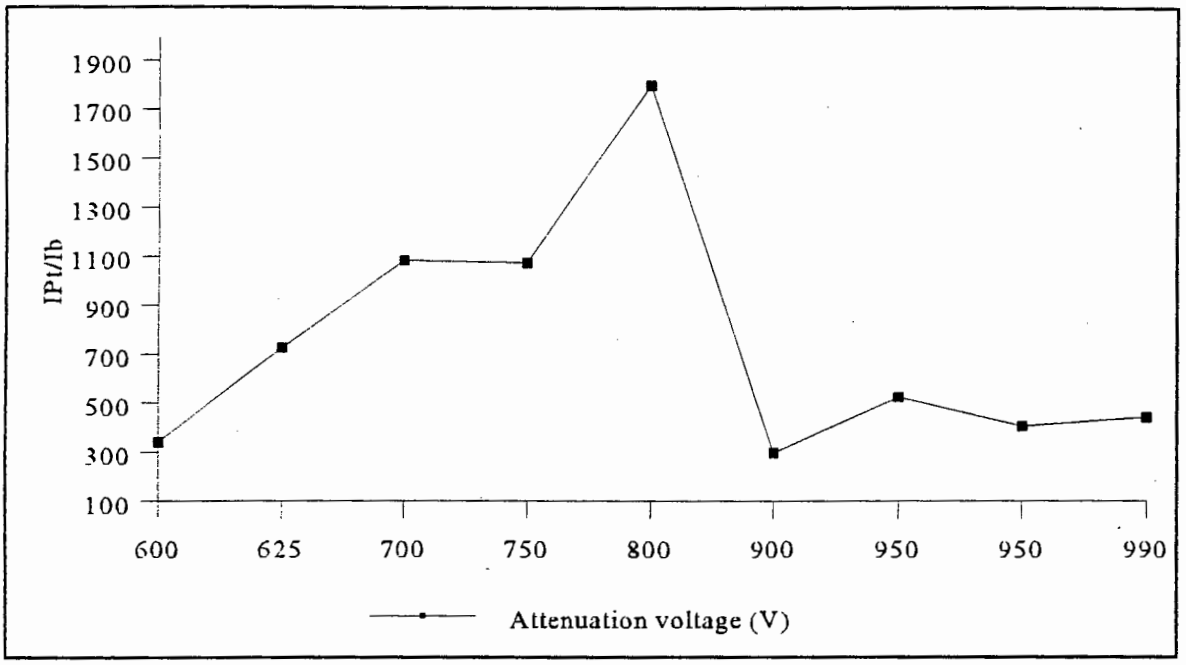

Figure 5.3.2: Effect of attenuation voltage on the signal to noise ratio of Pt(I) 265.945 nm

The Pt(I) 265.945 nm emission line exhibited a similar trend as the palladium atomic line studied. Increasing the attenuation voltage above 800 V led to a decrease in the signal to noise ratio, as background signal intensity increased. The higher excitation potential of platinum was believed to result in more favourable signal to noise ratios at higher voltages, compared to palladium where attenuation voltages greater than 625 V resulted in poor signal to noise ratios. The optimum attenuation voltage for Pd(I) 265.945 nm was selected as 800 V. This was checked with the JY 70C computed value obtained of 790 V, which was in agreement with the experimental value recorded.

5.4 Effect of aerosol gas flow rate on signal intensity of palladium(II) and platinum(IV/II)

The critical role played by the aerosol (nebulizer) argon gas flow rate on the signal intensity of Pd(I) 340.458 nm and Pt(I) 265.945 nm, was investigated by recording the analyte signal and blank intensities for a 2 $\mu g.cm^{-3}$ standard solution under compromise operating conditions (Table 5.2.2); and adjusting the aerosol gas flow valve setting and subsequently recording signal intensity again. The net analyte signal intensities determined are shown in Figure 5.4.1 and 5.4.2.

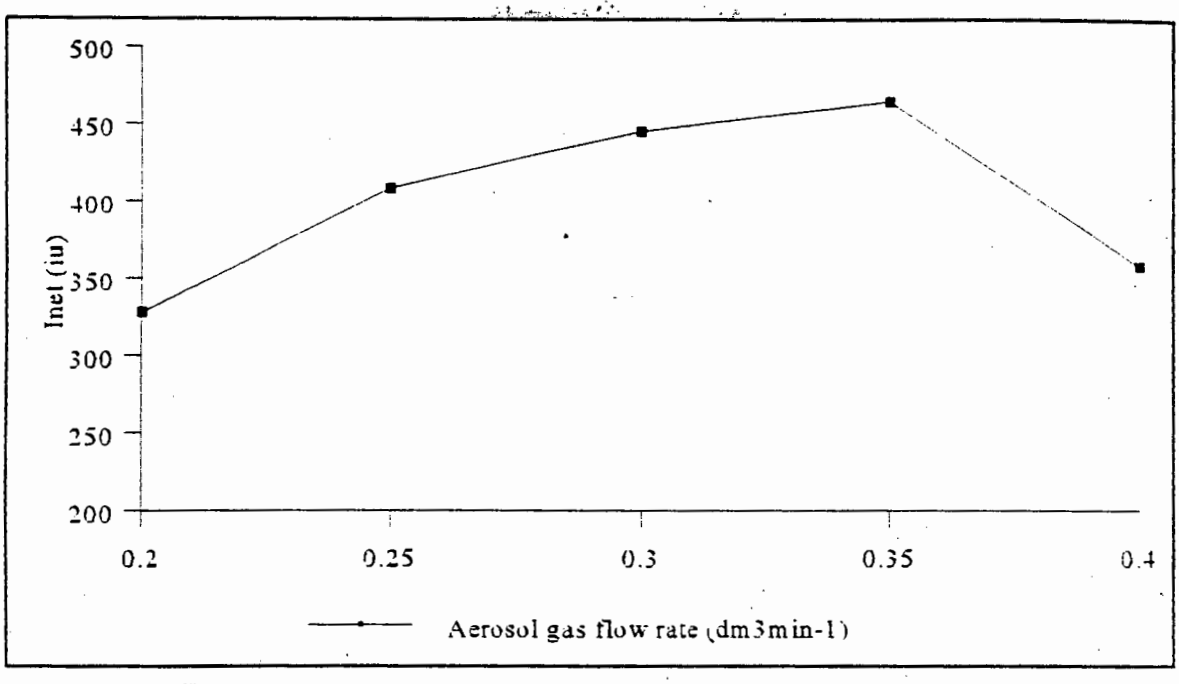

Figure 5.4.1: Effect of aerosol gas flow rate on signal intensity of Pd(I) 340.458 nm

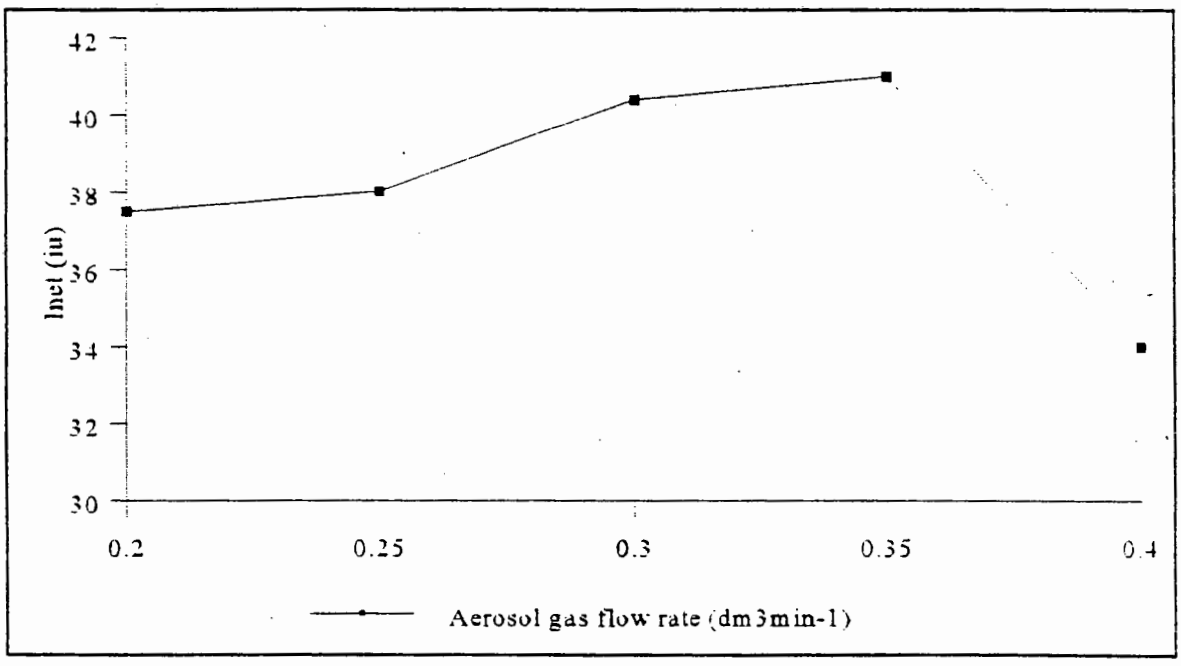

Figure 5.4.2: Effect of aerosol gas flow rate on signal intensity of Pt(I) 265.945 nm

The results were normalised to show relative magnitudes by ratioing to the mean net intensity at the compromise aerosol gas flow rate of 0.4 dm^3min^{-1}. An aerosol gas flow rate of 0.35 dm^3min^{-1} was judged to be optimum for both the atomic lines, as this flow rate yielded maximum net signal intensity and highest precision (8 % Pd(I) and 0.1 % Pt(I)) relative to the other flow rates studied.

It is of importance to note that the Pt(I) 265.945 nm emission line was less severely affected by a change in the aerosol gas flow rate than the Pd(I) 340.458 nm line. The intensity ratios of the Pd(I) line were found to be significantly different from the mean net intensity of the compromise aerosol gas flow rate and this difference was attributed to the lower excitation potential of palladium (relative to platinum), resulting in a greater change in intensity at various aerosol gas flow rates..

5.5 Effect of secondary argon feed pressure on signal intensity of Pd(II) and Pt(IV/II)

In order to demonstrate the effect of secondary argon feed pressure on analyte emission line intensity, the behaviour of the emission intensity of two palladium and two platinum lines were studied at feed pressures from 1.0 bar to 3.5 bar at an analyte concentration of 2 $\mu g.cm^{-3}$. The JY 70C spectrometer was used under compromise operating conditions (Table 5.2.2), with the observation height set at 14 mm above the load coil. The net analyte signal intensities determined are shown in Figures 5.5.1, 5.5.2, 5.5.3 and 5.5.4.

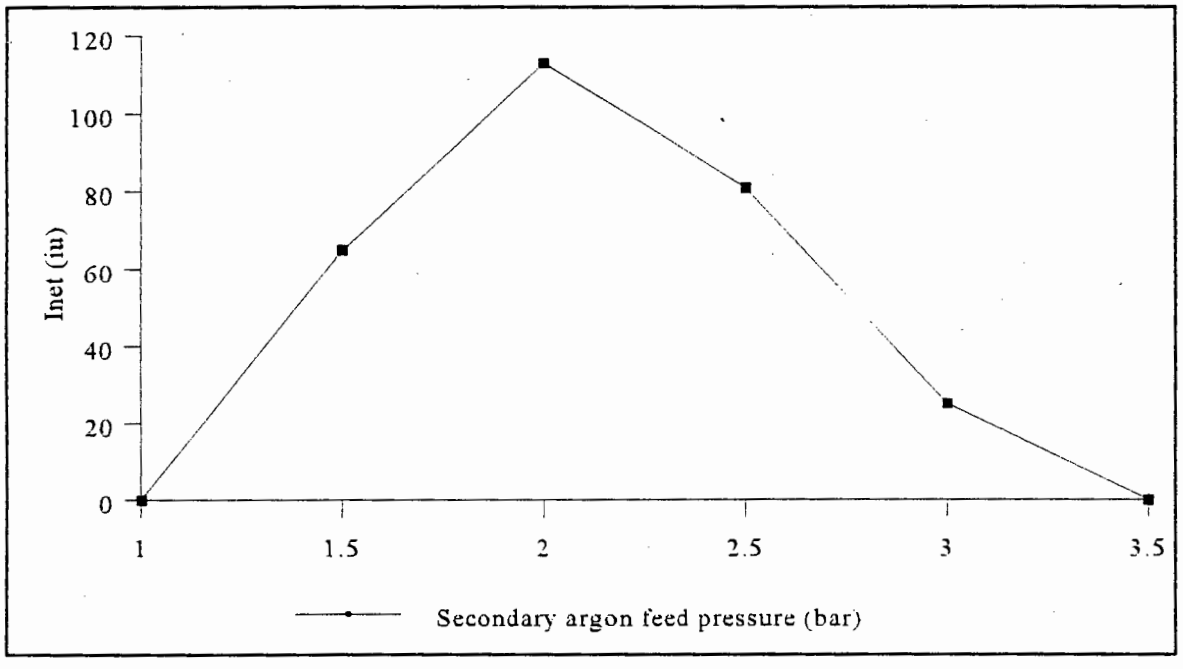

Figure 5.5.1: Effect of secondary argon feed pressure on signal intensity of Pd(I) 340.458 nm

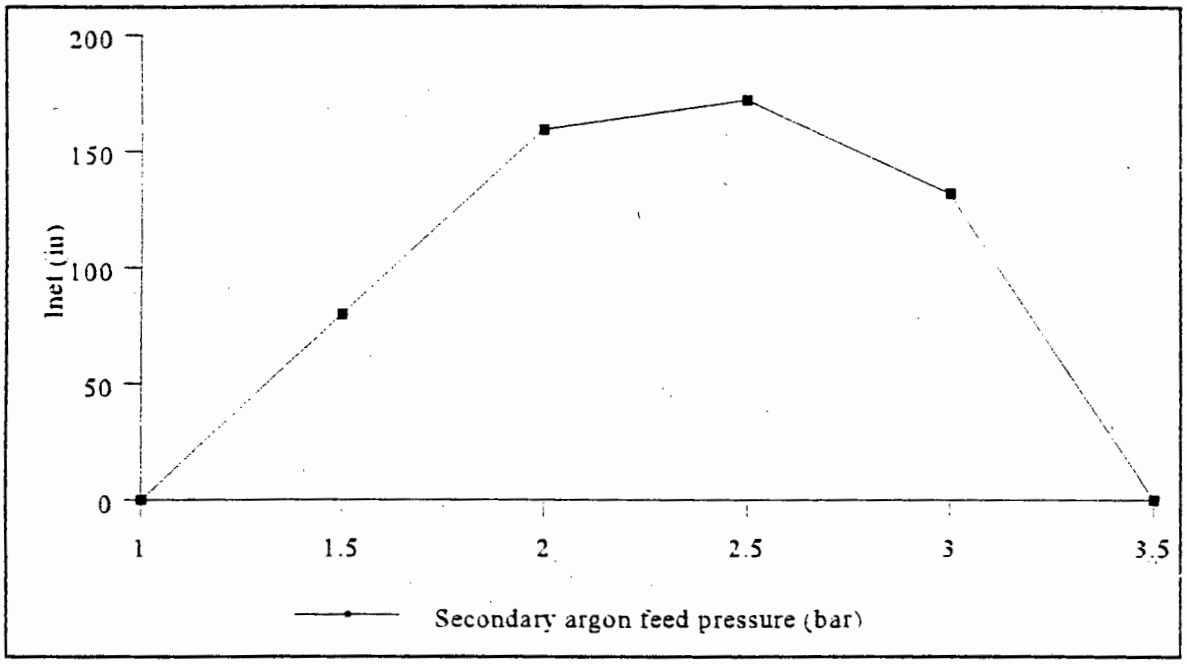

Figure 5.5.2: Effect of secondary argon feed pressure on signal intensity of Pd(II) 229.651 nm

For the palladium lines studied, secondary argon feed pressures below 1.5 bar resulted in an increase in the background intensity matching analyte intensity and consequently a net intensity of zero for the palladium lines studied. Feed pressures above 3 bar also resulted in a net intensity of zero as a result of plasma extinction and not as the result of an increase in background intensity.

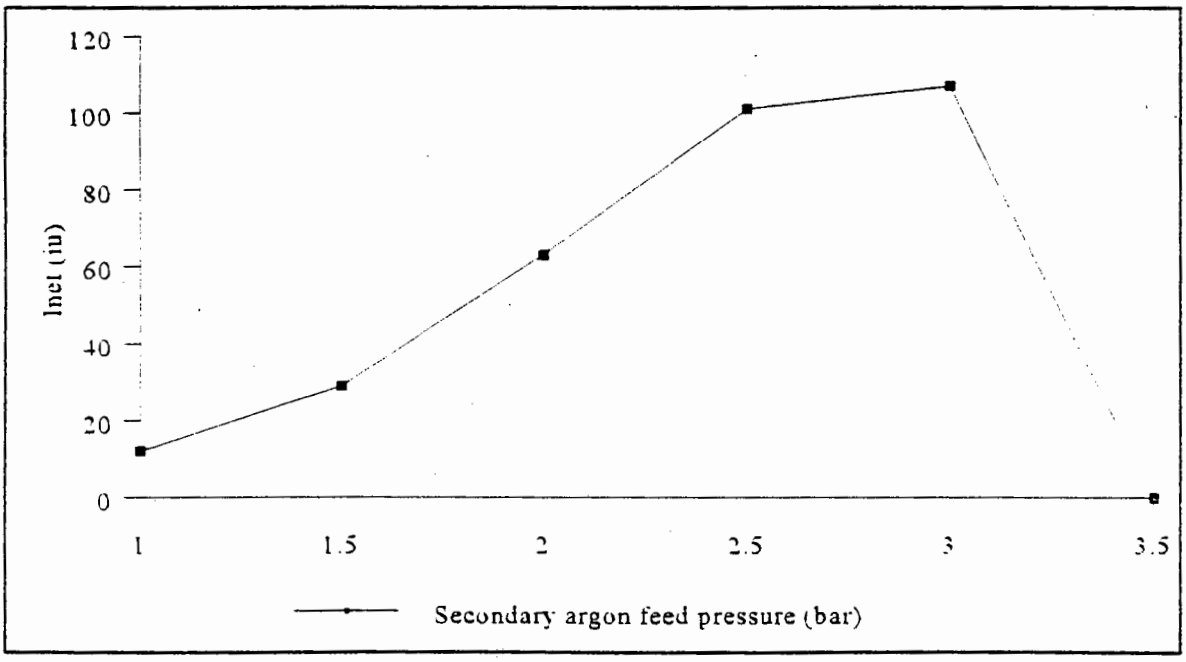

Figure 5.5.3: Effect of secondary argon feed pressure on signal intensity of Pt(I) 265.945 nm

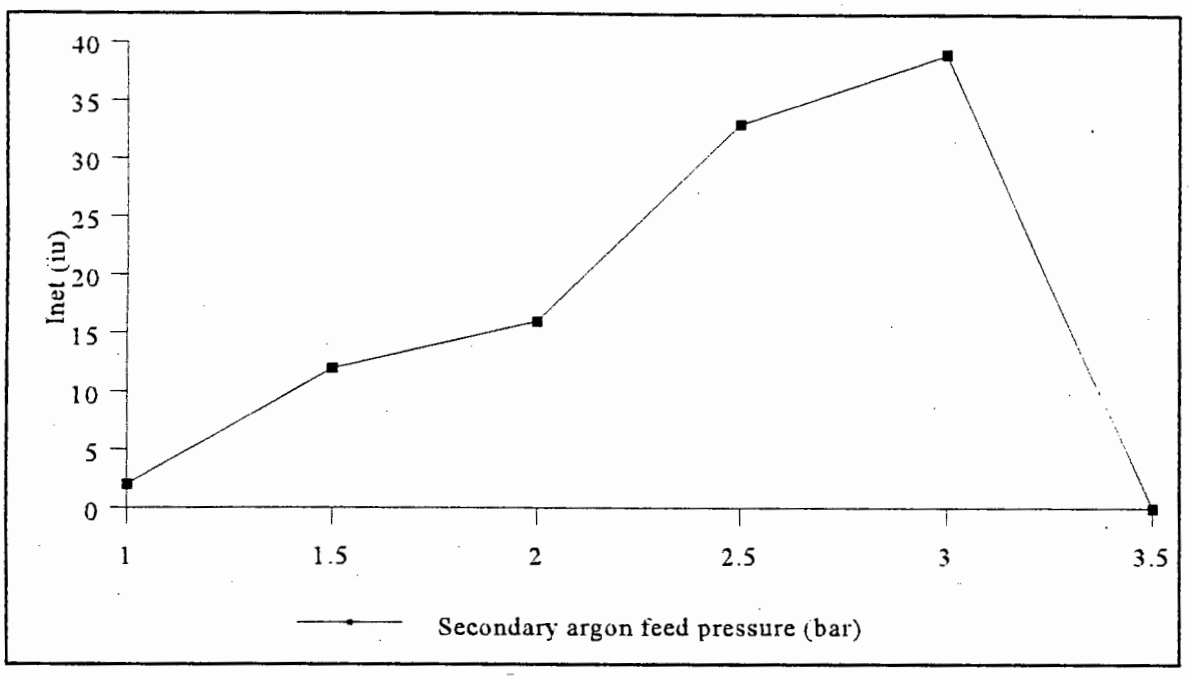

Figure 5.5.4: Effect of secondary argon feed pressure on signal intensity of Pt(II) 214.423 nm

For the platinum lines studied, secondary argon feed pressures below 1.5 bar exhibited similar behaviour as the palladium lines studied. Feed pressures above 3 bar resulted in a net intensity of zero as a result of plasma extinction and not from an increase in background intensity. However, the platinum lines were found to show a maximum net intensity at 3 bar compared to 2 bar for the palladium lines. This was believed to be the result of the higher excitation potential of platinum compared to palladium. The increased feed pressure would result in a higher population of ionised platinum atoms in the plasma with a concomitant increase in net analyte intensity. However, although higher net intensities were achieved at higher feed pressures, analysis precision decreased simultaneously.

