

**Comparison of silica-based poly(amine) containing ion exchangers and their guanidine derivatives for selective PGM recovery from authentic refinery process solutions**

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

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## Abstract

The platinum group metals (PGMs: Pt, Pd, Rh, Ir, Os and Ru) occur in nature in close association with other transition metals, such as Fe, Cu, Ni and Co in often large quantities. The separation and refinement of the PGMs largely uses solvent extraction, and ion exchange methods and finally incorporates precipitation and redissolution steps in order to obtain the pure PGM products at the end. During the refinement, precipitation and redissolution steps, PGM losses occur which give rise to process effluents which are termed authentic refinery process (ARP) solutions in this thesis. These process solutions have PGMs in low concentrations that could not be recovered by the present recovery processes. We have synthesised silica-based poly(amine)-containing ion exchangers (monoamine (**N1**); ethylenediamine (**N2**) and diethylenetriamine (**N3**)) and their corresponding dimethylguanidine derivatives (**N1G-N3G**) and have tested their Pt, Pd, Rh and Ir recovery behaviour from four ARP solutions. The ARP solutions vary considerably in compositions with the pH of the solutions ranging between -0.6 to 5.0.

Palladium showed up to quantitative extraction from ARP solutions with the highest pH's (pH 3.2 and 5.0) with both types of ion exchangers. However, the Pt, Pd, Rh and Ir extractions were not so good under very acidic conditions (pH -0.6 and 0.2) for both types of ion exchangers. Maximum extractions were achieved at 60% (Ir), 54% (Pt), 46% (Rh) and 17% (Pd) with the **N3** ion exchanger. A possible explanation for the incomplete PGM extractions was the high unbound chloride concentrations competing with the ion exchanger for the binding sites as well as the unknown speciation of individual PGM complexes in the ARP solutions. An increase in extraction followed a general trend from: **N1** < **N2** < **N3**. A very good PGM selectivity over Cu, Ni, Co and Fe under very acidic conditions was demonstrated by both types of ion exchangers. At increased pH, the selectivity dropped with the use of poly(amine) ion exchangers while the corresponding dimethylguanidine counterparts retained the selectivity due to their high  $pK_a$  value. Quantitative desorptions were attained for Pd with the use of 5M HCl and the combination of 0.5M thiourea / 1M HCl solutions for both types of ion exchangers, while 60%-90% Ir and Rh desorptions could be achieved with 2M HNO<sub>3</sub>. In terms of the re-usability of the ion exchangers, the poly(amine) ion exchange material was more stable than the dimethylguanidine ion exchange material, under harsh desorption conditions (5M HCl). Overall, best successive recoveries were obtained for Pd (ca 35.0 mg/g ion exchanger) with the **N3** ion exchanger after 5 cycles of adsorption and desorption.

## Uittreksel

Die platinumgroepmetale (PGM's: Pt, Pd, Rh, Ir, Os en Ru) kom in die natuur te same met dikwels groot hoeveelhede ander oorgangsmetale soos Fe, Cu, Ni en Co voor. Vir die skeiding en rafinering van die PGM's word grootliks gebruik gemaak van vloeistofekstraksie, ionuittreilings metodes en uiteindelik volg presipiterings- en heroplossingsstappe om suiwer PGM-produkte daar te stel. Tydens rafinering, presipiterings- en heroplossingsstappe kom PGM-verliese voor wat aanleiding gee tot proseseffluente wat outentieke rafineringsprosesoplossings (ARP) genoem word in die tesis. Hierdie prosesoplossings bevat PGM's in lae konsentrasies wat nie herwin kan word met die huidige herwinningsprosesse nie. Ons het silika-gebaseerde poliamienbevattende ionuittreilers (monoamine (**N1**); etileendiamien (**N2**) en diëtileentriamien (**N3**)) en hul ooreenkomstige dimetielguanidienafgeleides (**N1G-N3G**) gesintetiseer en het hul Pt-, Pd-, Rh- en Ir-herwinningseienskappe vanuit vier ARP-oplossings getoets. Die ARP-oplossings verskil aansienlik in samestelling met pH's wat strek van -0.6 tot 5.0.

Palladium het die beste vertoon met tot kwantitatiewe ekstraksie met beide tipes ionuittreilers vanuit die ARP-oplossings met die hoogste pH's (pH 3.2 en 5.0). Die Pt, Pd, Rh en Ir, het egter, nie so goed vertoon onder sterk suur kondisies (pH - 0.6 en 0.2) vir beide tipes ionuittreilers. Die maksimum ekstraksie wat verkry is is 60% (Ir), 54% (Pt), 46% (Rh) and 17% (Pd) met die **N3** ionuittreiler. 'n Moontlike verklaring vir die onvolledige PGM-ekstraksie is die hoë konsentrasies van ongebinde chloried wat kompeteer met die ionuittreiler vir die bindingsplekke sowel as die onbekende spesiëring van individuele PGM-komplekse in die ARP-oplossings. 'n Toename in ekstraksie het 'n algemene tendens getoon van **N1** < **N2** < **N3**. 'n Baie goeie PGM-seleksie bo Cu, Ni, Co en Fe onder suur kondisies is getoon deur beide ionuittreilers. By hoër pH het die selektiwiteit verminder met die gebruik van die poliamien ionuittreilers terwyl die ooreenkomstige dimetielguanidien ekwivalente selektiwiteit behou het as gevolg van hul hoë  $pK_a$ -waarde. Kwantitatiewe desorpsie is verkry vir Pd met gebruik van 5M HCl en die kombinasie van 0.5M tioureum/1M HCl-oplossings vir beide tipes ionuittreilers, terwyl 60%-90% Ir en Rh desorpsie verkry is met 2M HNO<sub>3</sub>. In terme van die hergebruik van die ionuittreilers is die poliamien ionuittreil-materiaal meer stabiele as die dimetielguanidien ionuittreil-materiaal onder strawwe desorpsiekondisies (5M HCl). Oorkoepelend is die beste agtereenvolgende herwinning verkry vir Pd (ca 35.0 mg/g ionuittreiler) met die **N3** ionuittreiler na 5 siklusse van adsorpsie en desorpsie.

## Isifundo ngokufingqiwe

Izinhlobo zensimbi eyiplatinamu (ezifingqwe zaba yiPGMs: Pt, Pd, Rh, Ir, Os kanye ne Ru) zenzeka ngokwemvelo ekuhlanganiseni nasekudluliseleni kwesinye isimo izinsimbi ezifana nalezi Fe, Cu, Ni kanye ne Co kusamba esikhulu. Ukwahlukanisa nokucwenga kwe PGMs kusebenzisa ukutatululwa okuncibilikisiwe kanye nezindlela zoshintsho lwe-ayoni okuzothi ekugcineni luhlanganise amaphuthu noma ukuzukiswa lokwaphula, wahlukanise nokuthephula ukuze kutholakale umkhiqikizo wePGM ongaxutshwe nalutho ekugcineni. Ngesikhathi sokucwenga, sokwenza amaphuthu noma ukuzukisa, kuba khona ingcithakalo kuPGM okwenza kube khona okugobhozayo okubizwa uketshezana oluwunqothu olungenamsebenzi olufinqwe nge-ARP. Lo mbhubhudlo oncibilikisiwe unePGMs onokuqoqana noma ukusinga okunezinga elehlile okunokwenzeka lingabuye lizuzeke kulolu luhla lwamanje lokutholwa futhi. Sihlele imiqondo saxubanisa isilika eyisisekelo. Le silika eyisisekelo ebizwa phecelezi 'ipoly(amine)' equkethe ukwenanana kwe-ayoni (monoamine (**N1**) ethylenediamine (**N2**) kanye ne diethylenetriamine (**N3**) kwase kuvela lo mkhiqizo obizwa (**N1G-N3G**) kwase kuvivinywa iPt, Pd, Rh kanye ne Ir okuyisenzo esitholiwe esiqhamuka emibhubhudlweni emine ye-ARP emahlandlamane. Lo mbhubhudlo oncibilikisiwe uyangokwehluka ekuhlanganisweni kanye ne pH yokuncitshilisiwe okumaphakathi kuka -0.6 ukuya ku 5.0.

Ubuningi bephaladiyamu bubonakalisiwe lapho bekutatululwa khona lo mbhubhudlo we-ARP onezinga eliphezulu le pH (pH 3.2 kanye ne 5.0) kuzo zozimbili lezi zinhlobo zokwenanana kwe-ayoni (ion). Noma kunjalo-ke utatuluko lwe Pt, Pd, Rh, kanye ne Ir belungeluhle neze neze ngaphansi kwemibandela noma-ke izimiselo ze-asidi (pH -0.6 kanye no 0.2) kuzo zombili lezi zinhlobo zokwenanana kwe-ayoni (ion). Isibalo esigcwele salokhu kutatululwa sitholakele kumaphesenti angama 60 (Ir), 54 (Pt), 46 (Rh) kanye no 17 we (Pd) eno **N3** wokwenanana kwe-ayoni. Incazelo enokunikezwa yokutatuluka kwe PGM engaphelele bekuwukuqoqana okuphezulu kwe klorayide engaboshiwe eqhudelana nokwenanana kwe-ayoni ukubopha amahlangothi kanye nokungaziwa kohlobo oludephile lwe-PGM ekumbhubhudlo oncibilikisiwe lwe-ARP. Ukwenyuka kotatuluko kulandele inkambiso ethe yemé ukusuka ku **N1** < **N2** < **N3**. Ukukhethwa kwe PGM okudla ubhedu okuwelisa iCu, Ni, Co kanye ne Fe ngaphansi kwesimo esiyi-asidi kuvezwe ngezinhlobo ezimbili zokwenanana ze-ayoni (ion). Ku pH enyukile, ukukhetha kudle ngokwehla lapho kusetshenziswe khona ipoly(amine) yokwenanana kwe-ayoni, kwathi idemethylguanidine engumvumelanisi yagcina noma yagodla ukhetho ngenxa ye  $pK_a$

ephezulu. Sithe lapho sikhulula iPd yatholakala ngobuningi lapho sisebenzise u5M HCl nenhlanguanisela ye 0.5M thiourea/1M HCl ewumbhubhudlo yazo zozimbili lezi zihlobo zokwenanana kwe-ayoni, ngesikhathi sokukhululwa kwe Ir ne Rh okungamaphesenti angama 60 ukuya kwangama 90 kungazuzeka nge2M HNO<sub>3</sub>. Emkhawulweni wokuphinda kusetshenziswe ukwenanana kwe-ayoni, ukwenanana kwe-ayoni okuyi poly(amine) kubonakale kungaguquki uma kuqathaniswa nokwenanana kwe-ayoni yedimethylguanidine, ngaphansi kwesimo esibukhali sokusetshenziswa kwamakhemikhali (5M HCl). Ngokulingene konke, ukufumana okulandelanayo okuyingqayizivele okutholelwe iPd (ca 35.0 mg/g ngokwenanana kwe-ayoni) ngokusetshenziswa kukaN<sub>3</sub> (ongukwenanana kwe-ayoni) ngemuva kokuyingiliza okuyisihlanu (5) ukutatuluka kanye nokukhulula.

*"Never regard study as a duty, but as the enviable opportunity to learn to know the liberating influence of beauty in the realm of the spirit for your own personal joy and to the profit of the community to which your later work belongs"*

*- Albert Einstein*

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(mg L<sup>-1</sup>): ARP solution 3: Ir < 3, Pt 99 ± 11, Rh 44 ± 1 and Pd 298 ± 31, Cu ~ 440, Fe~110, Ni ~ 20; ARP solution 4: Pt 44 ± 4 and Pd 109 ± 7, Cu ~ 10, Fe~ 10 and Ni ~ 110 65

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## Abbreviations

### General

ARP	authentic refinery process
BMs	base metals
CP-MAS	Cross Polarisation-Magic Angle Spinning
c/s	counts per second
DMG	dimethylguanidine
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
MRR	Matthey Rustenburg Refiners
MQ	Milli-Q water
NMR	Nuclear Magnetic Resonance
N1	monoamine ion exchanger
N2	ethylenediamine ion exchanger
N3	diethylenetriamine ion exchanger
N4	triethylenetetramine ion exchanger
N5	tetraethylenepentamine ion exchanger
N1G	guanidine derivative of a monoamine ion exchanger
N2G	guanidine derivative of an ethylenediamine ion exchanger
N3G	guanidine derivative of a diethylenetriamine ion exchanger
PGE	platinum group element
PGMs	platinum group metals
PMR	precious metal refinery
ppm	parts per million
ppb	parts per billion
RBMR	Rustenburg Base Metal Refinery
ROM	run-of-mine
RSD	relative standard deviation
R <sup>2</sup>	linear correlation
TDS	total dissolved solid
UV	Ultra Violet

**Chemicals**

AgCl	silver chloride
AgNO <sub>3</sub>	silver nitrate
KOH	potassium hydroxide
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	potassium dichromate
HCl	hydrochloric acid
H <sub>2</sub> SO <sub>4</sub>	sulphuric acid
MIBK	methyl-isobutyl ketone
Na	sodium
Na-benzoate	sodium-benzoate
NH <sub>4</sub> OH	ammonium hydroxide
NH <sub>4</sub> NO <sub>3</sub>	ammonium nitrate
NH <sub>4</sub> SCN	ammonium thiocyanate
Tu	thiourea

## Chapter 1: Introduction

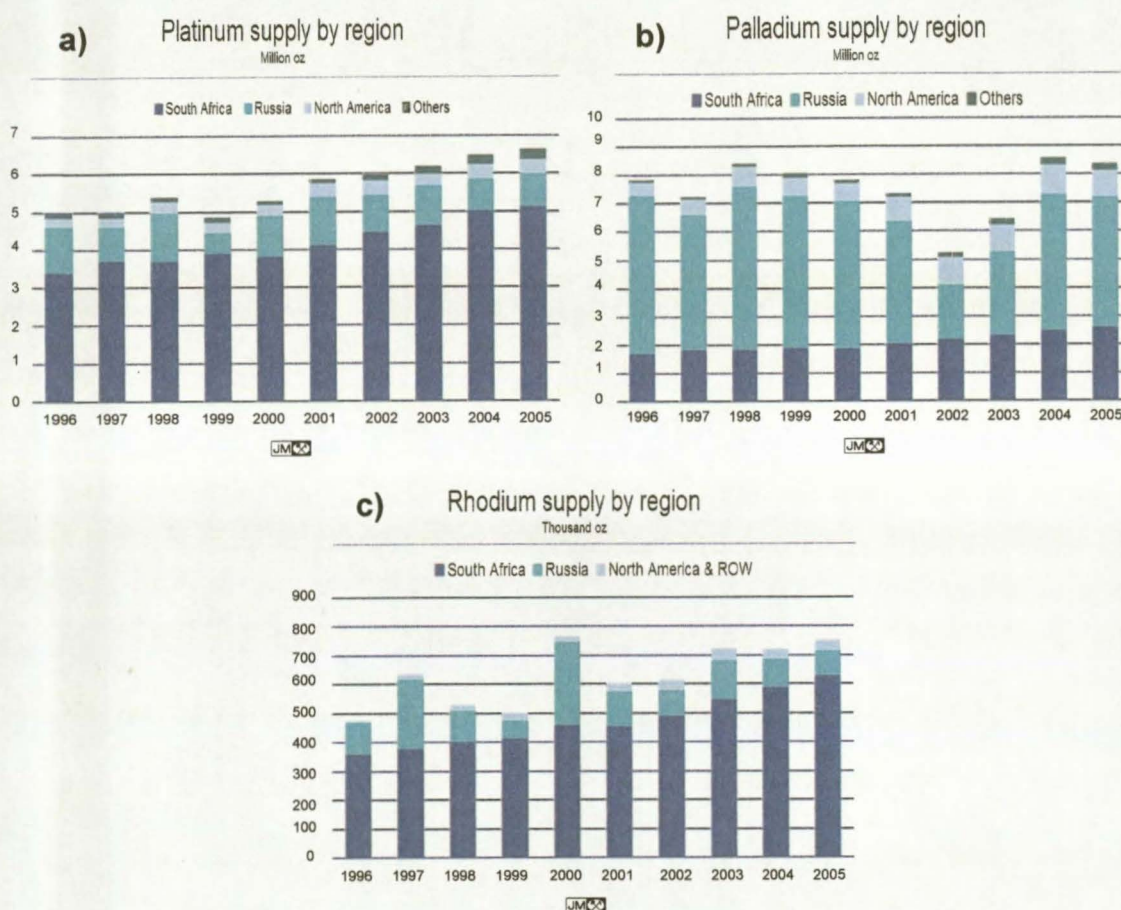
### 1.1 Discovery, Production and Application of the platinum group metals

The discovery of platinum dates back to 700 BC when it was found in ancient Egyptian artefacts, the famous one being the Casket of Thebes. In the 16th century, platinum was discovered by the Spanish Conquistadors whilst panning for gold in New Granada (now Colombia). The nuggets of gold were found to be mixed with some white metal nuggets, which were difficult to separate. The Spaniards named the white metal "*platina del Pinto*" or "little silver of the Pinto River". Scientific developments followed in the 18th century, where Scheffer, a Swedish researcher melted platinum by adding arsenic. In 1782, Lavoisier melted platinum completely by igniting it in charcoal and blowing upon it with oxygen <sup>[1-3]</sup>.

Another member of the platinum group metals, palladium, was discovered in 1802 by W. H. Wollaston through an investigation of refining of platinum in the 19th century, followed by the discovery of rhodium the following year. In the same year iridium and osmium were discovered by Smithson Tennant <sup>[1, 3]</sup>. Ruthenium is the last member of PGMs to be discovered by K. K. Klaus in 1844 <sup>[3]</sup>.

The work on refining the platinum group metals (PGMs: Pt, Pd, Rh, Ir, Ru and Os) also referred to as platinum group elements (PGE), began in England by Percival Norton John and George Matthey. In 1851, this collaboration gave birth to the partnership of Johnson and Matthey <sup>[1]</sup>. Johnson Matthey has continued to develop its technology for almost 200 years and their speciality focuses on its core skills such as catalysts, precious metals and fine chemicals. Their principal activities amongst other include refining, fabrication and marketing of precious metals <sup>[4]</sup>. Moreover, they are world leaders in precious metal refining technology <sup>[5]</sup>.

PGMs occur in nature in close association with one another and with other transition metals also called the base metals (BM), mainly copper, nickel, cobalt and iron [3, 6-8]. Over 98% of the world's PGM production is performed in three countries, South Africa, Canada and Russia [3]. Today, South Africa produces 74% of the world's platinum supply [9] and is also the predominant producer of Rh, whereas Russia has produced between 50-70% of Pd in the last decade (see *Figure 1.1*).



**Figure 1.1:** a) Platinum, b) palladium and c) rhodium supply by region for the past ten years [10-12].

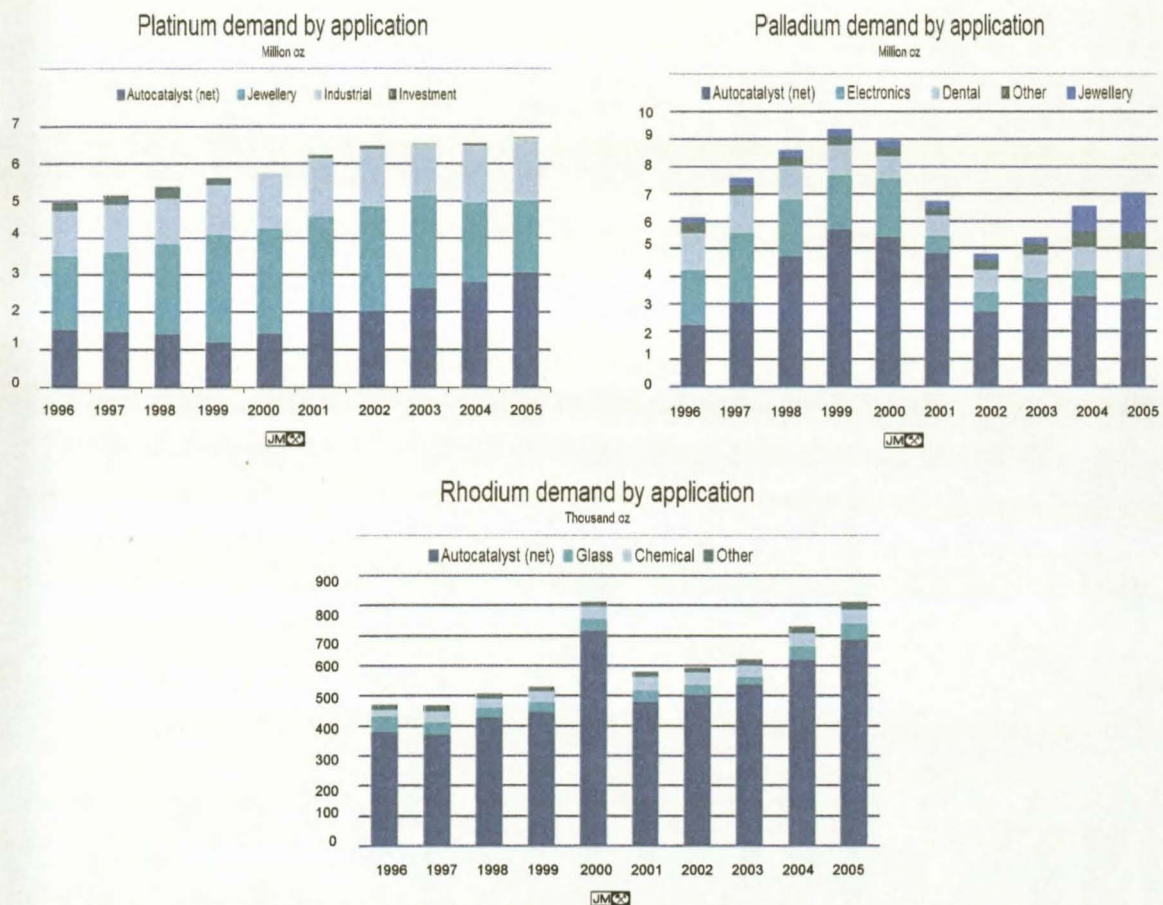
There is no question that South Africa and to a lesser extent, Russia will continue to dominate the world PGM output for the foreseeable future. These two countries have the largest deposits of Pt and Pd and thus produce the two metals as major products, respectively, while in other countries these metals are produced as by-

products. These other countries which also supply PGMs and whose ores are dominated by Ni-Cu deposits are in Canada (the Sudbury deposit), Russia (in Noril'sk-Talnakh), USA (in Duluth complex) and Northwest China (the Jinchuan deposits). The PGE-dominated deposits are the Merensky-type deposits which include the Platreef deposits, the UG2 chromitite, and the Merensky Reef itself located in South Africa. Zimbabwe (Great Dyke), Canada (Lac des Isles deposit) and the USA (Stillwater deposit) are among the few other countries with PGE-dominated deposits <sup>[13]</sup>.

The platinum-bearing ores in South Africa were discovered by Adolf Erasmus at the Waterburg District in the lode deposits in 1923. The next year, Andries Lombaard discovered the ores in Maandagshoek farm. From Lombaard's panning, the Pt-Fe alloy was identified by Hans Merensky and shortly afterwards within the broader Bushveld Igneous Complex, the Merensky reef was discovered. Today the Bushveld Complex hosts the world's largest reserves of PGMs. The ores also contain other transition metals such as Ni, Cu, Co and Fe in economically recoverable quantities <sup>[6, 13-15]</sup>.

The production of PGMs, in particular of Pt, has increased in the world over the years (shown in *Figure 1.1*). This growth is attributable to their increased use in a number of applications due to their technological importance (see *Figure 1.2*). The dominant and ever-growing application is in automobile exhaust emission control catalysts which accounted for 46% for Pt, 48% for Pd and 85% for Rh in 2005 as compared to other applications <sup>[10-12]</sup>. PGMs are also utilized in numerous other (industrial) applications including chemical catalysts, electronic components, dental alloys and computer hard discs, fuel cells for power generation, medicines and petroleum catalysts for gasoline refining. In the future, a potential application for

PGMs is fuel cells. The biggest PGM suppliers in South Africa are Anglo Platinum Limited, Impala Platinum Limited and Lonmin Platinum Limited. The mining industry is the key employer and has played the main role in the economic development of South Africa, as it contributed to 7% (in 2004) of the gross domestic product (GDP) [16]. High prices of these metals are also encouraging the development of PGM mining in other countries: currently (early October 2006), the individual PGMs cost around 1130 (Pt), 320 (Pd), 4800 (Rh), 400 (Ir) and 180 (Ru) (the prices are in US\$ per troy oz (~ 31.1 g)) [17].

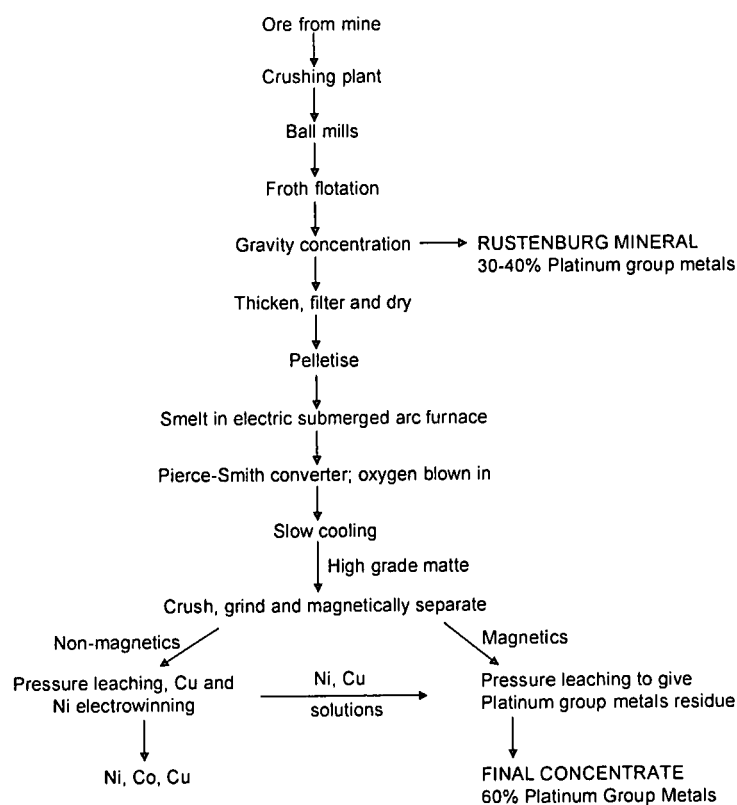


**Figure 1.2:** Various demand by application of Pt, Pd and Rh from 1996-2005 [10-12].

## 1.2 Primary versus secondary recovery

There are two types of recoveries of the PGMs: primary and secondary recovery. The latter involves the recovery of the precious metals after they have been used and they usually arise from different secondary sources. Some examples include the recovery of Pt from spent catalysts <sup>[18, 19]</sup> and scrapped catalytic converters <sup>[20, 21]</sup>. Furthermore, in the glass industry from the secondary Pt scrap containing Pd, Rh and Ir which arise from alloys or from enrichment due to multiple recycling of the construction elements <sup>[22]</sup>.

