

UNIVERSITY OF THE  
FREE STATE  
UNIVERSITEIT VAN DIE  
VRYSTAAT  
YUNIVESITHI YA  
FREISTATA



UFS  
UV



**T.T. CHIWESHE**

**QUANTIFICATION OF IRIDIUM AND OTHER PLATINUM GROUP  
METALS IN THE PRESENCE OF NATURALLY OCCURRING  
CONTAMINANTS IN GEOLOGICAL ORE**

*A thesis submitted to meet the requirements for the degree of*

Philosophiae Doctor

in the

FACULTY OF NATURAL AND AGRICULTURAL SCIENCES

DEPARTMENT OF CHEMISTRY

at the

UNIVERSITY OF THE FREE STATE

BLOEMFONTEIN

by

**TREVOR TRYMORE CHIWESHE**

*Promoter*

Prof. W. Purcell

*Co-promoter*

Dr. J.A. Venter

January 2014

UNIVERSITY OF THE  
FREE STATE  
UNIVERSITEIT VAN DIE  
VRYSTAAT  
YUNIVESITHI YA  
FREISTATA



UFS  
UV

**QUANTIFICATION OF IRIDIUM AND  
OTHER PLATINUM GROUP METALS  
IN THE PRESENCE OF NATURALLY  
OCCURRING CONTAMINANTS IN  
GEOLOGICAL ORE**



## **Declaration by candidate**

---

I hereby assert that the dissertation submitted for the degree of Philosophiae Doctorate in the department of Chemistry, at the University of the Free State is my own original work and has not been previously submitted to any other institution of higher education. I further declare that all sources cited or quoted are indicated and acknowledged by means of a comprehensive list of references.

**Signature** .....

*Chiweshe Trevor Trymore*

**Date** .....



# Acknowledgements

---

This work was carried out at the Department of Chemistry, University of the Free State during 2010 - 2013.

I thank God for all the people whom He has used to make this research study possible. I am very grateful to the University of the Free State for the opportunity to carry out this work and Inkaba yeAfrica for the financial assistance. I wish to express my deepest gratitude to my supervisors Prof W. Purcell and Dr J.A. Venter for their patient guidance and encouraging attitude during this work. I also want to thank all my colleagues in the Analytical Chemistry group (F. Koko, S. Lotter, L. Nkabiti, M. Nete, D. Nhlapo, S.M. Xaba and M. Conradie-Bekker) for creating a pleasant and supportive working atmosphere. Mnr M. Coetzee is kindly thanked for the Afrikaans translation and moral support. I am also grateful to all the staff and the postgraduate students in the Chemistry department of the University of the Free State for the support and creating such an inspiring working atmosphere.

I also wish to express my gratitude to my parents (Mrs S.R. Chiweshe and my late father Mr L. Chiweshe), my siblings (Pauline and Stembeni Chiweshe), Grandfather Mr T.J. Sibindi and the Chibindi family for their relentless support. Finally, I owe my deepest gratitude to Mrs K. Brown and the family for their love and support from the onset of my studies, thank you for your generosity.

*Trevor Trymore Chiweshe*



## List of original publications

---

This thesis is based on the following original publications, which are referred to in the text by their Roman numerals.

### Author's contribution

In all papers, the author has had a major role in the synthesis of the organometallic compounds, sample preparation and analysis of the inorganic and organometallic compounds as well as writing of the manuscripts.

- i) **T.T. Chiweshe**, W. Purcell and J.A. Venter, Quantification of Rhodium in a Series of Inorganic and Organometallic compounds using cobalt as internal standard, *South African Journal of Chemistry.*, (2012), 66, pp. 7 - 16.
- ii) Michael P. Coetzee, Walter Purcell, **Trevor T. Chiweshe**, Gideon Visser and Johan A. Venter, Characterisation of acetylacetonato carbonyl diphenyl-2-pyridylphoshine rhodium(I)., *Journal of Molecular Structure.*, (2013), 1038, pp. 220 - 229.
- iii) Walter Purcell, J. Conrandie, **Trevor T. Chiweshe**, Gideon Visser, Johan A. Venter L. Twigge and Michael P. Coetzee, Characterization and oxidative addition reactions of rhodium(I) carbonyl cupferrate diphenyl-2-pyridylphoshine complexes, *Journal of Organometallic Chemistry.*, (2013), 745 - 746, pp. 439 - 453.