A secondary argon feed pressure of 2 bar was selected as optimum as this pressure achieved maximum net intensity and precision for the palladium lines under study, in addition to adequate net intensities and enhanced analysis precision for the platinum lines.

5.6 Effect of observation height on signal intensity of Pd(II) and Pt(IV/II)

The critical role of observation height on the signal intensity of Pd(I) 340.458 nm, Pd(II) 229.651 nm, Pt(I) 265.945 nm and Pt(II) 214.423 nm, was investigated by recording the analyte signal and blank intensities for a 10 $\mu g.cm^{-3}$ standard solution under the compromise operating conditions

(Table 5.2.2); and adjusting the observation height screw to different settings above the coil (8 - 20 mm above the coil) and subsequently recording signal intensity again. The net analyte signal intensities determined versus analytical observation height are shown in Figure 5.6.1, 5.6.2, 5.6.3 and 5.6.4.

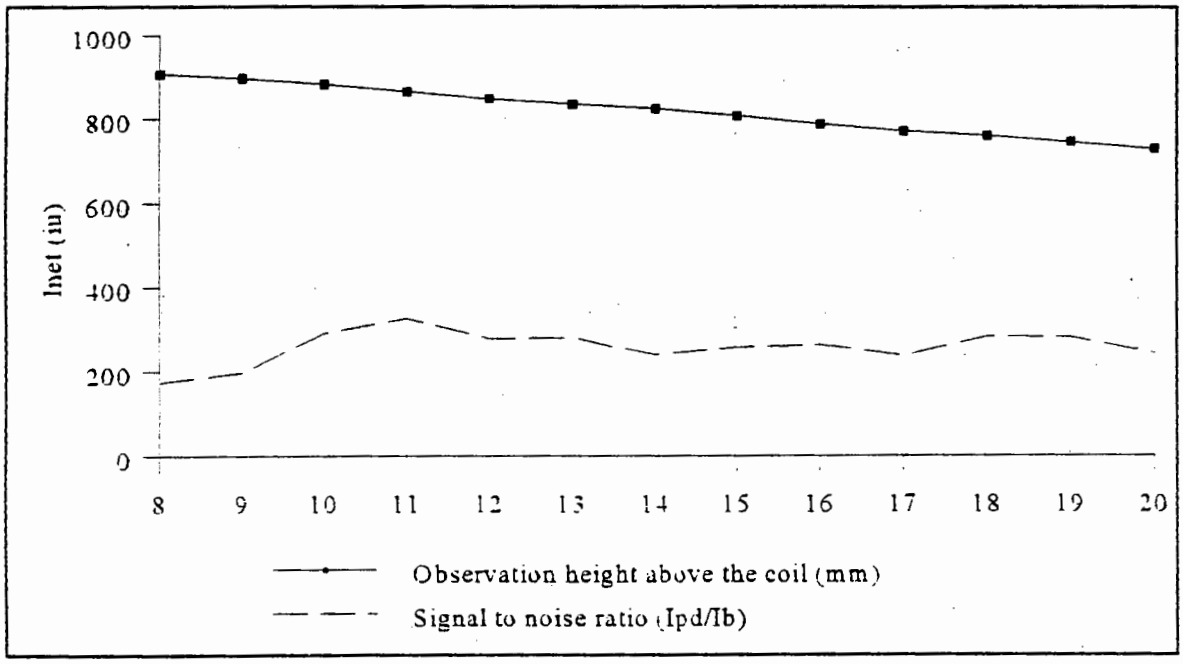

Figure 5.6.1: Effect of observation height on signal intensity of Pd(I) 340.458 nm

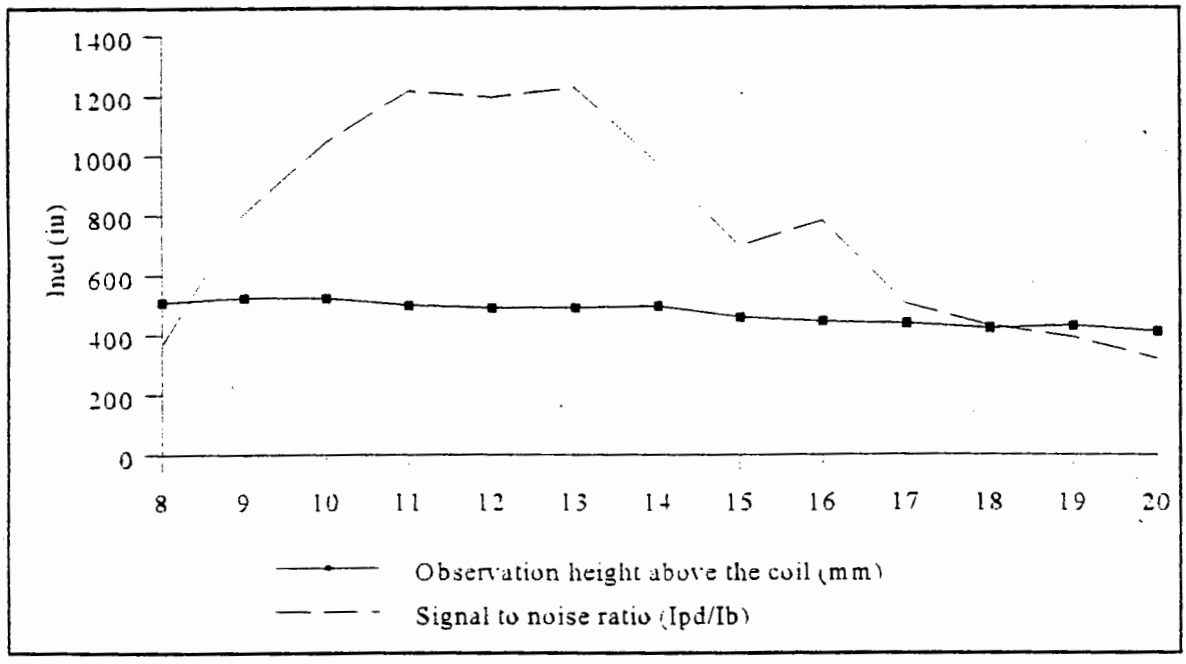

Figure 5.6.2: Effect of observation height on signal intensity of Pd(II) 229.651 nm

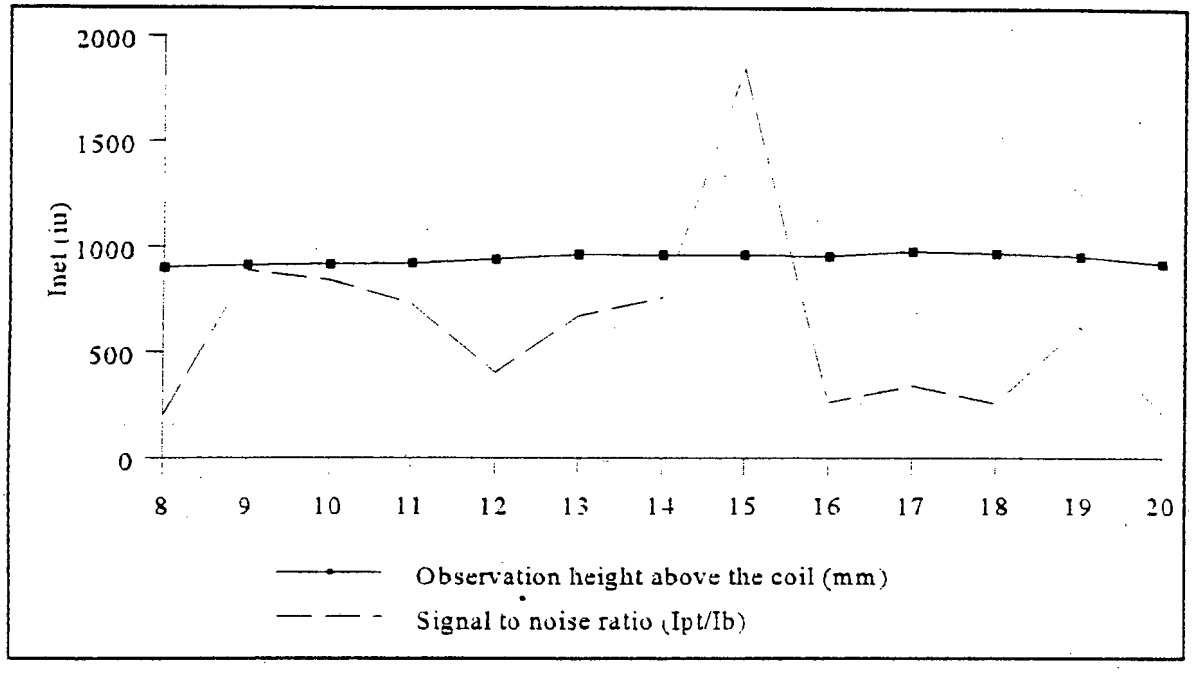

Figure 5.6.3: Effect of observation height on signal intensity of Pt(I) 265.945 nm

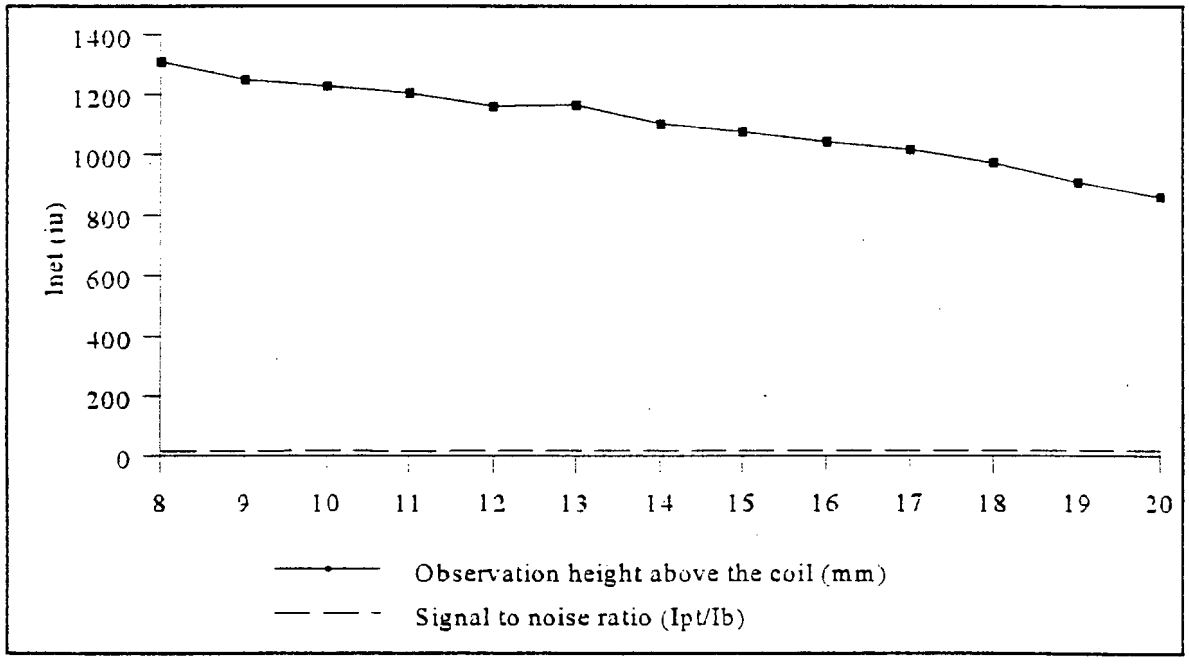

Figure 5.6.4: Effect of observation height on signal intensity of Pt(II) 214.423 nm

The observation height is an important parameter. Aerosol particles entering the plasma with the nebulizer gas, take a finite period to evaporate and decompose to form atoms or ions that are subsequently excited, the emission of which is monitored. Consequently, the process will be at different stages at different parts of the plasma. This means that the concentration of the species under observationis dependant on the plasma observation height. This is found to be valid for all

species in the plasma. Consequently it is important to determine the height in the plasma where the highest concentration of analyte is present with the least interfering radiation.

As expected from plasma theory (**3.7**), below the 'normal analytical zone' of 10 - 18 mm, emission intensities are highest between 8 and 9 mm above the load coil. This region of the plasma represents the initial radiation zone of the plasma and is the region responsible for excitation, ionisation and atomisation of analyte atoms in sample solutions. However below 10 mm above the load coil, so-called easily ionised elements (EIE) [8] such as the alkali metals (in particular, Na) were found to intefere significantly with the analysis of the platinum-group metals in the effluent solutions,. Interference by EIE on sample analysis is common in this region of the plasma as alkali metals are known to emit strongly in this region as a result of the low ionisation potential of this group of elements and the ease of excitation of the alkali metals in this energetic region of the plasma. This region (8 - 9 mm) was also characterised by a comparatively low signal to noise ratio resulting from the intense continuum emission from the surrounding plasma core, and unfavourable, elevated detection limits at these heights above the load coil, were recorded.

The effluent solutions under study were known to contain high quantities of sodium chloride, relative to the platinum-group metals (> 1000-fold higher), so observation heights below 10 mm above the coil were discounted.

The optimum observation height was selected as 18 mm above the load coil. This observation height resulted in a relatively high emission intensity and favourable (theoretical) detection limits for all the analytical wavelengths studied: Pd(I) 340.458 nm - 0.04 $\mu g.cm^{-3}$ (lit. - 0.04 $\mu g.cm^{-3}$ [9]); Pd(II) 229.651 nm - 0.06 $\mu g.cm^{-3}$ (lit. - 0.07 $\mu g.cm^{-3}$); Pt(I) 265.945 nm - 0.07 $\mu g.cm^{-3}$ (lit. - 0.08 $\mu g.cm^{-3}$) and Pt(II) 214.423 nm - 0.04 $\mu g.cm^{-3}$ (lit. - 0.03 $\mu g.cm^{-3}$). An additional advantage was the relatively high signal to noise ratio determined at this viewing height and the lowest relative standard deviation of intensity readings for all the observation heights and analytical wavelengths studied (Pd(I) 340.458 nm - 0.04%, Pd(II) 229.651 nm - 0.01%, Pt(I) 265.945 nm - 0.03% and Pt(II) 214.423 nm - 0.06%).

5.7 Effect of methanol on signal intensity of Pd(II) and Pt(IV/II)

Aspiration of non-aqueous solvents presents significant challenges in ICP-OES determinations. Organic solvents burn more efficiently in the plasma and are more efficiently vaporised due to lower viscosity and surface tension, than aqueous solutions. However, the introduction of organic solvents into the plasma results in a decrease in the plasma temperature and consequently, a decrease in the vaporisation efficiency of the analyte being studied [10]. The type of organic solvent selected can also significantly influence the magnitude of the emission signal recorded [11].

The most significant challenge to the routinue use of organic solvents in ICP-OES determinations is the formation of carbon radicals in the plasma when aspirating organic solvents. These carbon radicals collide with the energised electrons in the plasma, decreasing the electron density crucial to plasma maintenance. As the electron density of the plasma decreases, plasma instability arises and ultimately plasma extinction results.

The use of an eluent solution containing 20% methanol thus necessitated studying the effect of methanol on the signal intensity of palladium(II) and platinum(IV/II), to ensure long- and short-term reproducibility during the analysis of the effluent solutions. The introduction of small quantities of methanol into the plasma was found to quickly result in plasma extinction at the routine operating rf power of 1000 watt. To overcome this a rf power of 1200 watt was utilised, as this overcame the problem of plasma extinction by decomposing the carbon radicals rapidly, preventing depletion of the electron density within the plasma.

To study the effect of methanol on signal intensity of Pd(I) 340.458 nm, Pd(II) 229.651 nm, Pt(IV) 265.945 nm and Pt(II) 214.423 nm, the analyte signal and blank intensities for a 2 $\mu g.cm^{-3}$ standard solution, containing between 0 - 30% methanol (w/v), under the compromise operating conditions (Table 6.2.2) were recorded. The net analyte signal intensities determined versus % methanol content are shown in Figure 5.7.1, 5.7.2, 5.7.3 and 5.7.4.