Primary recovery is the actual 'winning' of the PGMs from primary sources such as ores, black sand and placer gold <sup>[23]</sup>. In this thesis the focus is on the primary recovery of PGMs which entail the recovery of the metals from their ores prior to use.



**Figure 1.3** Extraction of the PGMs at the Rustenburg Mines Plant in 1980 <sup>[24]</sup>.



Figure 1.3 illustrates the impressive variety of processes employed in the treatment of the ore before final recovery of the PGMs from what is called the final concentrate (see Section 1.3.3) and these processes will be discussed in more detail in the next sections.

### 1.3 PGM refining

In the Merensky and UG2 ores, the PGMs are largely associated with other transition metal sulphides in the minerals Braggite (Pt,Pd,Ni)S, Cooperite (PtS), Laurite (RuS<sub>2</sub>) and Ferroplatinum (Fe/Pt) [6, 25, 26]. The concentration of the PGMs in the run-of-mine (ROM) ores from the three major sources in South Africa (mentioned in Section 1.1) ranges between 2 to 10 g ton<sup>-1</sup> (or ppm).

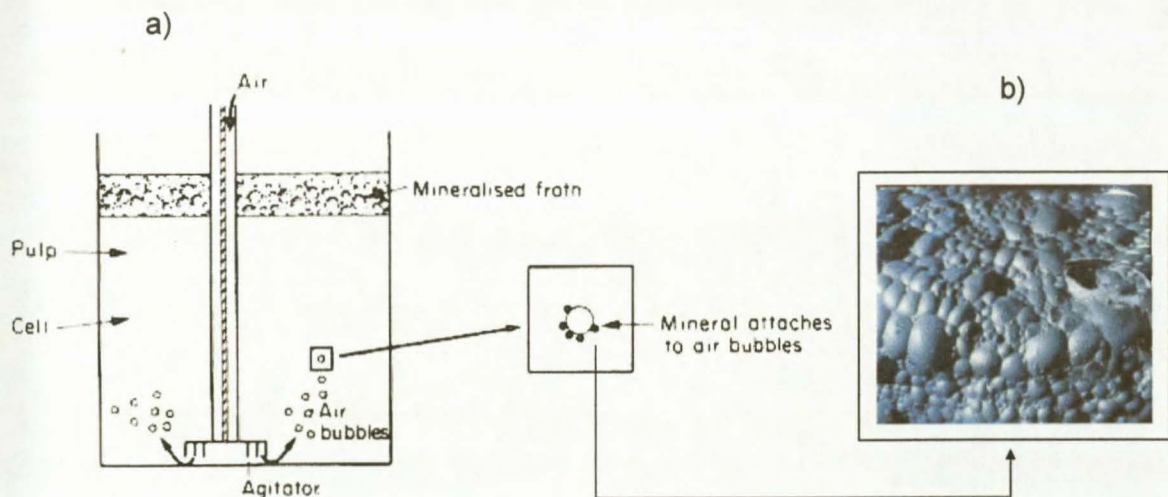
The separation processes required to yield a final saleable product are classified into three broad categories: (1) *mineral dressing* which employs crushing and separation of the ore into valuable substances using a variety of techniques [27] (2) *pyrometallurgy* is a process that utilizes chemical reactions at elevated temperature for the extraction of metals from the ores and concentrates [28] and (3) *hydrometallurgy* involves the extraction and recovery of metals from their ores via aqueous solution processes [29].

#### 1.3.1 Mineral Dressing

The first step in the production of the PGMs involves the treatment of the run-of-mine ore by *comminution*, which entails a sequence of crushing and grinding processes [30, 31]. These processes are initially performed underground and are employed further on the ore hoisted to the surface which eventually yields a product which has a particle size of between 1-6mm [31]. Water is added as a carrier to the crushed and

milled ore particles in order to produce a fine-grained product. This product is subjected to further size reduction by milling incorporating cyclone classifiers in order to liberate the minerals of interest from the silicate *gangue* (material of no economic value in the ore <sup>[32]</sup>).

The classifiers generally employed in industry are centrifugal (hydrocyclones) and mechanical (spiral and rake classifiers), and they are used to separate the coarse particles from the fine particles <sup>[33]</sup>. The fine-grained slurry product obtained is submitted to the flotation cells if the required particle size (200-300  $\mu\text{m}$ ) has been attained <sup>[31]</sup>, otherwise it undergoes a second-stage of grinding. This is then followed by the widely used operation in PGM mineral dressing called *froth flotation*, where the slurry product is treated with various chemicals rendering the minerals hydrophobic, before air is pumped through the liquid. As a result, the air bubbles rise to the surface and the reagents provide a stable froth to which PGM-particles and other minerals adhere to while the gangue particles are retained (see *Figure 1.4*).

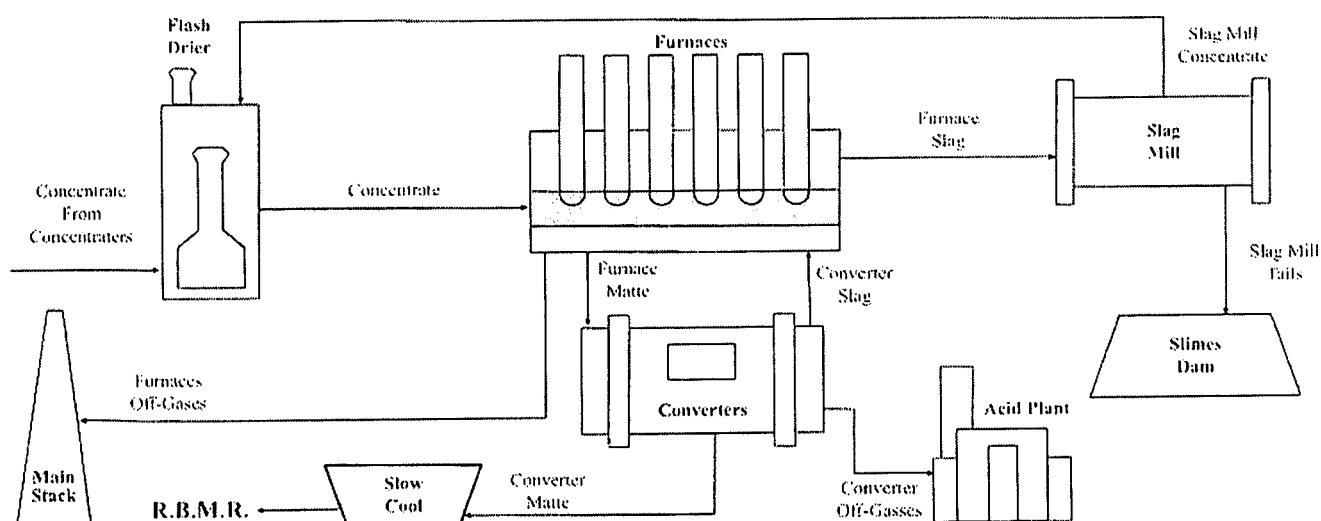


**Figure 1.4** a) Froth flotation process during PGM extraction from the ores and b) froth containing extracted PGMs and other minerals <sup>[30, 34]</sup>.

This process leads to a 97% gangue rejection hence a reduction from 1.000.000 tons of underground ore with an average PGM grade of 5 g ton<sup>-1</sup> to 30.000 tons of PGM grade at 135 g ton<sup>-1</sup> [25, 35]. Alternatively, gravity methods are also used to separate ore minerals from the gangue [13, 30].

### 1.3.2 Pyrometallurgy

This stage involves smelting of the flotation concentrates. A general flow sheet of the production of sulphur deficient Ni-Cu matte which is rich in PGMs as practised by Anglo Platinum in the Waterval Smelter of the Rustenburg Platinum Mines (in 2001) is depicted in *Scheme 1.1*. The concentrate is dried before it is fed directly into a furnace and smelted. The resulting heavy molten matte which collects at the base of the furnace is rich in Cu, Ni, other transition metals and the precious metals. The presence of other transition metal sulphides in the concentrates is essential, since they act as collectors of PGMs in the smelter furnaces [36]. The slag is then separated from the molten matte at about 1350 °C.



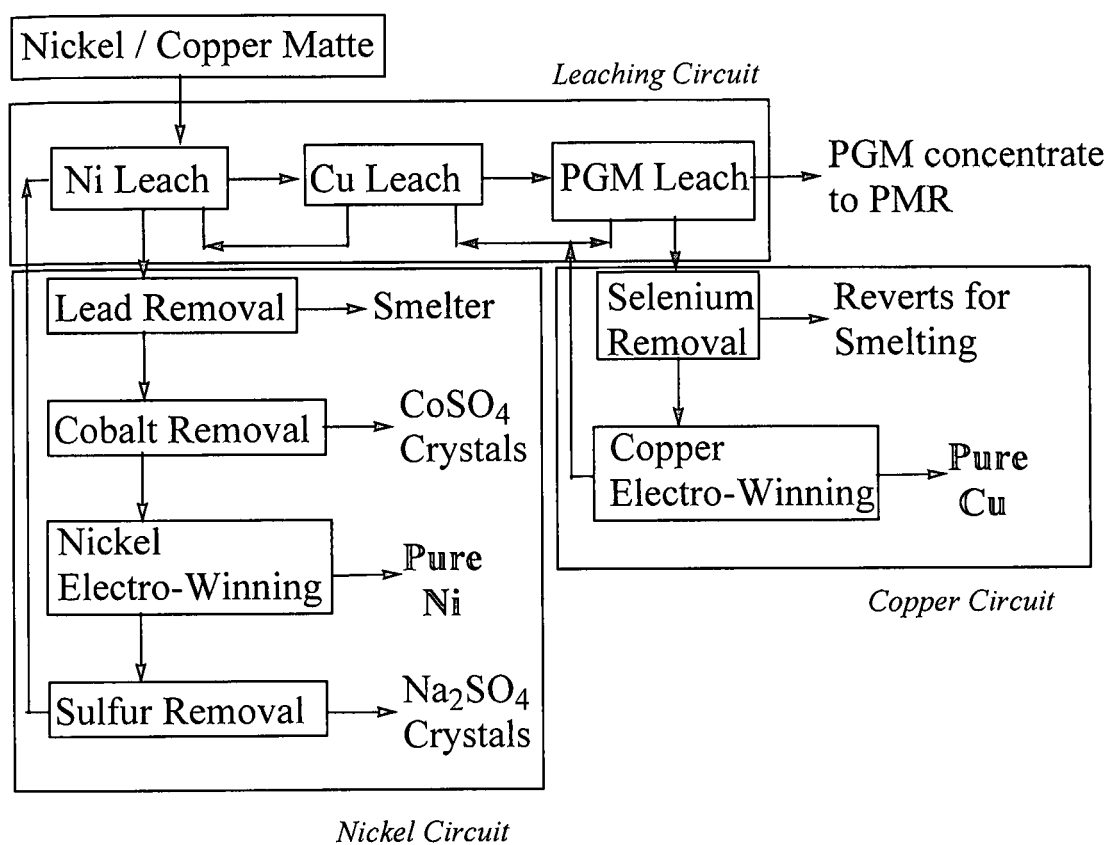
**Scheme 1.1** General flow sheet of the production of PGM-rich sulphur deficient Ni-Cu matte [37].

The slag which contains high metal content is usually granulated, refloats and returned to the furnace. The molten matte from the furnaces is tapped at about 1200 °C, poured into ladles and transported to the Pierce-Smith converters, where any iron present is oxidised with air or oxygen and subsequently removed to a great extent by the addition of silica sand to obtain iron silicates. Excess sulphur present in the matte is oxidised by air to form sulphur dioxide gas, which is then recovered as sulphuric acid or as elemental sulphur. The converter matte is allowed to cool to promote the formation and separation of the two phases, the Fe-Ni and the Cu-Ni phase. This cooled matte is crushed and ground into desired particle sizes to separate the two phases. The magnetic Fe-Ni matte which contains up to 95% of the precious metals passes through a series of magnetic separators leaving a Cu-Ni rich matte behind.

The PGM concentration from 30.000 tons grade of concentrate at 135 g ton<sup>-1</sup> is reduced to 1200 tons and thus yields 2000 to 4000 g ton<sup>-1</sup>. An average PGM percentage of approximately 0.32% is reached by now, and 99.8% gangue is rejected at this stage [25]. The magnetic concentrate is leached (selective aqueous acidic dissolution) in order to remove residual base metals, which is typically around 99% successful. The final PGM concentrate, containing between 50-60% PGMs at this stage) is transported to the precious metal refinery (PMR) where the PGMs are separated and refined (see next Section).

The non-magnetic Cu-Ni matte is treated at the base metal plant, which is divided into three major sections: the leaching circuit, the nickel circuit and the copper circuit (see *Scheme 1.2*) where Ni (and Co) and Cu are selectively extracted using sulphuric acid or by a chloride leaching route. The residue of these leaching stages is a PGM rich (30-60% PGMs) concentrate which is sent to the PMR. The

refining of Ni, Co and Cu takes place in separate circuits and Cu and Ni are finally won via electrolytic recovery.



**Scheme 1.2** Simplified Rustenburg Base Metal Refinery (RBMR) overview (in 2001) <sup>[37]</sup>

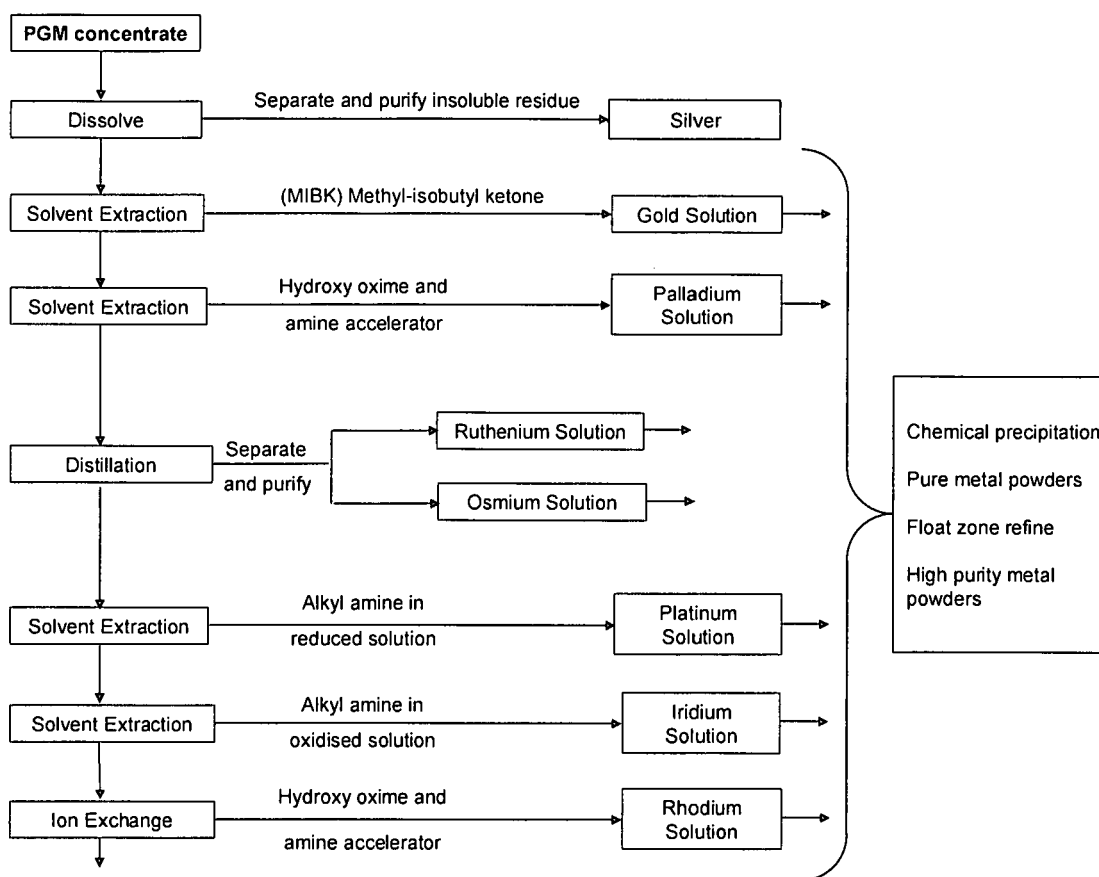
### 1.3.3 Hydrometallurgy

Refining comprises of a two-step operation, the first step being the recovery of other transition metals, followed by (second step) the recovery of precious metals. The precious metals solution and internal "reverts" which are then free of other transition metals are treated using conventional chloride technology. The primary step entails removal and separation of all the precious metals from the feed stock material received from the base metal refinery. The precious metals are then subjected to complete dissolution, and traditionally (up until mid 1970s <sup>[38]</sup>) selective precipitation

occurs, whereby the individual metals are separated and recovered as salts and impurities are eliminated. The purified salts of the precious metals are finally reduced by thermal decomposition leading to the production of the individual metals at very high purity of over 99.95% in their  $M^0$  oxidation state and final finishing into a saleable product which, dependent on the customers requirements, can be for instance as a sponge or as a bar or ingot <sup>[36, 39]</sup>.

*Scheme 1.3* shows an example of a typical modern refining method employed at the *Matthey Rustenburg Refiners* which incorporates ion exchange and solvent extraction techniques. These methods have been incorporated in the last decades to achieve a much more selective separation of the metals from one another.

It is clear that solvent extraction is prevalent in the separation steps. An important aspect in PGM refining involves the manipulation of the redox potential and the chloride ion concentration <sup>[31]</sup>.



**Scheme 1.3** Matthey Rustenburg Refiners (MRR) solvent extraction based precious metal refining flow-sheet in 2001 <sup>[25]</sup>.

A combination of hydrochloric acid and chlorine is commonly employed to dissolve the precious metals leading to a PGM concentrate containing about 60% PGMs <sup>[25, 38, 40]</sup>. Alternatively, *aqua regia* (a mixture of 1 HNO<sub>3</sub>:3 HCl) can be used to leach the precious metals because the mixture generates chlorine and nitrosyl chloride which are powerful oxidants <sup>[31]</sup>. Furthermore, hydrochloric acid complexes the metal ions leading to stable metal chlorides in solution (see Section 1.4.2).

Silver and gold are removed in the early stages of separations in order to avoid co-extraction of the metals later in the PGM extractions stages. Silver is precipitated as silver chloride with a low chloride concentration. Gold is then removed by solvent extraction using methyl-isobutyl ketone (MIBK).

The benefit of using MIBK is that it also extracts impurities such as iron and tellurium and consequently gives a cleaner solution for subsequent operations. The remaining PGMs are separated in their order of extractability. Although palladium ligand exchange is fast relative to the other PGMs (see *Table 1.3*) the extraction kinetics using hydroxy oximes are considered too slow, therefore this process is enhanced by the addition of amines <sup>[31]</sup>. Unfortunately, thereby the selectivity is decreased, i.e., without the addition of amines a palladium purity of > 99.9% can be attained, whereas with the amines a purity of > 99.5% can be achieved <sup>[41]</sup>.

Platinum is extracted under reducing conditions via a solvent extraction method using alkylamine (e.g. tri-n-octylamine <sup>[41]</sup>). The reducing conditions are applied to maintain the +3 oxidation state of Ir, thus avoiding co-extraction of this metal, since Ir in its +4 oxidation state is highly extractable by amines <sup>[40]</sup>. The subtle differences in extraction conditions demonstrate the complexity to achieve selective, fast and efficient recovery of the PGMs. Ruthenium and osmium are recovered by distillation as the tetraoxides (RuO<sub>4</sub> and OsO<sub>4</sub>) in their 8+ oxidation state <sup>[31, 38]</sup>. Iridium is then removed as Ir<sup>+4</sup> under oxidising conditions with an alkylamine <sup>[40]</sup>, leaving behind rhodium in the raffinate from the iridium solvent extraction. Rhodium is usually recovered last using ion exchange method. The time taken between mining of the ore to the final production of the pure metal requires complex processes that may take up to six months <sup>[35]</sup>. In case of Pd and Rh production time ranges between 6 to 20 weeks <sup>[39]</sup>.



## 1.4 Chemistry of PGMs in aqueous chloride media

### 1.4.1 Oxidation states

As already briefly touched upon in the previous section, the PGMs are characterized by their multiple oxidation states, something which is beneficial for their effective separation. These metals demonstrate an extremely varied chemical behaviour, which depends on their oxidation state and the chemical environment <sup>[26]</sup>. An overview of the oxidation states in 1 M HCl is given in *Table 1.1*.

**Table 1.1:** PGM oxidation states in 1M HCl <sup>[38]</sup>.

	<i>Ru</i>	<i>Rh</i>	<i>Pd</i>	<i>Os</i>	<i>Ir</i>	<i>Pt</i>
Reduction	<b>+3</b>	<b>+3</b>	<b>+2</b>	<b>+3</b>	<b>+3</b>	<b>+2</b>
↑	<b>+3</b>	<b>+3</b>	<b>+2</b>	<b>+4</b>	<b>+3</b>	<b>+4</b>
	<b>+4</b>	<b>+3</b>	<b>+2</b>	<b>+6</b>	<b>+4</b>	<b>+4</b>
↓	<b>+6</b>	<b>+4</b>	<b>+4</b>	<b>+8</b>	<b>+4</b>	<b>+4</b>
Oxidation	<b>+8</b>	<b>+4</b>	<b>+4</b>	<b>+8</b>	<b>+4</b>	<b>+4</b>

<sup>a</sup>The most stable oxidation states are denoted in bold.

### 1.4.2 PGM metal speciation

As an aqueous chloride environment is the most cost-effective medium in which all the PGMs can be brought into solution and concentrated, it is evident that a considerable amount of research has been performed into understanding the speciation of the PGM-halide complexes. An investigation of various PGM-halide and the mixed halide-aqua species (which form during aquation reactions, whereby a chloride ion is substituted by a water molecule in the PGM chloro complex) was carried out in the 1960-1970s with the use of electronic UV-visible absorption

spectrophotometry<sup>[42-44]</sup> and has been reviewed by Buslaeva and Simanova<sup>[45]</sup>. The PGM species found depend on the composition of the solution, in which the Cl<sup>-</sup> concentration and the pH of the solution plays a major role. An increase in the pH of the solution produce a mixture of complex species such as  $[MCl_{x-y-z}(H_2O)_y(OH)_z]^{n-x+y}$  and  $[MCl_{x-z}(OH)_z]^{n-x}$  which arise at different aquation and hydrolysis rates for individual metal ions<sup>[45]</sup>. Besides, dinuclear hydroxo or chloro bridged complexes and even polymeric complexes (for Rh) can also form, depending on the solution conditions.

The PGM chloro complexes shown in *Table 1.2* are described in an extensive review by Buslaeva and Simanova which is based on the findings of many different researchers. Most of the research done has been directed to Pt, Pd, Rh and Ir.

Leung and Hudson reported that Pt forms exclusively unaquated chloride complexes at all acid concentrations<sup>[46]</sup>. Indeed, Buslaeva *et. al.* confirmed that both Pt(II) and Pt(IV) form stable chloro complexes  $[PtCl_4]^{2-}$  and  $[PtCl_6]^{2-}$  in aqueous HCl and chloride solutions<sup>[45]</sup>. However from the data given in *Table 1.2*, it is evident that other Pt species will also be present in solution, depending on the conditions used:  $[PtCl_6]^{2-}$  is present from 0.05 M - 3.0 M and dominates at concentrations >3 M, whereas at 0.01 M HCl mixed complexes of chloro-aqua and chloro-hydroxo species exist.

Concerning Palladium, it becomes clear that the Pd(II) tetrachloro complex dominates and is exclusively present in >1 mol L<sup>-1</sup> HCl concentrations. Different from Pt, the complex is aquated with more ease, because  $[PdCl_4]^{2-}$  and  $[PdCl_3(H_2O)]^-$  chloro complexes coexist at  $0.1 < c_{Cl^-} < 0.5$  mol L<sup>-1</sup>.