- iv) E. Grobbelaara, J. Conradie, Johan A. Venter, W. Purcell, and **T.T. Chiweshe**, A kinetic investigation of the oxidative addition reactions of the dimeric  $\text{Bu}_4\text{N}[\text{Ir}_2(\mu\text{-Dcbp})(\text{CO})_2(\text{PCy}_3)_2]$  complex with iodomethane, *Journal of Organometallic Chemistry.*, (2011), 696, pp. 1990 - 2002.
- v) **Trevor T. Chiweshe**, Walter Purcell and Johan A. Venter, Determination of rhodium in inorganic  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  salt and the crystal waters, *The Southern Africa Institute of Mining and Metallurgy, Advanced Metals Initiative and Precious Metals, Symposium Series*, (2013), S77, pp. 327 - 337.



# Table of contents

---

<b>LIST OF FIGURES.....</b>	<b>vii</b>
<b>LIST OF TABLES.....</b>	<b>xiii</b>
<b>LIST OF SCHEMES.....</b>	<b>xx</b>
<b>LIST OF ABBREVIATIONS.....</b>	<b>xxii</b>
<b>KEYWORDS.....</b>	<b>xxiv</b>
1 Motivation of this study.....	1
1.1 Background .....	1
1.2 Aim of this study .....	5
2 Overview of PGM and gold .....	6
2.1 History and the discovery of PGM and gold.....	6
2.1.1 Discovery of platinum .....	6
2.1.2 Discovery of osmium .....	9
2.1.3 Discovery of iridium .....	10
2.1.4 Discovery of palladium.....	10
2.1.5 Discovery of rhodium .....	11
2.1.6 Discovery of ruthenium .....	12
2.1.7 Discovery of gold .....	13
2.2 Distribution of PGM and gold .....	14
2.2.1 Occurrence of PGM in the world.....	14
2.2.2 Distribution of gold in the world.....	19
2.3 Economic values of PGM and gold.....	21
2.4 Physical and chemical properties of PGM and gold.....	25
2.4.1 Chloride chemistry of PGM and gold .....	26
2.4.2 PGM and gold oxides .....	27
2.5 Separation of PGM and gold from the mineral ore .....	30
2.6 Uses of PGM and gold.....	32
2.7 Conclusion.....	37
3 Literature review .....	37
3.1 Introduction.....	37
3.2 A preview of the methods used for the determination of precious metals.....	38



---

## Table of contents

---

3.2.1	Spectrophotometric techniques .....	38
3.2.2	Chromatographic techniques .....	42
3.2.3	Gravimetric and titrimetric techniques.....	43
3.2.4	Spectrometric techniques .....	45
3.2.5	Calibration methods.....	49
3.2.6	Sample preparation .....	54
3.2.7	Conclusion .....	56
4	Selection of methods for precious metals determination.....	57
4.1	Introduction .....	57
4.2	Calibration methods in spectrometric analysis.....	58
4.2.1	Principles of spectral origin and measurements .....	58
4.2.2	Direct calibration method .....	59
4.2.3	Standard addition method.....	62
4.2.4	Internal standard addition method .....	63
4.3	Sample preparation methods of PGM and gold .....	71
4.3.1	Open beaker acid digestion/dissolution .....	72
4.3.2	Microwave dissolution.....	72
4.3.3	Fusion digestion.....	73
4.4	Validation parameters.....	75
4.5	Conclusion .....	77
5	Method development for the determination of precious metals.....	80
5.1	Introduction .....	80
5.2	Reagents and glassware .....	81
5.2.1	Chemicals and glassware.....	81
5.2.2	Preparation of double distilled and deionised water.....	81
5.2.3	House keeping.....	82
5.3	Equipments.....	82
5.3.1	Weighing.....	82
5.3.2	Microwave digestion .....	83
5.3.3	Fusion digestion.....	84
5.3.4	Inductive coupled plasma-optical emission spectrometry and mass spectrometry (ICP-OES/MS) .....	85
5.3.5	UV-vis spectrophotometer .....	87
5.3.6	Infrared (IR) spectroscopy .....	88