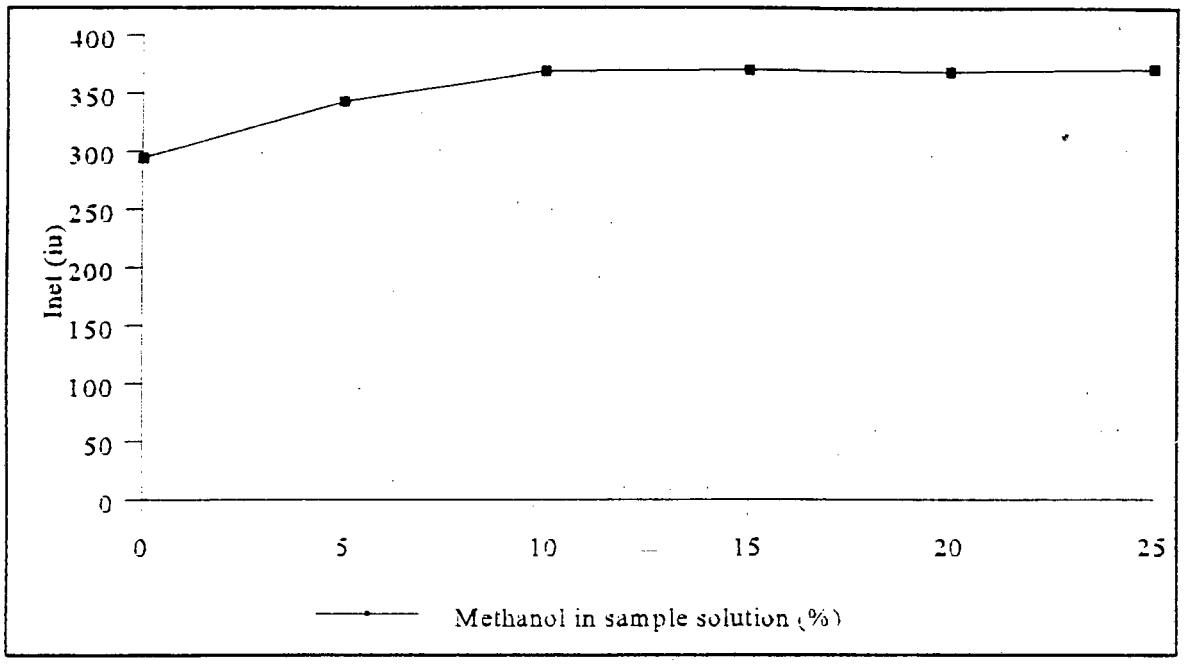

Figure 5.7.1: Effect of methanol on the signal intensity of Pd(I) 340.458 nm

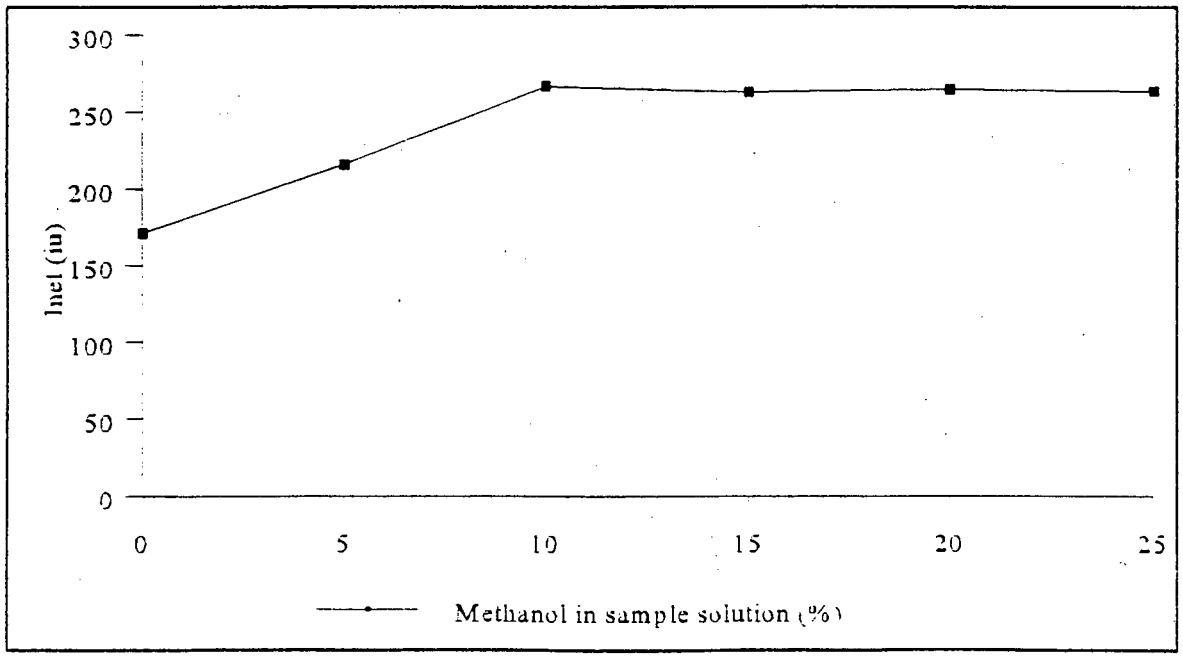

Figure 5.7.2: Effect of methanol on the signal intensity of Pd(II) 229.651 nm

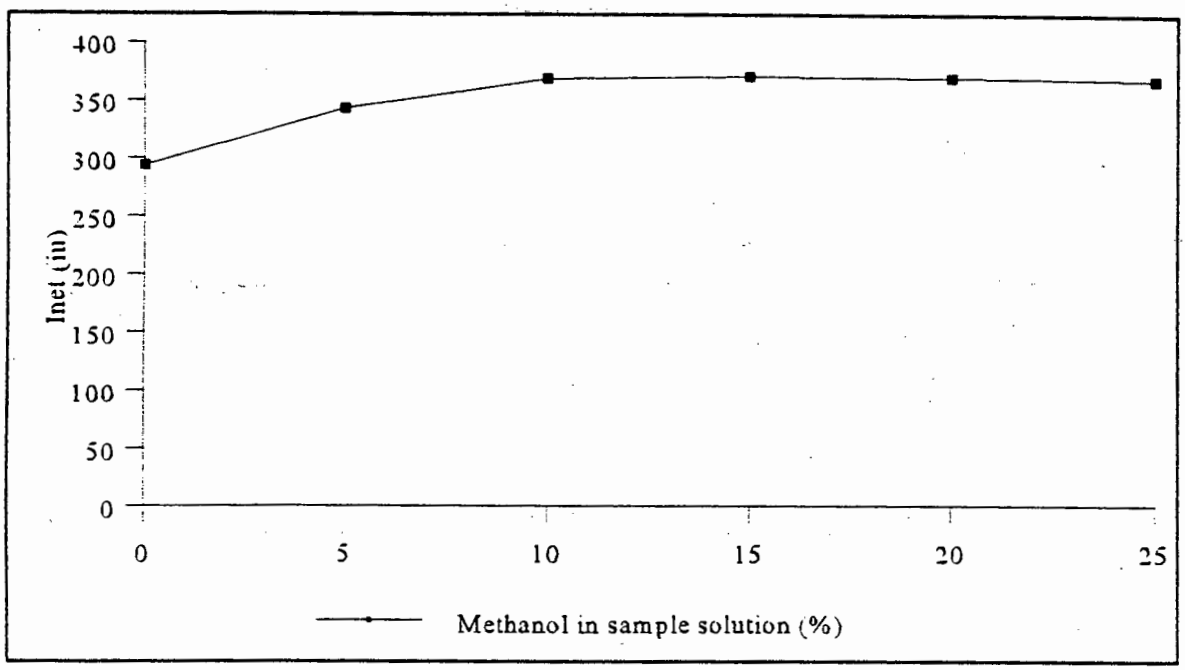

Figure 5.7.3: Effect of methanol on the signal intensity of Pt(I) 265.945 nm

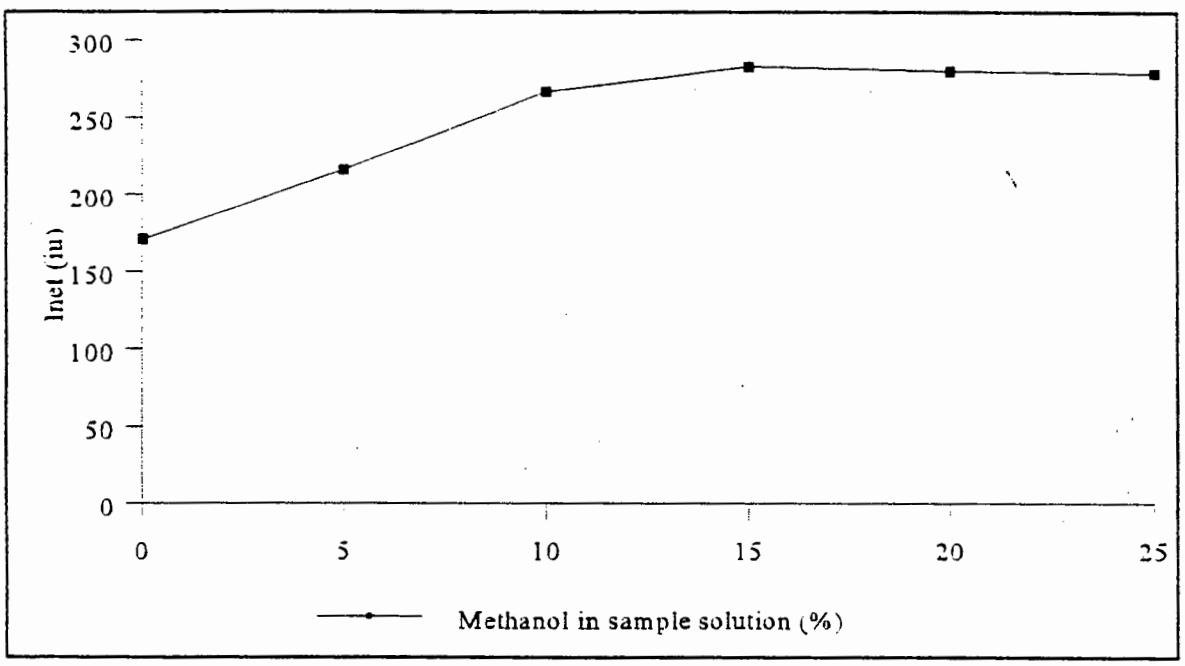

Figure 5.7.4: Effect of methanol on the signal intensity of Pt(II) 214.423 nm

A methanol content greater than 25% resulted in plasma instability and subsequent plasma extinction due to too high a carbon load in the plasma. For all of the analytical wavelengths studied, increasing the methanol content up to 10% resulted in significant enhancement (Pd(I) 340.458 nm - 92%, Pd(II) 229.651 nm - 105%, Pt(I) 265.945 nm - 78% and Pt(II) 229.651 nm - 66% to the emission intensities recorded (compared to an analyte solution containing no

methanol). Above 10% the enhancement was less significant, and effectively remained constant for a methanol content between 15 and 25%. The results indicated that a 20% methanol content in the eluent solution would not compromise the analysis of the effluent solutions and was found to be advantageous, as a result of the enhancement of the signal intensity of the analytical wavelengths.

5.8 Effect of thiourea on signal intensity of Pd(II)

As described in **5.7** above, the introduction of organic matter into the plasma seriously compromised plasma stability. The use of an eluent containing 5% (w/v) thiourea, necessitated the study of the effect of thiourea on signal intensity, to determine the plasma tolerance to thiourea in addition to possible interferences, that may arise due to the formation (and subsequent emission) of NO and CO in the plasma on the analytical wavelengths. To study the effect of thiourea on signal intensity of Pd(I) 340.458 nm and Pd(II) 229.651 nm, the analyte signal and blank intensities for a 2 $\mu g.cm^{-3}$ standard solution, containing between 0 - 10% thiourea (w/v), under the compromise operating conditions (Table 5.2.2) were recorded. The net analyte signal intensities determined versus % thiourea content are shown in Figure 5.8.1 and 5.8.2.

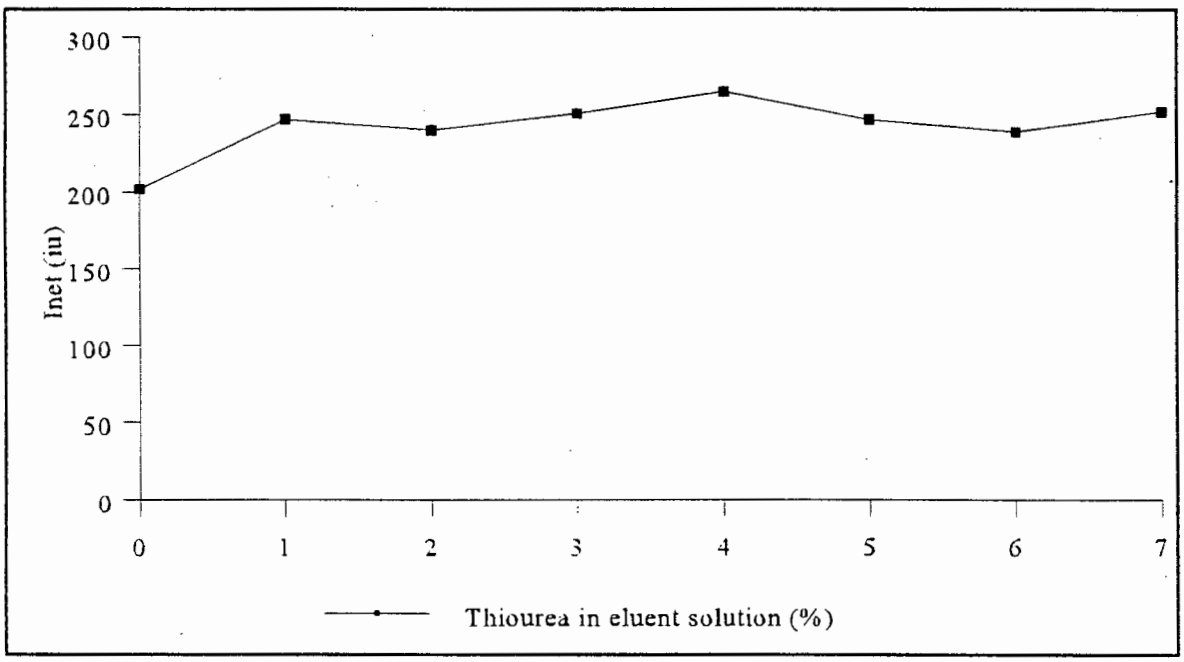

Figure 5.8.1: Effect of thiourea on the signal intensity of Pd(I) 340.458 nm

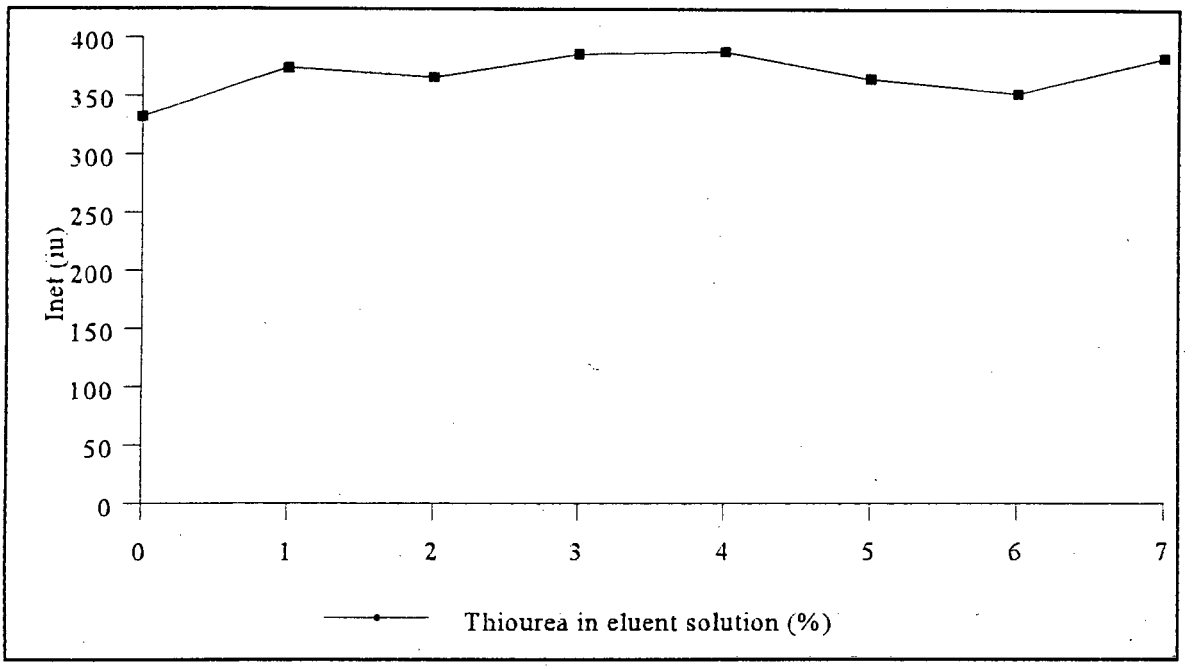

Figure 5.8.2: Effect of thiourea on the signal intensity of Pd(II) 229.651 nm

A thiourea content higher than 7% was found to result in an unacceptably high relative standard deviation for the measured intensities (> 5%), and poor system reproducibility as a result of the introduction of a significant quantity of carbon material into the plasma at high thiourea concentrations. For thiourea concentrations between 1 and 7%, a maximum of 10% (Pd(I) 340.458 nm) and 25% (Pd(II) 229.651 nm) enhancement of the signal intensity was observed, with little change in the enhancement over the range studied. The results indicated that the use of a 5% thiourea content in the eluent solution would not compromise the analysis of real effluent solutions and was found to be advantageous with respect to enhancement of the signal intensity of the analytical wavelengths.

5.9 Effect of surfactant on signal intensity of Pd(II)

The effect of a surfactant on the signal intensity of palladium(II) was studied in an effort to ascertain whether or not a surfactant would influence calibration sensitivity through a possible change in nebulization efficiency, resulting in more favourable detection limits for the analytical wavelengths under study.

Triton X-100 was utilised as the surfactant in this study and its effect on the signal intensity of a 2 $\mu g.cm^{-3}$ standard solution containing between 0 - 0.00015% Triton X-100 (w/v), under compromise operating conditions (Table 5.2.2) was recorded. The net analyte signal intensities determined versus % Triton X-100 content are shown in Figure 5.9.1 and 5.9.2.

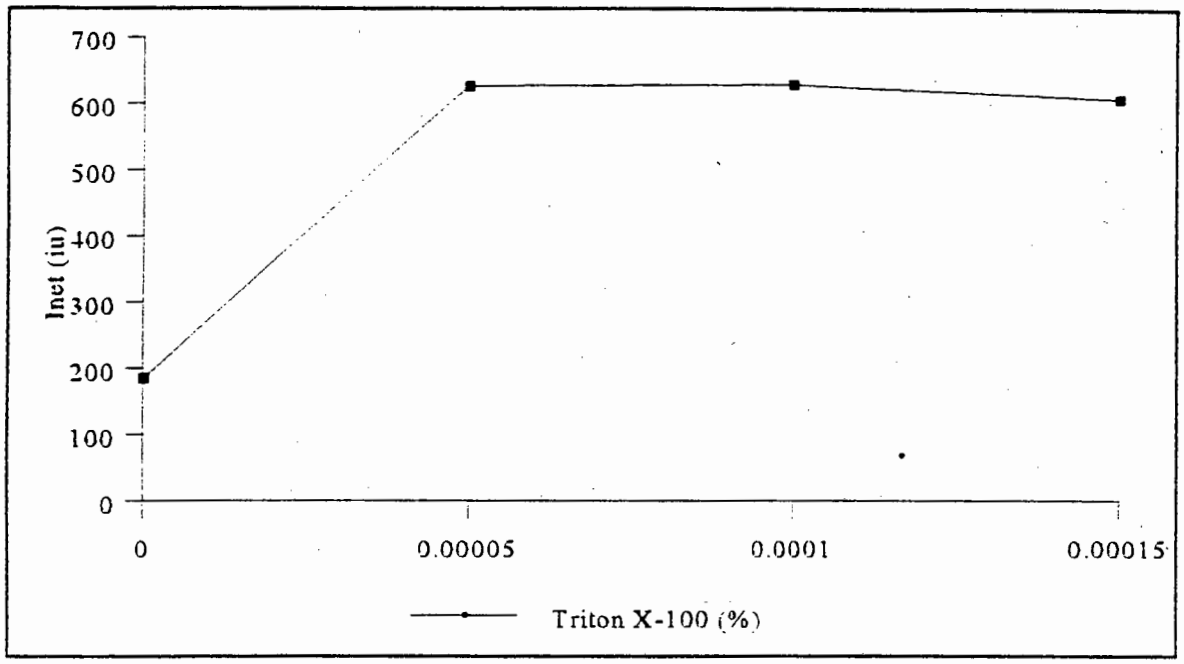

Figure 5.9.1: Effect of Triton X-100 on the signal intensity of Pd(I) 340.458 nm

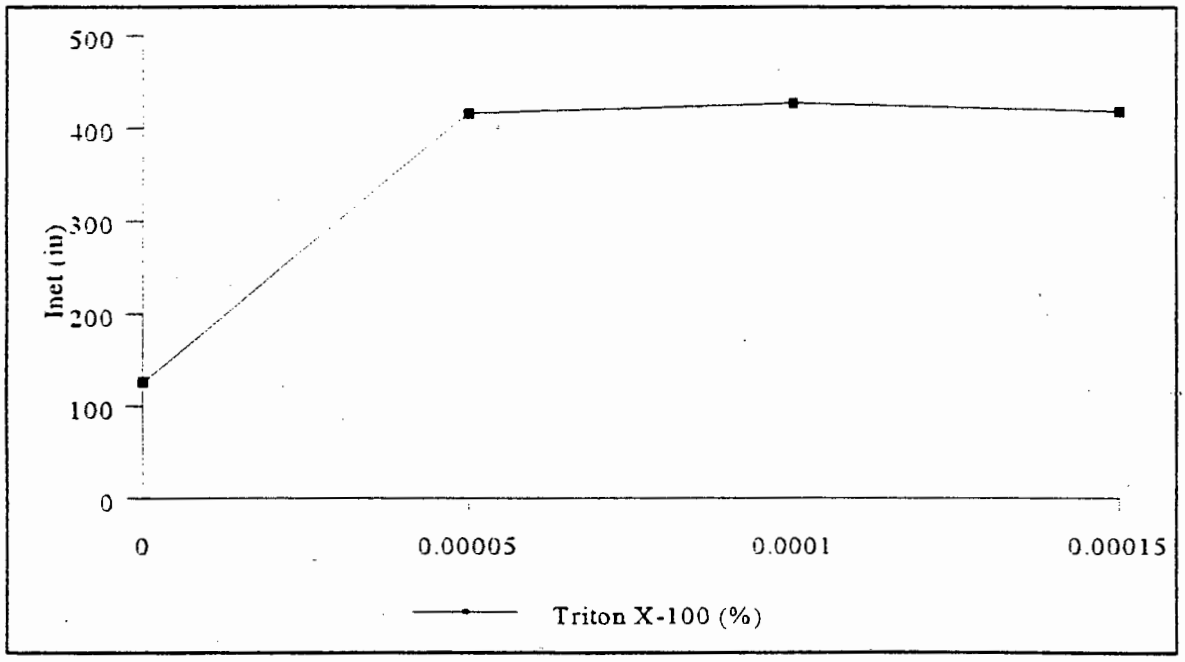

Figure 5.9.2: Effect of Triton X-100 on the signal intensity of Pd(II) 229.651 nm

The effect of Triton X-100 between 0.00005 and 0.00015%, resulted in a significant enhancement (Pd(I) 340.458 nm - maximum 240% and Pd(II) 229.651 nm - maximum 238%) to the recorded signal intensity for the two wavelengths studied. The identical signal enhancement (240 and 238%) observed for both wavelengths studied could be attributed to the expected increase in nebulization efficiency (and thus a corresponding increase in analyte emission intensity) upon aspiration of an

analyte solution containing a surfactant. Consequently, all subsequent analyte solutions were spiked with 0.0001% Triton X-100 prior to determination by ICP-OES.

5.10 Linearity of concentration range

ICP-OES is known as a technique with a wide linear dynamic concentration range, that allows for analysis of sample sets containing like analytes with high or low concentrations, utilising only one calibration data set. Few descriptions are to be found in the literature with regard to the linearity of the concentration range for the platinum-group metals, using ICP-OES. As a result, determination of the precision and linearity of the analytical wavelengths as measured at line centre position was required.