**Table 1.2:** PGM oxidation states and their possible chloro (aqua/hydroxo) complexes  
[25, 31, 41, 45, 47]

Metal	Oxidation state	Co-ordination number	Structure	Complex	Composition of solution
Pt	+2	4	Square	$[\text{PtCl}_4]^{2-}$	> 0.1 M $\text{Cl}^-$
			planar	$[\text{PtCl}_4]^{2-}$ , $[\text{PtCl}_3(\text{H}_2\text{O})]^-$	1mM < $c_{\text{Cl}^-}$ < 0.1 M
	+4	8	Octahedral	$[\text{PtCl}_6]^{2-}$	>3 M HCl
				$[\text{PtCl}_6]^{2-}$ , $[\text{PtCl}_5(\text{H}_2\text{O})]^-$	0.1 M HCl
				$[\text{PtCl}_5(\text{H}_2\text{O})]^-$ ,	0.01 M HCl
				$[\text{PtCl}_5(\text{OH})]^{2-}$ ,	
				$[\text{PtCl}_4(\text{H}_2\text{O})_2]$ ,	0.05 M HCl
$[\text{PtCl}_4(\text{OH})_2]^{2-}$					
$[\text{PtCl}_5(\text{H}_2\text{O})]^-$ , $[\text{PtCl}_6]^{2-}$ ,					
$[\text{PtCl}_5(\text{OH})]^{2-}$					
Pd	+2	4	Square	$[\text{PdCl}_4]^{2-}$	>1 M HCl
			planar	$[\text{PdCl}_4]^{2-}$ , $[\text{PdCl}_3(\text{H}_2\text{O})]^-$	0.1 M < $c_{\text{Cl}^-}$ < 0.5 M
	+4	8	Octahedral	$[\text{PdCl}_6]^{2-}$	Highly oxidising conditions
Rh	+3	6	Octahedral	$[\text{RhCl}_6]^{3-}$	6.3-13 M HCl
				$[\text{RhCl}_6]^{3-}$ ,	4.5-6.0 M HCl
				$[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$	2.0-4.5 M HCl
				$[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$ , $[\text{RhCl}_6]^{3-}$	0.5-2.0 M HCl
				$[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$ ,	0.25-0.5 M HCl
				$[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$	0.0-0.25 M HCl
				$[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$	pH > 3
				$[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$ ,	
$[\text{RhCl}_3(\text{H}_2\text{O})_3]$					
$[\text{RhCl}_{6-n}(\text{H}_2\text{O})_{n-1}(\text{OH})]^{n-4}$					
Ir	+3	6	Octahedral	$[\text{IrCl}_6]^{3-}$	>3.0 M HCl
				$[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$ ,	0.1-3.0 M HCl
				$[\text{IrCl}_4(\text{H}_2\text{O})]^-$ ,	
				$[\text{IrCl}_4(\text{OH})_2]^{3-}$	0.01-0.05 M HCl
	$[\text{IrCl}_4(\text{H}_2\text{O})_2]^-$ ,				
	$[\text{IrCl}_4(\text{H}_2\text{O})_2]^-$ ,				
+4	6	Octahedral	$[\text{IrCl}_4(\text{OH})_2]^{3-}$ ,	>3.0 M HCl	
			$[\text{IrCl}_2(\text{H}_2\text{O})_4]^+$	0.1-3.0 M HCl	

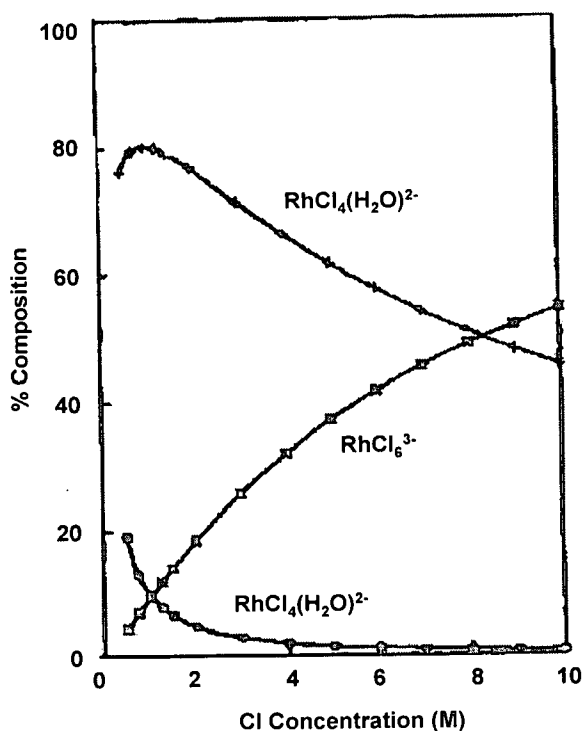
**Table 1.2: continued.**

				$[\text{IrCl}_6]^{2-}$ $[\text{IrCl}_6]^{2-}$ , $[\text{IrCl}_5(\text{H}_2\text{O})]^-$ , $[\text{IrCl}_4(\text{OH})_2]^{2-}$ $[\text{IrCl}_6]^{2-}$ , $[\text{IrCl}_5(\text{H}_2\text{O})]^-$ , $[\text{IrCl}_4(\text{OH})_2]^{2-}$	0.01-0.05 M HCl
Ru	+3	6	Octahedral	$[\text{RuCl}_6]^{3-}$	<sup>[b]</sup>
	+3	6	Octahedral	$[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$	—
	+4		Octahedral	$[\text{RuCl}_6]^{2-}$	
Os	+3	6	Octahedral	$[\text{OsCl}_6]^{3-}$ , $[\text{OsCl}_5(\text{H}_2\text{O})]^{2-}$	<sup>[b]</sup>
	+4	6	Octahedral	$[\text{OsCl}_6]^{2-}$	> ~1 M HCl
				$[\text{OsCl}_6]^{2-}$ , $[\text{OsCl}_5(\text{H}_2\text{O})]^-$	0.1-1.0 ( $\text{C}_{\text{Cl}^-}$ )

<sup>[a]</sup> Dinuclear and polymeric species are omitted for clarity <sup>[47]</sup>

<sup>[b]</sup> Concentrations unknown.

Alternatively, the speciation of Rh(III) under industrially relevant conditions is at considerable variance with both Pd and Pt. It is documented that Rh(III) forms significant concentrations of the hexachloro complexes  $[\text{RhCl}_6]^{3-}$  only at high hydrochloric acid concentrations (see *Figure 1.5*) and considerable concentrations of chloro-aqua  $[\text{RhCl}_{6-n}(\text{H}_2\text{O})_n]^{n-3}$  species ( $n=1-3$ ) at intermediate acid concentrations <sup>[46]</sup>, with  $n$  increasing with a decrease in  $\text{Cl}^-$  concentration <sup>[47]</sup>. Importantly, the Rh chloro-aqua species are considered to be difficult to extract <sup>[45, 48-50]</sup>.



**Figure 1.5** Rhodium chloride speciation diagram at 25°C <sup>[47]</sup>.

Even though Rh(III) can form seven complexes in HCl solutions it is expected that under industrial conditions, where the feed solutions will have acidities where the pH is  $\ll 3$ , where reasonably high chloride concentrations prevail,  $[\text{RhCl}_6]^{3-}$  and the aquated  $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$  and  $[\text{RhCl}_4(\text{H}_2\text{O})_2]^{-}$  complexes will be the main species present in solution <sup>[47]</sup>. The complexes,  $[\text{RhCl}_6]^{3-}$  and  $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$  dominate at high Cl<sup>-</sup> concentration (10 M) as shown in the Rh chloro speciation diagram in *Figure 1.5*. It must be noted though, that the relevance of this speciation diagram to real industrial solutions greatly depends on the source and type of thermodynamic stability constants data <sup>[47]</sup>.

Warszawsky has demonstrated the existence of some of the Ir chloro complexes displayed in *Table 1.2* <sup>[51]</sup>. The presence of hexachloro complexes of Ir at high acid concentrations and a tendency of forming mixed chloro-aqua anionic complexes at intermediate acid concentrations is noted also by Leung *et.al.* <sup>[46]</sup>. It is

clear that the fully chlorinated complexes of Ir in +3 and +4 oxidation states exist at concentrations  $>3$  M HCl. Moreover, at concentration range: 0.1 M - 3.0 M, the presence of chloro-aqua and chloro-hydroxo species has been demonstrated, whereby Ir(III) is somewhat more prone to undergo aquation than Ir(IV).

Ruthenium and osmium chloro complexes are less relevant to the modern refining industry, since the metals are recovered as the tetroxides (see *Section 1.3.3*). However, classically, the separation of the distilled Ru and Os tetroxide is achieved by adsorption in HCl solution, where Ru is reduced to Ru(IV) chloro complex. On the other hand, Os remains as the tetroxide and can be redistilled [31, 41, 52]

From the data given in *Table 1.2*, it can be concluded that  $[\text{PdCl}_4]^{2-}$  and  $[\text{PtCl}_4]^{2-}/[\text{PtCl}_6]^{2-}$  complexes are much less susceptible to undergo aquation than  $[\text{RhCl}_6]^{3-}$  or  $[\text{IrCl}_6]^{2-}/[\text{IrCl}_6]^{3-}$ . Furthermore, under oxidising conditions found in industrial solutions, Pt will most likely be present in the 4+ oxidation state. When the pH of the solution increases, hydrolysis will play a major role, with the formation of e.g.  $[\text{PtCl}_{6-n}(\text{OH})_n]^{2-}$  complexes.

### 1.4.3 Ligand exchange kinetics

Differences in ligand exchange kinetics clearly also play a major part in the refining of the PGMs as separation between species can be effected by the often considerable differences in ligand exchange rates. The relative ligand substitution kinetics for the PGMs in their most common oxidation states (relative to  $[\text{PdCl}_4]^{2-}$  set at 1) is as follows [25] (*Table 1.3*):

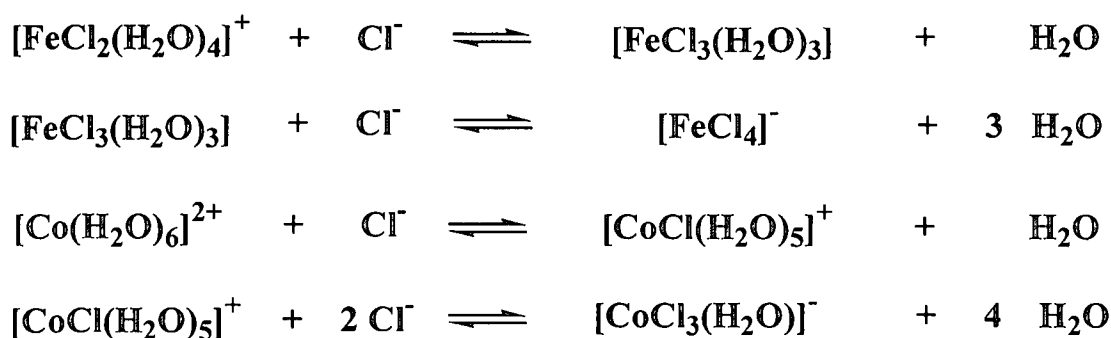
**Table 1.3** *The relative ligand substitution kinetics in PGM complexes at different oxidation states.*

<b>Metal</b>	<b>Ru(III)</b>	<b>Rh(III)</b>	<b>Pd(II)</b>	<b>Ag(I)</b>
Rate	$10^{-2} - 10^{-4}$	$10^{-3} - 10^{-4}$	1	$10^4 - 10^6$
<b>Metal</b>	<b>Ru(IV)</b>	-	-	-
Rate	$10^{-4} - 10^{-6}$			
<b>Metal</b>	<b>Os(III)</b>	<b>Ir(III)</b>	<b>Pt(II)</b>	<b>Au(I)</b>
Rate	$10^{-7} - 10^{-9}$	$10^{-4} - 10^{-6}$	$10^{-3} - 10^{-5}$	$10^2 - 10^3$
<b>Metal</b>	<b>Os(IV)</b>	<b>Ir(IV)</b>	<b>Pt(IV)</b>	<b>Au(I)</b>
Rate	$10^{-9} - 10^{-12}$	$10^{-8} - 10^{-10}$	$10^{-10} - 10^{-12}$	$10^1 - 10^{-1}$

Selective precipitation of the metals can sometimes be achieved by exploiting the differences in kinetics. Of notable interest is the huge difference in ligand substitution kinetics reported between Pt(II) and Pt(IV) chloro complexes. The latter are generally considered to be very slow (see *Table 1.3*) since these are known to be highly stable and kinetically inert complexes <sup>[45]</sup> although in practise Pt(IV) ligand exchange reactions are strongly catalysed by the presence of traces of Pt(II).

#### 1.4.4 Speciation of other transition metals

Since other transition metals co-exist with the PGMs in the refining solutions, as shown earlier, it is worthwhile looking at their behaviour in aqueous chloride solutions. These metals are characterized by fast ligand exchange kinetics and as a result they seldom form fully chlorinated species except at very high chloride concentrations <sup>[25, 53, 54]</sup>.



A general reaction (e.g. Cu) depicting equilibrium established (very rapidly) by transition metals is also shown below <sup>[55]</sup>:



Investigation by Lindenbaum and Boyd showed that nickel (II) does not form anionic chloro complexes in aqueous solutions <sup>[56]</sup>. Alternatively, Iron exists in aqueous solution as both cationic and anionic species, and is known to form stable chloro complexes,  $[\text{FeCl}_4]^-$  in high HCl concentrations <sup>[57]</sup>.

## 1.5 Different recovery methods

### 1.5.1 Classical precipitation methods

Although precipitation methods which were classically used for PGM recovery are relatively cheap in terms of single step separation they are nowadays considered to be inefficient. In order for the desired degree of purity to be achieved, several successive precipitation and redissolution stages are required <sup>[41]</sup>. In addition, the recovery efficiency for low metal concentrations is too low. Furthermore, selectivity is a challenge in precipitating PGMs due to the presence of other transition metals. Taking this into consideration, these processes are long and labour intensive <sup>[8]</sup>.



It has been mentioned earlier that the co-existence of other transition metals with the PGMs, makes selective precipitation difficult <sup>[8]</sup>.

The long processing times are not desirable for the material of this value. Single pass recoveries take at best a week, but given the fact that significant recycles are involved, the net processing can even take much longer. With the number of recycle streams being large due to the inefficiency of the processing steps, a significant lock-up of the precious metals in the refinery occurs, in particular with iridium. This is not only economically unfavourable, it also creates health hazards, as workers in the refinery can be exposed to potential allergenic reactions due to a large number of processing steps conducted for example platinum <sup>[41]</sup>.

The refined PGMs are 99.90% for Rh, Ru, Os and 99.95% for Pd, Pt, respectively <sup>[13]</sup>. It is evident that some PGMs are lost during this process and the so called "lost PGMs" are not recovered and are consequently left in the authentic refinery process solutions.

However, in spite of its clear disadvantages, precipitation reactions are to this date still indispensable at certain stages of the refining process, and here are some examples of its application: the use of sodium formate as a precipitating agent for PGM recovery from acidic effluents containing base metals <sup>[58]</sup>. Moreover, polyamine-containing such as diethylenetriamine have also been tested for the precipitation of a rhodium hexachloro anion complex and for Ir, Ru, and Os in the (III) oxidation state <sup>[59]</sup>. Furthermore, ammonium chloride has been investigated as well for precipitation of PGMs arising as secondary scrap from the glass industry <sup>[22]</sup>.

### 1.5.2 Solvent extraction

The final refining stage for the production of individual PGMs has fuelled the use of solvent extraction<sup>[60]</sup>. The advantage of using solvent extraction technique is that metals of interest can be quantitatively and selectively recovered from the complex processing streams<sup>[41]</sup>. Moreover, the technique also provides a much cleaner separation of PGMs relative to the classical process. The drawback of this technique is that the stripped liquor obtained are not pure enough for direct conversion to the product metal and thus further refining steps such as precipitations similar to those employed in classical process are required<sup>[31]</sup>. Unfortunately, solvent extraction is not applicable to very dilute solutions containing metal ions at relatively low concentrations (100-200 ppm). For the process to be efficient, the distribution coefficient of the metal ions to be extracted should be high ( $D > 10^2$ ), that is, the aqueous organic phase ratio must be high, leading to high organic losses through cross-contamination in the aqueous phase<sup>[41, 53, 61]</sup>.

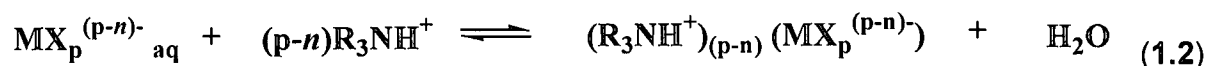
Solvent extraction is also referred to as liquid/liquid extraction, separation or in simplest terms, as liquid ion exchange. This extraction technique involves the selective transfer of certain ionic species in an aqueous solution to an organic solvent. Depending on what is desired to be isolated or collected in the solvent, there is a variety of solvent extraction reagents one can choose from, e.g. cationic, anionic or neutral. The extraction process entails the reaction of the metal of interest with the solvent to form a chemical compound which is much more stable in the organic phase. Following the successful extraction of the metal from an inorganic phase to the organic phase, the metal is stripped into an aqueous phase with somewhat differing properties (such as pH or redox ions).

There are four types of solvent extraction reagents employed in hydrometallurgical operations <sup>[25]</sup>: the first type involve *acidic extractants*. Some well known examples of these extractants are sulphonic acids (RS(OH)O<sub>3</sub>) and carboxylic acids (RCOOH). An example of a cationic reaction is displayed in *equation 1.1* where the solvent extraction reagent is represented by RH. The resulting extractant-metal ion complex is denoted by MR<sub>n</sub>.



This reaction strongly depends on the pH. The acidic extractant has ionisable hydrogen atoms that can be substituted by a metal ion to give an overall neutral species.

The second type incorporates *basic extractants* which comprises of amines: primary (RNH<sub>2</sub>), secondary (R<sub>2</sub>NH), tertiary (R<sub>3</sub>N) and quaternary (R<sub>3</sub>N<sup>+</sup>). The amines can accept a proton or possess a positive charge and form ion pairs with the anionic species, as a result, reducing the effective charge of the latter (see *equation 1.2*).



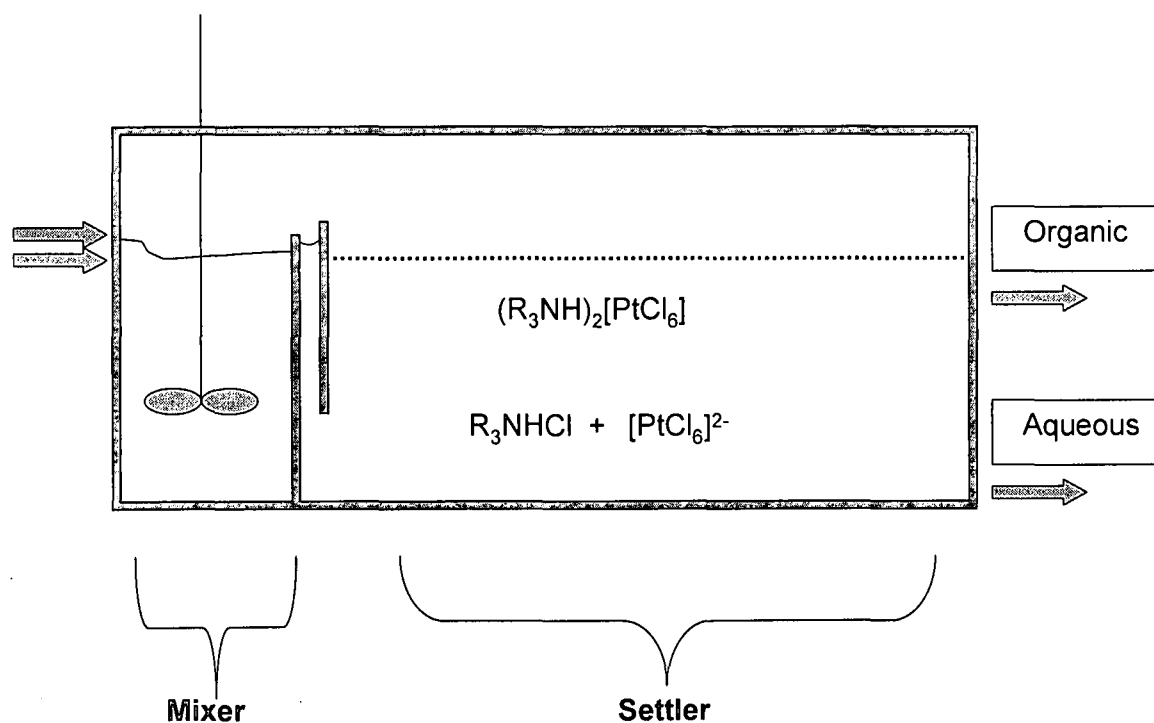
The third type entails *solvating extractants*, and these extractants compete with water for the first solvation sphere of the metal atom/ion (demonstrated in *equation 1.3*). Some examples include ketones (RCOR') such as MIBK (CH<sub>3</sub>COCH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>), amides (RCONR'<sub>2</sub>) and phosphine sulphides (RSR').



The last type comprises of *chelating acidic extractants* which possess ionisable hydrogen atoms that can be replaced by a metal ion to give a neutral species but also participate in the coordination sphere of the metal. A few examples include quinolines,  $\alpha$ -hydroxyoximes  $(\text{RC}(\text{NOH})\text{CH}(\text{OH})\text{R}')$  and the  $\beta$ -hydroxyoximes  $(\text{RC}(\text{NOH})\text{CR}'\text{C}(\text{OH})\text{R}_2)$ .

In most cases, anionic or neutral extractants are used for precious metals <sup>[23]</sup>.

Figure 1.6 depicts the box type equipment termed a mixer-settler which is commonly employed in hydrometallurgy. This system shows a single contact, consisting of an organic phase and an aqueous phase.



**Figure 1.6** Basic solvent extraction mixer settler arrangement for  $[\text{PtCl}_6]^{2-}$  extraction by a tertiary amine reagent <sup>[25]</sup>.

For example, *Figure 1.6* illustrates an extraction of  $[\text{PtCl}_6]^{2-}$  complex from an acidic aqueous phase that is treated with an organic phase containing a tertiary amine reagent as an extractant, and extraction takes place as indicated in *equation 1.2*. The two phases are mixed together in a mixing chamber and are subsequently allowed to separate in a settling chamber. Upon mixing the amine becomes protonated ( $\text{R}_3\text{NH}^+$ ) and solubilised in the aqueous phase. This results in the formation of neutral ion pairs  $(\text{R}_3\text{NH})_2 [\text{PtCl}_6]^{2-}$  which are soluble in the organic phase and are consequently extracted.

Some examples exist on extraction of PGMs from chloride media incorporating solvent extraction <sup>[8, 62, 63]</sup> and their recovery from spent catalysts <sup>[64]</sup>.

### 1.5 3 Ion Exchange

#### 1.5.3.1 Introduction

Ion exchange is yet another branch of *separation science*, and it is incorporated in fields of application that are parallel to solvent extraction, since the principles of extraction are very similar <sup>[65]</sup>. Ion exchangers are materials that are insoluble in the solvents in which they are utilized. An exchange reaction takes place between the counter-ions (the ions in the exchanger) and the ions in the solution. Two of the key features of a good ion exchanger are a high degree of selectivity (an ability to exchange certain ions only) and good metal ion exchange capacity (the amount of ions that are exchangeable per unit of ion exchanger) <sup>[66]</sup>. Furthermore, ion exchange is suited to high cost and low throughput purification processes <sup>[67]</sup>, and metals can be concentrated from very dilute solutions <sup>[68]</sup>.

In the 1850s, Thompson and Way, the British soil scientists studied the exchange of ammonium ions for calcium ions <sup>[69-71]</sup>. With progressing industrialisation

the focus shifted to plant scale water softening, initially with natural and later on with synthetic inorganic ion exchangers <sup>[72]</sup>. Synthetic materials are usually superior because their properties can be better controlled <sup>[66]</sup>, and they can be subdivided into classical (charged) ion exchangers and chelating ion exchangers (see below). The comprehensive history and development of chelating ion exchangers and the synthetically classical (charged) ion exchangers has been reviewed <sup>[72]</sup>. Classical ion exchangers can be classified as either cationic or anionic exchangers (see *Section 1.5.2* for the corresponding extraction mechanisms). An example of a cationic reaction is displayed in *equation 1.1*.

Chelating ion exchangers contain metal-ion complexing groups rather than the ion exchange groups <sup>[73]</sup>. The bond formation is promoted by chelation of positively charged metal ions via the non-bonding electron-pairs of donor atoms on the backbone, or on covalently bonded side chains <sup>[74]</sup>. Some examples of chelating ion exchangers include iminodiacetate, and aminophosphonate functional groups and benzoylthiourea modified polyamidoamine dendrimers for the recovery of heavy metals like Ni, Co and Cu <sup>[40, 75, 76]</sup>.

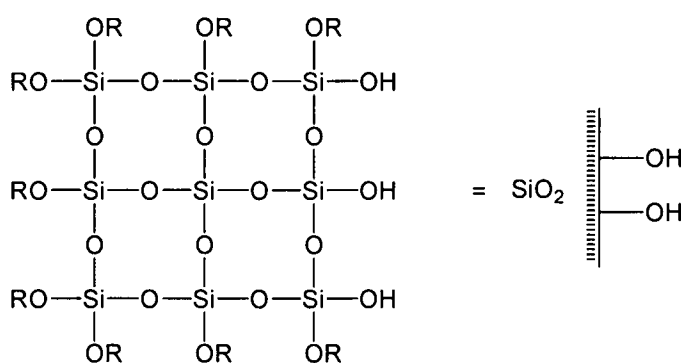
### 1.5.3.2 Ion Exchanger Composition

In general, ion exchangers consist of a functional group that is bound onto a solid support (backbone), the backbone is either an organic or an inorganic material. The organic backbones are also called resins or polymeric backbones. Ion exchangers with the organic backbones have been made from a variety of both natural e.g. chitosan, sulfonated coals <sup>[77, 78]</sup> and synthetic materials. The English chemists Adams and Holmes invented synthetic ion exchangers in 1935. Some of their classic work involved the preparation of anion exchange resins by the polymerization of

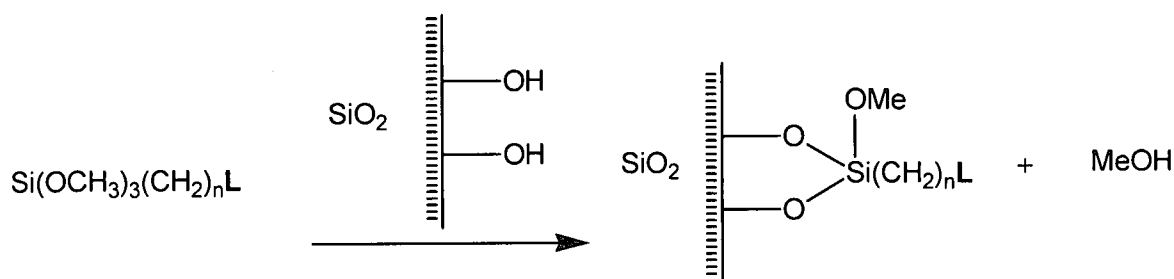
the amines such as aniline and metaphenylene diamine with formaldehyde <sup>[79]</sup>. The earliest organic anion exchangers contained weak-base amine groups and were followed later by the preparation of the resins with strong-base quaternary ammonium groups and this contribution is owed to Adam and Holmes <sup>[72]</sup> and these first ion-exchange resins are condensation polymers.