---

## Table of contents

---

5.4 Qualitative analysis and the determination of limits of detection and quantitation (LOD and LOQ) of precious metals in the CRM .....	89
5.4.1 Description of the CRM.....	89
5.4.2 Qualitative analysis of the CRM and the selection of the precious metals and the internal standards wavelength.....	89
5.4.3 Determination of LOD and LOQ of precious metals.....	90
5.5 Experimental determination of PGM and gold (Method development) .....	92
5.5.1 Determination of a suitable internal standard for precious metals using a CRM .....	92
5.5.2 Robustness of the selected scandium internal standard method towards acids and EIE's .....	94
5.6 Determination of precious metals in the geological certified reference material (CRM) .....	96
5.6.1 Description of the geological CRM.....	96
5.6.2 Digestion of the CRM.....	97
5.7 Discussion of results.....	101
5.7.1 Selection of an internal standard element.....	101
5.7.2 Determination of the suitable internal standard for the quantification of precious metals in the CRM.....	105
5.7.3 Robustness of the selected scandium internal standard method towards acids and EIE's .....	108
5.8 Determination of precious metals in the geological certified reference material (CRM) .....	115
5.8.1 Determination of precious metals in the geological CRM after microwave digestion .....	115
5.9 Conclusion.....	119
6 Quantification of osmium (method development).....	121
6.1 Introduction.....	121
6.2 Reagents and glassware .....	121
6.3 Equipment .....	122
6.4 Experimental procedures.....	122
6.4.1 Preliminary determination of the optimum conditions for osmium analysis.....	122

---

## Table of contents

---

6.4.2	Stability test of the Os standard, $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ , in different acidic mediums (HX where X = F, Cl and Br) .....	123
6.4.3	Stability test of osmium standards $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in different basic mediums (NaOH, KOH and $\text{NH}_4\text{OH}$ ) .....	125
6.4.4	UV-vis analysis of the Os standards $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in acidic medium (HF, HCl and HBr).....	126
6.4.5	UV-vis analysis of the Os standards $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in basic medium (NaOH, KOH and $\text{NH}_4\text{OH}$ ).....	127
6.4.6	Application of the scandium internal standard in osmium determination.....	130
6.4.7	Selection of an alternative osmium standard .....	131
6.5	Discussion of the experimental results .....	138
6.5.1	Preliminary determination of the optimum conditions for osmium analysis.....	138
6.5.2	Stability test of the Os standards $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in acidic medium (HF, HCl and HBr) .....	139
6.5.3	Stability of osmium standards $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in basic medium (NaOH, KOH and $\text{NH}_4\text{OH}$ ).....	142
6.5.4	UV-vis determination of Os standard $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in basic and acidic medium.....	144
6.5.5	Stability of the Os standards $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in HCl in different storage conditions.....	145
6.5.6	Chemistry/Explanation of $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ instability in solution .....	148
6.5.7	Selection and evaluation of an alternative osmium standard.....	153
6.6	Conclusion.....	156
7	Determination of precious metal content: Evaluation of scandium as internal standard .....	161
7.1	Introduction.....	161
7.2	Reagents and glassware .....	162
7.3	Equipment .....	162
7.3.1	X-ray fluorescence spectrometry .....	163
7.4	Determination of PGM and gold in inorganic and organometallic compounds .....	164
7.4.1	General experimental procedures.....	164