To determine the linearity and precision of the concentration range, a series of palladium(II) and platinum(IV) standards between 0 - 100 $\mu g.cm^{-3}$ were aspirated to obtain a calibration curve and emission intensity data (Figure 5.10.1, 5.10.2, 5.10.3 and 5.10.4). Linearity was determined via least-squares regression analysis of the calibration curve and the correlation coefficient determined. The value of the correlation coefficient was used to evaluate the linearity of the concentration range studied. A linear regression correlation coefficient value R^2, of 0.9999 (Pd(I) 340.458 nm), 0.9988 (Pd(II) 229.651 nm), 0.9971 (Pt(I) 265.945 nm) and 0.9901 (Pt(II) 214.423 nm) was obtained for the range 0 - 10 $\mu g.cm^{-3}$. Inclusion of emission intensities of concentrations greater than 10 $\mu g.cm^{-3}$ in the linear regression analysis of the experimental calibration curve, resulted in deterioration of the linear regression correlation coefficient. This deterioration was attributed to a decline in linearity over the extended concentration range and as a result, a 0 - 10 $\mu g.cm^{-3}$ concentration range was deemed to be the optimum analysis window particularly since effluent solutions were unlikely to contain concentrations of platinum-group metals exceeding 10 $\mu g.cm^{-3}$. In subsequent analyses with samples containing higher concentrations of platinum-group metals, appropriate dilutions were performed to allow for analysis within this optimum linear concentration range.

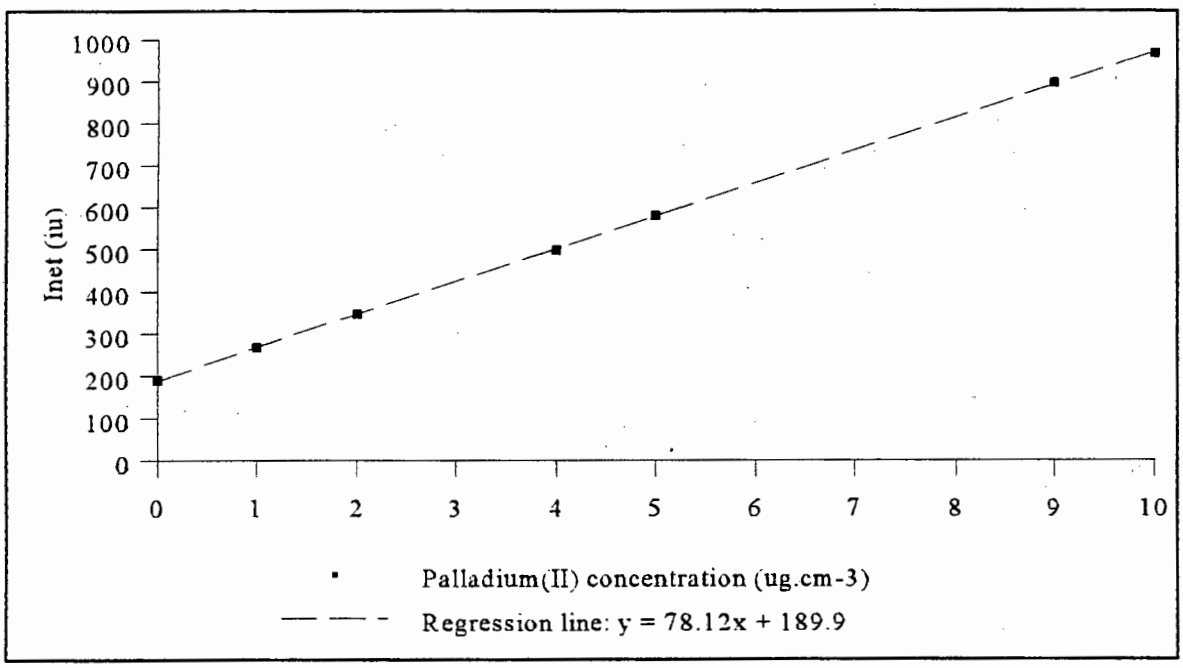

Figure 5.10.1: Linearity of Pd(I) 340.458 nm line

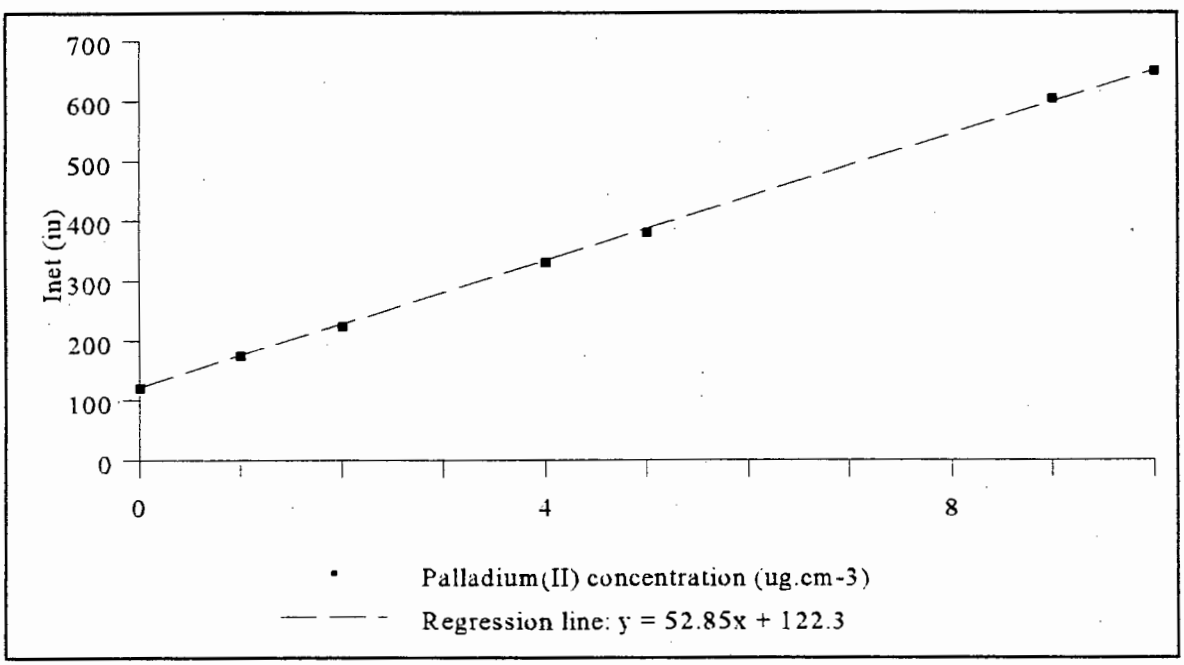

Figure 5.10.2: Linearity of Pd(II) 229.651 nm line

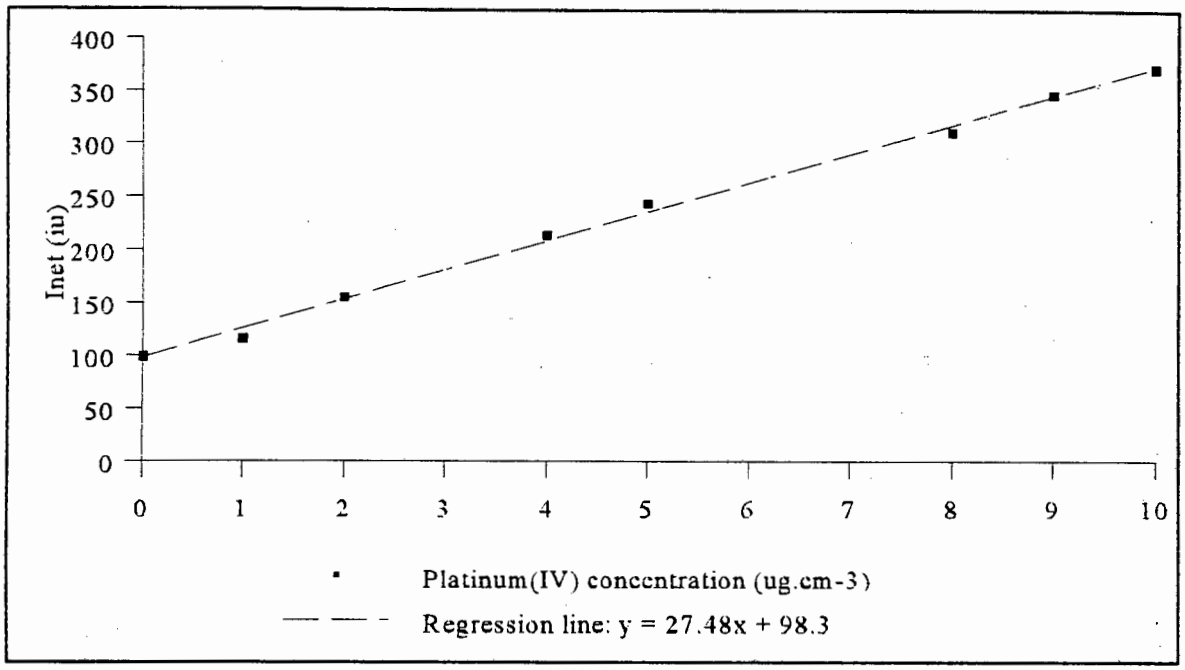

Figure 5.10.3: Linearity of Pt(I) 265.945 nm line

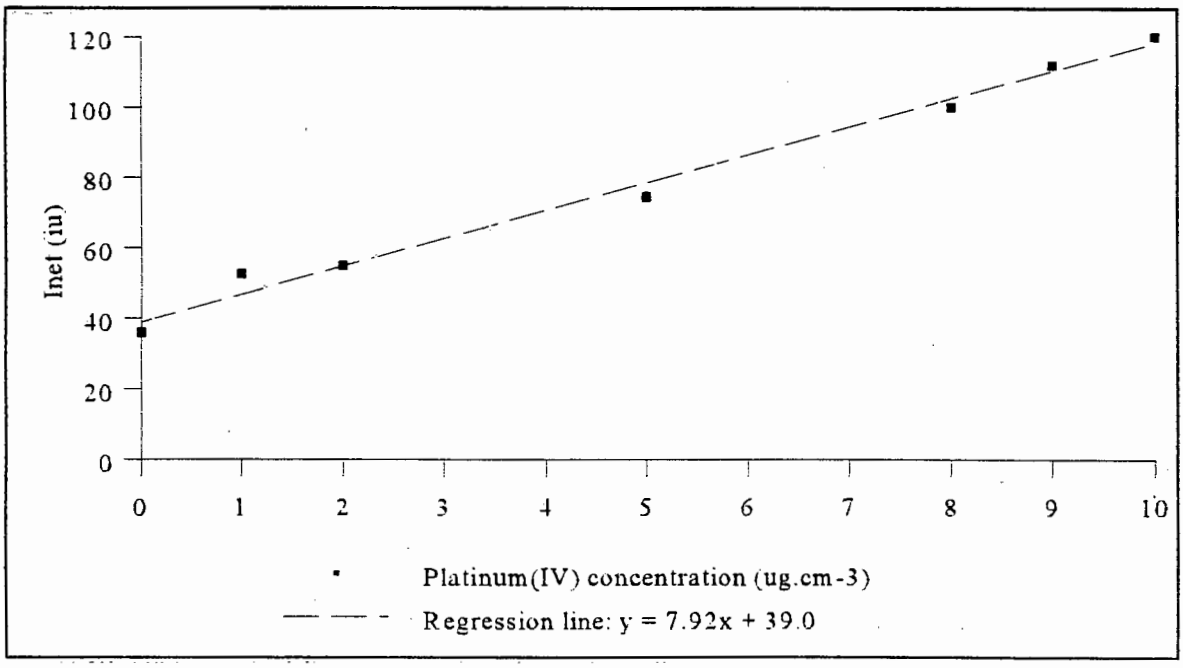

Figure 5.10.4: Linearity of Pt(II) 214.423 nm line

5.11 Conclusion

It was evident from the results of this chapter that optimisation of the determination of the platinum-group metals in effluent samples by ICP-OES involved consideration of the response of the detection system to changes in various parameters, in order to obtain experimental conditions that ensured optimum maxima for all parameters. The selection of optimum ICP-OES operating

parameters for the platinum-group metals under study, required careful consideration of the sensitivity, accuracy and precision obtained with the selected operating parameters.

5.12 References

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Chapter 6

Validation of Developed Pre-concentration and Determination System

6.1 Introduction

Prior to analysis of real effluent samples with the developed system, it was necessary to first validate the pre-concentration and determination systems. Accuracy, precision and system reproducibility were evaluated by means of recovery and spiking experiments. Results pertaining to the single- and multi-component analysis of platinum(IV/II) and palladium(II) with *N*-benzoyl-*N'*, *N'*-di(2-hydroxyethyl)thiourea from synthetic solutions, are detailed below:

1. Palladium(II) recovery from synthetic effluent
2. Platinum(IV) recovery from synthetic effluent
3. Platinum(II) recovery from synthetic effluent
4. Interference of Ni^{2+}, Fe^{3+} and Cu^{2+} on palladium(II) and platinum(IV/II) recovery
5. Mixed metal recovery from synthetic effluent

The effect of the oxidation state of the platinum was simultaneously investigated by preparation of separate solutions containing identical amounts of Pt(IV) and Pt(II) respectively. The concentrations were verified to be the same by flame atomic-absorption spectrometry and ICP-OES. All else being equal, any variation in percentage recovery would be due to the different oxidation states of the platinum.

6.2 Palladium(II) recovery from synthetic effluent

A series of 20 (0.5 $\mu g.cm^{-3}$) synthetic Pd(II) solutions were prepared and analysed after measurement of Pd(II) calibration standards. A pre-concentration factor of 4 was previously found to be optimum (**4.9**) thus sample aliquots of 40 cm^3 were pre-concentrated onto the column, followed by 10 cm^3 of eluent solution after column rinsing (theoretical content of Pd(II) = 2 $\mu g.cm^{-3}$). The eluent aliquots were then presented to the JY 70C for determination of the palladium(II) content, at the most sensitive atomic line Pd(I) 340.458 nm and subsequently palladium(II) percentage recovery evaluated (Table 6.2.1), against the theoretical content of Pd(II).

Table 6.2.1: Palladium(II) percentage recovery from synthetic effluent solutions

Sample no.	Mean Pd(II) content determined ($\mu g.cm^{-3}$)	* Mean percentage recovery (%)	* 95% Confidence interval of mean percentage recovery (%)
1	2.02	100.8 +- 0.25	100.2 - 101.4
2	1.94	97.0 +- 0.14	96.6 - 97.4
3	1.94	97.0 +- 0.03	96.9 - 97.1
4	2.02	100.8 +- 0.25	100.2 - 101.4
5	1.99	99.6 +- 0.15	99.2 - 100.0
6	2.03	102.0 +- 0.01	102.0
7	1.94	97.0 +- 0.07	96.8 - 97.2
8	1.94	97.0 +- 0.21	96.5 - 97.5
9	1.89	94.5 +- 0.83	92.4 - 96.6
10	1.99	99.6 +- 0.10	99.3 - 99.9
11	1.96	98.1 +- 0.10	97.8 - 98.4
12	1.99	99.8 +- 0.30	99.1 - 100.5
13	1.91	95.6 +- 0.20	95.1 - 96.1
14	1.92	96.2 +- 0.21	95.7 - 96.7
15	1.85	92.4 +- 0.11	92.1 - 92.7
16	1.99	99.9 +- 0.40	98.9 - 100.9
17	1.94	97.0 +- 0.00	97.0
18	1.97	98.4 +- 0.10	98.1 - 98.7
19	1.93	96.5 +- 0.00	96.5
20	1.88	94.0 +- 0.36	93.1 - 94.9

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t =4.30 for N = 3

The mean recovery (at the 95% confidence limit) for the 20 samples was found to be 97.7 +- 4.5%. This equated to an experimental concentration of 1.95 $\mu g.cm^{-3}$ palladium(II) compared to the theoretical concentration of 2 $\mu g.cm^{-3}$.

6.3 Platinum(IV) recovery from synthetic effluent

A series of 20 (0.5 $\mu g.cm^{-3}$) synthetic Pt(IV) solutions were prepared and analysed after

measurement of Pt(IV) calibration standards. Sample aliquots of 40 cm^3 were pre-concentrated onto the column, and eluted with 10 cm^3 of eluent solution after column rinsing (theoretical content of Pt(IV) = 2 $\mu g.cm^{-3}$). The eluent aliquots were then presented to the JY 70C for determination of the platinum(IV) content, at the most sensitive atomic line Pt(I) 265.945 nm and subsequently platinum(IV) percentage recovery was evaluated (Table 6.3.1), against the theoretical content of Pt(IV).

Table 6.3.1: Platinum(IV) percentage recovery from synthetic effluent solutions

Sample no.	Mean Pt(IV) content determined ($\mu g.cm^{-3}$)	* Mean percentage recovery (%)	* 95% Confidence interval of mean percentage recovery (%)
1	1.98	98.8 +- 0.20	98.3 - 99.3
2	1.90	95.2 +- 0.21	94.7 - 95.7
3	2.00	100.0 +- 0.04	99.9 - 100.1
4	1.91	95.4 +- 0.10	95.2 - 95.6
5	1.95	97.5 +- 3.79	88.1 - 106.9
6	2.00	100.0 +- 0.06	99.8 - 100.2
7	1.97	98.5 +- 0.16	98.1 - 98.9
8	2.01	100.6 +- 0.70	98.9 - 101.7
9	1.83	91.7 +- 0.22	91.1 - 92.2
10	1.98	99.2 +- 0.18	98.8 - 99.6
11	1.98	98.9 +- 0.10	98.6 - 99.2
12	1.86	93.1 +- 0.11	92.8 - 93.4
13	1.97	98.5 +- 0.03	98.4 - 98.6
14	2.19	109.3 +- 0.13	109.0 - 109.6
15	1.99	99.6 +- 0.02	99.5 - 99.7
16	1.97	98.7 +- 4.07	88.6 - 108.8
17	1.91	95.4 +- 0.85	93.3 - 97.5
18	1.95	97.4 +- 0.66	95.8 - 99.0
19	1.92	96.1 +- 0.01	96.1
20	1.86	93.0 +- 2.36	87.1 - 98.9

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t = 4.30 for N = 3

The mean recovery (at the 95% confidence limit) for the 20 samples was found to be 97.8 +-

3.8%. This equated to an experimental concentration of 1.96 $\mu g.cm^{-3}$ platinum(IV) compared to the theoretical concentration of 2 $\mu g.cm^{-3}$.

6.4 Platinum(II) recovery from synthetic effluent

As in experiments **6.2** and **6.3** above, a series of 20 (0.5 $\mu g.cm^{-3}$) synthetic Pt(II) solutions were prepared and analysed after measurement of Pt(II) calibration standards. Sample aliquots of 40 cm^3 were pre-concentrated onto the column, and eluted with 10 cm^3 of eluent solution after column rinsing (theoretical content of Pt(II) = 2 $\mu g.cm^{-3}$). The eluent aliquots were then presented to the JY 70C for determination of the platinum(II) content at the most sensitive atomic line Pt(I) 265.945 nm and subsequently platinum(II) percentage recovery was evaluated (Table 6.4.1), against the theoretical content of Pt(II).

Table 6.4.1: Platinum(II) percentage recovery from synthetic effluent solutions

Sample no.	Mean Pt(II) content determined ($\mu g.cm^{-3}$)	* Mean percentage recovery (%)	* 95% Confidence interval of mean percentage recovery (%)
1	1.81	90.6 +- 0.49	89.4 - 91.8
2	1.99	99.7 +- 0.06	99.5 - 99.7
3	1.87	93.8 +- 0.32	93.0 - 94.6
4	1.90	94.9 +- 0.53	93.6 - 96.2
5	1.99	99.6+- 0.10	99.3 - 99.9
6	2.04	101.8 +- 0.19	101.3 - 102.3
7	1.88	94.1 +- 0.72	92.3 - 95.9
8	1.88	93.8 +- 0.31	93.0 - 94.6
9	1.94	97.2 +- 0.12	96.9 - 97.5
10	2.03	101.7 +- 0.19	101.2 - 102.2
11	2.20	110.2 +- 0.18	109.7 - 110.7
12	1.88	94.0 +- 0.51	92.7 - 95.3
13	1.83	91.3 +- 0.22	90.7 - 91.9
14	1.97	98.5 +- 0.03	98.4 - 98.6
15	1.82	91.0 +- 1.8	86.5 - 95.5
16	1.86	92.8 +- 0.22	92.2 - 93.4
17	1.98	99.2 +- 0.34	98.4 - 100.0

Sample No.	Pt(II) content Determined ($\mu g.cm^{-3}$)	* Mean percentage recovery (%)	* 95% Confidence interval of mean percentage recovery (%)
18	1.78	89.1 +- 0.11	88.8 - 89.4
19	1.88	93.8 +- 0.21	93.3 - 94.3
20	2.06	102.8 +- 0.19	102.3 - 103.3

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t = 4.30 for N = 3

The mean recovery (at the 95% confidence limit) for the 20 samples was found to be 96.5 +- 3.7%. This equated to an experimental concentration of 1.93 $\mu g.cm^{-3}$ platinum(IV) compared to the theoretical concentration of 2 $\mu g.cm^{-3}$.