Some examples of inorganic backbones include synthetic zeolites, alumina ( $\text{Al}_2\text{O}_3$ ) and silica ( $\text{SiO}_2$ ) <sup>[78]</sup>. Silica is an abundant, geological material that is found in an aquatic environment and its surface is covered with hydroxyl groups <sup>[80]</sup>. This material is by far the most extensively used inorganic support and is commercialised as silica gel (see *Figure 1.7*). The functional group (L) is connected with the backbone via the hydroxyl groups, either via a spacer or directly (see *Figure 1.8*).

Silica-based sorbents have high thermal and mechanical strength <sup>[81]</sup>. Silica is very stable in the range of pH 0-8. A disadvantage of the silica matrix is its relatively low stability in alkaline conditions as it dissolves significantly above pH 9.



**Figure 1.7** The silica structure, where R represents the lattice <sup>[82]</sup>.



**Figure 1.8** Immobilisation of the functional groups (amine ligands) onto a silica backbone via a trimethoxysilane. The functional group is represented by  $L$  and it is separated from the silica backbone by an alkyl spacer group  $(CH_2)_n$ , where  $n = 0-6$  <sup>[82]</sup>.

### 1.5.3.3 Silica-based amine containing ion exchangers

Due to the tendency of PGM ions to form stable anionic complexes in aqueous chloride solutions, clearly, a common way to recover the PGMs is by using anion exchangers. There is an increasing demand for economic and newer processes for the recovery of metal ions from industrial effluents and this is a very difficult task. Concerted efforts to synthesize PGM-selective ion exchangers have been reported by several authors who have illustrated PGM recovery from the chloride media using different ion exchange materials. Leung and Hudson have given a notable example of an ion exchange copolymer based on poly(styrene-co-divinylbenzene) with covalently bound 1,3,4-thiadiazole-2-amino-5-thiol groups in hydrometallurgical studies for selective extraction of PGMs <sup>[46]</sup>. Warshawsky has demonstrated the use of isothiuronium resins for the separation of PGMs in chloride media <sup>[51]</sup>. Gaita also illustrated the selective separation of Pt, Pd and Rh from automotive catalytic converters by ion exchange <sup>[21]</sup>. Guibal studied the sorption of Pt and Pd with chitosan <sup>[77]</sup>.

The research described in this thesis will focus on anion exchangers containing N donor atoms. It is known that a large variety of amines are highly efficient and selective extractants for PGMs <sup>[77, 83, 84]</sup>. The nature of the alkyl group



plays an important role in extraction. It has been noticed that in general aliphatic amines are better extractants than aromatic groups that are directly attached to the nitrogen since the extraction ability weakens. Furthermore, extraction is also reduced by too much chain branching <sup>[40]</sup>.

In this context our PGM recovery studies will focus on silica-based (poly)amine containing ion exchangers. (Poly)amine containing ion exchange materials can function as anionic exchangers under acidic conditions since they are protonated in *equation 1.4*. It is believed that extraction takes place via substitution of  $\text{Cl}^-$  by the anionic PGM complexes of the type  $[\text{MCl}_x]^{n-x}$  as shown in *equation 1.5*, where M is the metal,  $n$  is the oxidation state of the metal and  $x$  is typically 4 or 6 <sup>[47]</sup>.



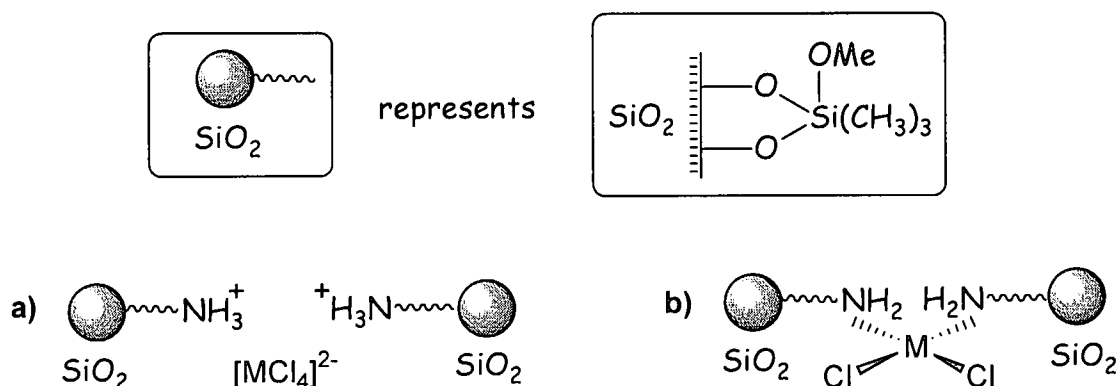
Stability of the ion-pair for a given ion exchange resin seem to be related to the overall charge on the anion. Importantly, the tendency for ion pairing between the metal-chloro complexes and the anion exchangers is in the order:



The order of ion pairing is determined by the charge to size ratio, or by the charge density of the species. Anions with a charge of 1 or 2 tend to be extracted more than those with a 3<sup>-</sup> charge <sup>[75]</sup>. This concept may be used as well to separate PGMs from one another. Since species with low charge density are paired with more ease than

the species with higher charge density, this is probably due to the size of the hydration shell surrounding the ions. Consequently, densely charged species containing larger hydration shells have lower coulombic interaction with their counterions than those with smaller hydration shells <sup>[38]</sup>. Therefore, differences in PGM anion stability are expected to create selectivity under these conditions of high acidity.

However, as the pH increases, protonation becomes less predominant and binding is expected to take place increasingly via coordination of the lone-pairs of the amine group to the metal ion (M) depicted in *Figure 1.9*.



**Figure 1.9** Expected extraction principle of  $[MCl_4]^{2-}$  complexes: **a)** at low pH where protonation occurs and anion pairing takes place and **b)** as the pH increases, protonation decreases and results into coordination through the lone-pairs.

Since it is known that amine ion exchangers have a high affinity for other transition metals under these conditions <sup>[84]</sup>, increasing competition and hence decreasing selectivity of PGM extraction over the other transition metals might be anticipated with increasing pH.

#### 1.5.3.4 Silica-based guanidine containing ion exchangers

In order to maintain our desired selectivity over other transition metals a longer pH range, new ion exchange materials will be compared. These ion exchangers are the guanidine derivatives of the amine ion exchangers (see *Scheme 3.1*). The weak base anion exchangers bearing guanidine ligands have been investigated for gold extraction in chloride solutions <sup>[76, 85]</sup>. Furthermore, studies were extended to PGM and gold sorption in the chloride media containing base metals <sup>[86]</sup> However, no studies exist on the use of guanidinium groups for PGM recovery from authentic precious metal refinery process solutions.

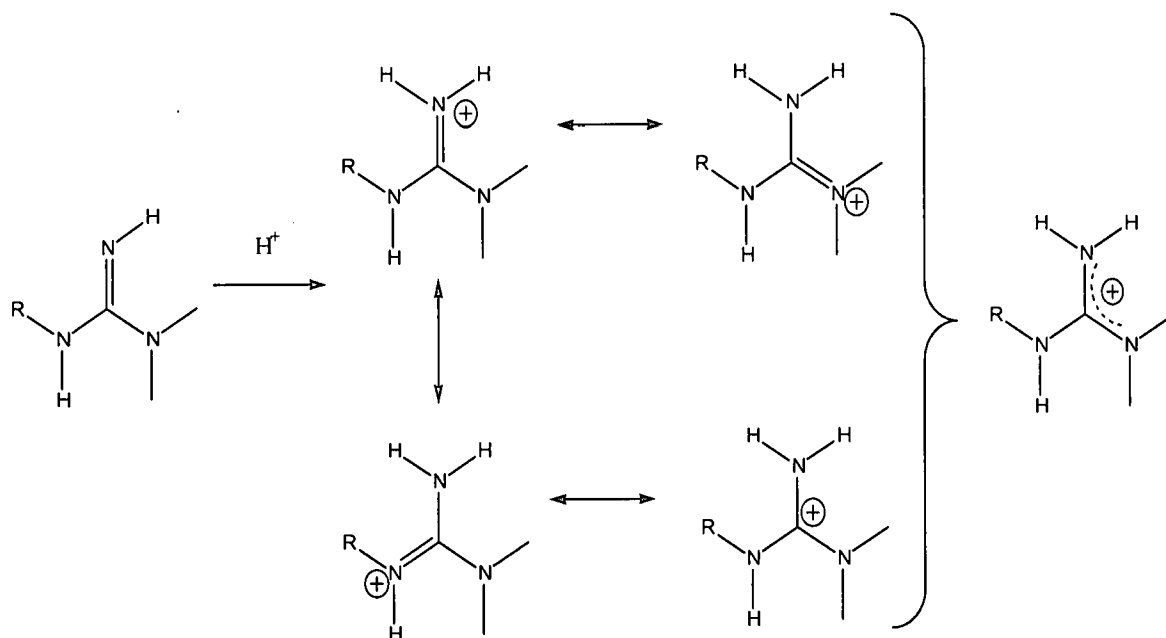
At low pH, it is expected for the guanidine containing ion exchangers to become protonated and therefore bind to anionic PGM complex similar to the (poly)amine containing derivatives. Alternative to these (poly)amine containing ion exchangers, guanidine containing ion exchangers are expected to remain protonated much longer at higher pH conditions because of their high pKa (13.4) <sup>[87]</sup>. Hence, *anion pairing* is hopefully retained and the materials are anticipated to remain PGM selective.

### 1.6 Desorption

Although for quantitative extraction a high affinity of the ion exchanger for PGMs is desirable, this might be disadvantageous for good subsequent desorption. Weak base ion exchangers are therefore recommended instead of strong base anion exchangers which might form too stable binding that could be difficult to desorb, as pointed out by Kolarz et al <sup>[87]</sup>.

An advantage of using a weak base ion exchanger is illustrated by the use of guanidine containing ion exchangers, whereby during protonation, the positive

charge is delocalised (see *Figure 1.10*). This phenomenon is anticipated to promote a weaker binding of the ion exchanger to the PGM complex and to encourage much easier stripping.



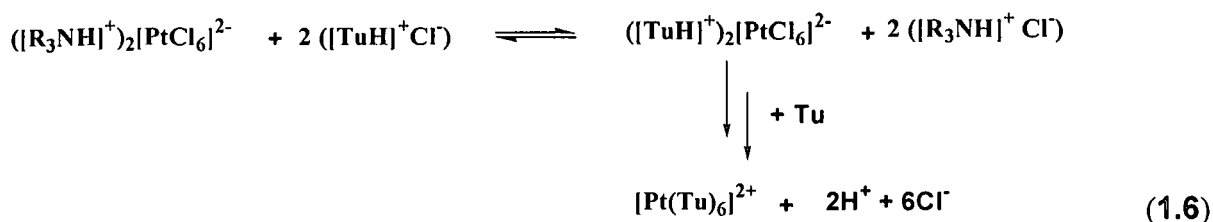
**Figure 1.10** Resonance structures of the dimethylguanidium group.

There are three possibilities via which the metals from the loaded ion exchangers can be desorbed.

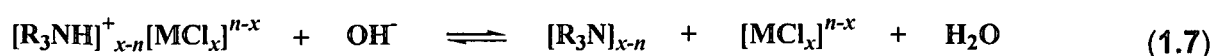
The first method is to introduce competing species; for example an HCl solution of high concentration might be used to desorb metals from the loaded ion exchanger. Chloride ions compete with the PGM anion for the binding sites on the protonated ion exchangers in PGM extractions, therefore the high chloride concentration pushes an equilibrium to the left as shown in *equation 1.5* <sup>[46, 76]</sup>.

The second method, involves the use of a stronger competing ligand like thiourea ( $\text{NH}_2\text{-C=S-NH}_2 = \text{Tu}$ ) in acidic medium (displayed in *equation 1.6*) which has the ability to form stronger complexes with the desired metals <sup>[46, 60]</sup>. The protonated

thiourea binds fast with the anionic complex through ion pairing. An exchange mechanism takes place very slow. Initially an anionic mixed-chloro-thiourea complex form followed by a conversion to a neutral complex and finally to a fully substituted cationic PGM thiourea complex <sup>[51]</sup>, as indicated for Pt(IV) in *equation 1.6*.



Thirdly, introducing alkaline conditions would render the ion exchangers no longer protonated and might even lead to deprotonation, as shown in *equation 1.7*. Clearly, the ion exchanger is no longer capable of forming stable ion pairs and the PGM anion is released from the extractant. Care must be taken though, when alkaline conditions are applied using silica-based ion exchangers, since exposure to high pH will seriously dissolve and hence damage the ion exchange materials <sup>[84]</sup>.



## 1.7 Research Aim

The aim of this research is to investigate PGM extraction efficiency and selectivity of various silica-based (poly)amine and dimethylguanidine-containing ion exchangers from authentic refinery process (ARP) solutions. Since the origin of these solutions has not been revealed, our only information is the fact that these solutions originate from different stages of the PGM refining processes, and contain PGMs as well as other transition metals (e.g. Cu, Ni, Fe and Co) in often significant concentrations.

This poses an obvious challenge to the research, bearing in mind the large variation in the PGM speciation dependent on the composition of the solution and the corresponding variation in their extractabilities, as described in the current chapter. An even greater challenge is to selectively extract PGMs since the ARP solutions were found to vary significantly in composition and pH.

The aim of this chapter has been to present a general overview on PGMs, and it includes their occurrence in nature, the processes employed in industry to recover the metals from the ores up to the final stages of refinement. A brief review is given on the research work that had been done on this subject.

Chapter 2 comprises of a detailed experimental approach on the synthesis of the amine ion exchangers and the determination of the metal concentrations in ARP solutions. A procedure undertaken in performing extractions, desorptions and successive recovery studies is illustrated.

Chapter 3 covers the PGM recovery and selectivity performance of the ion exchangers from the studied ARP solutions of various pHs. The results on the re-usability of the ion exchangers are also discussed. Part of the work described in this chapter has been published <sup>[88]</sup>. A brief summary of the findings is presented in chapter 4 together with some recommendations for future work.

## Chapter 2: Experimental Section

### 2.1 Reagents and apparatus

All reagents and solvents for the synthesis of the ion exchangers were purchased from commercial sources and were used without further purification unless otherwise stated. The free amine ligands (bonded to a trimethoxy silane), 3-(trimethoxysilyl) propylamine, N-[3-(trimethoxysilyl) propyl] ethylenediamine and N-[3-(trimethoxysilyl) propyl] diethylene-triamine were purchased from Aldrich. Toluene was distilled from Na with benzophenone as an indicator and stored over activated molecular sieves (3Å beads). Syntheses of the ion exchangers were conducted under nitrogen with standard Schlenk techniques.

Silica gel (Aldrich Davisil™) with surface area of 480 m<sup>2</sup>/g, pore volume of 0.75 cm<sup>3</sup>/g and size of 4-20 μm (further referred to as *fine silica*) and 250-500 μm (*coarse silica*) was used. The silica gels were activated by heating at 65°C in vacuo (<50 mbar) until constant weight before use to remove adsorbed water. Elemental analyses of C, H and N were performed by the Microanalytical Laboratory of the University College in Dublin. Solid-state cross polarisation magic angle spinning (CP-MAS) <sup>13</sup>C NMR spectra were recorded on a Bruker MSL 400 spectrometer, with a rotational spin speed of 10.5 kHz, operating at 100.6 MHz at Leiden University, the Netherlands.

HCl (37% v/v) and H<sub>2</sub>SO<sub>4</sub> (95-98% v/v) were purchased from Aldrich and Riedel-de Haën respectively. The calibration standards were purchased from J.F.J Industries CC. The purity of the PGM (Pt, Pd, Ir and Rh) standards was 99.99% and the concentration of single elements was 1000 mg L<sup>-1</sup> in HCl (5 or 10% v/v) matrix. The purity of the other transition metals (Fe, Ni, Cu and Co) 1000 mg L<sup>-1</sup> standards

was 99.999% and the single elements were dissolved in  $\text{HNO}_3$  (4% v/v). All solutions were prepared using Milli-Q water (MQ,  $> 18 \Omega$ ).

Authentic refinery process (ARP) solutions 1-4 were obtained from a Precious Metal Refining Company in South Africa. All metal ion determinations were performed with an Inductively Coupled Plasma–Optical Emission Spectrometer (Varian Liberty II ICP-OES) using linear calibration curves (see *Section 3.2*).

## 2.2 Determination of pH and chloride in the ARP solutions

The pH of the ARP solutions was measured with a Metrohm 744 pH meter, which was calibrated with buffers of pH 4.00 and pH 7.00. The unbound chloride concentration in the ARP solutions was determined using the Mohr method<sup>[89]</sup>. The method involves titration of the chloride ions with standard silver nitrate solution of 0.075 M concentration. The silver nitrate solution was standardised with 25 mL of a 0.03 M sodium chloride solution. Potassium dichromate (0.25 M) was used as an indicator.

The ARP solutions were diluted with water (see *Appendix 3*). Dilution of these solutions ranged from 50 to 200-fold for a detectable endpoint to be reached after addition of ca 10 mL of  $\text{AgNO}_3$  solution. A few drops of 1 M KOH or  $\text{HNO}_3$  were added to attain the desired pH (between 6 and 8) before titration. Those ARP solutions, in which the other transition metals were present in high concentrations, were diluted with a pH 4.00 buffer solution composed of sodium acetate in acetic acid. The acetate buffer was applied to reduce interferences of these metals in the determination of the endpoint of the titrations<sup>[90]</sup>. An indicator blank was performed and subtracted from the titration values to correct for errors. The endpoint was marked by a colour change from yellow to orange-red. The yellow colour was



observed after the addition of an indicator,  $K_2Cr_2O_7$  in an AR P solution before titration. The latter colour was distinguished after the precipitation of silver chloride (AgCl) was completed upon the formation of silver dichromate <sup>[89]</sup>.

### 2.3 Immobilisation of amine-containing ligands onto silica

The silica-based amine-containing ion exchangers **N1-N3** (shown in *Scheme 3.1*) were synthesized as described by Kramer *et al* <sup>[91]</sup>, as follows: a 250 mL two-necked flask was flame dried under vacuum and kept under nitrogen before addition of 20 g silica. The flask was flame dried again after addition of silica to eliminate any moisture adsorbed during weighing. 1.7 mmol of free amine ligand per gram of silica was added to a suspension of silica in dry toluene (5-10 mL per gram of silica). In case of the *coarse* particles, the mixture was stirred with a magnetic stirrer for a few seconds at room temperature to attain homogeneity of the suspension, followed by manual stirring at regular intervals to avoid crushing of the silica particles by the magnetic stirrer and was left to stand for 48 h. The mixture was subsequently filtered and washed with toluene (6x 20 ml) to remove residual reagents. The ion exchangers were purified further by refluxing toluene in a Soxhlet apparatus for 24 h. After overnight evaporation of excess solvent the extractants were further dried at 65°C *in vacuo* (< 50 mbar) until constant weight. The procedure for the *fine* particles was identical, apart from the fact that the fine size of the particles allowed for *magnetic* stirring of the suspensions.

The corresponding dimethylguanidine (DMG) containing (**N1G-N3G**) ion exchangers were obtained as a gift from J. Kramer, and were prepared via addition of dimethylcyanamide to **N1**, **N2** or **N3** ion exchangers, respectively, as described by Korlaz *et al* <sup>[92]</sup>.

## 2.4 The instrumental working conditions

Most ICP-OES measurements were carried out with two interference-free emission lines of high intensity (shown in *Table 3.2*), and the instrument working conditions are shown in *Table 2.1*.

The (interdaily) instrumental variation in the sensitivity (in counts/sec) was measured prior to each measurement series via a time scan of a 10 mg L<sup>-1</sup> standard solution.

**Table 2.1** ICP-OES working conditions.

Power/kW	1.20
Plasma flow rate (L / min)	15.0
Auxiliary gas flow rate (L / min)	1.50
Nebulizer	glass concentric
Nebulizer pressure (kPa)	160
Viewing	radial
Viewing height (mm)	5 - 8
Instrument stabilization delay (s)	15
PMT Voltage (V)	650
Spray chamber	Sturman-Masters
Sample uptake delay (s)	25
Pump rate (rpm)	15
Acid rinse time (s)	60

## 2.5 Calibration solutions and determination of ARP metal ion concentrations

A series of 10 mixed PGM (Pd, Pt, Rh, Ir) calibration standard solutions were prepared in a 0.1-100 mg L<sup>-1</sup> range, while the mixed standards of the other transition metal ions (Cu, Co, Fe, Ni) were prepared from 0.5-50 mg L<sup>-1</sup>. PGM and other transition metal ion concentrations in the ARP solutions were determined using calibration standards prepared in 0.9 M H<sub>2</sub>SO<sub>4</sub>. This acid proved to be the most suitable for matrix matching due to the relatively high viscosity resulting from the high total dissolved solid (TDS) concentration of these samples. Thus, ARP samples for metal ion concentration determinations were diluted with 0.9 M H<sub>2</sub>SO<sub>4</sub>, as follows: ARP solution 1-2: 2.5 mL was diluted to 25 mL, and ARP solution 3-4: 5 mL was diluted to 25 mL. All the standard solutions and the samples were then spiked with 500 mg L<sup>-1</sup> yttrium (Y) internal standard to a final concentration of 5 mg L<sup>-1</sup> before measurements. The addition of Y was used for extra compensation of the matrix effects<sup>[93]</sup> and as correction for variations in the analyte response<sup>[94]</sup>. Cross contamination was avoided by 60 s rinse between samples using the matrix acid solution.

To improve the accuracy of the measurements, the average concentration obtained from two different interference-free spectral lines for each element was taken (see previous section), each of which concentrations was based on four replicate measurements. Additionally the samples were occasionally remeasured to establish the interdaily variation in the ICP measurements, resulting in the concentrations as given in *Table 3.3*. Metal ions in ARP solutions with very low concentrations (*i.e.* < 3 mg L<sup>-1</sup>) relative to other metal ions present were not mentioned in the text.

## 2.6 Extraction experiments

ARP solutions 1-4 (10.0 mL) were mixed with 300 mg of silica-based ion exchangers (N1-N3 and N1G-N3G) and with 500 mg in the case of ARP 4. The suspensions were mounted on a shaker and agitated (175 rpm) for 24 h at room temperature to ensure equilibrium had been reached. After shaking, the samples containing *fine* silica-based ion exchangers were centrifuged at 4000 rpm for 4 min. Then, 5 mL of the supernatant was transferred into a volumetric flask and diluted to 25 mL with 0.9 M H<sub>2</sub>SO<sub>4</sub> in the case of ARP 3-4, whereas 2.5 mL of ARP 1-2 was transferred and diluted to 25 mL. All samples were then spiked with a 500 mg L<sup>-1</sup> Y internal standard solution to a final concentration of 5 mg L<sup>-1</sup> Y and extraction efficiencies were determined using calibration standards prepared in 0.9 M H<sub>2</sub>SO<sub>4</sub>. The samples which contained *coarse* silica ion exchangers were filtered instead of centrifuged to separate the ion exchangers from the solutions and treated likewise.

All extraction efficiencies (as a percentage) were determined via comparison of the metal ion content of the ARP solutions before and after treatment with the extractants. Since the matrix of the sample before and after extraction is virtually identical, it was found not necessary to apply Y corrections in determining the extraction efficiencies. The largest relative standard deviation (RSD) was found mostly not to exceed 5%. Consequently, a RSD of 5% is given for all extraction efficiencies except for those samples where the variation in average concentration obtained from the two emission lines was larger; in these cases the larger RSD is given.

Mass balance calculations were performed to investigate the reliability of this method of establishing extraction efficiencies, using *equation 2.1*:

$$\text{Mass balance (\%)} = ((\text{amount left in the ARP solution after extraction (mg L}^{-1}\text{)} + \text{amount adsorbed on extractant (mg L}^{-1}\text{)} / (\text{amount initially present in the ARP solution (mg L}^{-1}\text{)}) * 100 \quad (2.1)$$

The amount of PGMs adsorbed onto the ion exchangers was determined as follows: The loaded *fine* ion exchangers were washed with 25 mL water (3x), followed by centrifugation and decanting. The ion exchangers were then suspended in acetone and were thoroughly air dried on the filter. For mass balance determinations, 100 mg portions of the loaded ion exchangers were digested overnight by gently refluxing in 5.0 mL of concentrated H<sub>2</sub>SO<sub>4</sub>. A few drops of concentrated HNO<sub>3</sub> were added until the solutions became clear. The digested samples were transferred into 50.0 mL volumetric flasks, diluted with water and spiked with a 500 mg L<sup>-1</sup> Y internal standard solution to a final concentration of 5 mg L<sup>-1</sup> Y. The samples were then filtered (with P4 filter paper) to remove the residual, undigested silica. The filtrate was measured for the metal content using 0.9 M H<sub>2</sub>SO<sub>4</sub> calibration standards and Y correction was applied.

## 2.7 Desorption experiments

Coarse silica-based ion exchangers **N3** and **N3G** (1000 mg) were mixed with 30.0 mL of ARP solutions **2** and **3** and the suspensions were mounted on a shaker and agitated for 24 h (175 rpm) at room temperature to ensure equilibrium had been reached. The loaded ion exchangers were then vacuum filtered and washed with 25 mL water (3x) and allowed to dry on the filter for few seconds before desorption was performed. The loaded ion exchangers were divided into equal weights, which were then contacted with 15.0 mL desorbent and agitated as described above. The tested

desorbents were, 1.0 M HCl, 5 M HCl, 0.5 M thiourea (Tu), 0.5 M Tu / 1.0 M HCl, 2 M HNO<sub>3</sub>, 2 M H<sub>2</sub>SO<sub>4</sub>, 2.7 M NH<sub>4</sub>OH / 0.5 M NH<sub>4</sub>NO<sub>3</sub>, 2.7 M NH<sub>4</sub>OH / 0.5 M Na-benzoate and 0.5 M NH<sub>4</sub>SCN. When agitation stopped, the suspension quickly settled and 10.0 mL of the 15.0 ml supernatant was subsequently transferred into an ICP tube, spiked with Y (to a final concentration of 5 mg L<sup>-1</sup>) and desorption efficiencies were determined using calibration standards prepared in 2 M HCl. Desorption efficiencies were calculated in the following way:

- Firstly, the concentration of the element of interest in the ARP solution was determined and expressed in an amount of metal present (in mg) in the volume used during the extraction.
- Secondly, this amount (in mg) was multiplied by the extraction %, in order to get the actual amount loaded on the ion exchanger to be desorbed.
- From this extraction efficiency, the concentration after maximum desorption could be calculated taking into account the volume of the desorbent (15.0 mL). This concentration could then be compared with the measured concentration using ICP, after applying Y corrections, resulting in the desorption efficiency.