---

## Table of contents

---

7.4.2	Qualitative and quantitative determination of iridium in inorganic and organometallic compounds.....	165
7.4.3	Qualitative and quantitative determination of gold in inorganic and organometallic compounds.....	171
7.4.4	Qualitative and quantitative determination of osmium in inorganic and organometallic compounds.....	177
7.4.5	Qualitative and quantitative determination of palladium in inorganic and organometallic compounds.....	184
7.4.6	Qualitative and quantitative determination of platinum in inorganic and organometallic compounds.....	190
7.4.7	Qualitative and quantitative determination of rhodium in inorganic and organometallic compounds.....	195
7.4.8	Qualitative and quantitative determination of ruthenium in inorganic and organometallic compounds.....	201
7.4.9	Overall assessment of the use of scandium as internal standard in quantifying precious metals in inorganic and organometallic compounds ..	205
7.5	Determination of precious metals from the mineral ores.....	206
7.5.1	Microwave digestion of the chromitite mineral ore .....	207
7.5.2	Fusion of the chromitite mineral ore.....	210
7.5.3	Quantitative determination of precious metals in the Merensky reef mineral ore after fusion with flux mixture of $\text{Na}_2\text{HPO}_4$ and $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ..	223
7.6	Determination of precious metals in mineral ores using X-ray fluorescence (XRF).....	227
7.6.1	Determination of precious metals in the chromitite mineral ore .....	227
7.7	Conclusion.....	230
8	Statistical validation of results .....	231
8.1	Introduction.....	231
8.2	Validation of the CRM results and the experimental parameters.....	232
8.2.1	Validation of the experimental parameters and results in the determination of precious metal and from the liquid CRM .....	233
8.2.2	Validation of the osmium results in the liquid CRM.....	234
8.2.3	Validation of the experimental parameters and results obtained in the determination of precious metals from geological CRM.....	238
8.3	Validation of the inorganic salts results.....	239

---

## Table of contents

---

8.3.1	Validation of osmium results and experimental conditions in the determination of osmium from $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ using $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ calibration standards kept at room temperature in the presence of light.....	240
8.4	Validation of the organometallic compounds results.....	242
8.5	Validation of geological samples results .....	244
8.5.1	Validation of the experimental parameters and results in the determination of precious metals from the chromitite mineral ore .....	244
8.5.2	Validation of the experimental results and conditions in the determination of precious metals in the Merensky reef mineral ore.....	246
8.6	Conclusion.....	248
9	Evaluation of this study and future work.....	250
9.1	Degree of success with regard to the set objectives.....	250
9.2	Future work.....	251
	<b>Summary</b> .....	254
	<b>Opsomming</b> .....	256
	<b>Appendix</b> .....	CD

# List of figures

---

<b>Figure 1.1:</b> The platinum group metals together with gold and silver form the precious metals .....	1
<b>Figure 2.1:</b> Spanish military leader Antonio de Ulloa (1735 - 1748) .....	7
<b>Figure 2.2:</b> The analysis of crude platinum by a group of English, French, German and Swedish scientists .....	7
<b>Figure 2.3:</b> James Smithson Tennant (1761 - 1815) and William Hyde Wollaston (1766 - 1828).....	8
<b>Figure 2.4:</b> A fragment of Wollaston's notebook when he named rhodium in 1803 ....	56
<b>Figure 2.5:</b> William Hyde Wollaston's Copley Medal by the Royal Society and the 250 <sup>th</sup> anniversary medal made in recognition of Smithson Tennant's work.....	12
<b>Figure 2.6:</b> World PGM reserves.....	14
<b>Figure 2.7:</b> The Bushveld Igneous Complex of South Africa.....	15
<b>Figure 2.8:</b> Cross-section through the Bushveld Igneous Complex (BIC) .....	16
<b>Figure 2.9:</b> Cross-section of the Merensky reef showing PGM deposits in an open pit mine.....	16
<b>Figure 2.10:</b> Types of PGM mineral ores (i) Osmoiridium mineral ore (Os and Ir), (ii) Sperrylite (Pt), (iii) Plumbopalladinite (Pd) and (iv) Irarsite (Ir, Ru, Rh and Pt). .....	17
<b>Figure 2.11:</b> Witwatersrand basin, which contains nearly half the world's gold reserves.....	19
<b>Figure 2.12:</b> Features within the gold-bearing conglomerates in the Witwatersrand basin.....	19
<b>Figure 2.13:</b> Witwatersrand gold conglomerate.....	20
<b>Figure 2.14:</b> Monthly average prices of PGM for the last few years (2008 - 2012) ....	21
<b>Figure 2.15:</b> The increase in gold price over the past 5 years (2008 - 2012) ....	21