6.5 Interference of Ni^{2+}, Fe^{3+} and Cu^{2+} on palladium(II) and platinum(IV/II) recovery

Since first row transition elements were likely to be found in solutions of real effluent samples (**1.1**) at high concentrations relative to the concomitant platinum-group metals, it was important to determine the tolerance of the developed system for these interferents and additionally whether approaches circumventing their interference were possible. To this end, a preliminary interference study was conducted for the reaction of palladium(II) and platinum(IV/II) with *N*-benzoyl-*N'*, *N'*-di(2-hydroxyethyl)thiourea.

The potential interference for the reaction between *N*-benzoyl-*N'*, *N'*-di(2-hydroxyethyl)thiourea and palladium(II)/platinum(IV/II) was likely to be of one of two types: (1) a non-selective complexation reaction of *N*-benzoyl-*N'*, *N'*-di(2-hydroxyethyl)thiourea with elements other than the platinum-group metals or (2) an oxidative interference, leading to competitive consumption of the *N*-benzoyl-*N'*, *N'*-di(2-hydroxyethyl)thiourea in solution. In general, the established [1,2] high selectivity of the reaction of *N*-benzoyl-*N'*, *N'*-dialkylthioureas with the platinum-group metals made interference of type 1 unlikely (although interferences from other platinum-group metals and gold may be expected).

The sample and eluent solutions were both in 2 M perchloric acid, with the result that substantial interferences of type 2 from the first row transition metals were unlikely, with the possible exception of Fe^{3+} and Ni^{2+} which would be present in relatively high concentrations.

Interference tolerances at 0.5 $\mu g.cm^{-3}$ levels for palladium(II) and platinum(IV/II) were

investigated in triplicate, by monitoring the experimental percentage recovery (final PGM content = 2 $\mu g.cm^{-3}$) after pre-concentration of a 40 cm^3 aliquot of sample solution and subsequent elution with 10 cm^3 eluent solution (Table 6.5.1, 6.5.2 and 6.5.3). The maximum amount of each interferent tested was 500 $\mu g.cm^{-3}$.

Table 6.5.1: The effect of interferents on the percentage recovery of palladium(II)

Base metal added ($\mu g.cm^{-3}$)	Mean Pd(II) content determined ($\mu g.cm^{-3}$)	* Mean percentage recovery (%)	* 95% Confidence interval of mean percentage recovery (%)
Cu^{2+}			
0	2.04	102.0 +- 0.31	101.2 - 102.8
50	1.98	99.0 +- 0.05	98.9 - 99.1
100	1.92	96.0 +- 2.54	89.7 - 102.3
250	1.95	97.5 +- 0.26	96.8 - 98.2
500	2.02	101.0 +- 0.07	100.8 - 101.2
Fe^{3+}			
0	2.04	102.0 +- 0.20	101.5 - 102.5
50	2.02	101.0 +-0.75	99.1 - 102.9
100	2.02	101.0 +- 0.42	100.0 - 102.0
250	2.08	104.0 +- 0.19	103.5 - 104.5
500	1.97	98.7 +- 0.36	97.8 - 99.6
Ni^{2+}			
0	1.94	97.0 +- 0.15	96.6 - 97.4
50	1.96	98.0 +- 0.49	96.8 - 99.2
100	1.92	96.0 +- 0.93	93.7 - 98.3
250	2.02	101.0 +- 0.78	98.2 - 103.8
500	2.00	100.0 +- 0.09	99.8 - 100.2

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t = 4.30 for N = 3

The interferent concentration, in the case of palladium(II), that could be handled was such that the percentage recovery determined did not differ by more than 2% from that of a pure standard solution, in the case of Ni^{2+} (98.8%) and Fe^{3+} (101.2%), and by less than 4% in the case of Cu^{2+} (98.4%). Consequently, it was clear that palladium(II) could be determined in the presence of relatively large amounts of Ni^{2+}, Fe^{3+} and Cu^{2+}.

Table 6.5.2: The effect of interferents on the percentage recovery of platinum(IV)

Base metal added ($\mu g.cm^{-3}$)	Mean Pt(IV) content determined ($\mu g.cm^{-3}$)	* Mean percentage recovery (%)	* 95% Confidence interval of mean percentage recovery (%)
Cu^{2+}			
0	1.95	97.4 +-0.10	97.1 - 97.7
50	0.09	4.9 +- 0.85	2.8 - 7.0
100	0.10	5.0 +- 0.02	4.9 - 5.1
250	0.09	4.7 +- 0.41	3.7 - 5.7
500	0.09	4.8 +- 0.67	3.1 - 6.5
Fe^{3+}			
0	1.99	99.6 +- 0.51	98.3 - 100.9
50	0.12	6.2 +- 3.33	0.0 - 14.5
100	0.11	5.9 +- 7.20	0.0 - 23.8
250	0.11	5.5 +- 0.79	3.5 - 7.5
500	0.11	5.7 +- 4.11	0.0 - 15.9
Ni^{2+}			
0	1.98	98.9 +- 0.96	96.5 - 101.3
50	0.10	4.9 +- 0.15	4.5 - 5.3
100	0.10	5.0 +- 0.02	4.9 - 5.1
250	0.09	4.7 +- 0.93	2.4 - 7.0
500	0.09	4.5 +- 2.00	0.0 - 10.0

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t = 4.30 for N = 3

The interferent concentration, in the case of platinum(IV), that could be handled was such that the percentage recovery determined significantly differed from that of a pure standard solution, for all three interferents studied. The results showed that in the presence of moderate to high concentrations of Ni^{2+}, Fe^{3+} and Cu^{2+}, platinum(IV) pre-concentration was severely impaired.

This loss in recovery was attributed to a type 2 interference (competitive consumption of the ligand). Platinum(IV) undergoes substitution reactions slowly compared to the interferents studied and so failed to form the neutral platinum(IV) metal-ligand chelate necessary for retention (and resultant pre-concentration) on the reverse-phase column, instead passing through into the waste solution instead. It was clear that platinum(IV) could not be measured, without interference, in

the presence of relatively large to moderate amounts of Ni^{2+}, Fe^{3+} and Cu^{2-}, without pretreatment prior to determination to remove the first-row transition elements in solution.

Table 6.5.3: The effect of interferents on the percentage recovery of platinum(II)

Base metal added ($\mu g.cm^{-3}$)	Mean Pt(II) content determined ($\mu g.cm^{-3}$)	* Mean percentage recovery (%)	* 95% Confidence interval of mean percentage recovery (%)
$\underline{Cu^{2+}}$			
0	1.88	94.1 +- 0.06	93.9 - 94.3
50	0.91	45.3 +- 0.44	44.2 - 46.4
100	0.82	41.0 +- 0.32	40.2 - 41.8
250	0.97	48.7 +- 0.41	47.7 - 49.7
500	0.78	39.0 +- 0.57	37.6 - 40.4
$\underline{Fe^{3+}}$			
0	1.97	98.6 +- 0.10	98.3 - 98.9
50	2.20	110.0 +- 0.03	109.9 - 110.1
100	1.95	97.3 +- 0.21	96.8 - 97.8
250	1.97	98.7 +- 0.20	98.2 - 99.2
500	1.94	96.9 +- 0.11	96.6 - 97.2
$\underline{Ni^{2+}}$			
0	1.95	97.3 +- 0.94	95.0 - 99.6
50	0.10	5.1 +- 2.0	0.1 - 10.0
100	0.09	4.4 +- 2.3	0.0 - 10.1
250	0.10	4.8 +- 4.2	0.0 - 14.8
500	0.10	5.0 +- 3.7	0.0 - 14.2

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test. t = 4.30 for N = 3

The interferent concentration, in the case of platinum(II), that could be handled was such that the percentage recovery determined, significantly differed from that of a pure standard solution, for Ni^{2+} and Cu^{2+}. The results showed that in the presence of moderate to high concentrations of Ni^{2+} and Cu^{2+}, platinum(II) pre-concentration was severely impaired. Suprisingly, Fe^{3+} was found not to interfere with the percentage recovery (100.7%) of platinum(II).

This loss in recovery was again attributed to a type 2 interference (competitive consumption of

the ligand). Platinum(II) undergoes substitution reactions slowly compared to the interferents studied, but is significantly more labile than platinum(IV). This resulted in a shortage of ligand to complex with the platinum(II) and hence the platinum(II) was unretained on the reverse-phase material of the column.

The unexpected result was that the experimental data obtained suggested that the following overall order of reaction between *N*-benzoyl-*N'*, *N'*-di(2-hydroxyethyl)thiourea and the elements under study applied: Pd(II)>Ni(II)>Cu(II)>Pt(II)>Fe(III)>Pt(IV). It was clear that platinum(II) could not be measured, without interference, in the presence of relatively large to moderate amounts of Ni^{2+} and Cu^{2+}, without pretreatment prior to determination to remove these first-row transition elements from the sample solution.

6.6 Mixed Metal Recovery

Successful optimised conditions having been established for single component determinations of palladium(II) and platinum(IV/II) with *N*-benzoyl-*N'*, *N'*-di(2-hydroxyethyl)thiourea, the next stage in the validation of the developed system was to analyse these two platinum-group metals simultaneously.

Synthetic mixtures of platinum(IV/II) and palladium(II) were prepared, pre-concentrated (pre-concentration factor of 4) and analysed using the simultaneous channel of the JY 70C ICP spectrometer and respective standard solutions. Mixtures contained varying amounts of platinum(IV/II) and palladium(II) in the range 0.1 - 1.0 $\mu g.cm^{-3}$. The ratios of one platinum-group metal to another varied between 1:10 and 10:1. Percentage recoveries of the two metals were recorded and the mutual interference (if any) evaluated (Table 6.6.1 and 6.6.2). No synergistic effects between the metals were observed within the ranges used. Consequently, the responses of the mixtures were independent of their respective component concentrations.

Table 6.6.1: Percentage recovery of palladium(II) and platinum(IV) for simultaneous analysis

Pd(II) added to sample ($\mu g.cm^{-3}$)	Mean Pd(II) determined ($\mu g.cm^{-3}$)	* Mean Pd(II) percentage recovery (%)	* 95% Confidence interval of mean Pd(II) percentage recovery (%)	Pt(IV) added to sample ($\mu g.cm^{-3}$)	Mean Pt(IV) determined ($\mu g.cm^{-3}$)	* Mean Pt(IV) percentage recovery (%)	* 95% Confidence interval of mean Pt(IV) percentage recovery (%)
1.0	3.95	98.8 +- 0.90	96.6 - 101.0	0.1	0.39	99.7 +- 3.00	92.3 - 107.1
0.5	1.88	93.8 +- 0.31	93.0 - 94.6	0.2	0.77	96.8 +- 2.60	85.6 - 108.0
0.4	1.63	102.0 +- 0.75	100.1 - 103.9	0.3	1.21	101.0 +- 1.00	98.5 - 103.5
0.3	I.18	98.1 +- 0.34	97.3 - 98.9	0.4	1.58	99.0 +- 2.10	93.8 - 104.2
0.2	0.81	101.0 +- 0.42	100.0 - 102.0	0.5	2.01	100.4 +- 1.80	95.9 - 104.9
0.1	0.38	94.1 +-1.10	91.4 - 96.8	I.0	3.87	96.8 +- 0.30	96.1 - 97.6

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t = 4.30 for N = 3

The results obtained indicated that there was no loss in the analytical performance of the developed system when simultaneously analysing mixtures of palladium(II) and platinum(IV), as in real effluent samples. The percentage recoveries (Pd(II) - 97.9 +- 3.5% and Pt(IV) - 98.9 +- 1.8%) were effectively unchanged when comparing the results obtained with those recorded in the single component analysis (Pd(II) - 97.7 +- 4.5% and Pt(IV) - 97.8 +- 3.8%).

Table 6.6.2: Percentage recovery of palladium(II) and platinum(II) for simultaneous analysis

Pd(II) added to sample ($\mu g.cm^{-3}$)	Mean Pd(II) determined ($\mu g.cm^{-3}$)	* Mean Pd(II) percentage recovery (%)	* 95% Confidence interval of mean Pd(II) percentage recovery (%)	Pt(II) added to sample ($\mu g.cm^{-3}$)	Mean Pt(II) determined ($\mu g.cm^{-3}$)	* Mean Pt(II) percentage recovery (%)	* 95% Confidence interval of mean Pt(II) percentage recovery (%)
1.0	3.76	94.1 +- 0.10	93.8 - 94.4	0.1	0.39	97.6 +- 1.70	93.4 - 101.8
0.5	2.02	101.0 +- 0.14	100.6 - 101.4	0.2	0.79	99.6 +- 1.60	95.6 - 103.6
0.4	1.57	98.3 +- 0.57	96.9 - 99.7	0.3	1.17	97.2 +- 1.10	94.5 - 99.9
0.3	1.14	95.0 +- 0.08	94.8 - 95.2	0.4	1.60	100.2 +- 1.80	95.7 - 104.7
0.2	0.76	94.9 +- 0.60	93.4 - 96.4	0.5	1.92	95.8 +- 1.30	92.6 - 99.0
0.1	0.38	95.4 +-3.00	88.0 - 102.8	1.0	4.00	100.0 +- 0.90	97.8- 102.2

*mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t = 4.30 for N = 3

The results obtained, once again indicated that there was no loss in the analytical performance of the developed system when simultaneously analysing mixtures of palladium(II) and platinum(II), as in real effluent samples. The percentage recoveries recorded simultaneously (Pd(II) - 96.5 +- 2.8% and Pt(II) - 98.4 +- 1.8%) were effectively unchanged when comparing the results obtained with those recorded in the single component analysis (Pd(II) - 97.7 +- 4.5% and Pt(II) - 96.5 +- 3.7%).

6.7 Conclusion

The results of the recovery experiments with single component solutions and synthetic mixtures proved that separate and simultaneous analysis of platinum(IV/II) and palladium(II) was possible and that the developed system appeared to have the potential to analyse real effluent samples (7.1) precisely, accurately and reproducibly. Since the analytical performance of the developed system had been evaluated, the next focus of the research was the analysis of real effluent samples and ultimately evaluating the analytical performance of the developed system in the determination of the platinum-group metal content of real effluent solutions.

6.8 References

1. Schuster, M. J., *J. Anal. Chem.*, 1992, **342**, 791

2. Koch, K. R., Sacht, C., Grimmbacher, T. and Bourne, S., *S. Afr. J. Chem.*, 1995, **48(1/2)**, 71

Chapter 7

Real Effluent Analysis

7.1 Introduction

The results of the developed system using synthetic effluent solutions (**6.1**) indicated that the underlying principle of the developed system had exceptional merit for the pre-concentration and determination of the platinum-group metals from synthetic matrices, at trace concentrations. The refined pre-concentraton and determination steps as developed in this study, resulted in accurate and reproducible pre-concentration and determination of the platinum-group metals from synthetic effluent solutions. The advantage of such accurate and reproducible pre-concentration and determination for synthetic effluent analysis appeared to be supported by the experimental data presented.

Since the fully optimised pre-concentration and determination system had been developed and tested on synthetic effluent solutions only, the analytical and system performance of the developed system using two real post-processing effluents, loaned from different South African platinum-group metal producers, had to be evaluated. For this purpose the following experiments were investigated with real post-processing effluents, using the refined system (**4.1** and **5.1**) and the analytical and system performance evaluated:

1. Palladium(II) recovery from real post-processing effluent
2. Platinum(IV) recovery from real post-processing effluent
3. Platinum(II) recovery from real post-processing effluent
4. Standard addition recovery from real post-processing effluent

The effect of the oxidation state of the platinum was simultaneously investigated by reduction of the platinum(IV) found in the real post-processing effluent with tin(II) chloride, prior to pre-concentration and determination. All else being equal, any variation in percentage recovery would be due to the different oxidation states of the platinum.

7.2 Palladium(II) content in real post-processing effluent

A series of 5 aliquots (15 - 40 cm^3) of two real post-processing effluents (designated IP and AP for anonymity), from two different South African platinum-group metal producers, with an unknown palladium(II) content were diluted by half with 2 M perchloric acid to prevent column overload and to ensure that an excess of ligand was present in the effluent. The effluent solutions were then pre-concentrated and analysed, in triplicate, by ICP-OES. An initial palladium(II) concentration in the effluent of 2 $\mu g.cm^{-3}$ (maximum) was assumed and thus a theoretical upper limit of palladium(II) to be determined, after a maximum of 40cm^3 effluent had been pre-concentrated, was 8 $\mu g.cm^{-3}$. Consequently, palladium(II) calibration standards in the 0 - 10 $\mu g.cm^{-3}$ range were measured, prior to determination of the palladium(II) effluent content by ICP-OES (Table 7.2.1).

Table 7.2.1: Palladium(II) content determined in real post-processing effluent

Sample no.	Volume of effluent pre-concentrated (cm^3)	Eluent volume (cm^3)	* Mean palladium(II) content in effluent ($ng.cm^{-3}$)	* 95 % Confidence interval of mean ($ng.cm^{-3}$)
IP-1	16.5	9.0	500 +- 37	408 - 592
IP-2	19.9	10.0	550 +- 32	471- 621
IP-3	20.0	7.2	486 +- 30	412 - 560
IP-4	15.1	9.5	530 +- 13	498 - 562
IP-5	17.7	9.8	520 +- 25	458 - 582
AP-1	40.0	13.1	74 +- 12	44 - 104
AP-2	30.0	9.6	88 +- 18	43 - 121
AP-3	18.8	10.0	90 +- 23	33 - 123
AP-4	22.0	10.0	64 +- 8	44 - 84
AP-5	21.8	9.3	84 +- 24	24 - 144

* mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t = 4.30 for N = 3

The mean Pd(II) content determined (at the 95% confidence limit, t = 2.78 for N = 5) for the 5 IP effluent samples was 517 +- 31 $ng.cm^{-3}$, with a 95% confidence interval of the mean Pd(II) content of 486 - 548 $ng.cm^{-3}$, for the IP effluent sample. The mean Pd(II) content determined (at

the 95% confidence limit, t = 2.78 for N = 5) for the 5 AP effluent samples was 80 +- 14 $ng.cm^{-3}$, with a 95% confidence interval of the mean Pd(II) content of 66 - 94 $ng.cm^{-3}$, for the AP effluent sample.

Additionally, profile scans of the real effluent samples across the analytical wavelength, were recorded to elucidate the 'true' composition of the effluent (**Appendix A**). Significant quantities (relative to the platinum-group metal content) of Zn (1.5 $\mu g.cm^{-3}$), Fe (4 $\mu g.cm^{-3}$), Cu (0.8 $\mu g.cm^{-3}$), Ni (4 $\mu g.cm^{-3}$), Na (800 $\mu g.cm^{-3}$) and Cr (3 $\mu g.cm^{-3}$) were found to be present in the effluent.

7.3 Platinum(IV) content in real post-processing effluent

A series of 5 aliquots (15 - 40 cm^3) of two real post-processing effluents, from two different South African platinum-group metal producers, with an unknown platinum(IV) content were diluted by half with 2 M perchloric acid to prevent column overload and to ensure that an excess of ligand was present in the effluent. The effluent solutions were then pre-concentrated and analysed, in triplicate, by ICP-OES. An initial platinum(IV) concentration in the effluent of 2 $\mu g.cm^{-3}$ (maximum) was assumed and thus a theoretical upper limit of platinum(IV) to be determined, after a maximum of 40cm^3 effluent had been pre-concentrated, was 8 $\mu g.cm^{-3}$. Consequently, platinum(IV) calibration standards in the 0 - 10 $\mu g.cm^{-3}$ range were measured, prior to determination of the platinum(IV) effluent content by ICP-OES (Table 7.3.1).

Table 7.3.1: Platinum(IV) content determined in real post-processing effluent

Sample no.	Volume of effluent pre-concentrated (cm^3)	Eluent volume (cm^3)	* Mean platinum(IV) content in effluent ($ng.cm^{-3}$)	* 95 % Confidence interval of mean ($ng.cm^{-3}$)
IP-1	18.8	10.0	39 +- 2	34 - 44
IP-2	22.0	10.0	35 +- 3	28 - 42
IP-3	21.8	9.3	30 +- 4	20 - 40
IP-4	20.0	10.0	33 +- 1	30 - 36
IP-5	15.0	10.0	32 +- 0.7	30 - 34

Sample no.	Volume of effluent pre-concentrated (cm^3)	Eluent volume (cm^3)	* Mean platinum(IV) content in effluent ($ng.cm^{-3}$)	* 95 % Confidence interval of mean ($ng.cm^{-3}$)
AP-1	20.0	10.0	36 +- 5	24 - 48
AP-2	20.0	9.9	33 +- 1	30 - 36
AP-3	30.0	10.0	28 +- 0.4	27 - 29
AP-4	40.0	10.1	30 +- 0.6	28 - 32
AP-5	40.0	12.4	35 +- 3	28 - 43

* mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t = 4.30 for N = 3

The mean Pt(IV) content determined (at the 95% confidence limit, t = 2.78 for N = 5) for the 5 IP effluent samples was 34 +- 4 $ng.cm^{-3}$, with a 95% confidence interval of the mean Pt(IV) content of 30 - 38 $ng.cm^{-3}$, for the IP effluent sample. The mean Pt(IV) content determined (at the 95% confidence limit, t = 2.78 for N = 5) for the 5 AP effluent samples was 32 +- 4 $ng.cm^{-3}$, with a 95% confidence interval of the mean Pt(IV) content of 28 - 36 $ng.cm^{-3}$, for the AP effluent sample.