Average RSD values for desorption efficiencies were taken from the RSD values in the measured metal concentrations of the ARP solutions (see *Table 3.3*), since these were higher than the RSD values for extraction determinations.

## 2.8 Successive recovery experiments

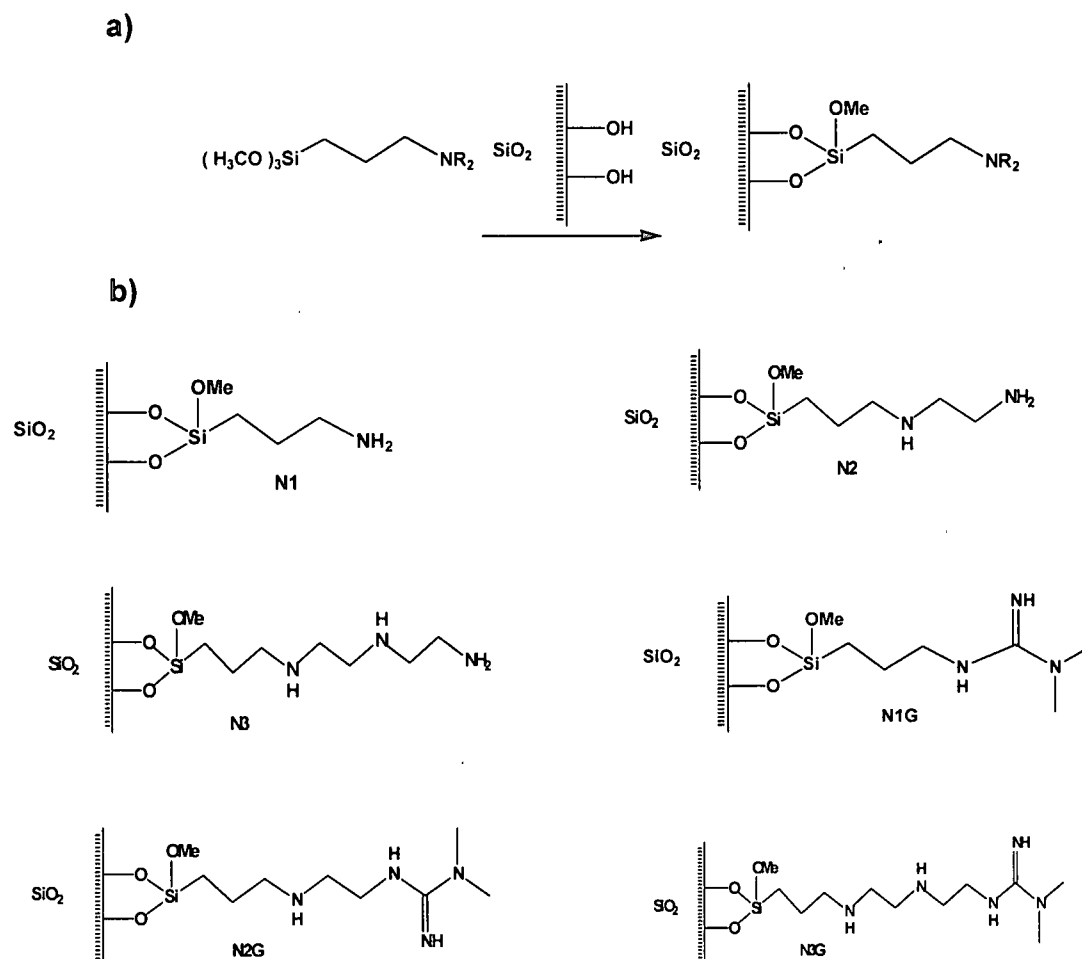
400 mg of *coarse* ion exchangers **N3** and **N3G** were preconditioned overnight with 0.5 M HCl to ensure the ion exchangers were protonated, and washed with water until the pH of the filtrate was pH 6-7. The ion exchangers were mixed with 15.0 mL

of ARP solutions. The extractions were performed via agitation of the suspensions for 1 h at room temperature. After filtering and washing with water (3x 50 mL) the residual ion exchangers were treated with 15.0 mL of 5 M HCl desorbent. The suspensions were again shaken for 1 h at room temperature, filtered and washed with water, and then the next recovery cycle was started. Five cycles were completed using the same ion exchangers. The extraction percentages for all cycles were calculated as discussed in *Section 2.6*. Desorption efficiencies from the second cycle onward were calculated based on the amount adsorbed during the new extraction cycle and taking into consideration the total amount of PGMs still left on the extractant after the previous desorption cycle, when applicable.

## Chapter 3: Results and Discussion

### 3.1 Immobilisation of amines onto silica

The free amine trimethoxysilane ligands, 3-(trimethoxysilyl) propylamine, N-[3-(trimethoxysilyl) propyl] ethylenediamine and N-[3-(trimethoxysilyl) propyl] diethylene-triamine were immobilised onto the surface of the silanol groups of silica via a methanolysis reaction (see *Scheme 3.1*). This resulted in ion exchangers **N1-N3** containing a monoamine (**N1**), ethylenediamine (**N2**), and diethylenetriamine (**N3**) functionality. Their corresponding dimethylguanidine-containing equivalents (**N1G-N3G**) are also shown in *Scheme 3.1* <sup>[88]</sup>.



**Scheme 3.1** a) Immobilisation of free amine-containing ligands onto silica particles via methanolysis reaction and b) Ion exchangers **N1-N3** and their corresponding dimethylguanidine-containing equivalents, **N1G-N3G**.



Characterisation of the ion exchangers was performed via elemental analysis and solid state  $^{13}\text{C}$  NMR measurements. The elemental analysis results are listed in *Table 3.1* and the  $^{13}\text{C}$  spectra are shown in *Figure 3.1*. The ligand concentrations of the functionalised silica were calculated from the weight percentage of nitrogen, as is generally done <sup>[95, 96]</sup> while the C and H percentages, which are based on this ligand concentration, are given in parentheses (*Table 3.1*). As was observed previously <sup>[91]</sup> the ligands are grafted, on the average, via two methoxy groups.

It is observed that the ligand concentration for both types of ion exchangers decreases as the number of nitrogen atom increases regardless of the silica particle size used. This is probably due to the porous structure of the silica: small ligands can fit better through the pores of the silica resulting in a decreasing accessibility with increasing ligand size.

**Table 3.1** Elemental analyses (C, H and N) and the ligand concentrations of the fine silica-based ion exchangers **N1-N3** and **N1G-N3G**.

Ion exchangers	%C (calc <sup>[b]</sup> )	%H (calc <sup>[b]</sup> )	%N <sup>[a]</sup>	Ligand Conc. (mmol / g) <sup>[a]</sup>
<b>N1</b>	4.80 (4.78)	0.90 (1.10)	1.40	1.00
<b>N2</b>	5.82 (5.99)	1.04 (1.34)	2.33	0.83
<b>N3</b>	7.32 (7.03)	1.28 (1.55)	3.08	0.73
<b>N1G</b>	4.38 (2.78)	0.88 (0.57)	1.39	0.33
<b>N2G</b>	6.75 (6.94)	1.13 (1.42)	3.60	0.64
<b>N3G</b>	8.24 (8.66)	1.34 (1.78)	4.59	0.66

<sup>[a]</sup> Ligand concentrations were calculated based on the nitrogen content

<sup>[b]</sup> Based on the results of the nitrogen content.

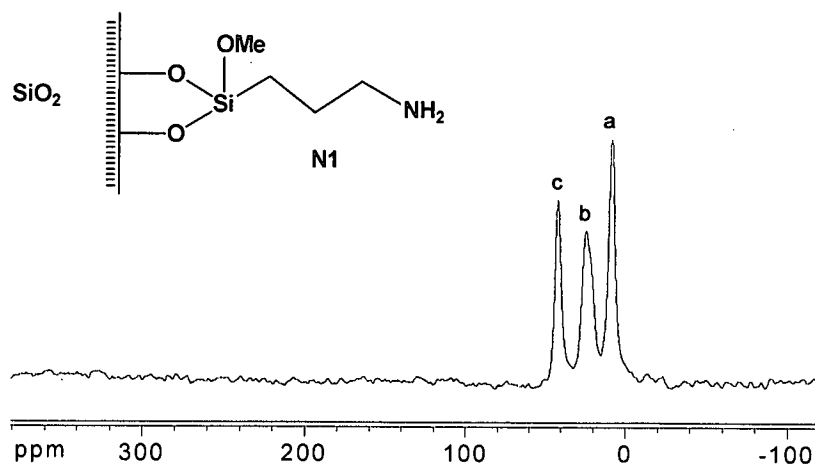
Moreover, as was expected, conversion of the (poly)amine-containing ion exchangers into their corresponding DMG-containing analogues showed a significant increase in nitrogen content, as well as in carbon content with exception to **N1** and **N1G** ion exchangers.

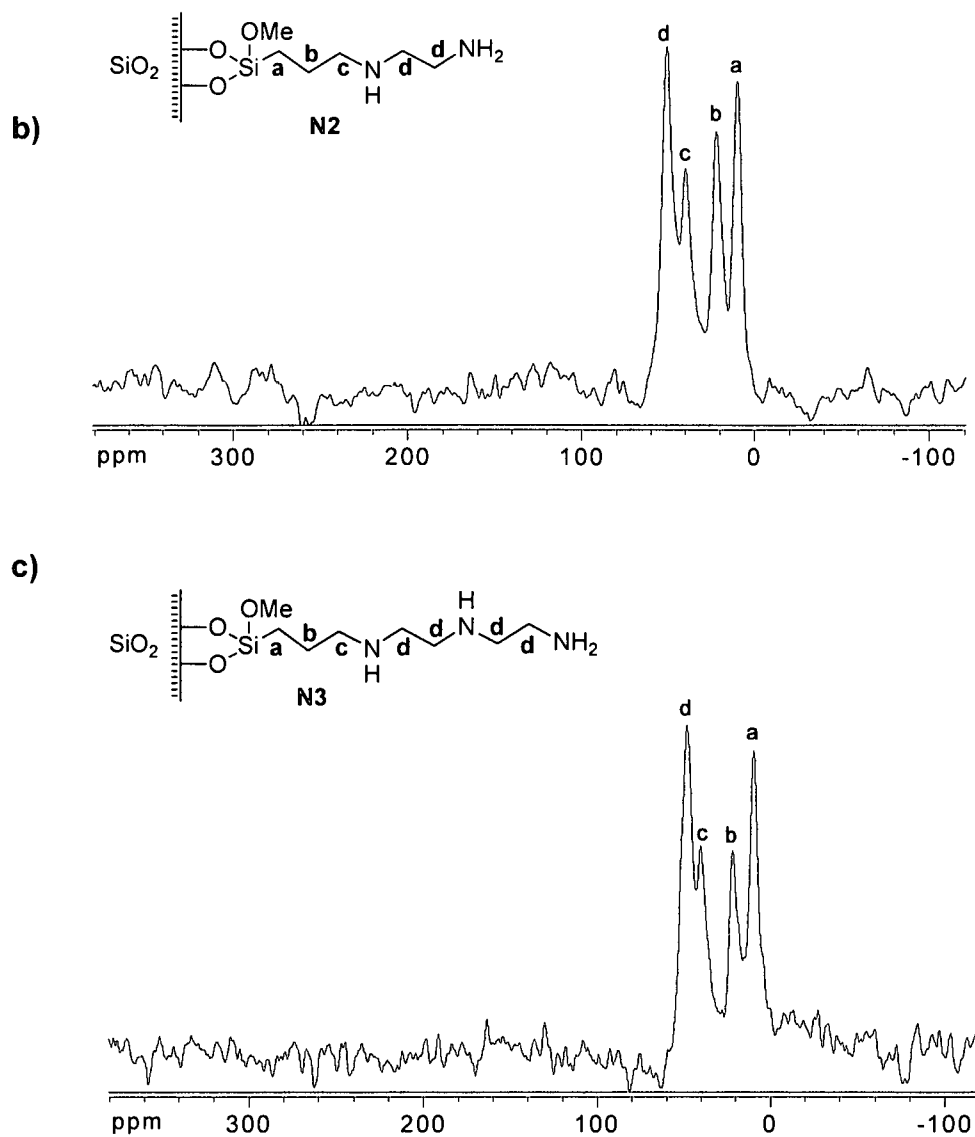
The conversion of the secondary amine groups of ion exchangers **N2** and **N3** into the corresponding DMG functionality is not expected to occur, due to the reduced accessibility of these groups, which are closer to the silica surface. This assumption is supported by the relatively moderate increase in nitrogen percentage observed as well as by the apparent lower reactivity of propylamine-containing ion exchanger **N1** where incomplete conversion of the amine into the corresponding guanidine is likely to be the reason for the discrepancy between the observed and calculated C and H percentages. Finally, the lower ligand concentration of ion exchangers **N1G-N3G** as compared to ion exchangers **N1-N3** is probably caused by

the detachment of part of the ligands under the harsh conditions (high temperatures and low pH for extended times) required for good conversions to take place <sup>[88, 92]</sup>.

The solid state <sup>13</sup>C NMR spectra of **N1-N3** ion exchangers are displayed below in *Figure 3.1*. The most upfield peaks at about 9 ppm depicted by **a**, originate from the carbon attached to the silicon group ((R)<sub>3</sub>SiCH<sub>2</sub>-) where R represents the methoxy group. The signals at about 20-25 ppm shown by **b** originate from the middle carbon in the alkyl chain ((R)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH-). The two downfield peaks at about 41 and 50 ppm indicated by **c** and **d** originate from the carbons attached to the amine moiety. The other ion exchangers, **N1G-N3G** which were synthesised as described elsewhere <sup>[88]</sup> looked very similar to their corresponding amine-containing counterparts. The only exception is a strong peak around 160 ppm which is attributable to the quaternary carbon of the guanidine group <sup>[88]</sup>.

a)





**Figure 3.1** Solid state  $^{13}\text{C}$  NMR spectra of silica-based ion exchangers containing **a)** monoamine (N1), **b)** ethylenediamine (N2) and **c)** diethylenetriamine (N3) functionalities.

### 3.2 Calibration graphs

As discussed in Section 2.5, all metal ion concentrations of the ARP solutions, as well as their extraction efficiencies were established applying 0.9 M  $\text{H}_2\text{SO}_4$  linear calibration standards, whereas desorption efficiencies were determined via measurement of the PGM concentrations with 2 M HCl linear calibration standards.

(see Table 3.2), and typical calibration graphs using 2 M HCl linear calibration standards of the most sensitive interference-free lines (as indicated by the slope) are shown in Figure 3.2.

**Table 3.2** Wavelengths of selected analytical lines used for ICP-OES measurements in 2 M HCl (PGMs) and 0.9 M H<sub>2</sub>SO<sub>4</sub> (BM).

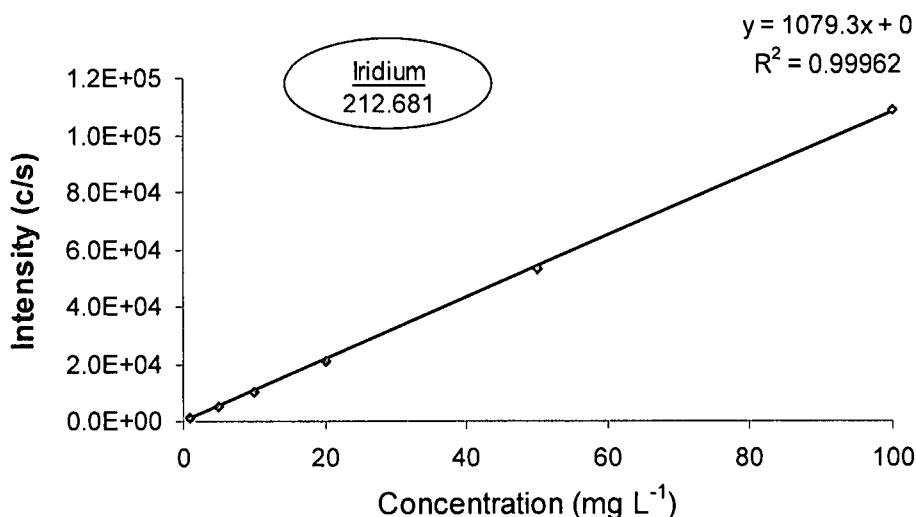
Element	Wavelength (nm)	Limit of detection ( $\mu\text{g L}^{-1}$ )		Linear correlation	
		(average: number of measurements = n)		(average: number of measurements = n)	
Pd	340.458	5 ± 4	(2)	0.99997	(2)
	324.270	29 ± 10	(4)	0.99997	(4)
	355.308 <sup>[a]</sup>	56	(1)	0.99990	(1)
Pt	214.423	9 ± 3	(4)	0.99981	(4)
	265.945	17 ± 5	(3)	0.99994	(3)
Rh	343.489	16 ± 7	(4)	0.99990	(4)
	369.236	22 ± 10	(3)	0.99995	(3)
Ir	212.681	6 ± 1	(4)	0.99985	(4)
	322.078	129 ± 47	(3)	0.99970	(3)
Fe	259.940	2 ± 1.4	(4)	0.99989	(3)
	238.204	4 ± 2.0	(3)	0.99988	(4)
Cu	324.754	2 ± 0.96	(4)	0.99994	(4)
	327.396	3 ± 0.58	(3)	0.99997	(3)
Ni	221.647	3 ± 1.7	(4)	0.99992	(4)
	232.003	23 ± 19.1	(2)	0.99993	(2)
	231.604	25	(1)	0.999986	(1)
Co	228.616	2	(1)	0.99990	(1)
	237.862	7	(1)	0.99988	(1)
Y	371.030	— <sup>[a]</sup>		— <sup>[a]</sup>	

<sup>[a]</sup> Concentration in calibration standards and samples ca 1.00 mg L<sup>-1</sup> (in ICP measurements).

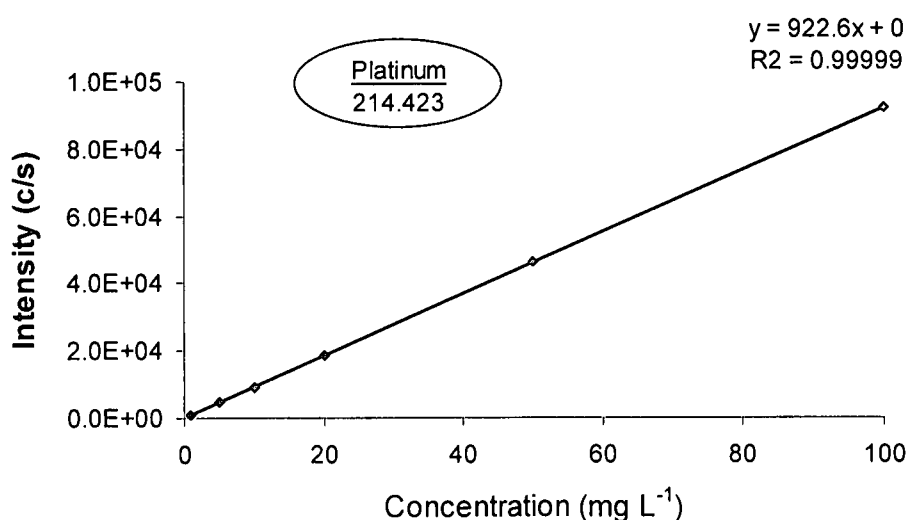
Limit of detection was calculated based on (3x) standard deviation of the blank and the slope of the graph as described by Miller <sup>[97]</sup>. PGMs and BM show good to excellent linearity. Sensitivity is down to 5 (Pd)  $\mu\text{g L}^{-1}$  (or ppb) well below lowest concentration observed in authentic refinery solutions. In addition, PGMs in 2 M HCl demonstrate equal to slightly better sensitivity than in  $\text{H}_2\text{SO}_4$ . However, BM exhibit somewhat better sensitivity than PGMs.

All calibration lines (Figure 3.2) displayed excellent linearity over three orders of magnitude in concentration.

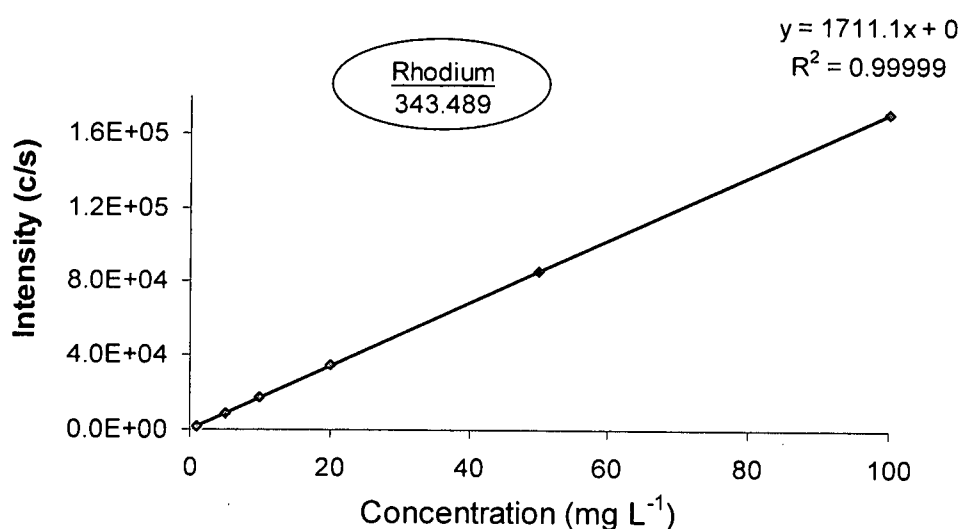
a)



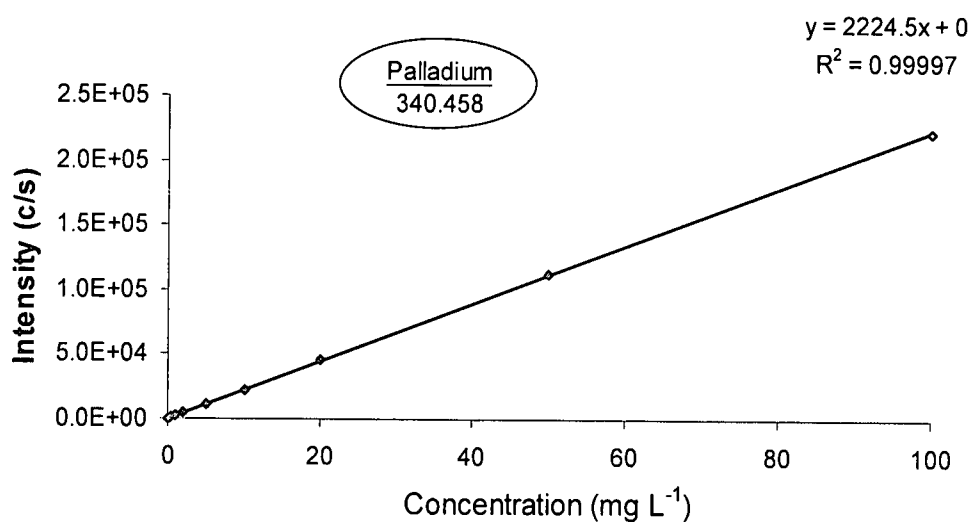
b)



c)



d)



**Figure 3.2** Calibration graphs of **a)** Ir (212.681 nm), **b)** Pt (214.423 nm), **c)** Rh (343.489 nm) and **d)** Pd (340.458 nm). The standards were prepared in 2 M HCl.

As mentioned in Section 2.5, the PGM standards were prepared in a 0.9 M H<sub>2</sub>SO<sub>4</sub> matrix solution for the extraction samples and in 2 M HCl matrix solution for the desorption samples. Sulphuric acid proved to be an appropriate acid for matrix matching the ARP solutions although the sensitivity in calibration graphs of the PGMs in 0.9 M H<sub>2</sub>SO<sub>4</sub> matrix solution is observed to be lower than the ones in 2 M

HCl. The reason for this low sensitivity is attributed by the viscosity of  $H_2SO_4$  which results to changes in the nebulization and the aspiration of the solution. Furthermore, the density of an acid affects the transport of an aerosol through the spray chamber [93].

### **3.3 The composition of the authentic refinery process solutions**

The unbound chloride content, pH as well as PGM and other transition metal concentrations, of the four different authentic refinery process solutions at our disposal are displayed in *Table 3.3*. Since the origin of the solutions has not been revealed to us, the speciation of the PGMs is unknown. We have restricted our focus to the determination of the most important platinum group metals (Pd, Pt, Ir and Rh) as well as the 'undesired' other transition metals which are most sensitive to being co-extracted under our recovery conditions, i.e. Cu, Ni, Fe and Co.



**Table 3.3** The PGM and other transition metals concentrations (in  $\text{mg L}^{-1}$ ), pH and unbound chloride concentrations (in  $\text{mol L}^{-1}$ ) as determined in authentic precious metal refinery process solutions ARP 1-4.

Metal ion	ARP solution			
	1	2	3	4
	pH:	- 0.6	0.2	3.2
	[Cl] ( $\text{mol L}^{-1}$ ): $4.9 \pm 0.03$	$1.7 \pm 0.01$	$1.6 \pm 0.02$	$3.1 \pm 0.07$
Pd	$641 \pm 57$	~ 3	$298 \pm 31$	$109 \pm 7$
Pt	$393 \pm 94$	$26 \pm 2$	$99 \pm 11$	$44 \pm 4$
Ir	$475 \pm 27$	$387 \pm 40$	< 3	< 1
Rh	$216 \pm 21$	$742 \pm 61$	$44 \pm 1$	< 3
Fe	> 15000	~ 1270	~ 110	~ 10
Cu	> 43000	~ 160	~ 420	~ 10
Ni	~ 1500	~ 8	~ 20	~ 110
Co	~ 100	~ 1	~ 1	0

\* A rough scan using ICP-MS performed by R. Rossouw (University of Stellenbosch, Central Analytical Facility) at the Council for Geosciences, Pretoria revealed the presence of the majority of the elements in the Periodic Table in these solutions in varying concentrations

Strikingly, vast quantities of the other analysed transition metals were measured, to an impressive  $> 60 \text{ g L}^{-1}$ , something which is supported by the colour of the solution.