---

## List of figures

---

<b>Figure 2.16:</b> Companies affected by the recent labor strife in South Africa between the year 2011 and 2014 .....	23
<b>Figure 2.17:</b> A section through a catalytic converter .....	32
<b>Figure 2.18:</b> Use of iridium in the Cativa process .....	33
<b>Figure 2.19:</b> Use of rhodium in the Monsanto process .....	33
<b>Figure 2.20:</b> A section through a platinum-coated fuel cell .....	34
<b>Figure 3.1:</b> Complexation of Rh(III) with 5-Br-PAPS .....	41
<b>Figure 3.2:</b> Different 5-Br-PAPS derivatives used for the selective determination of PGM and gold .....	42
<b>Figure 3.3:</b> Effects of EIE's in rhodium recovery from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in different chloride salt solutions .....	47
<b>Figure 3.4:</b> Effects of acid matrix in rhodium recovery from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in different acidified solutions .....	47
<b>Figure 3.5:</b> The direct proportion between the analyte and the internal standard intensities .....	50
<b>Figure 3.6:</b> Analyte to internal standard intensity ratio .....	51
<b>Figure 4.1:</b> Energy level diagram showing energy transitions where (a) and (b) represents excitation, (c) is ionization, (d) is ionization/excitation, (e) is ion emission (ionic line), and (f, g and h) are atom emission (atomic lines) .....	58
<b>Figure 4.2:</b> The direct calibration curve .....	60
<b>Figure 4.3:</b> A calibration curve plot showing limit of detection (LOD), limit of quantitation (LOQ), dynamic range and limit of linearity (LOL) .....	61
<b>Figure 4.4:</b> Comparison of the analyte signal to the standard signal .....	62
<b>Figure 4.5:</b> Standard addition calibration curve .....	63
<b>Figure 4.6:</b> The internal standard calibration curve .....	64
<b>Figure 4.7:</b> Concentration range of an internal standard solution .....	65
<b>Figure 4.8:</b> Sensitivity error ( $M_{\text{max}}$ and $M_{\text{min}}$ ) as a result of acid matrix .....	67
<b>Figure 4.9:</b> AA, ICP-OES and ICP-MS measuring devices .....	69
<b>Figure 4.10:</b> Skimmer cone with salt (EIE's) build up .....	70
<b>Figure 4.11:</b> The normal distribution for the z-statistic at 95 % confidence interval .....	76
<b>Figure 5.1:</b> Scaltec (SBA 33) and Sartorius (CPA26P Series) electronic balances .....	82
<b>Figure 5.2:</b> Anton Paar Perkin-Elmer Multiwave 3000 microwave .....	82