7.4 Platinum(II) content in real post-processing effluent

A series of 5 aliquots (15 - 40 cm^3) of two real post-processing effluents, from two different South African platinum-group metal producers, with an unknown platinum(II) content were diluted by half with 2 M perchloric acid to prevent column overload and to ensure that an excess of ligand was present in the effluent. The effluent solutions were then pre-concentrated and analysed, in triplicate, by ICP-OES. An initial platinum(II) concentration in the effluent of 2 $\mu g.cm^{-3}$ (maximum) was assumed and thus a theoretical upper limit of platinum(II) to be determined, after a maximum of 40cm^3 effluent had been pre-concentrated, was 8 $\mu g.cm^{-3}$. Consequently, platinum(II) calibration standards in the 0 - 10 $\mu g.cm^{-3}$ range were measured, prior to determination of the platinum(II) effluent content by ICP-OES (Table 7.4.1).

Table 7.4.1: Platinum(II) content determined in real post-processing effluent

Sample no.	Volume of effluent pre-concentrated (cm^3)	Eluent volume (cm^3)	* Mean platinum(II) content in effluent ($ng.cm^{-3}$)	* 95 % Confidence interval of mean ($ng.cm^{-3}$)
IP-1	19.9	10.1	36 +- 0.5	35 - 37
IP-2	40.0	9.8	34 +- 0.2	33 - 35
IP-3	23.0	11.2	31 +- 0.8	29 - 33
IP-4	19.6	10.0	39 +- 1.0	37 - 41
IP-5	20.0	10.0	35 +- 0.3	34 - 36
AP-1	40.0	10.0	32 +- 0.6	31 - 33
AP-2	20.0	10.0	35 +- 2.0	30 - 40
AP-3	35.0	9.5	37 +- 0.5	36 - 38
AP-4	21.3	9.2	34 +- 0.8	32 - 36
AP-5	19.8	9.0	30 +- 0.4	29 - 31

* mean +- std. deviation, 95 % confidence interval calculated using the student t-test, t = 4.30 for N = 3

The mean Pt(II) content determined (at the 95% confidence limit, t = 2.78 for N = 5) for the 5 IP effluent samples was 34 +- 4 $ng.cm^{-3}$, with a 95% confidence interval of the mean Pt(II) content of 30 - 38 $ng.cm^{-3}$, for the IP effluent sample. The mean Pt(II) content determined (at the 95% confidence limit, t = 2.78 for N = 5) for the 5 AP effluent samples was 32 +- 4 $ng.cm^{-3}$, with a 95% confidence interval of the mean Pt(II) content of 28 - 36 $ng.cm^{-3}$, for the AP effluent sample.

The results additionally indicated that the oxidation state of the platinum had no effect on the percentage recovery of the platinum in the effluent samples. Null hypothesis testing of the mean platinum content determined by either direct pre-concentration of the platinum(IV) in the effluent samples or by reduction of the platinum(IV) to platinum(II) before pre-concentration, indicated that there was no significant difference between the two determined means and that the difference between the means was due to indeterminate errors only (**Appendix B**).

7.5 Standard addition recovery from real post-processing effluent

The platinum-group metal content of the real post-processing effluent samples were evaluated in

the previous experiments (**7.2**, **7.3** and **7.4**) by simple pre-concentration and subsequent determination with the developed system. However, the results obtained needed to be further evaluated before attesting to the reliability of the developed method in the pre-concentration and determination of the platinum-group metal content of the real post processing effluent samples. Since no standard reference materials (SRM) of post-processing effluent were available for validation of the developed method, it was necessary to employ standard addition methodology to determine the effectiveness of the developed method by evaluating the extent of recovery of an added quantity of platinum-group metal. The recovery of the standard addition method would then reveal any errors from the way the sample was treated or from the presence of the other elements and/or compounds in the sample matrix. The standard addition curve thus derived allowed evaluation of the original content of platinum-group metal by extrapolation, at $y = 0$, of the derived linear regression line obtained with this method.

Aliquots of the effluent sample were pre-concentrated with the addition of increasing amounts of the platinum-group metal being studied, and subsequently eluted off the column and determined by ICP-OES (Table 7.5.1 and 7.5.2). The linear regression line was derived (Figure 7.5.1, 7.5.2, 7.5.3 and 7.5.4) and the original content of platinum-group metal determined and compared to the previous results obtained. Since the recovery of platinum, as either Pt(IV) or Pt(II), was shown to be unaffected by the oxidation state of the metal (**7.3** and **7.4**) only standard addition of platinum(IV) was studied.

Table 7.5.1: Palladium(II) content determined in real post-processing effluent by standard addition

Effluent sample	Pd(II) added to effluent sample prior to pre-concentration ($ng.cm^{-3}$)	Volume of effluent pre-concentrated (cm^3)	Eluent volume (cm^3)	Mean uncorrected intensity of the sample (iu)	Mean corrected intensity of the sample ($I_b = 3.95$) (iu)
IP	0	20.0	10.2	45.47	41.52
	50	20.3	9.7	51.55	47.60
	100	20.1	9.5	54.05	50.10
	150	25.8	10.0	59.26	55.31
AP	0	21.8	9.3	11.82	7.87
	50	28.0	9.7	17.90	13.95

Effluent sample	Pd(II) added to effluent sample prior to pre-concentration ($ng.cm^{-3}$)	Volume of effluent pre-concentrated (cm^3)	Eluent volume (cm^3)	Mean uncorrected intensity of the sample (iu)	Mean corrected intensity of the sample (I_b = 3.95) (iu)
AP	100	30.0	13.3	23.40	19.45
	150	25.0	9.8	28.40	24.45

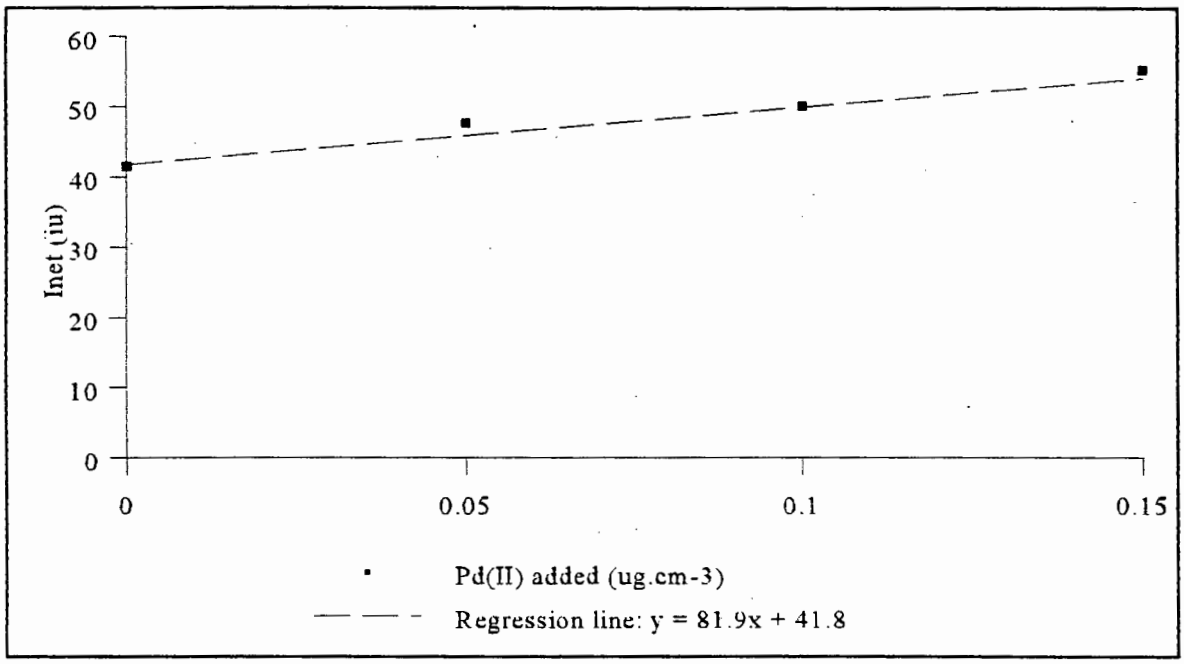

Figure 7.5.1: Palladium(II) standard addition curve for the IP effluent sample

Solving the linear regression line ($R^2 = 0.996$) at y = 0, yields an initial palladium(II) concentration of 510 +- 17 $ng.cm^{-3}$ for the IP effluent sample. This compared well to the palladium(II) concentration of 517 +- 31 $ng.cm^{-3}$ obtained previously by direct determination of the pre-concentrated IP effluent in **7.2**.

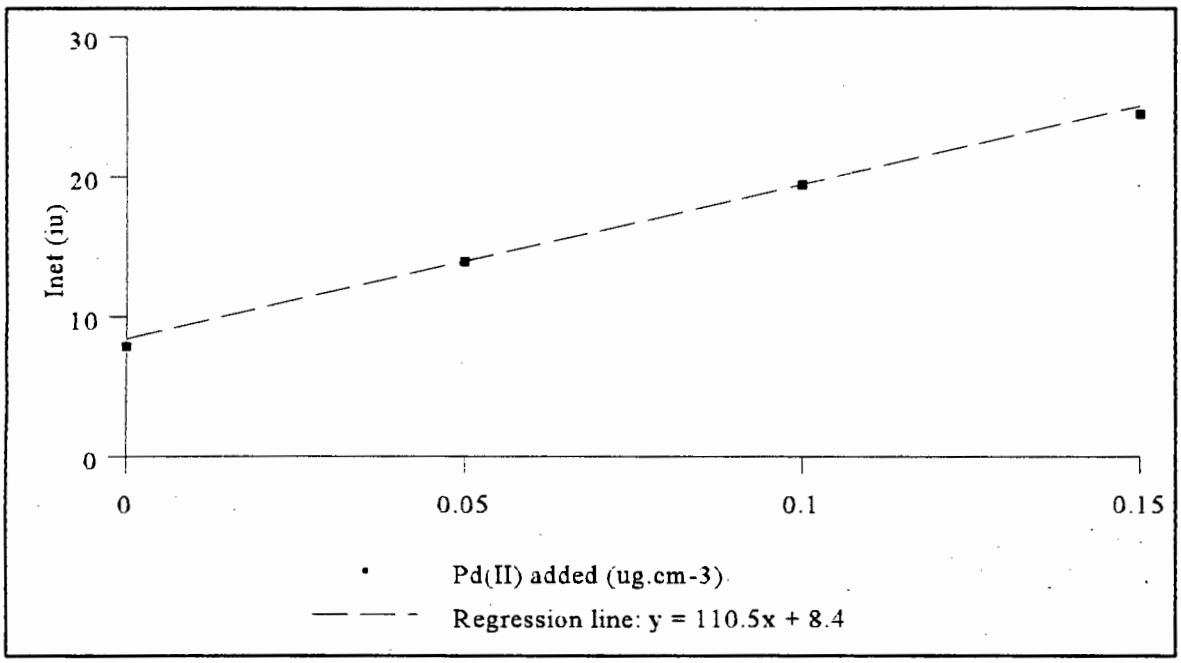

Figure 7.5.2: Palladium(II) standard addition curve for the AP effluent sample

Solving the linear regression line ($R^2 = 0.998$) at $y = 0$, yields an initial palladium(II) concentration of 74 +- 1 $ng.cm^{-3}$ for the AP effluent sample. This compared well to the palladium(II) concentration of 80 +- 11 $ng.cm^{-3}$ obtained previously by direct determination of the pre-concentrated AP effluent in **7.2**.

Table 7.5.1: Platinum(IV) content determined in real post-processing effluent by standard addition

Effluent sample	Pt(IV) added to effluent sample prior to pre-concentration ($ng.cm^{-3}$)	Volume of effluent pre-concentrated (cm^3)	Eluent volume (cm^3)	Mean uncorrected intensity of the sample (iu)	Mean corrected intensity of the sample ($I_b = 1.13$) (iu)
IP	0	18.6	9.5	2.18	1.05
	50	20.1	9.7	3.71	2.58
	100	25.2	10.0	5.33	4.20
	150	19.9	10.2	6.89	5.76
AP	0	22.4	9.6	1.38	0.25
	50	19.6	9.5	1.68	0.55
	100	21.3	9.3	2.02	0.89

Effluent sample	Pt(IV) added to effluent sample prior to pre-concentration ($ng.cm^{-3}$)	Volume of effluent pre-concentrated (cm^3)	Eluent volume (cm^3)	Mean uncorrected intensity of the sample (iu)	Mean corrected intensity of the sample (I_b = 1.13) (iu)
AP	150	20.0	10.4	2.33	1.20

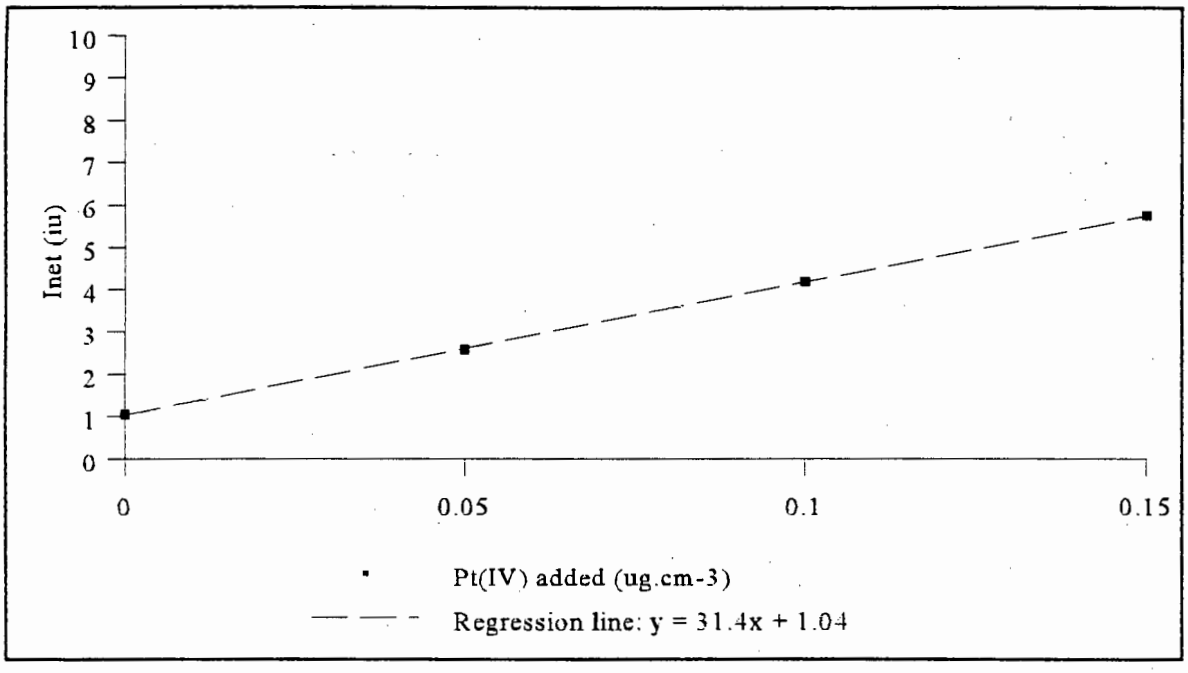

Figure 7.5.3: Platinum(IV) standard addition curve for the IP effluent sample

Solving the linear regression line ($R^2 = 0.995$) at y = 0, yields an initial platinum(IV) concentration of 33 +- 1.7 $ng.cm^{-3}$ for the IP effluent sample. This compared well to the platinum(IV) concentration of 34 +- 3.4 $ng.cm^{-3}$ obtained previously by direct determination of the pre-concentrated IP effluent in **7.3**.

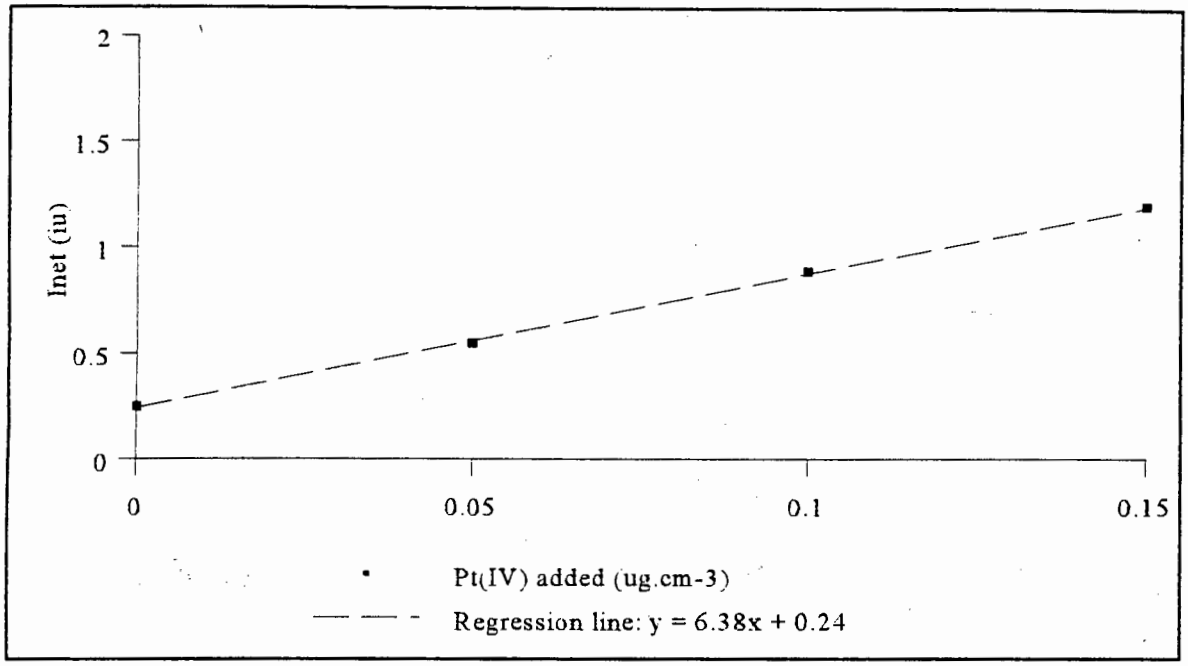

Figure 7.5.4: Platinum(IV) standard addition curve for the AP effluent sample

Solving the linear regression line ($R^2 = 0.999$) at $y = 0$, yields an initial platinum(IV) concentration of 38 +- 1.9 $ng.cm^{-3}$ for the AP effluent sample.

At these trace concentration levels, this was in agreement with the platinum(IV) concentration of 32.4 +- 3.4 $ng.cm^{-3}$ obtained previously by direct determination of the pre-concentrated AP effluent in **7.3**.

7.6 Conclusion

Through the use of real post-processing effluent samples, it has been demonstrated that the developed system quantitatively pre-concentrates palladium(II) and platinum(IV/II), accurately and reproducibly, from the complex matrices of the real post-processing effluent samples. The actual oxidation state of the platinum in the samples was found not to reduce the sensitivity of the analysis, nor did the oxidation state of the platinum affect the percentage recovery of the platinum from the pre-concentrated samples (**7.3** and **7.4**). Additionally, high relative concentrations of the 1st row transition metals (**7.2**) concomitant with the platinum-group metals present in the effluent samples, were found not to interfere with the pre-concentration and quantitative recovery of the palladium(II) and platinum(IV/II).

The data obtained from pre-concentration and subsequent determination of the post-processing

effluent samples was supported by results obtained from the standard addition experiments performed on the post-processing effluent samples.

Chapter 8

Final Conclusions

8.1 Summary

Conventional treatment of the effluent solutions produced in the recovery and refining processes (**1.4**) of the platinum-group metals is known to recover most of the residual platinum-group metals (mainly platinum and palladium). However, considering the volumes of post-processing effluent cycled to waste by South African producers, even trace levels of unrecovered platinum and palladium in post-processing effluent accumulate to represent a substantial annual loss of income. Additionally, classical chemical and instrumental methods (**2.1 and 3.1**) for platinum-group metal analysis were found not to be well suited to routinue analysis, at trace and ultra trace concentrations, of a complex, chemical matrix, such as post-processing effluent and the more successful methods were time-consuming and cumbersome. Consequently, failure to accurately and reproducibly quantify the platinum-group metal content of post-processing effluent cycled to waste results in a significant error in plant process control.

In this work a pre-concentration system with subsequent ICP-OES determination was developed, fully optimised and evaluated first on synthetic effluent solutions and finally, on two real effluent samples. The results of the developed system using synthetic effluent solutions (**6.1**) indicated that the underlying principle of the developed system had exceptional merit for the pre-concentration and determination of the platinum-group metals from complex matrices, at trace concentrations. The refined pre-concentraton and determination steps as developed in this study resulted in accurate and reproducible pre-concentration and determination of the platinum-group metals from synthetic effluent solutions. The advantage of such accurate and reproducible pre-concentration and determination for synthetic effluent analysis were supported by the experimental data presented.