The large number of these undesired metal ions, as well as the high concentration of TDS (originating from the alkali and alkali earth metal ions) explains our considerable difficulty to accurately determine the concentration of the PGM; this is reflected in the relatively large RSD found for this ARP solution, as both spectral and importantly non-spectral matrix interferences clearly play a significant role under these conditions. The RSD of the ARP concentrations is determined by taking the average

from measurements performed on different days. Apart from the difficulties mentioned above of getting reproducible measurements, metal salt precipitation over time contributed to variation of the actual concentration over time, leading to larger RSD.

ARP solution **2** is a clear, orange/brown solution. This colour indicates the presence of considerable amounts of Rh(III) bound to halide ions which forms complexes that are characterised by a distinctive red colour. This ARP solution contains a relatively high concentration ( $>700 \text{ mg L}^{-1}$ ) of Rh and Ir relative to the other PGMs. Solution **2** is also acidic with a lower concentration of unbound chloride but contains considerably less of the other transition metals than ARP solution **1**, with exception to Fe which is almost double the concentration of Rh. It is likely that this ARP solution originates from a process stream at the end of the precious metal refinery, because it is rich in Rh and Ir and these metals are mostly recovered last (see *Section 1.3.3*).

ARP solution **3** is characterised by its yellow/orange colour. The unbound chloride concentration is similar to ARP solution **2**. The pH of the solution is slightly higher at 3.2. Iridium is present in minute quantities (as shown in *Table 3.3*), therefore the focus of the extraction studies will be mainly on Pd, Pt and Rh as they are present in substantial amounts. The ARP solution also consists of more than  $500 \text{ mg L}^{-1}$  Cu, Ni, and Fe in total. Hence the total PGM concentration ( $> 400 \text{ mg L}^{-1}$ ) almost equals the total concentration of other transition metals.

ARP solution **4** is light peach-brown in colour. The unbound chloride concentration is slightly higher at 3.1 M than in ARP solutions **2** and **3** but is still lower than in ARP solution **1**. This ARP solution contains Rh and Ir in lesser amounts and suggests being a Pd/Pt stream. The other transition metals are present in lower

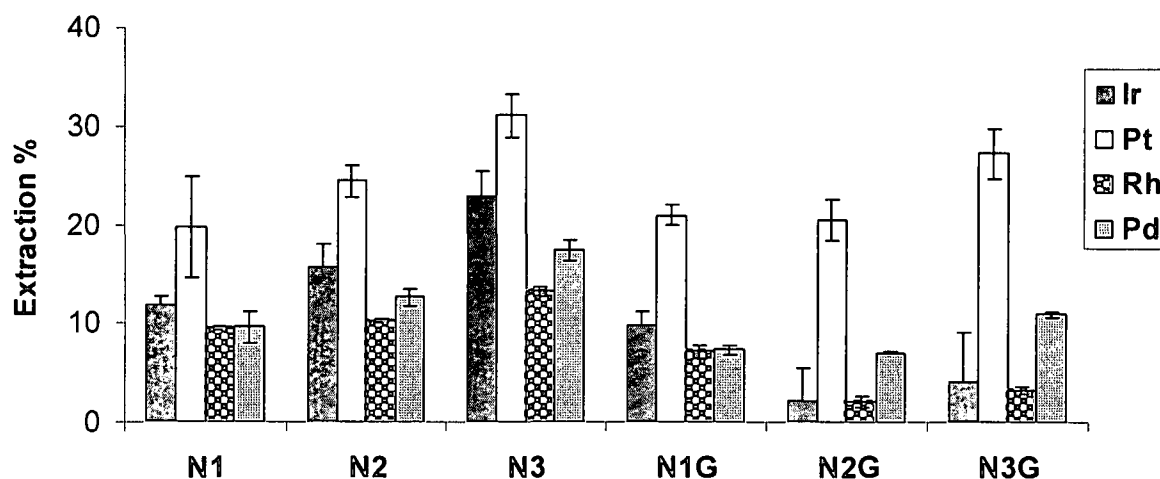
concentrations ( $< 10 \text{ mg L}^{-1}$ ), with the exception of Ni at a higher concentration ( $110 \text{ mg L}^{-1}$ ) and very close to the Pd concentration. Lastly, it is important to note that this solution is not very acidic ( $\text{pH} \sim 5$ ), which clearly poses the biggest challenge of all the ARP solutions with regard to selective PGM recovery.

### **3.4 Extraction studies using N1-N3 and N1G-N3G ion exchangers**

Ion exchangers **N1-N3** and their corresponding dimethylguanidine-containing equivalents (**N1G-N3G**) were compared in their PGM extraction efficiency (*Section 3.4.1*) and their selectivity of PGM extraction over other transition metals (*Section 3.4.2*). Extraction experiments were conducted on ARP solutions **1-4** which consist of different metal concentrations as displayed in *Table 3.3*. In all extraction experiments, it was ensured that ligands (ion exchangers) were always added in molar excess to total PGMs in the ARP solution under study.

### 3.4.1 Platinum group metal extractions

Figure 3.3 shows PGM extraction efficiencies obtained when both types of ion exchangers are used for PGM uptake in ARP solution 1.



**Figure 3.3** PGM extractions from ARP solution 1 using ion exchangers **N1-N3** and **N1G-N3G**. Initial metal ion concentrations (in  $\text{mg L}^{-1}$ ): Ir  $475 \pm 27$ , Pt  $393 \pm 94$ , Rh  $216 \pm 21$ , and Pd  $641 \pm 57$ . Other transition metal concentrations (in  $\text{mg L}^{-1}$ ): Cu  $> 43.000$ , Fe  $> 15.000$ , Ni  $\sim 1.500$  and Co  $\sim 100$ ,  $[\text{Cl}^-]$ :  $4.9 \text{ mol L}^{-1}$  and pH - 0.6.

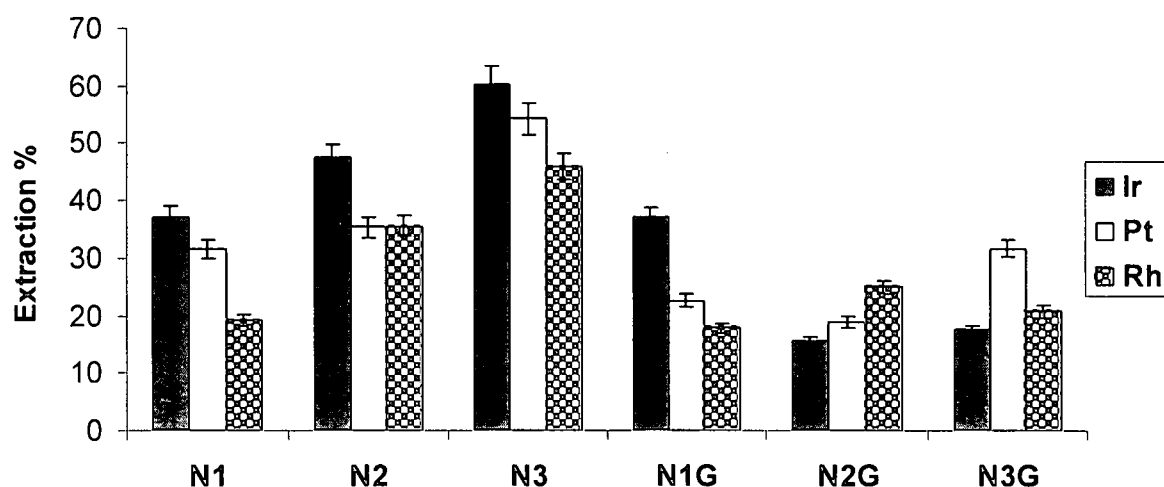
Although both types of ion exchangers become protonated under these acidic conditions and thus establish an ideal situation for PGM anionic complexes to be extracted via anion pairing, the extraction efficiency observed clearly is not very good for any of the ion exchangers **N1-N3** and **N1G-N3G** (note that the maximum extraction is set to 40%): The Ir, Pt, Rh and Pd uptake ranges from 9% to 31% with the former ion exchangers, with maximum extractions being observed for Pt. Even less adsorption was demonstrated at 2% (for Ir and Rh) to 27% (for Pt) by the latter ion exchangers. The general PGM extraction order for **N1-N3** ion exchangers is as follows: Pt > Ir > Pd > Rh.

The suppressed extractions can be explained in terms of the high concentration of unbound chloride ions ( $[\text{Cl}^-] \sim 4.9 \text{ mol L}^{-1}$ ), and other, not analysed,

anions present in this ARP solution, resulting in an increase in competition between the chloride anions and the PGM chloro complexes for binding sites on the protonated ion exchangers <sup>[46, 76]</sup>.

All the PGMs depict the general extraction trend, which is an increase in extraction from **N1** < **N2** < **N3** ion exchangers. This increase in adsorption is obtained as the number of nitrogen atoms increases in the ion exchanger. That is, more positive charges on the ion exchanger can effectively compensate for the negative charge of the PGM anions.

Figure 3.4 displays extraction efficiencies in ARP solution 2 with both types of ion exchangers.



**Figure 3.4** PGM extractions from ARP solution 2 using ion exchangers **N1-N3** and **N1G-N3G**. Initial metal concentrations (in  $\text{mg L}^{-1}$ ): Ir  $387 \pm 13$ , Pt  $26 \pm 2$ , Rh  $742 \pm 27$ . Other transition metal concentrations (in  $\text{mg L}^{-1}$ ): Cu  $\sim 160$ , Fe  $\sim 1270$ , Ni  $\sim 8$ , [Cl<sup>-</sup>]:  $1.7 \text{ mol L}^{-1}$  and pH  $\sim 0.2$ .

Although none of the PGMs were extracted quantitatively, generally a considerable increase in extraction with the ion exchangers is seen for all the PGMs compared with ARP solution 1, with Ir extractions ranging from 37% to 60%, whilst Pt ranges from 32% to 54% and Rh varies from 19% to 46% in case of the **N1-N3** ion exchangers. The same extraction trend displayed from ARP solution 1, **N3** > **N2** > **N1**, is seen here.

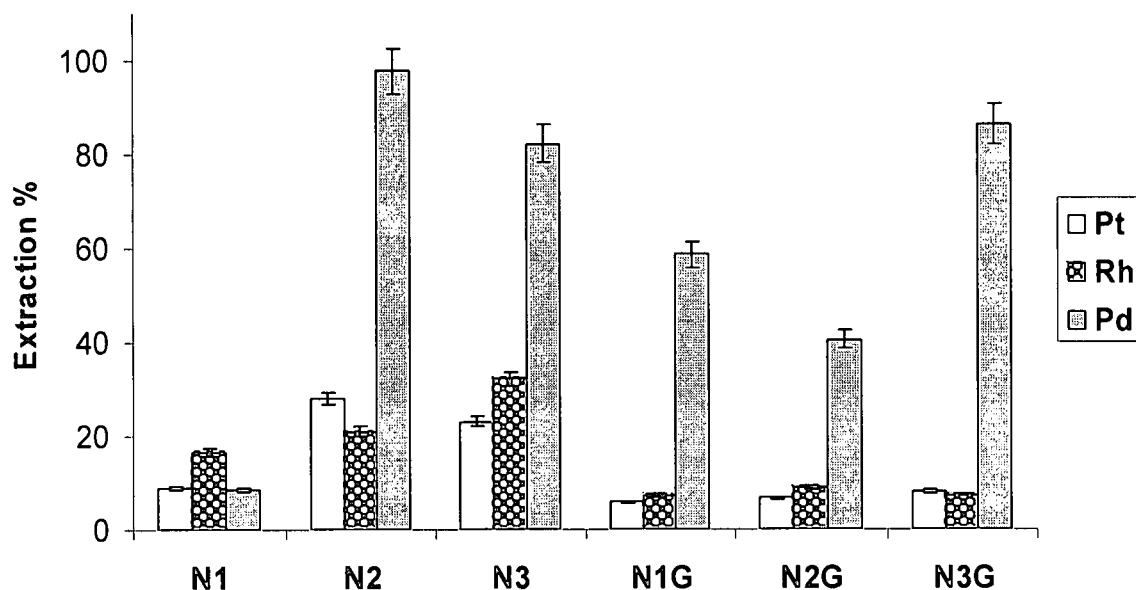
Alternatively, the PGM extraction exhibited by the DMG-containing ion exchangers differs for each metal and shows no consistent pattern from **N1G** to **N2G** and **N3G**; Ir extraction improves from **N2G** to **N3G** to **N1G**. Platinum sorption increases in the order: **N2G** to **N1G** to **N3G** and the rhodium uptake increases from **N1G** to **N3G** to **N2G**. A general feature of the DMG-containing ion exchangers is their depressed PGM adsorption as compared with extraction using the **N1-N3** ion exchangers. It appears that the affinity of guanidinium-containing ion exchangers for

these PGMs (Ir, Pt and Rh) is somewhat less than that of the (poly)amines, which might also explain why ion exchanger **N1** and **N1G** are most alike in adsorption pattern: incomplete conversion of the amine into the corresponding guanidine occurred for this ion exchanger (see *Section 3.1*).

A plausible explanation for the improved extractions is the decreased competition of free unbound  $\text{Cl}^-$  (and other anions) in this solution. Adversely, under these conditions of lower  $[\text{Cl}^-]$ , Rh (III) and Ir (III) can exist in the following complex forms:  $[\text{MCl}_6]^{3-}$ ,  $[\text{MCl}_5(\text{H}_2\text{O})]^{2-}$  or  $[\text{MCl}_4(\text{H}_2\text{O})]^-$  ( $\text{M} = \text{Ir}^{3+}$  and  $\text{Rh}^{3+}$ ), respectively <sup>[47, 98]</sup>. These different aquated species are considered to be less readily extractable (see *Section.1.4.2*) <sup>[48, 49]</sup>. The reasonably high Ir extractions could be due to the predominant existence of the metal in its 4+ oxidation state in this solution, and it is known that  $[\text{IrCl}_6]^{2-}$  is much less susceptible to aquation reactions <sup>[45, 49, 99-101]</sup>. Support for this assumption comes from our observations during digestion studies of ion exchangers loaded with ARP solution **1** and **2**: The colour changed from deep purple to yellow/green upon diluting the samples, indicative of Ir (IV) reduction under influence of water <sup>[102]</sup>.

At relatively high chloride concentrations Pt(II)/Pt(IV) and Pd(II) form similar complexes, essentially  $[\text{PtCl}_4]^{2-}/[\text{PtCl}_6]^{2-}$  and  $[\text{PdCl}_4]^{2-}$  <sup>[45]</sup>. In general, these  $[\text{MCl}_4]^{2-}$  and  $[\text{MCl}_6]^{2-}$  complexes are more readily extractable than the hydrolysed species. Apparently the competition between unbound  $\text{Cl}^-$  and Pt chloro complexes for binding sites is still significant judging from a maximum Pt extraction not exceeding 60% for any of the ion exchangers.

Figure 3.5 shows the PGM extractions from the ARP solution 3 with a higher pH of 3.2 and much lower in concentration of the other transition metals than the previously discussed ARP solutions.



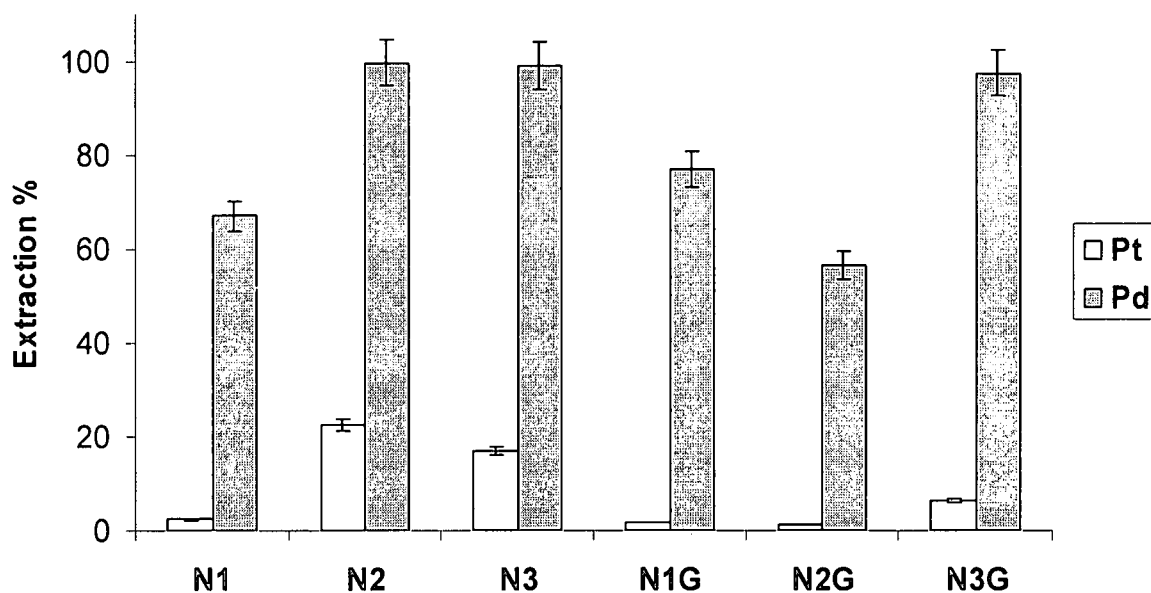
**Figure 3.5** PGM extractions from ARP solution 3 using ion exchangers **N1-N3** and **N1G-N3G**. Initial metal ion concentrations (in  $\text{mg L}^{-1}$ ): Pt  $99 \pm 11$ , Rh  $44 \pm 1$  and Pd  $298 \pm 31$ . Other transition metals concentrations (in  $\text{mg L}^{-1}$ ): Cu  $\sim 420$ , Fe  $\sim 110$ , Ni  $\sim 20$ , [Cl]:  $1.6 \text{ mol L}^{-1}$  and pH 3.2.

Palladium extractions were most successful and a close to quantitative extraction ( $\sim 98\%$ ) of the metal ion is observed using **N2** ion exchanger. Although the **N2G** ion exchangers is much less efficient (for unknown reasons), the average Pd sorption for the DMG-containing ion exchangers was also around 60%. Rhodium and Pt sorption are again not very successful, the first probably due to the co-presence of aquated species as explained before. The relatively low Pt extraction, with a maximum of 28% observed for the **N2** ion exchanger, is more difficult to explain. One explanation might be connected with the increased pH of the solution (pH  $\sim 3.2$ ) allowing the presence of hydrolysed  $[\text{PtCl}_{6-n}(\text{OH})_n]^{2-}$  species since the reported  $\text{pK}_a$  value for the deprotonation of  $[\text{PtCl}_5(\text{H}_2\text{O})]^-$  is  $\sim 3.5$  <sup>[103]</sup>. Although no data have been found on the



relative extractabilities of these hydrolysed species compared to  $[\text{PtCl}_6]^{2-}$ , it is not unreasonable to assume that these species will be more hydrophilic hence more difficult to remove from an aqueous solution. Furthermore it is noticeable that **N1G-N3G** ion exchangers are much more selective to Pd extraction, since a strong reduction in adsorption of Pt and Rh with the DMG-containing ion exchangers is furthermore distinguished.

Figure 3.6 shows the PGM extraction from ARP solution 4 with a somewhat higher pH of 5.0 than the ARP solution 3 and very similar extraction behaviour to that observed in Figure 3.5 is seen.



**Figure 3.6** PGM extractions from ARP solution 4 using ion exchangers **N1-N3** and **N1G-N3G**. Initial metal ion concentrations (in  $\text{mg L}^{-1}$ ): Pt  $44 \pm 4$  and Pd  $109 \pm 7$ . Other transition metals concentrations (in  $\text{mg L}^{-1}$ ): Cu  $\sim 10$ , Fe  $\sim 10$ , Ni  $\sim 110$ ,  $[\text{Cl}^-]$ :  $3.1 \text{ mol L}^{-1}$  and pH 5.0.

Clearly, an increase in uptake is displayed for all the ion exchangers as compared to extraction from ARP solution 3 (see Figure 3.5). Quantitative extraction of Pd is demonstrated with the **N2**, **N3** as well as with the **N3G** ion exchangers. Interestingly, the overall Pd extraction is not affected by the high chloride content ( $> 3 \text{ M}$ ) present

in this ARP solution. Although a molar excess of ligand to total PGM anions has been deployed in all solutions, less competition from other metal ions in this particular solution might have enhanced Pd extraction with the ion exchangers.

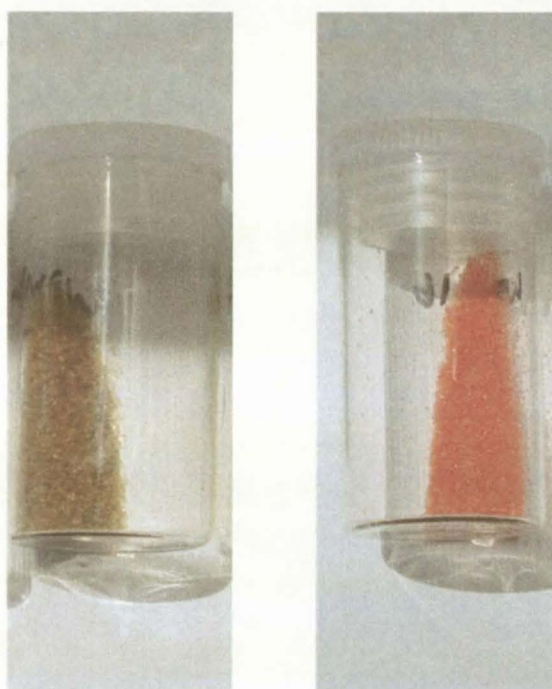
Maximum Pt uptake is attained at 22% in this ARP solution and hydrolysis species are expected to be even more abundant at this pH. Platinum extraction is greatly reduced in the case of the **N1G-N3G** ion exchangers. The highest uptake accomplished with **N3G** ion exchanger is at 6% which is very close to 8%, as previously identified in ARP solution **3**. Possibly the replacement of the rather small and flexible  $\text{NH}_2$  groups with the bulkier dimethylguanidine group forces the extractions to take place via ion pairing with more than one ligand whereby the square planar  $[\text{PdCl}_4]^{2-}$  complex which is smaller in size than  $[\text{PtCl}_6]^{2-}$  or related octahedral species can be preferentially extracted.

#### 3.4.2 Assessment of PGM extraction selectivity

Ion exchangers **N1-N3** and **N1G-N3G** proved to be very selective towards PGM extractions at low pH (pH range of - 0.6 to 0.2): *No other transition metal extractions* were observed from ARP solutions **1** and **2** (see *Table 3.3*). It is remarkable to note the extremely high selectivity for PGMs over the other undesired metal ions, in particular ARP solution **1**, where the total concentration of Cu, Ni, Fe and Co is more *than 35-fold* that of the total PGM concentration.

As discussed earlier (see Chapter 1) <sup>[88, 91, 104]</sup> under these very acidic conditions, all the ion exchangers are expected to be protonated and thus bind selectively to anionic PGM complexes, since the other transition metals do not form stable anionic complexes. An important factor accounting for the incomplete PGM extractions is certainly high concentration of other transition metals present in these

ARP solutions, giving rise to high concentration of competing ions for extraction sites. The colour of the loaded **N1-N3** ion exchanger contacted with ARP solution 1 confirms PGM uptake, as the materials are orange-brown. Ion exchangers brought into contact with ARP solution 2 gave different colours, namely an orange colour for the **N1** and **N2** ion exchangers and a pink colour for the **N3** ion exchanger, which colour is characteristic of the uptake of Rh and Ir-chloride complexes. *Figure 3.7* shows **N3** ion exchanger contacted with ARP solution 1 and 2.



**Figure.3.7.** *N3* ion exchanger after contact with authentic refinery process solution 1 (left) and 2 (right)

Quite a different result is obtained when Cu, Ni and Fe extractions were tested from ARP solution 3 and 4 (see *Table 3.4*) with a considerably higher pH relative to ARP solution 1 and 2. A quantitative extraction of Fe with the **N1-N3** ion exchangers is observed from ARP solution 3.

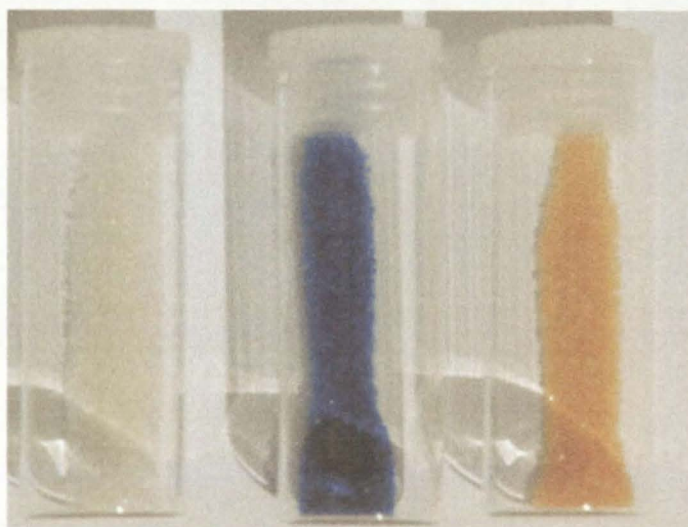
**Table 3.4:** Extractions of base metals: Cu, Fe and Ni from ARP solutions 3 (pH ~ 3.2, [Cl<sup>-</sup>]: 1.6 mol L<sup>-1</sup>) and 4 (pH 5.0, [Cl<sup>-</sup>]: 3.1 mol L<sup>-1</sup>). Metal ion concentrations (mg L<sup>-1</sup>): ARP solution 3: Ir < 3, Pt 99 ± 11, Rh 44 ± 1 and Pd 298 ± 31, Cu ~ 440, Fe ~110, Ni ~ 20; ARP solution 4: Pt 44 ±4 and Pd 109 ± 7, Cu ~ 10, Fe ~ 10 and Ni ~ 110.