---

## List of figures

---

<b>Figure 5.3:</b> Barnstead Thermolyne furnace .....	84
<b>Figure 5.4:</b> Shimadzu ICPS-7510 ICP-OES .....	85
<b>Figure 5.5:</b> Shimadzu ICPM-8500 ICP-MS.....	85
<b>Figure 5.6:</b> Varian Cary UV-vis spectrophotometer .....	87
<b>Figure 5.7:</b> A Digilab (FTS 2000) spectrometer .....	87
<b>Figure 5.8:</b> Iridium calibration curve obtained using the direct calibration method .....	90
<b>Figure 5.9:</b> Experimental procedure for the determination of PGM and gold in the CRM using the fusion method .....	99
<b>Figure 5.10:</b> Average percentage recovery of precious metals from the liquid CRM in the determination of the best internal standard .....	105
<b>Figure 5.11:</b> Effects of unmatched HCl acid matrix in the determination of precious metals using the direct calibration curve.....	108
<b>Figure 5.12:</b> Effects of unmatched HCl acid matrix in the determination of precious metals using the Sc internal standard .....	109
<b>Figure 5.13:</b> The effects of increasing HCl acid matrices on the Sc emission intensities .....	110
<b>Figure 5.14:</b> Effects of increasing Na ions concentrations (EIE's) in the determination of precious metals using the direct calibration method .....	111
<b>Figure 5.15:</b> Effects of Na content (EIE's) in PGM and gold recovery using the Sc internal standard method .....	112
<b>Figure 5.16:</b> Effects of increasing Na content (EIE's) on the Sc internal standard in the determination of precious metals using the ICP-OES at 361.384 nm .....	114
<b>Figure 5.17:</b> Infrared spectrum of the digested CRM residues in different mineral acids .....	115
<b>Figure 5.18:</b> Quantitative results of the CRM digested using the direct calibration method after microwave digestion in <i>aqua regia</i> , HCl and HNO <sub>3</sub> ....	116
<b>Figure 5.19:</b> Quantitative results of the CRM acid digested using the Sc internal standard method after microwave digestion .....	117
<b>Figure 5.20:</b> Quantitative results of CRM digested using NH <sub>4</sub> HF <sub>2</sub> flux .....	118
<b>Figure 6.1:</b> UV-vis determination of the stability of osmium standard, (NH <sub>4</sub> ) <sub>2</sub> [Os(Cl) <sub>6</sub> ], in acidic medium (HF, HCl and HBr).....	126



---

## List of figures

---

<b>Figure 6.2:</b> Spectrophotometric determination of the stability of Os standard $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in basic medium ( $\text{NH}_4\text{OH}$ , $\text{NaOH}$ and $\text{KOH}$ ).....	127
<b>Figure 6.3:</b> Infrared spectrum of $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ .....	132
<b>Figure 6.4:</b> Decrease in osmium percentage recovery from the liquid CRM using the direct calibration method with $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ as calibration standard .....	137
<b>Figure 6.5:</b> Influence of time on the slope of the Os calibration curves of $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in $\text{HCl}$ matrix using the direct calibration method .....	139
<b>Figure 6.6:</b> Change in calibration curve sensitivity with time using different halide acids $\text{HX}$ ( $\text{X} = \text{F}$ , $\text{Cl}$ and $\text{Br}$ ) and the direct calibration .....	139
<b>Figure 6.7:</b> Influence of Os recovery concentration as a function of time in $\text{HCl}$ matrix .....	140
<b>Figure 6.8:</b> A yellow-black coating observed on the volumetric flask stoppers containing the osmium calibration standards.....	141
<b>Figure 6.9:</b> Osmium calibration curves in the basic medium ( $\text{NH}_4\text{OH}$ ) as a function of time (48 and 72 Hrs are superimposed) .....	142
<b>Figure 6.10:</b> Comparison of sensitivity of the osmium calibration curves in $\text{NaOH}$ , $\text{KOH}$ and $\text{NH}_4\text{OH}$ base matrix .....	143
<b>Figure 6.11:</b> Spectrophotometric analysis of $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in basic medium (a) $\text{NH}_4\text{OH}$ and (b) $\text{NaOH}$ and $\text{KOH}$ .....	144
<b>Figure 6.12:</b> Os calibration standards solutions stored in different conditions: (1) kept left exposed to the light, (2) kept in the cupboard (dark) and (3) kept at ca. $10^\circ\text{C}$ .....	145
<b>Figure 6.13:</b> Determination of Os content in liquid CRM using $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ calibration standards kept at $10^\circ\text{C}$ in the absence of light.....	146
<b>Figure 6.14:</b> Reactions of $[\text{OsCl}_6]^{2-}$ used in the synthesis of numerous osmium compounds .....	147
<b>Figure 6.15:</b> A postulate of the increase in osmium emission intensities as a result of the $\text{OsO}_4$ or $\text{OsO}_2$ production .....	149
<b>Figure 6.16:</b> Stability test of Os calibration standards in $\text{HCl}$ medium prepared from the newly synthesized $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ compound.....	154
<b>Figure 7.1:</b> Series of steps involved in sample preparation for XRF analysis (A) Sample poured in the dies (B) Pressing instrument (C) Compressed pellets (D) Sample holder.....	160