Pre-concentration and determination of the platinum-group metals present in real post-processing effluent was the ultimate goal of this work and experimental work conducted on two real post-processing effluent samples with the developed system, proved acceptably accurate and reproducible, and appeared to be quite suitable for routine application by South African platinum-

group metal producers.

An unexpected result of the research was the uncatalysed complexation of Pt(IV) with *N-benzoyl-N', N'-di(2-hydroxyethyl)thiourea*. This class of ligands, whilst selective for the platinum-group metals in acidic solutions, has not been known to complex with Pt(IV) until this study. Pt(II) co-ordination with this class of ligands is well-understood and well documented, but the complexation of Pt(IV) has not been described. This is due to the Pt(IV) ion low-spin d^6 electronic configuration, resulting in characteristically inert substitution reactions for Pt(IV).

This unexpected complexation between *N-benzoyl-N', N'-di(2-hydroxyethyl)thiourea* and Pt(IV) directly in the effluent led to a preliminary investigation into the specific speciation of the Pt(IV)-ligand complex in the effluent samples - in order to understand the fundamental chemistry of the pre-concentration step and so to control it more effectively. To elucidate the speciation of the Pt(IV)-ligand complex, experiments were designed utilising UV-Vis Spectrophotometry and NMR techniques (Figure 8.1.1 and 8.1.2).

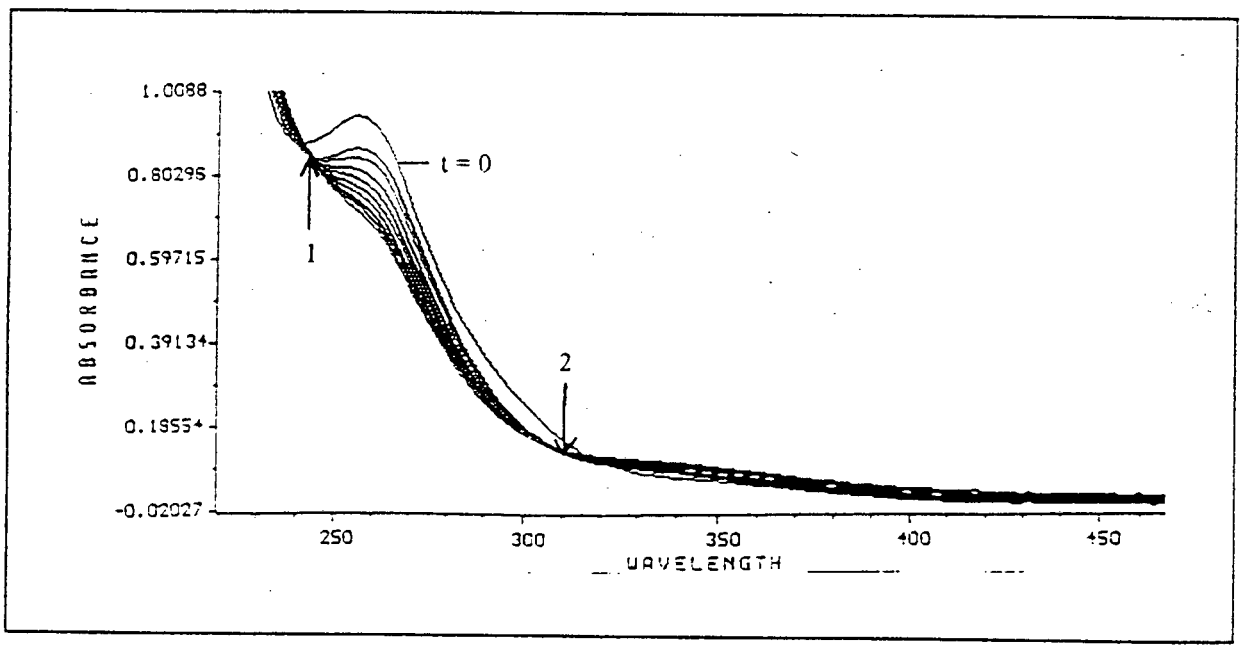

Figure 8.1.1: UV spectrum of the Pt(IV)-ligand complex vs time (Scanned at 5 min intervals at 60 °C)

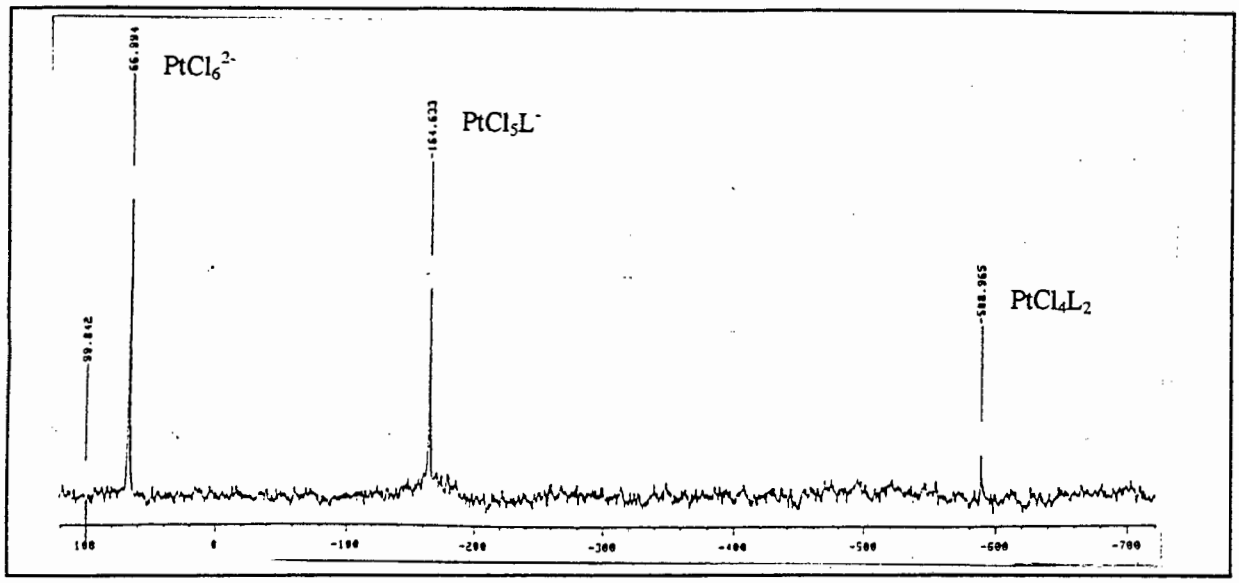

Figure 8.1.2: ^{195}Pt NMR spectrum of the Pt(IV)-ligand complex (where L=*N-benzoyl-N', N'-di(2-hydroxyethyl)thiourea*)

The UV spectrum of the Pt(IV)-ligand complex showed the presence of two isosbestic points at 245 nm and 310 nm respectively. The presence of two isosbestic points indicated that in the complexation of the ligand with Pt(IV), there were two reaction equilibria and therefore at least three species present in solution.

The ^{195}Pt NMR spectrum of the Pt(IV)-ligand complex, was in agreement with the UV spectra. Three ^{195}Pt peaks were present in the spectra at 66.9, -164.6 and -588.9 ppm, respectively (the preliminary assignment of the species is indicated in Figure 8.1.2) [1].

8.2 Future Work

The ability to pre-concentrate and determine platinum-group metals, at trace concentrations, in post-processing effluents introduced in this work should be expanded to encompass a greater variety of real post-processing effluents. The analysis of real post-processing effluents was limited to two samples in this study, due to the resistance from South African platinum-group metal producers in supplying effluent samples for investigation, for company confidentiality and security reasons.

For commercial application of the developed method a polymeric sorbent would be preferred, based on the monomer utilised in this study, further reducing the pre-concentration complexity of the developed sytem. This polymeric sorbent would need to be synthesised, possibly by grafting the monomer utilised in this work onto a polycarbamate or polyethylene 'backbone'.

The preliminary investigation into the Pt(IV)-ligand complex species formed during pre-concentration deserves further in-depth study, ultimately resulting in a conclusive elucidation of all of the Pt(IV)-ligand complex species present, thus contributing substantially to the knowledge of uncatalysed substitution reactions and kinetics of Pt(IV).

8.3 References

1. Pregosin, P.S., *Coord. Chem Rev.*, 1982, **44**, 247

Chapter 9

Experimental

9.1 Chemicals, Reagents and Glassware

All experimental work was carried out using analytically pure chemicals and reagents from various suppliers. 99.97 +- 0.01% pure palladium and platinum metal was loaned from Impala Platinum Limited. $RhCl_3 \cdot nH_2O$ was loaned from Johnson Matthey Chemicals Limited. $(NH_4)_2PtCl_6$ was loaned from Amplats Limited. Thiourea, $(NH_2)_2CS$ (Analar grade); benzoyl chloride, C_6H_5Cl (Analar grade); potassium thiocyanate, KSCN (Analar grade); diethanolamine, $(HOCH_2CH_2)_2NH$ (Analar grade) and tin(II) chloride, $SnCl_2 \cdot 2H_2O$ (Analar grade) were obtained from E. Merck, Darmstadt. Acetone, $(CH_3)_2CO$ (Analar grade) and methanol, CH_3OH (Analar grade) were obtained from Sigma-Aldrich.

Thiourea solutions were prepared weekly by dissolving 50 g thiourea in 10 cm^3 deionised water and 169.4 cm^3 concentrated perchloric acid, in a 1000 cm^3 volumetric flask. The cloudy solution was allowed to stand for ten minutes in a warm water bath until the solution cleared. The clear solution was then cooled and diluted to volume with deionised water (MQW). Perchloric acid concentrations were kept at 2 M to prevent hydrolysis of the thiourea. Tin(II) chloride solutions were freshly prepared by dissolution of the desired amount of salt in 50 cm^3 concentrated hydrochloric acid. The initially cloudy solution was allowed to stand for 15 - 20 minutes in a warm water bath until the solution cleared. The solution was then cooled and diluted to volume with MQW. Metallic tin pieces (5 g) were added to all the tin(II) chloride solutions to prevent oxidation of the solution by atmospheric oxygen. Hydrochloric acid concentrations of the final solutions were kept at 0.5 M to prevent the hydrolysis of the tin(II) chloride [1]. All tin(II) chloride solutions were used within 48 hours of preparation.

All solutions were prepared using fresh MQW. Analytical grade concentrated hydrochloric acid (31.5 % - 10 M) and concentrated perchloric acid (70% - 12 M) were used directly. The concentrations of the noble metal stock solutions were standardised against commercially available atomic absorption standards, by inductively coupled plasma-optical emission spectrometry.

Glassware was soaked in diluted TRITON X-100, and subsequently overnight in 10% nitric acid. Glassware was rinsed thoroughly several times with MQW and allowed to dry on a drying rack, before use. A mixture of A and B grade glassware (volumetric apparatus) was used throughout. Two Gilson adjustable pipettes (1 cm^3 and 10 cm^3 dispensing capacities) previously calibrated by weighing the dispensed volumes, were used. Grade A pipettes (10 - 50 cm^3) were used for larger volumes. A Mettler four decimal place balance was used for all weighing and an electronic top-loading balance for all rough weighing. Ultraviolet and visible spectrophotometry was performed on a HP UV-VIS diode-array spectrophotometer with a path length (l) of 5 mm. Inductively coupled plasma-optical emission spectrometry was performed on a Jobin Yvon JY 70C combined simultaneous and sequential instrument with a 486 DX 33 MHz IBM computer with VGA monitor and JY version 4.0 Quantitative and control software package.

9.2 Preparation of *N-benzoyl-N', N'-di(2-hydroxyethyl)thiourea*

Under nitrogen, dry KSCN (0.8096 g, 0.016 mol) was dissolved in dry acetone (50 cm^3) in a 2-necked round-bottomed flask fitted with a pressure compensated dropping funnel and a condensor. Benzoyl chloride (1.0544 g, 0.015 mol) dissolved in dry acetone (60 cm^3) was then added dropwise to the stirred KSCN solution, precipitating potassium chloride in the process. The solution was then heated under reflux for 45 min. Subsequently, diethanolamine (2.1014 g, 0.020 mol) dissolved in dry acetone (50 cm^3), was added dropwise to the mixture, which was heated under reflux for a further 45 min. The reaction mixture was allowed to cool before pouring into ice water (160 cm^3), followed by refrigeration overnight to precipitate the product. After refrigeration of the reaction mixture, the acetone was evaporated off and the product collected by filtration and dried *in vacuo* for 4 hours. The dry crystals were recrystallised from water/ethanol [2]. Crude yield: 3.5473 g (13.236 mmol, 88.2%). Recrystallised yield. 3.1171 g (11.631 mmol, 77.5%); m.p. 121-123°C (lit.[3] m.p. 123-125°C). Elemental analysis, calculated for $C_{12}H_{16}N_2O_3S$: C, 53.7; H, 6.0; N, 10.4; S, 11.9%. Found: C, 53.7; H, 6.0; N, 10.5; S, 11.2%.

9.3 Platinum-Group Metal Pre-concentration Studies

Synthetic effluent solutions were made up in 500 cm^3 pyrex bottles. The required quantity of palladium(II) and/or platinum(IV) and/or platinum(II) was pipetted directly into the bottle, along

with the various interfering elements (e.g. Na^+, Cl^-, Cu^{2+}, etc.) for the parameters being studied. Subsequently, the required amount of ligand was added to equal a 1:20 (metal: ligand) ratio (optimised). The solution was then made to volume (100 cm^3) with 2 M perchloric or 2 M hydrochloric acid. In the case of palladium(II) or platinum(II), the prepared solution was directly presented to the semi-automated pre-concentration instrument for pre-concentration onto the C_{18} reverse-phase column (**9.5**). Platinum(IV) solutions, after addition of the ligand, were heated at 60°C in a warm water bath for 30 min. This heating procedure was required for complexation to occur between the ligand and the platinum(IV) in solution.

9.4 Inductively-Coupled Plasma-Optical Emission Spectroscopy of Palladium and Platinum

Palladium(II) stock solutions were prepared by the addition of 0.506 g (99.97% pure) palladium metal added to aqua regia (20 cm^3) in a 400 cm^3 beaker and allowed to stand, covered, for one hour. Subsequently, the solution was placed on a gentle hotplate for one to two hours, until all the nitric acid had boiled off as NO_2. The solution was then cooled and washed, quantitatively, into a 500 cm^3 volumetric flask using MQW. After quantitative transferal of the solution, 42.5 cm^3 concentrated hydrochloric acid was added and the solution cooled and made to volume with MQW. The solution was mixed and compared to a commercial atomic absorption standard. Platinum(IV) stock solutions were prepared by dissolving the desired amount of solid $(NH_4)_2PtCl_6$ in 10 cm^3 concentrated hydrochloric acid, and making up to volume with MQW, to the appropriate hydrochloric acid concentration. Platinum(II) stock solutions were prepared by reduction of a platinum(IV) stock solution, with a 0.025 M tin(II) chloride solution, and diluted to volume with 2 M perchloric acid.

Palladium(II) and platinum(IV/II) calibration standards were prepared from the above stock solutions, by weighing the appropriate mass of stock solution into a 100 cm^3 volumetric flask and diluting to volume with a 20% methanol, 5% w/v thiourea solution in 2 M perchloric acid, to match the matrix of the standard to that of the eluted synthetic solutions being analysed. This negated the use of elaborate background corrections. A blank solution was prepared without the addition of palladium(II) or platinum(IV/II).

The JY 70C combined simultaneous and sequential instrument was used in all measurements. The

system was optimised (**5.1**) by aspirating a 2 $\mu g.cm^{-3}$ standard solution and adjusting all system variables to give maximum sensitivity and stability. The optimised ICP-OES system operating parameters are given in Table 9.4.1. These optimised parameters were used for the analysis of all synthetic and real effluent solutions. All analyses were performed in at least triplicate.

Table 9.4.1: Optimised ICP-OES system operating parameters

Instrumental parameters	Optimised value
Gas:	
Argon feed pressure	600 kPa
Secondary regulator (in source box)	200 kPa
Inner (aerosol) gas flow	0.35 dm^3min^{-1}
Intermediate (plasma) gas flow	0.10 dm^3min^{-1}
Outer (coolant) gas flow	18 dm^3min^{-1}
Observation height	18 mm above coil
Sample uptake	2.5 cm^3min^{-1}
RF power:	
Incident	1200 watt
Reflected	< 5 watt
Integration:	
Time	10 s
Replicates	3 - Simultaneous channels
	3 - Sequential channel
Analytical wavelengths	Pd(I) - 340.458 nm (seq.)
	Pd(I) - 340.458 nm (sim.)
	Pt(I) - 265.945 nm (sim.)
	Rh(I) - 343.439 nm (sim.)
	Pd(II) - 229.651 nm (seq.)
	Pt(II) - 214.423 nm (seq.)

The calibration curves for the atomic line - palladium(I) 340.458 nm, ionic line - palladium (II)

229.651 nm, atomic line - platinum(I) 265.945, ionic line - platinum(II) 214.423 nm and atomic line - rhodium(I) 343.489 nm were linear to 100 $\mu g.cm^{-3}$ (the maximum tested). Weekly verifications of the palladium(II) and platinum(IV/II) concentration in the standards and mixture solutions were performed. The sequential and simultaneous operational modes were both used in this work. No significant differences were found. Calibrations were repeated at regular intervals, before and after each batch of samples. Additionally a 5 $\mu g.cm^{-3}$ standard solution (appropriate to the platinum-group metal being studied) was sampled before, between and after each batch of samples, to evaluate instrumental short-and long -term reproducibility. Instrumental long term precision was better than 0.5% over the duration of the measurements.

Calibrations, using a minimum of four standards were repeated when the correlation was poor ($r < 0.997$), or in the case of a high relative standard deviation of individual data points. Some typical experimental calibration least-squares results are shown in Table 9.4.2.

Table 9.4.2: Linear least-squares equations for calibration curves of platinum, palladium and rhodium by ICP-OES.

Element	Wavelength (nm)	Slope	y-Intercept	Correlation coefficient (R^2)
Pd	340.458 (I)	79.2	183.3	0.999
Pd	229.651 (II)	52.7	118.9	0.999
Pt	265.945 (I)	10.4	0.056	0.998
Pt	214.423 (II)	11.7	74.24	0.999
Rh	343.489 (I)	0.01	0.053	1.000

9.5 Semi-automated Pre-concentration Apparatus

A Knapp logistics pre-concentration instrument (Figure 9.5.1) was used in this work, consisting of computer operated peristaltic pumps (P1, P2, P3 - 10 rollers), three internal selection valves (V1, V2, V3) and tubing connecting the whole system to a packed cellulose pre-concentration column (11 mm long, 7 mm i.d.). Pump flow tubing of 1.42 mm i.d. (Yellow tags) and 0.35 mm

i.d. (Black tags) was used. All tubing consisted of poly(tetrafluoroethylene) (PTFE). Tubing connections were made either with commercially available Omnifit PTFE or PEEK™ threaded connectors, or by push-fit connections. All long lengths of tubing were fixed to prevent movement and influence on the flow characteristics. Pump tubing was replaced periodically, depending on the condition of the tubes.