ARP solutions, ion exchanger	Cu (%)	Fe (%)	Ni (%)
3, N1	10	93	0
3, N2	99	99	1
3, N3	89	99	95
3, N1G	0	0	0
3, N2G	0	29	0
3, N3G	0	64	0
4, N1	3	96	0
4, N2	99	98	8
4, N3	97	96	82
4, N1G	2	87	0
4, N2G	2	81	0
4, N3G	71	79	0

A quantitative extraction of the > 400 mg L<sup>-1</sup> Cu ions initially present in solution is seen with the **N2-N3** ion exchangers. Although Ni is not extracted by the **N1** and **N2** ion exchanger, a close to quantitative sorption is displayed by **N3** ion exchanger. This lack of extraction selectivity becomes also evident from the blue/purple to blue colours of the loaded **N2** and **N3** ion exchanger solutions indicating significant Cu uptake (see *Figure 3.8*), whereas the **N1** ion exchanger displayed a cream white colour marking the lack of any significant metal ion uptake.

On the other hand, the PGM selectivity over Cu, Ni and Fe is retained for the **N1G** ion exchanger, and no detectable Cu or Ni was removed from solution using the other two DMG-containing ion exchangers. The retained Pd extraction selectivity is evidenced by the yellow-brown colour of the **N2G** ion exchanger, in stark contrast

to the blue colour of its **N2** counterpart (*Figure 3.8*). Iron uptake is observed, increasing from the **N2G** and **N3G** ion exchangers, at 29% and 64% respectively.



**Figure 3.8** Ion exchangers **N2** (middle) and **N2G** (right) after contact with authentic refinery process solution **3**. The vial on the left shows unfunctionalised silica for comparison.

The lack of Cu and Ni extraction observed for the latter materials supports our expectation (see *Section.1.5.3.4*) that the much higher  $pK_a$  of guanidine-containing ligands<sup>[87]</sup> as compared to amine groups would result in the ligands to be present as a dimethylguanidinium group extracting exclusively anionic complexes.

Adversely, as extensively discussed, in these pH conditions, the (poly)amine containing ion exchangers are found to be less protonated which promotes the formation of (chelating) coordination bonds through the lone-pairs of the nitrogen atom. As a result, the PGM selectivity is increasingly less, as Cu and Ni are known to form very stable chelating complexes with aliphatic amine ligands<sup>[77, 87]</sup>. The order of extraction of these transition metals is **N1** < **N2** < **N3**. The trend correlates with the increasing availability of lone-pairs from the monoamine to the ethylenediamine to the diethylenetriamine, as a study by Nesterenko *et al.* indicated an increasingly low  $pK_a$  of the amine groups in the same order<sup>[84]</sup>.

Alternatively to Cu and Ni, in relatively chloride rich (either as HCl or other salts) solutions, Fe is possibly extracted as  $[\text{FeCl}_4]^-$  complex or as  $\text{Fe}^{3+}$ -containing complexes<sup>[40, 57, 105]</sup>.

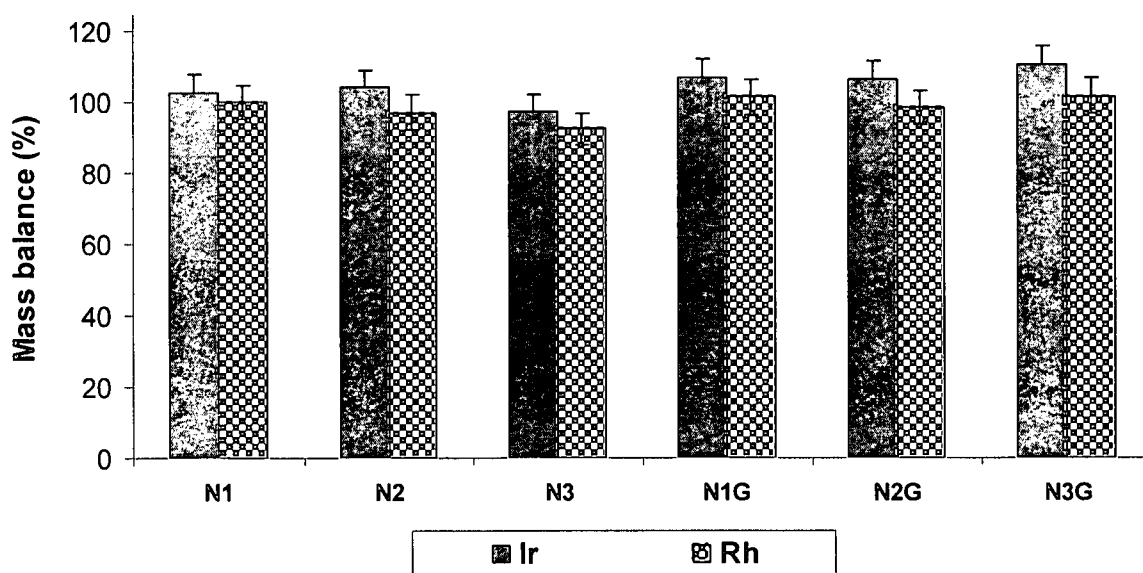
Therefore the quantitative extraction of Fe observed with the **N1-N3** ion exchangers and its considerable extraction with **N3G** ion exchanger under the experimental conditions could be possible due to binding via anion pairing as  $[\text{R}_3\text{NH}]^+[\text{FeCl}_4]^-$  or via coordination.

The lack of selectivity already displayed at pH 3.2 is even more strongly exhibited when the (poly)amine containing ion exchangers are contacted with ARP solution 4 (pH 5.0). *Table.3.4* shows the complete removal of Cu and Fe by the **N2** and **N3** ion exchangers whereas Ni is not taken up by **N1** ion exchanger, some extraction is observed (ca 8%) with **N2** and a high extraction is noticeable at 82% with the **N3** ion exchanger.

On the other hand, the DMG-containing ion exchangers (**N1G** and **N2G**) are still remarkably selective over Ni and Cu and only with the **N3G** ion exchanger, a 71% uptake of Cu is displayed. Probably, due to an increase in pH, the remaining amine groups in this ion exchanger which have not been converted into a dimethylguanidine group are no longer protonated. Therefore, coordination (possibly even via chelation) will play an increasingly large role at higher pH. Hence, the challenge is to convert the other remaining amine groups into guanidine groups. A strong increase in the Fe uptake from 79-87% with the **N3G** to **N1G** dimethylguanidine ion exchangers is seen as well. The reason for this uptake is caused by the higher  $[\text{Cl}^-]$ , which then leads to more  $[\text{FeCl}_4]^-$  in the solution.

### 3.4.3 PGM extractions: Mass balance determinations

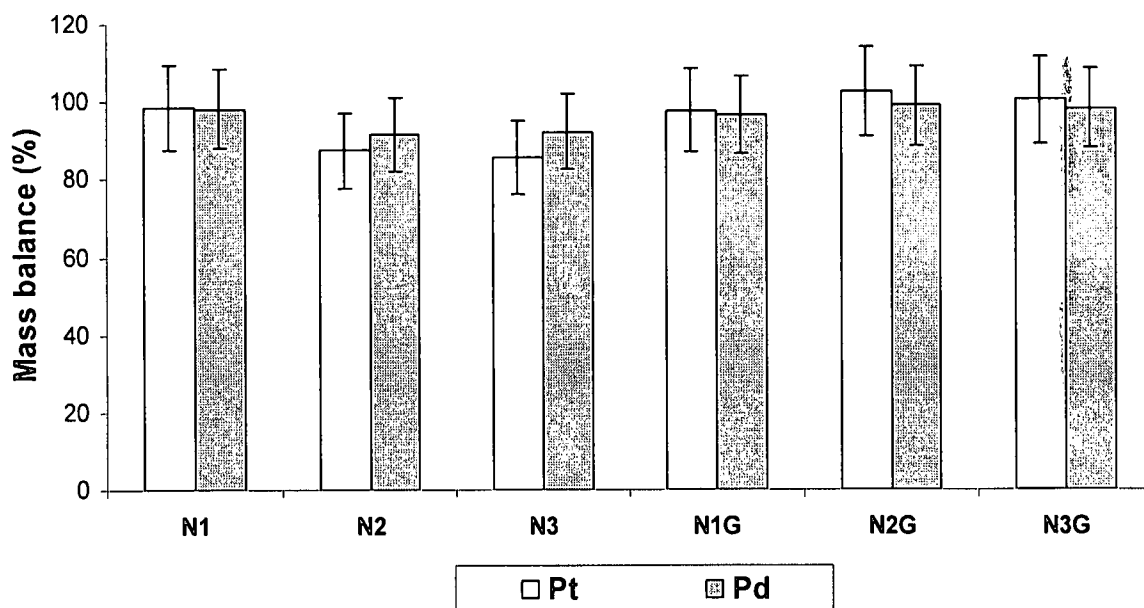
Mass balance determinations were performed occasionally to verify the reliability of our method to determine the PGM extraction efficiencies (see *equation 2.1*, *Section 2.6*). The error bars supplied in the mass balance results are based on the standard deviation in the PGM concentrations of the ARP solutions in *Figure 3.9* which shows mass balance for Ir and Rh in ARP solution 2. The results are very good since a mass balance of around 100% is obtained for both elements, in spite of the difficulties to determine the PGM concentration very reliably (see *Section 3.3*), which clearly affects *equation 2.1* (mass balance equation). In a few cases the Ir values are slightly higher than 100%, which reflect the difficulty in completely accurate quantification of these precious metal ions in these ARP solutions.



**Figure 3.9** Mass balances for Ir and Rh from ARP solution 2.

*Figure 3.10* displays the mass balance for Pt and Pd in ARP solution 3. A slight decrease in mass balance is experienced for Pt ranging from 86-103%. This depression is much less pronounced for Pd, as mass balance for Pd were found to

be ranging from 92%-99%. The somewhat lower mass balance has been observed before <sup>[91]</sup> and the error lies with the amount of extracted Pt (and Pd), based on the content of the ion exchangers. In the case of Pt, the amounts of extracted metal ions based on the content of the ion exchanger are often lower than those based on the content of the filtrate. This is the result of partial reduction of the Pt (and Pd) metal ions to  $M^0$  and subsequent precipitation during the digestion of the ion exchangers in concentrated  $H_2SO_4$ , needed to prepare the samples for analysis (see *Section 2.6*). Hence, the extraction results based on the amount of PGMs left in the filtrate are the most reliable, and were consequently, throughout this study.



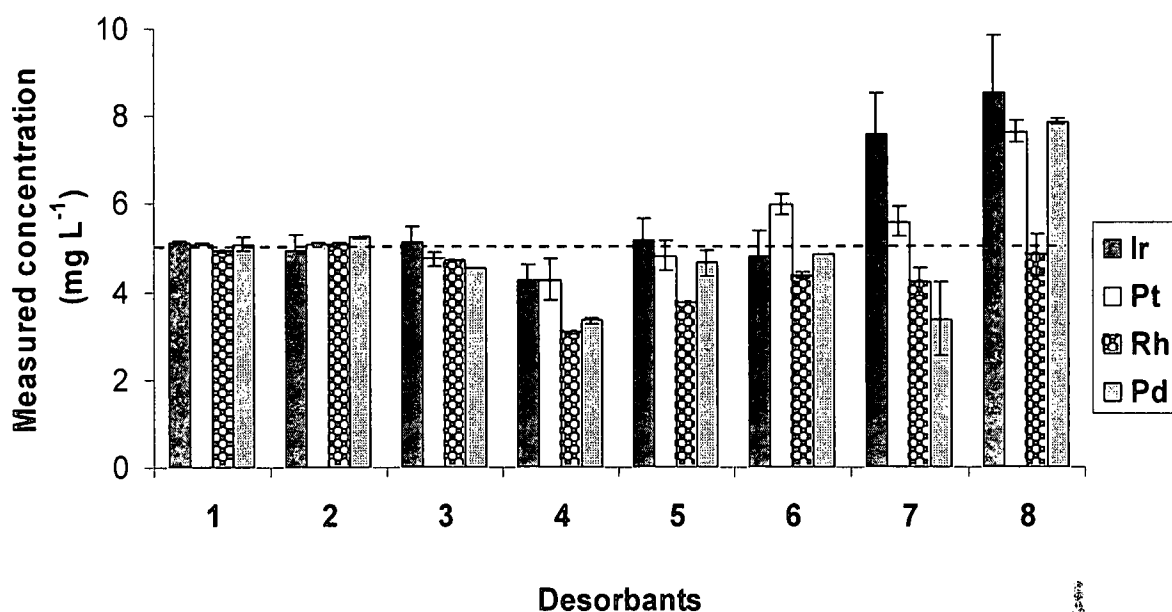
**Figure 3.10** Mass balances for Pt and Pd from ARP solution 3.

### 3.5 Matrix effects on PGM concentrations obtained with ICP-OES

Various stripping agents were investigated for the recovery of the adsorbed PGMs on the ion exchanger. Prior to this experiment the matrix effect of the desorbent on the outcome of the ICP-OES instrument results was tested as follows: A series of potential desorbents (see *Section 2.7*) was spiked with the PGMs (Pd, Pt, Ir and Rh)



to a final concentration of  $5 \text{ mg L}^{-1}$  and concentrations were determined using PGM standards in  $2 \text{ M HCl}$ .



**Figure 3.11** PGM concentrations measured by means of ICP-OES in a  $5 \text{ mg L}^{-1}$  solution of Ir, Pt, Rh and Pd in the following stripping agents (entries 1-8): 1)  $5 \text{ M HCl}$  2)  $1 \text{ M HCl}$  3)  $2 \text{ M HNO}_3$  4)  $2 \text{ M H}_2\text{SO}_4$  5)  $0.25 \text{ M Tu} / 1 \text{ M HCl}$  6)  $0.5 \text{ M Tu}$  7)  $2.7 \text{ M NH}_4\text{OH} / 0.5 \text{ M NH}_4\text{NO}_3$  and 8)  $0.5 \text{ M NH}_4\text{SCN}$ . The dotted line represents the actual concentration present in solution ( $5 \text{ mg L}^{-1}$ ).

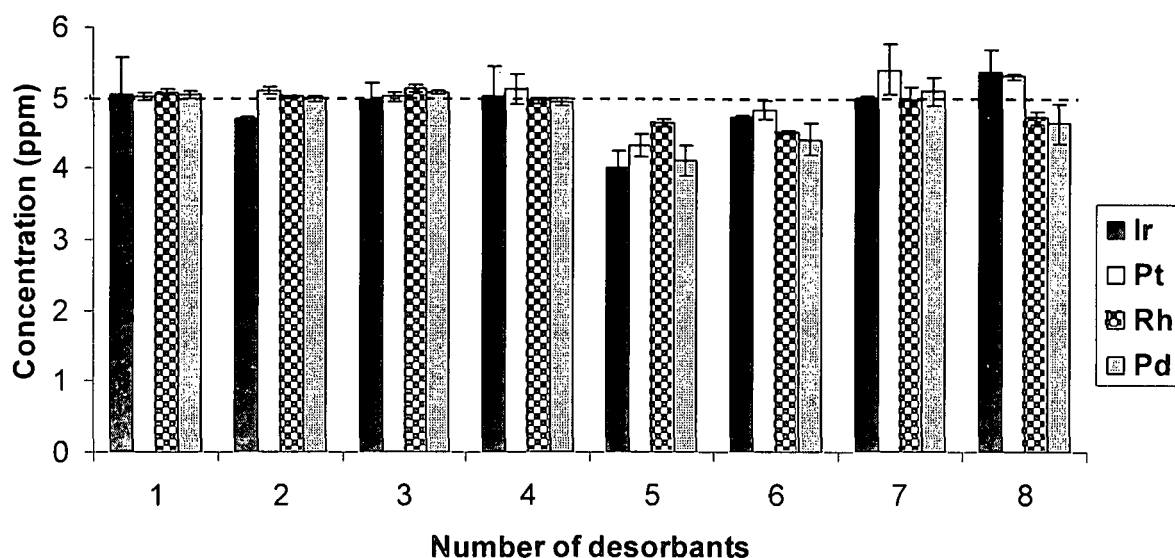
Figure 3.11 shows only small matrix effects of HCl or HNO<sub>3</sub> (entry 1, 2 and 3) on any of the measured PGM concentrations. However, a clear effect is visible when H<sub>2</sub>SO<sub>4</sub> (entry 4) is used, with an up to 40% depression of the signal due to the high viscosity of sulphuric acid. The measured PGM concentrations when thiourea is present (entries 5 and 6) are also less reliable, possibly resulting from the large total dissolved solid concentration. Under alkaline conditions (entries 7 and 8) very large deviations from the correct  $5 \text{ mg L}^{-1}$  value are observed for most PGMs, ranging from as low as  $3 \text{ mg L}^{-1}$  to as high as  $8 \text{ mg L}^{-1}$ , rendering these conditions very unreliable without any matrix correction. Spiking of the solutions with Y ( $5 \text{ mg L}^{-1}$ ) as an internal standard increases the PGM signals obtained in H<sub>2</sub>SO<sub>4</sub> by some 20%. However, the

measured PGM concentrations in the Tu-containing agents or alkaline conditions did not show considerable improvement (data not shown), so when a high concentration of TDS is present, this method is insufficient.

Therefore the samples were 'matrix matched' with the 2 M HCl standards as follows: 5mL of a 10 mg L<sup>-1</sup> PGM solution in the selected desorbent was mixed with 5mL of a 4 M HCl solution resulting in a 5 mg L<sup>-1</sup> PGM solution that contained a final concentration of 2 M HCl aside the desorbent matrix.

*Figure 3.12* shows a considerable improvement for especially the alkaline desorbent (entry **8**), clearly demonstrating the necessity to always acidify the samples before measurement is commenced. The risk of formation of hydroxides which might precipitate and clog the ICP tubing system is thereby also reduced.

Unfortunately this method of matrix matching is very labour intensive, and therefore impractical, so for future studies our focus will be on acidic desorption conditions only, using Y corrections.



**Figure 3.12** Yttrium corrected concentrations of the PGMs in a variety of stripping agents that are 'matrix matched': 1) 1.5 M HCl 2) 3.5 M HCl 3) 1 M HCl / 1 M HNO<sub>3</sub> 4) 1 M HCl / 1 M H<sub>2</sub>SO<sub>4</sub> 5) 0.25 M Tu / 1.5 M HCl 6) 0.25 M Tu / 1 M HCl 7) 1.3 M NH<sub>4</sub>OH / 0.25 M NH<sub>4</sub>NO<sub>3</sub> / 1M HCl and 8) 0.25 M NH<sub>4</sub>SCN / 1 M HCl.

### 3.6 PGM recoveries

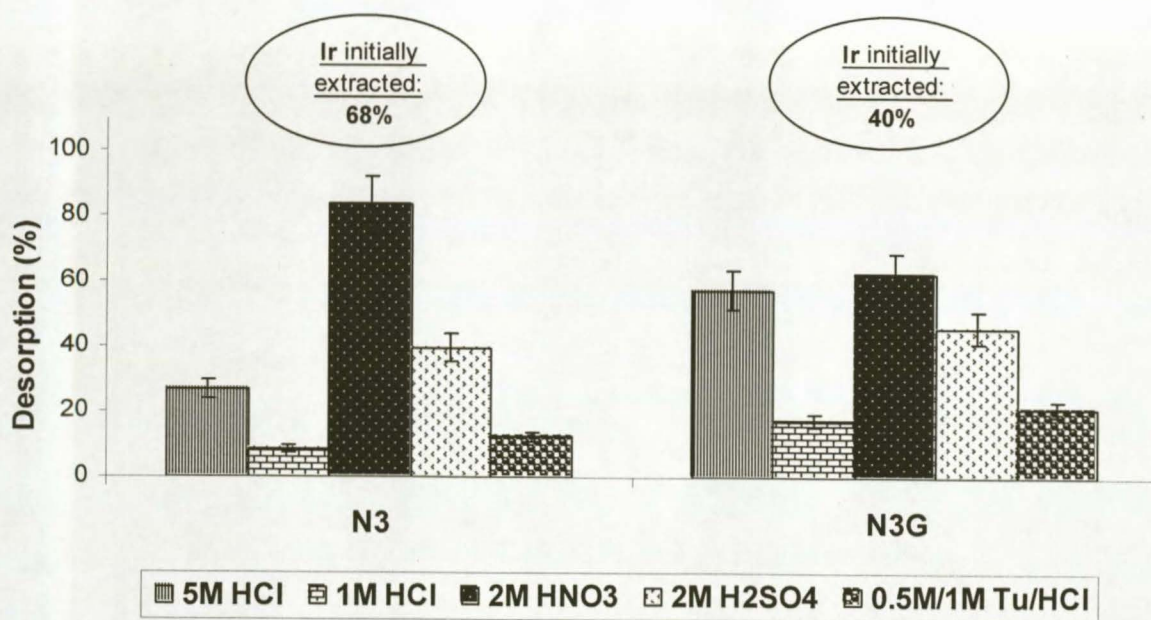
Desorption studies were carried out using **N3** and **N3G** ion exchangers. These ion exchangers were chosen based on the fact that they displayed generally the most efficient extraction amongst the polyamine and the corresponding DMG-containing ion exchangers. The focus was on PGM desorption from the ion exchangers loaded with the elements which were present in substantial amounts: Rh and Ir desorption was investigated from ion exchangers loaded with ARP solution **2** (Section 3.6.1), followed by Pd and Pt desorption from ion exchangers contacted with ARP solution **3** (Section 3.6.2). Finally, the total recovery of the PGMs is given in Section 3.6.3 and Section 3.6.4, respectively.

All the recovery studies were performed using ion exchangers based on coarse silica particles, as these proved much easier to handle (less time-consuming) than the fine materials. The corresponding ligand concentrations are somewhat

higher than those listed in *Table 3.1* for the fine materials:  $0.92 \text{ mmol g}^{-1}$  and  $0.75 \text{ mmol g}^{-1}$  for **N3** and **N3G**, respectively.

### 3.6.1 Iridium and rhodium desorption using various stripping agents

*Figure 3.13* shows Ir desorption efficiencies from **N3** and **N3G** ion exchangers with various acidic desorbents. All the desorption results are based on solutions that were spiked with  $5 \text{ mg L}^{-1}$  Y as an internal standard, since this correction proved to be reliable for acidic desorbents. The other potential desorbents, displayed in *Figure 3.11* were also tested, i.e. alkaline desorbents and competing ligands (thiourea,  $\text{NH}_4\text{OH} / \text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{OH} / \text{Na-Benzoate}$ , and  $0.5 \text{ M NH}_4\text{SCN}$ ). However, the results were not very reliable, as could be expected based on the results of the previous section, and are therefore not shown.



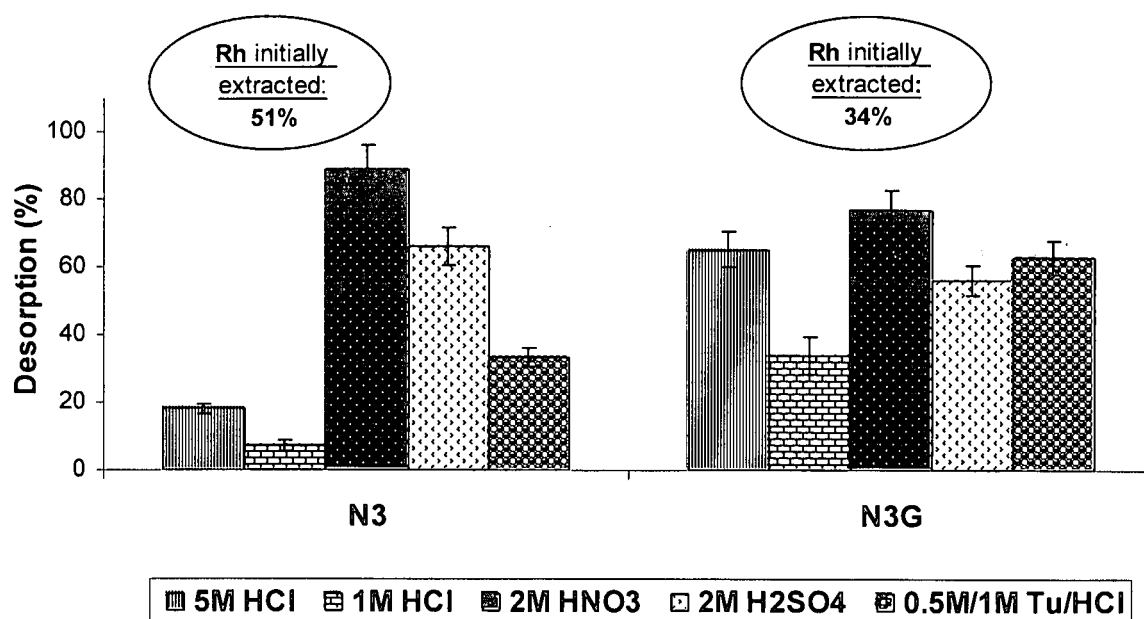
**Figure 3.13** Iridium desorption from loaded **N3** and **N3G** ion exchangers using various stripping agents subsequent to adsorption with ARP solution 2.

An extraction efficiency of 68% and 40% was obtained for **N3** and **N3G** ion exchangers, respectively, and samples were divided into equal portions, and

contacted with the various desorbents. The somewhat improved extraction result as compared to *Figure 3.4 (in Section 3.4.1)* is attributable to the slightly higher ligand to metal molar excess applied in this experiment.

For both ion exchangers, the best desorption is demonstrated with 2 M HNO<sub>3</sub> at 84% by **N3** ion exchanger and at 63% with **N3G** ion exchanger, respectively. With the other stripping agents, up to 40% desorption was achieved with the **N3** ion exchanger.

By contrast desorption of iridium using the other desorbants (5 M HCl and 2 M H<sub>2</sub>SO<sub>4</sub>) is generally somewhat better from the **N3G** ion exchanger than from the **N3** ion exchanger, ranging from 18% for 1 M HCl to 58% for 5 M HCl.



**Figure 3.14** Rhodium desorption from loaded **N3** and **N3G** ion exchangers using various stripping agents subsequent to adsorption from ARP solution 2.