---

## List of figures

---

<b>Figure 7.2:</b> Molecular structure of $[\text{Ir}(\text{cod})\text{Cl}]_2$ .....	163
<b>Figure 7.3:</b> Structure of $(\text{Bu}_4\text{N})[\text{Ir}_2(\mu\text{-Dcbp})(\text{CO})_2(\text{PCy}_3)_2]$ .....	164
<b>Figure 7.4:</b> Infrared spectrum of $(\text{Bu}_4\text{N})[\text{Ir}_2(\mu\text{-Dcbp})(\text{CO})_2(\text{PCy}_3)_2]$ .....	165
<b>Figure 7.5:</b> Molecular structure of $[\text{Ir}(\text{CO})(\text{Cl})(\text{PPh}_3)_2]$ .....	165
<b>Figure 7.6:</b> Infrared spectrum of $[\text{Ir}(\text{CO})(\text{Cl})(\text{PPh}_3)_2]$ .....	166
<b>Figure 7.7:</b> Molecular structure of $[\text{Au}(\text{opd})(\text{Cl})_3]$ .....	169
<b>Figure 7.8:</b> Infrared spectrum of $[\text{Au}(\text{opd})(\text{Cl})_3]$ .....	170
<b>Figure 7.9:</b> Molecular structure of $[\text{Au}(2,9\text{-Me}_2\text{phen})(\text{Cl})_3]$ . ....	170
<b>Figure 7.10:</b> Infrared spectrum of $[\text{Au}(2,9\text{-Me}_2\text{phen})(\text{Cl})_3]$ .....	171
<b>Figure 7.11:</b> Molecular structure of $[\text{Au}(\text{en})_2]\text{Cl}_3$ .....	171
<b>Figure 7.12:</b> Infrared spectrum of $[\text{Au}(\text{en})_2]\text{Cl}_3$ .....	172
<b>Figure 7.13:</b> Increase in Os emission intensity for the $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ analyte sample .....	177
<b>Figure 7.14:</b> Molecular structure of acetylosmium.....	178
<b>Figure 7.15:</b> Molecular structure of $[\text{Os}(\text{bpy})_2(\text{Cl})_2]$ .....	178
<b>Figure 7.16:</b> Infrared spectrum of $[\text{Os}(\text{bpy})_2(\text{Cl})_2]$ .....	179
<b>Figure 7.17:</b> Molecular structure of $[\text{Os}(\text{opd})(\text{Cl})_3]$ .....	179
<b>Figure 7.18:</b> Infrared spectrum of $[\text{Os}(\text{opd})(\text{Cl})_3]$ .....	180
<b>Figure 7.19:</b> Molecular structure of $[\text{Pd}(\text{cod})(\text{Cl})_2]$ .....	183
<b>Figure 7.20:</b> Molecular structure of $[\text{Pd}(\text{acac})(\text{PPh}_3)(\text{Cl})]$ .....	184
<b>Figure 7.21:</b> Infrared spectrum of $[\text{Pd}(\text{acac})(\text{PPh}_3)(\text{Cl})]$ .....	184
<b>Figure 7.22:</b> Molecular structure of $[\text{Pd}(\text{phen})(\text{Cl})_2]$ .....	185
<b>Figure 7.23:</b> Infrared spectrum of $[\text{Pd}(\text{phen})(\text{Cl})_2]$ .....	185
<b>Figure 7.24:</b> Molecular structure of $[\text{Pt}(\text{cod})(\text{Cl})_2]$ .....	188
<b>Figure 7.25:</b> Molecular structure of $[\text{Pt}(\text{Cl})_2(\text{PPh}_3)_2]$ .....	189
<b>Figure 7.26:</b> Infrared spectrum of $[\text{Pt}(\text{Cl})_2(\text{PPh}_3)_2]$ .....	189
<b>Figure 7.27:</b> Structure of $[\text{cis-PtCl}_2(\text{PhCH}=\text{CH}_2)_2]$ .....	190
<b>Figure 7.28:</b> Infrared spectrum of $[\text{cis-PtCl}_2(\text{PhCH}=\text{CH}_2)_2]$ .....	190
<b>Figure 7.29:</b> Molecular structure of $[\text{Rh}(\text{hfaa})(\text{CO})_2]$ .....	194
<b>Figure 7.30:</b> Infrared spectrum of $[\text{Rh}(\text{tfaa})(\text{CO})_2]$ .....	194
<b>Figure 7.31:</b> Molecular structure of $[\text{Rh}(\text{tfaa})(\text{dpp})(\text{CO})]$ .....	195
<b>Figure 7.32:</b> Infrared spectrum of $[\text{Rh}(\text{tfaa})(\text{dpp})(\text{CO})]$ .....	195
<b>Figure 7.33:</b> Molecular structure of $[\text{Rh}(\text{cupf})(\text{PPh}_3)(\text{CO})]$ .....	196
<b>Figure 7.34:</b> Infrared spectrum of $[\text{Rh}(\text{cupf})(\text{CO})(\text{PPh}_3)]$ .....	196