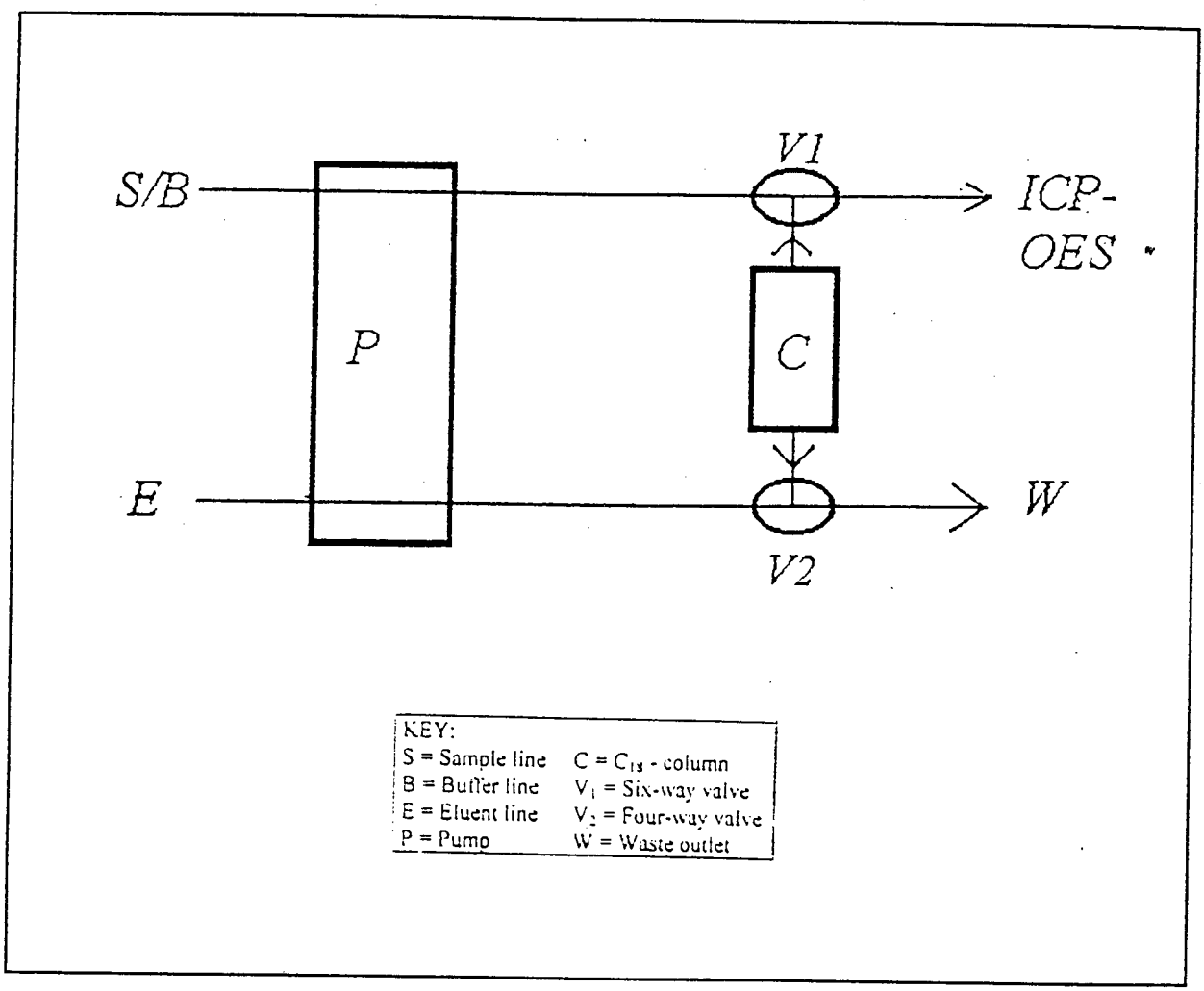

Figure 9.5.1: Schematic of the Knapp Logistics instrument and pre-concentration steps

The internal selection valves and cellulose column were not used in this work, instead the column was packed (to a height of 3 cm) with commercially available Isolute™ EC C_{18} reverse phase material (0.121 g) and two external selection valves from Rheodyne (Rheodyne, California, USA) were connected to the system. A model 5010 4-position selection valve and a model 5011 6-position selection valve were used. Both have uniform flow passages of 0.8 mm i.d. and internal

surfaces made of fluoropolymers - Teflon™ (stator) and Kel-F™ (rotor). The selection valves were pneumatically operated, manually, via an override switch. Pneumatic operators (operating at 70 psi minimum) and solenoid control valve kits (240-VAC) were supplied by Rheodyne. Nitrogen was used to drive the actuators.

Pump flow rates, for all pumps, were calibrated daily by volume vs time measurements and reproducible, computer-controlled pumping-times verified sample volumes pumped on the column at all times.

The use of a C_{18} reverse-phase packed column, required the column to be preconditioned with pure methanol (5 cm^3), followed by MQW (5 cm^3) before and after each analysis was run. This preconditioning of the column before and after each acidic sample, increased column lifetime by regeneration of the C_{18} reverse-phase material.

9.6 References

1. Auer, D., PhD Thesis, 1995, 198

2. Douglass, I. B. and Dains. F. B., *J. Am. Chem. Soc.*, 1934, **56**, 719

3. Koch, K. R., Sacht, C. and Bourne, S., *Inorg. Chim. Acta*, 1995, **232**, 109

Appendix A

Effluent Profile Scans

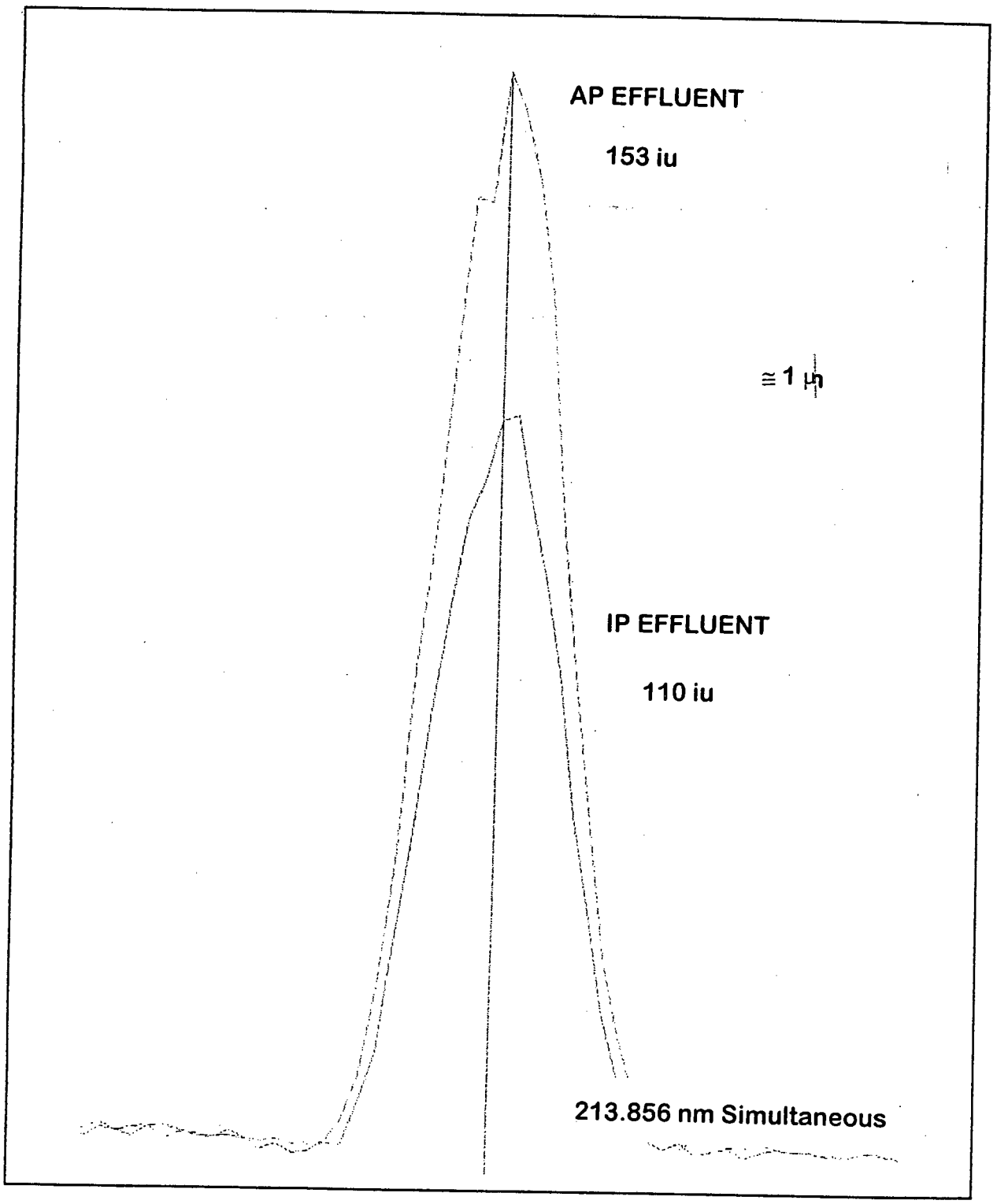

Figure A1: Presence of Zn in IP and AP effluent samples

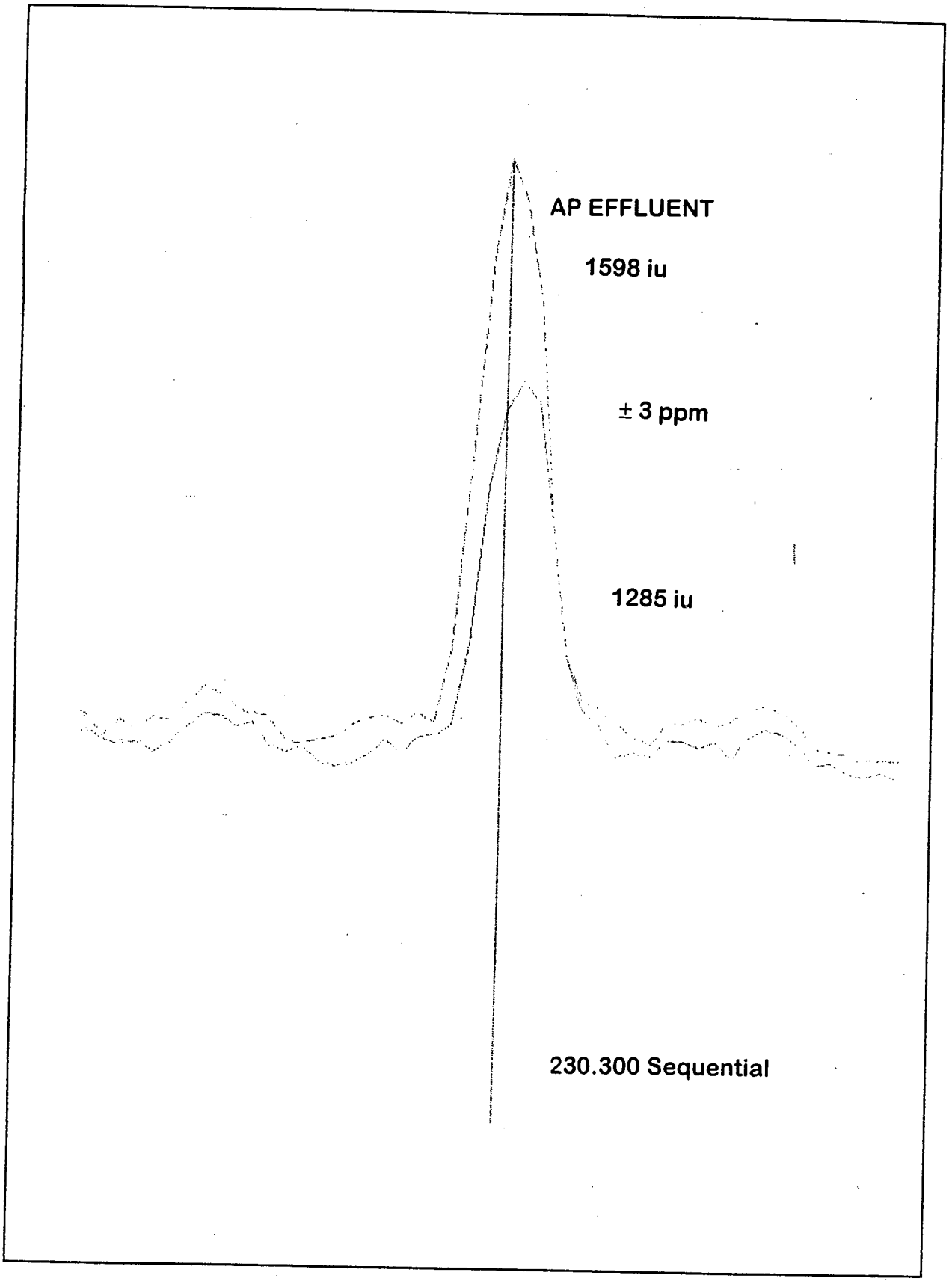

Figure A2: Presence of Ni in IP and AP effluent samples

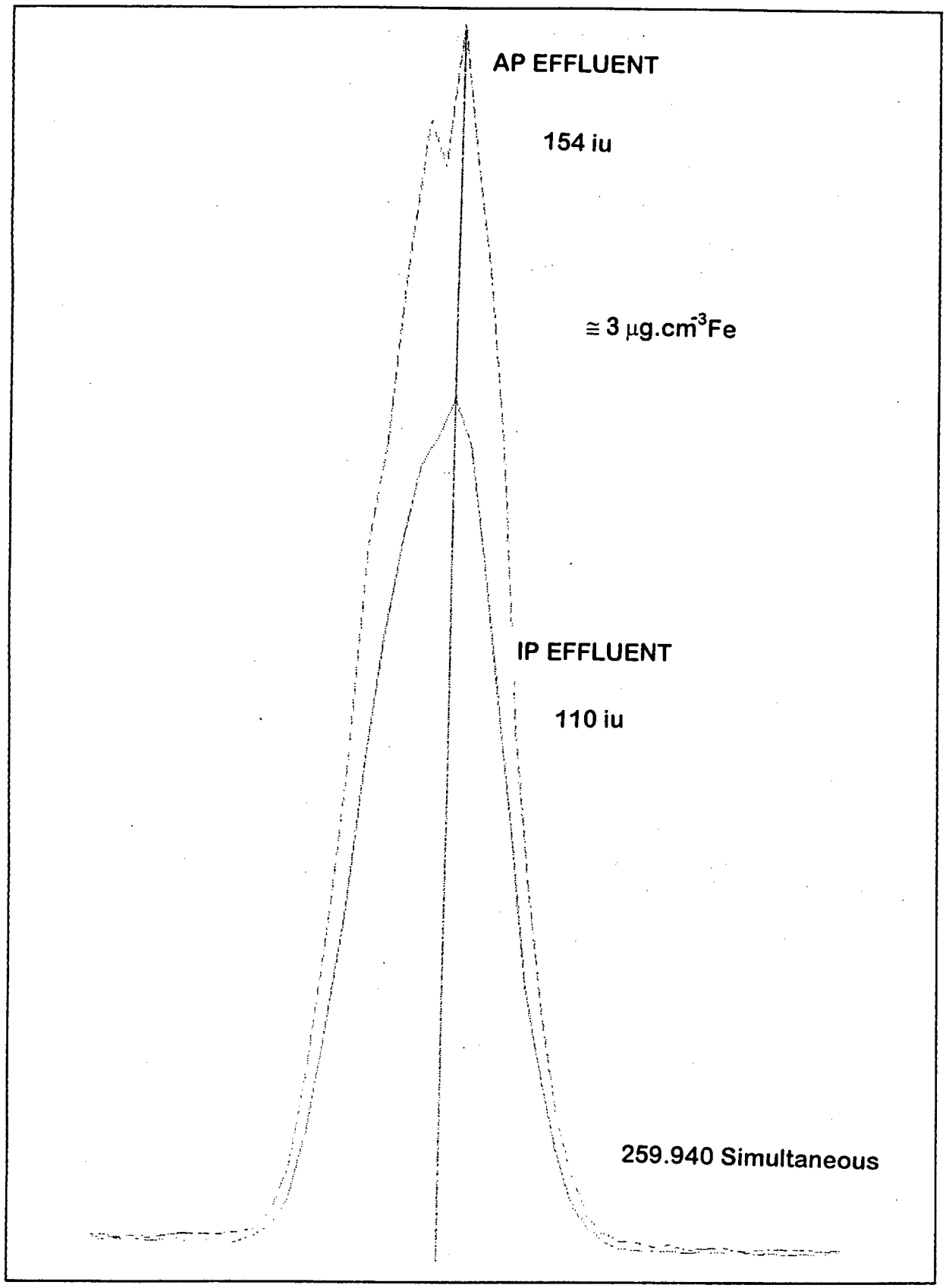

Figure A3: Presence of Fe in IP and AP effluent samples

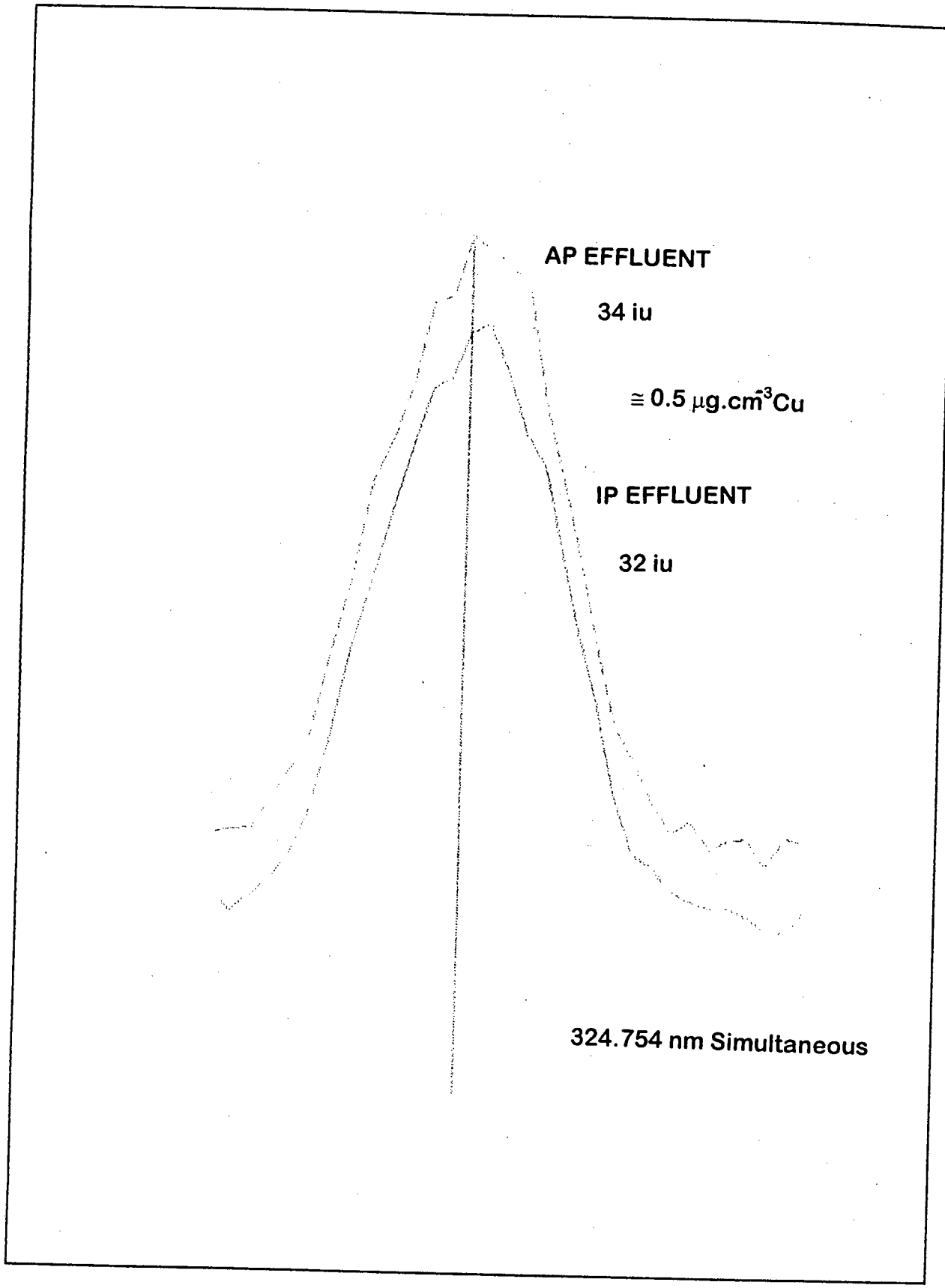

Figure A4: Presence of Cu in IP and AP effluent samples

Appendix B

Null Hypothesis Testing of Pt(IV) and Pt(II) content of IP and AP effluent samples

H_0: $\overline{x}_{(PtIV)} = \overline{x}_{(PtII)}$ and $H_1 = \overline{x}_{(PtIV)} \neq \overline{x}_{(PtII)}$

The critical value for the rejection of the null hypothesis is calculated by:

$\overline{x}_{(PtIV)} - \overline{x}_{(PtII)} = +- ts_{pooled} (N_1 + N_2/N_1N_2)^{1/2}$

For the IP effluent sample:

$\overline{x}_{(PtIV)} - \overline{x}_{(PtII)} = 34 - 35 = -1$ ng.cm^{-3}

$s_{pooled} = 3.06$ ng.cm^{-3} and $+- ts_{pooled} (N_1 + N_2/N_1N_2)^{1/2} = +- 4.47$ ng.cm^{-3} (where t = 2.31 for 8 degrees of freedom at the 95% Confidence Interval)

Since $\overline{x}_{(PtIV)} - \overline{x}_{(PtII)} < +- ts_{pooled} (N_1 + N_2/N_1N_2)^{1/2}$ then no difference in the IP effluent platinum content determined, as either Pt(IV) or Pt(II), has been established and the difference in the mean platinum content determined is due to indeterminate error only and H_0 is accepted.

For the AP effluent sample:

$\overline{x}_{(PtIV)} - \overline{x}_{(PtII)} = 32 - 34 = -1$ ng.cm^{-3}

$s_{pooled} = 2.94$ ng.cm^{-3} and $+- ts_{pooled} (N_1 + N_2/N_1N_2)^{1/2} = +- 4.29$ ng.cm^{-3} (where t = 2.31 for 8 degrees of freedom at the 95% Confidence Interval)

Since $\overline{x}_{(PtIV)} - \overline{x}_{(PtII)} < +- ts_{pooled} (N_1 + N_2/N_1N_2)^{1/2}$ then no difference in the AP effluent platinum content determined, as either Pt(IV) or Pt(II), has been established and the difference in the mean platinum content determined is due to indeterminate error only and H_0 is accepted.

Thus a change in the oxidation state of the platinum, does not affect the percentage recovery of platinum from the effluent samples.