*Figure 3.14* demonstrates the stripping of Rh with the same desorbents under investigation. Nitric acid proved to be the best desorbent for Rh as well, as observed with **N3** ion exchanger at some 90% and 75% after Rh loading onto the **N3G** ion

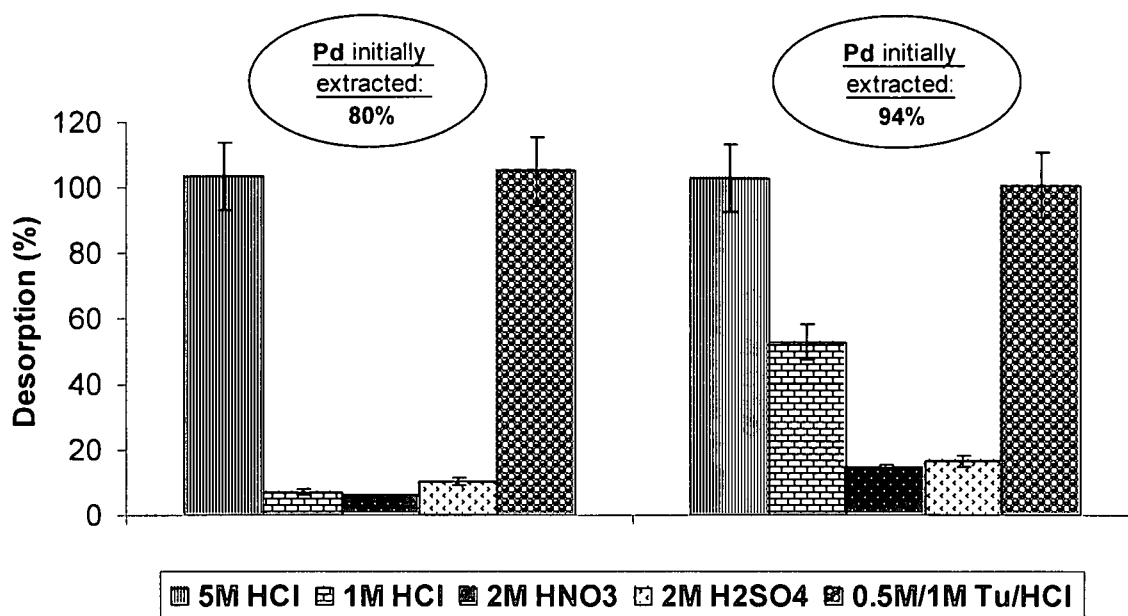
exchanger. Moreover, Rh desorptions were somewhat better than Ir for the other desorbents as well.

Since Rhodium and iridium desorptions are notoriously difficult due to irreversible binding <sup>[47, 106]</sup>, the maximum observed desorptions are promising.

It is clear that both Rh and Ir are stripped better from the **N3G** than from the **N3** ion exchanger with most desorbents. A possible explanation might be the anticipated weaker binding of the dimethylguanidinium group, as a result of the charge delocalisation as compared to the more localised positive charge on the amine groups. This hypothesis appears to be supported by the generally observed lower extraction using the DMG-containing ion exchangers.

### 3.6.2 Palladium and platinum desorption using various stripping agents

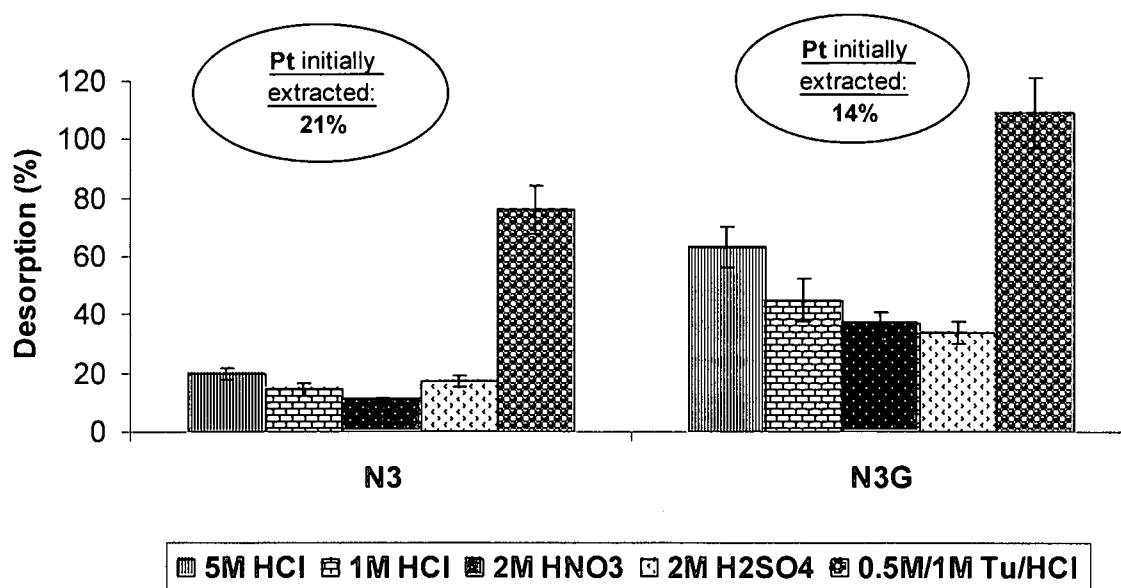
Desorptions of Pd and Pt from **N3** and **N3G** ion exchangers loaded with APR solution **3** were performed using the same acidic desorbents and results are shown in *Figure 3.15 and 3.16*. Extractions of 80% and 94% Pd were obtained with **N3** and **N3G** ion exchangers, respectively. Platinum extractions were much lower at 21% for **N3** and 14% for **N3G** ion exchangers, as observed in *Figure 3.5 (see Section 3.4.1)*.



**Figure 3.15** Palladium desorption from loaded **N3** and **N3G** ion exchangers using various stripping agents subsequent to adsorption with ARP solution 3.

Quantitative desorptions were effected with 5 M HCl and Tu / HCl for Pd using **N3** ion exchangers whereas very low desorptions of only up to 10% were achieved with 1 M HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. Further excellent desorptions are observed for Pd with **N3G** ion exchanger by 5 M HCl and Tu / HCl. An improvement from 7% desorption with **N3** ion exchanger to 53% with **N3G** ion exchanger is noticed when more dilute HCl (1 M) was used.

The resistance of Pd to be desorbed with HNO<sub>3</sub> might be used to our advantage: it could provide a way to selectively strip Rh and Ir from the loaded ion exchanger, as both these metals proved to be most removed by this stripping agent.



**Figure 3.16** Platinum desorption from loaded **N3** and **N3G** ion exchangers using various stripping agents subsequent to adsorption with ARP solution 3.

The Pt desorption trend is very similar to that seen for Pd, and demonstrates the similarity of the metal ions thus exemplifying the relative difficulty to separate these two precious metal ions from each other.

The desorptions are more modest than for Pd though, with the highest Pt desorption achieved at 76% using Tu / HCl from **N3** ion exchanger. Desorption with other acids is very poor, a maximum of 20% was reached with 5 M HCl. Platinum is considerably better stripped from the **N3G** ion exchangers. An increase in desorption with 5 M HCl is achieved at 63%, and quantitative desorption with Tu / HCl is possible.

Again the best stripping for both metal ions seems to be achieved with the dimethylguanidinium-containing ion exchanger, and these findings are consistent with the results obtained in *Figure 3.13* and *3.14* for Ir and Rh.



### 3.6.3 Iridium and rhodium recovery

Clearly it is crucial to calculate the total recoveries of the individual metal ions as well, as this will give a correct representation of the relative efficiency of the different ligands for recovery of the individual metal ions. The recoveries of Ir and Rh are displayed in *Table 3.5*.

**Table 3.5** *Iridium and rhodium recoveries (in % and mg/g ion exchanger) obtained for N3 and N3G ion exchangers from ARP solution 2.*

Ion Exchanger, Metal ion	Desorbent Used				
	5 M HCl	1 M HCl	2 M HNO <sub>3</sub>	2 M H <sub>2</sub> SO <sub>4</sub>	0.5 M Tu / 1 M HCl
<b>N3, Ir</b>	18%	6%	57%	27%	8%
	2.1 mg/g	0.7 mg/g	6.6 mg/g	3.1 mg/g	1.0 mg/g
<b>N3G, Ir</b>	23%	7%	25%	18%	8%
	2.7 mg/g	0.8 mg/g	2.9 mg/g	2.1 mg/g	1.0 mg/g
<b>N3,Rh</b>	9%	4%	45%	34%	17%
	2.1 mg/g	0.8 mg/g	10.1 mg/g	7.5 mg/g	3.8 mg/g
<b>N3G,Rh</b>	22%	12%	26%	19%	22%
	5.0 mg/g	2.6 mg/g	5.8 mg/g	4.3 mg/g	4.8 mg/g

The recoveries of both Rh and Ir obtained with the **N3** and **N3G** ion exchangers are best using either nitric acid or sulphuric, and recoveries using the **N3** ion exchanger are superior to those of the **N3G** ion exchanger. Recoveries using **N3** in fact were the highest out of all the ion exchangers tested since the extractions were found to increase in the order **N1** < **N2** < **N3** (shown in *Figure 3.4*).

### 3.6.4 Palladium and platinum recovery

Total recoveries for Pd and Pt ions were calculated as well to sum up the performance of both types of ion exchangers for the recovery of these individual metal ions. The results of Pd and Pt recoveries are displayed in *Table 3.6*.

**Table 3.6.** *Palladium and platinum recoveries (in % and mg/g ion exchanger) obtained for N3 and N3G ion exchangers from ARP solution 3.*

Ion Exchanger, Metal ion	Desorbent Used				
	5 M HCl	1 M HCl	2 M HNO <sub>3</sub>	2 M H <sub>2</sub> SO <sub>4</sub>	0.5 M Tu / 1 M HCl
<b>N3, Pd</b>	83%	6%	4%	8%	84%
	7.4 mg/g	0.5 mg/g	0.4 mg/g	0.7 mg/g	7.5 mg/g
<b>N3G, Pd</b>	97%	49%	13%	16%	95%
	8.6 mg/g	4.4 mg/g	1.2 mg/g	1.4 mg/g	8.4 mg/g
<b>N3, Pt</b>	4%	3%	2%	4%	16%
	0.1 mg/g	0.1 mg/g	0.1 mg/g	0.1 mg/g	0.5 mg/g
<b>N3G, Pt</b>	9%	6%	5%	5%	15%
	0.3 mg/g	0.2 mg/g	0.2 mg/g	0.1 mg/g	0.4 mg/g

A good Pd recovery is achieved using the **N3** ion exchanger when either 5 M HCl or a combination of thiourea and HCl was used. Close to quantitative recoveries are achieved with the **N3G** ion exchanger. The importance in choosing the correct acidic desorbent to get to good recoveries is clearly displayed, since very poor Pd recoveries (<20%) were obtained with the other stripping agents.

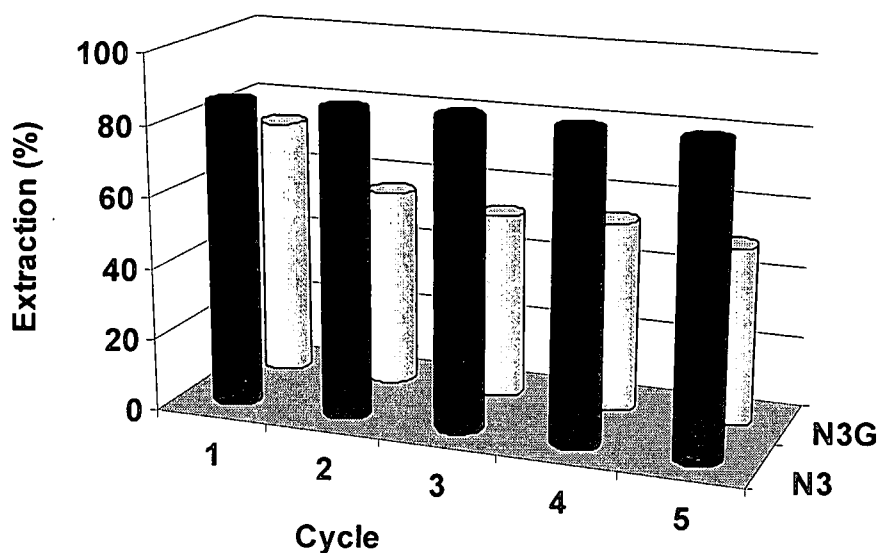
It is clear that Pt recovery is poor for both types of ion exchangers, which is the obvious result of the low extraction efficiencies observed for both ion exchangers. Up to 0.5 mg/g and 0.4 mg/g are recovered from the **N3** and **N3G** ion exchangers, respectively with the Tu / HCl desorbent.

In summary, although nitric acid is the best stripping agent for Ir and Rh, it is the least effective desorbent for the recovery of Pd and Pt, offering a means to separate these PGMs in the desorption step.

### 3.7 Successive recovery studies

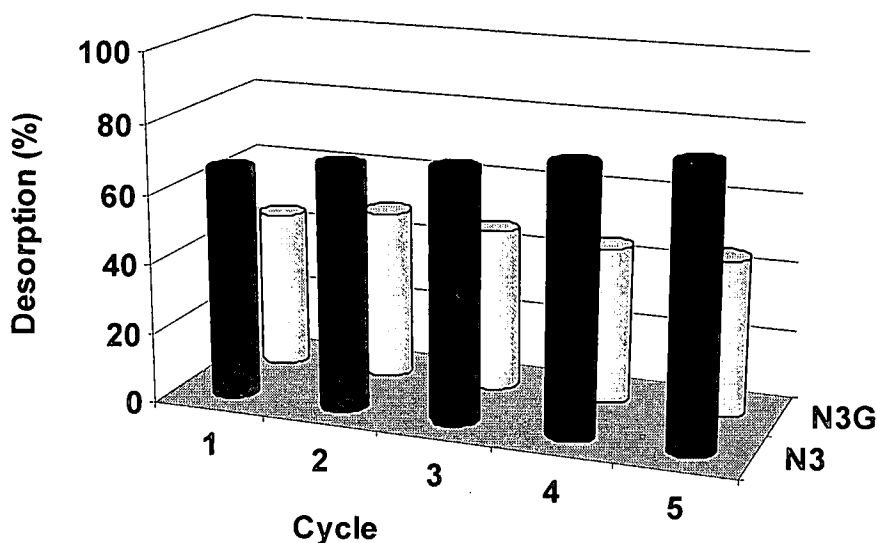
In spite of the relatively low synthesis costs of these ion exchange materials, sustainability of the materials is an important issue. Therefore, the ion exchangers were subjected to several recovery cycles in order to assess their re-usability during repeated exposure to the ARP solutions and minerals acids required for desorption.

Consequently, a series of five cycles of Pd adsorption-desorption was performed with a considerable (>5 fold) molar ligand to total PGM excess using the most efficient ion exchangers **N3** and **N3G**. The focus has been on Pd since the most efficient recovery results were obtained for this PGM. After a fresh batch of ion exchanger was contacted with ARP solution **3**, desorption was performed using 5 M HCl. This desorbent was chosen in view of the favourable results obtained (see *Figure 3.15*) and the fact that HCl is most desirable from an industrial point of view due to its abundance in the refinery processes. Subsequently, the same materials were exposed to a fresh batch of ARP solution in the next extraction cycle.



**Figure 3.17** Successive Pd extractions with **N3** (■) and **N3G** (□) ion exchangers from ARP solution 3. Initial Pd concentration:  $298 \pm 31 \text{ mg L}^{-1}$ .

Figure 3.17 shows that good, consistent extraction is maintained of just over 85% throughout the cycles for Pd with **N3** ion exchanger. Alternatively, the adsorption of Pd on **N3G** drops some 20% after the first extraction cycle, where Pd is adsorbed at 73%. In the following cycles, the extraction stabilises at just over 50%. The DMG ligands apparently are more vulnerable to degradation under strongly acidic conditions applied than amines. This results in lower ligand concentration, so less ligands are available for the same amount of metal ions which then leads to a decrease in uptake.

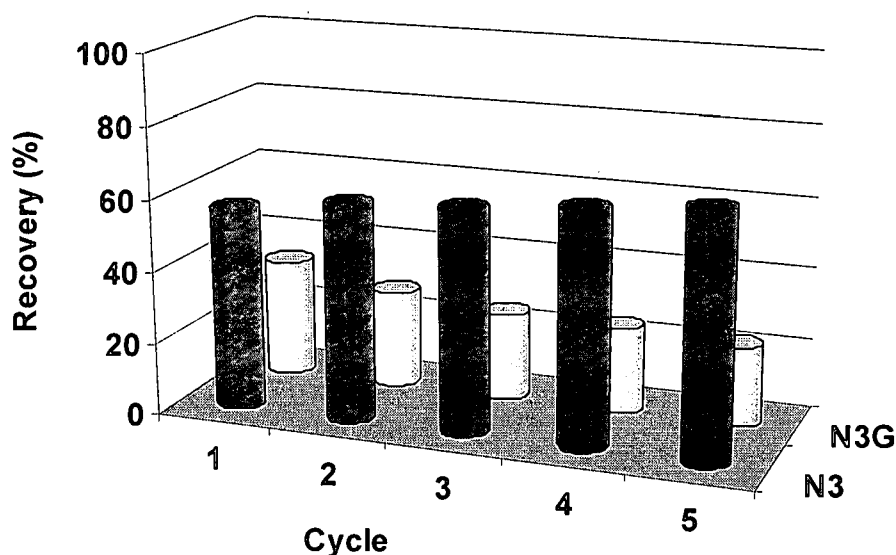


**Figure 3.18** Successive Pd desorptions using 5 M HCl, from **N3** (▨) and **N3G** (no colour □) ion exchangers loaded with ARP solution 3. Initial Pd concentration:  $298 \pm 31 \text{ mg L}^{-1}$ .

Consistently a little less than half of the Pd metal ions initially extracted were found desorbed from the **N3G** ion exchanger using 5 M HCl. Desorption with HCl proved better with **N3** than with the **N3G** ion exchanger. Interestingly, the attained desorption for Pd initially at 66%, gradually increased to almost 70% in the last cycle with **N3** ion exchanger. The slight increase might imply that part of the Pd ions are bound more strongly, probably via chelation, and that metal ions bound in this fashion are only removed from the ion exchanger upon repeated contact with the desorbent. This could explain why no such increase is observed for **N3G**, as anion pairing is the only mode of binding envisaged.

For both types of ion exchangers, incomplete desorptions were observed, and efficiencies were considerably lower than observed earlier (*Figure 3.15*). Less desorbent (15 mL) relative to amount of ion exchanger (400 mg) and ARP solution was used whereas *Figure 3.15* demonstrates quantitative desorption of Pd with 5 M HCl. In those experiments, the same amount of desorbent was used to strip only 100

mg of loaded ion exchanger. In the present experiment, 400 mg ion exchanger was used to ensure enough binding sites throughout the 5 extraction cycles performed, and this might explain the drop in desorption efficiency, the desorbed  $[\text{PdCl}_4]^{2-}$  anionic complexes present in a much higher concentration in the current solution might re-attach to the polymer after initial desorption. So there will be an equilibrium under these batch conditions that is not expected to occur in a continuous system. In other words, in a recovery set-up where a column is used, the equilibrium in *equation 1.5* will be pushed strongly to the left due to a continuous supply of 'fresh'  $\text{Cl}^-$  ions.



**Figure 3.19** Successive Pd recoveries, from ARP solution 3 using **N3** (■) and **N3G** (□) ion exchangers.

About 56-68% (between 6-8 mg/g) of Pd could be recovered with **N3** ion exchanger from the ARP solution during each recovery cycle with the recoveries increasing as a result of the above-discussed small increase in desorption with each contact. This implies that a recovery of roughly ca 35 mg Pd per g of **N3** ion exchangers is achieved after five cycles. The **N3G** ion exchanger is considerably less efficient (with 22-33% Pd recovery obtained), which is largely attributable to the lower desorption percentage as compared to **N3** ion exchanger, differences that were not observed

when the amount of desorbent per amount of ion exchanger was larger  
(*Figure.3.15*).

## Chapter 4: Conclusions

A series of (poly)amine containing silica-based anion exchangers (**N1-N3**) and their corresponding dimethylguanidine (DMG) derivatives (**N1G-N3G**) have been successfully synthesised and subsequently tested on their ability to recover the platinum group metals Pd, Pt, Ir and Rh from authentic refinery process (ARP) solutions, as relevant to the South African industry. In spite of the considerable difficulties to accurately determine metal concentrations in these solutions (details of which composition were not given to us) which contained large numbers of total dissolved solids (resulting from the presence of other transition metal ions and unbound counter ions such as chloride), the PGM concentrations could be determined to within a reasonable accuracy of 5-10%.

Of the PGMs studied, palladium extraction proved to be most successful, with up to quantitative extraction achievable with both types of ion exchangers. These metal extraction results are dependent on a number of factors like the pH, the unbound chloride ions (and other anions) as well as often relatively high concentrations of the other undesired transition metal ions in the ARP solutions. Aquation in particular of Rh and Ir also negatively influences their extraction. Despite these aforementioned factors, palladium exhibited good extractions regardless of the high unbound chloride ions which are known to compete for the binding sites in the protonated ion exchangers. However, the extractions of the other PGMs (Pt, Rh and Ir) are negatively affected by competing anions as was the case from ARP solution 1, which was very high ( $5.0 \text{ mol L}^{-1}$ ) in unbound chloride ions as compared to other studied ARP solutions. A decrease in the chloride concentration in the ARP solution 2 ( $1.7 \text{ mol L}^{-1}$ ) showed improved PGM extractions and maximum extractions of 54% for Pt, 46%, for Rh and 60% for Ir were obtained using **N3** ion exchanger. The best



extraction behaviour was generalised as follows: **N3** > **N2** > **N1** and has been demonstrated that the polyamines are superior to the DMG-containing ion exchangers. Palladium is excluded in the series as is present in insignificant amounts in this ARP solution. However the DMG-containing ion exchangers are more interPGM selective, hence for Pd.

Under very acidic conditions (pH <0.5) displayed in ARP solution **1** and **2** the ion exchangers **N1-N3** and **N1G-N3G** are very PGM selective over the other transition metals tested (Cu, Ni, Fe and Co), since the protonated ion exchangers bind to the anionic PGM complexes, and these so-called base metals form much less stable anionic complexes under these conditions. All the ion exchangers were remarkably selective as no undesired metal ions were extracted from ARP solution **1** in spite of their large (>35 times) excess to the PGMs in this solution. It should be noted though that selectivity was a great challenge with an increase in the pH of the ARP solutions. As was anticipated, under these conditions the poly(amine) containing ion exchangers have a high affinity to coordinate to other transition metals. In general the guanidine containing ion exchangers proved to be very selective especially over Ni and to a large extent also over Cu, presumably since the high pKa (>13) ensures protonation of these ligands over a much larger pH range. Fe extraction, though considerably less for the DMG-containing ion exchangers, was considerable for most of the ion exchangers, likely due to the tendency of this metal ion to form  $[\text{FeCl}_4]^-$  complexes.

The presented desorption studies were conducted with two ion exchangers (**N3** and **N3G**), since they generally showed the most efficient extraction relative to the other polyamines and the corresponding DMG-containing ion exchangers. Of the five acidic desorbing agents tested, being 5 M HCl, 1 M HCl, and 2 M HNO<sub>3</sub>, 2 M

H<sub>2</sub>SO<sub>4</sub> and 0.5 M Tu / 1 M HCl for stripping the PGM loaded ion exchangers, maximum desorption was dependent on the type of metal to be desorbed. For instance, best desorption was displayed with 2 M HNO<sub>3</sub> for Ir at 63% and 84%, **N3** and **N3G** ion exchangers, correspondingly. Even better desorptions were obtained for Rh at 75% and 90% with **N3** and **N3G** ion exchangers, respectively. These figures are promising since both metal ions are notoriously difficult to strip. Although nitric acid proved to be the best desorbing agent for Ir and Rh, it is the worst desorbing agent for Pd and Pt as only 14% and 37%, respectively could be removed using 2 M HNO<sub>3</sub> with both types of ion exchangers. However these findings can be beneficial in the separation of Pd/Pt from Rh/Ir *during the desorption step*, as quantitative desorption of Pd was attained with the use of 5 M HCl and 0.5 M Tu / 1 M HCl. Moreover, excellent Pt desorption was also effected with the combination of Tu /HCl stripping agent for both types of ion exchangers.

Studies were also performed on the re-usability of the ion exchange materials, which is an important parameter to test for a possible application of the ion exchangers. The **N3** and **N3G** ion exchangers were subjected to five cycles of extraction-desorption. HCl as a desorbing agent was chosen due to its cost effectiveness. Best successive recoveries were obtained with Pd at ca 35 mg/g using **N3** ion exchanger, whilst **N3G** ion exchanger showed some 16 mg/g of Pd recovery. Overall, **N3** ion exchange material gave stable results (extraction and desorption), whereas **N3G** ion exchanger showed degradation of the material caused by the exposure to harsh desorption conditions (5 M HCl).

In summary, the (poly)amine containing ion exchangers were found to be more efficient for the recovery of PGMs from the available authentic refinery process solutions compared to their dimethylguanidine-containing equivalents. However,

when selectivity over other transition metal ions such as Cu and Ni is an issue, the latter materials are considered favourable since they retain their PGM selectivity over a wider pH range.

### **Future Recommendations**

It would be worthwhile to tune the conditions of adsorption of the PGMs in order to effect maximum extraction efficiencies from these ARP solutions. More specifically, the addition of extra hydrochloric acid would prevent aquation which would hopefully improve the extractions, although care must be taken not to have too high concentration of unbound competing ions present.

Furthermore, the degradation of the ion exchange material observed in the successive recovery studies can be avoided by conducting the experiments under more mild desorbing conditions. Alternatively, an organic backbone other than an inorganic backbone like silica can be used since silica cannot be used at higher pHs (dissolves in pHs >9) which limits its desorption conditions.

Since desorption studies were carried out using the batch method, it was suspected that optimum desorption was not achieved due to the fact that the desorbed PGM complexes in the solution were re-adsorbed on the ion exchanger. Therefore, a column method can be investigated for effective PGM recoveries.

Lastly, potential ligands with longer polyamines (e.g. triethylenetetramine (N4) and tetraethylenepentamine (N5)) could be investigated, and their guanidine derivatives for PGM extractions from acidic solutions. Other guanidine-type derivatives such as diguanidines could be explored as well.

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