---

## List of figures

---

<b>Figure 7.35:</b> Molecular structure of $[\text{Ru}(\text{cod})(\text{Cl})_2]$ .....	199
<b>Figure 7.36:</b> Molecular structure of acetyl ruthenium .....	199
<b>Figure 7.37:</b> Molecular structure of $[\text{Ru}(\text{en})_2(\text{Cl})_2]$ .....	200
<b>Figure 7.38:</b> Infrared spectrum of $[\text{Ru}(\text{en})_2(\text{Cl})_2]$ .....	200
<b>Figure 7.39:</b> Chromitite mineral ore mined from the Rustenburg platinum mine.....	203
<b>Figure 7.40:</b> Determination of PGM in the chromitite mineral ore using the direct calibration method .....	206
<b>Figure 7.41:</b> Determination of PGM in the chromitite mineral ore using scandium as internal standard .....	206
<b>Figure 7.42:</b> (a) Original ICP-OES flame (b) Effects of sodium phosphate flux on the ICP-OES flame .....	212
<b>Figure 7.43:</b> A section through an ICP-OES torch nozzle showing a clog.....	213
<b>Figure 7.44:</b> The spinel structure of $\text{Cr}_2\text{O}_3$ .....	217
<b>Figure 8.1:</b> Method validation procedure .....	231

# List of tables

---

<b>Table 2.1:</b> Characteristics of Bushveld Igneous Complex PGM ore types .....	18
<b>Table 2.2:</b> Physical properties of PGM and gold.....	24
<b>Table 2.3:</b> Common properties PGM and gold in chlorido complexes .....	25
<b>Table 2.4:</b> Relative substitution kinetics of the precious metal chlorido-complexes .....	26
<b>Table 2.5:</b> Common oxidation states of PGM and gold .....	29
<b>Table 2.6:</b> PGM consumption (in million troy ounces) in different sectors in the year 2012 .....	36
<b>Table 3.1:</b> Summary of the ICP-OES methods of analysis .....	63
<b>Table 3.2:</b> Validation criteria .....	66
<b>Table 4.1:</b> The most commonly used fluxes in various PGM and gold mineral ore .....	74
<b>Table 5.1:</b> Microwave optimum conditions for the PGM and gold mineral ore digestion (PGM XF100-8).....	83
<b>Table 5.2:</b> ICP-OES optimum operating conditions for PGM and gold analysis	86
<b>Table 5.3:</b> ICP-MS optimum operating conditions for PGM and gold analysis...	86
<b>Table 5.4:</b> Selected ICP-OES ionic wavelengths for the internal standards .....	89
<b>Table 5.5:</b> Selected ICP-OES atomic and ionic wavelengths for PGM and gold determination.....	89
<b>Table 5.6:</b> Experimentally determined LOD and LOQ for PGM and gold .....	91
<b>Table 5.7:</b> Average percentage recoveries of the precious metals from the liquid CRM.....	93
<b>Table 5.8:</b> Effects of increasing HCl matrix in the determination of precious metals using the direct calibration method .....	94
<b>Table 5.9:</b> Effects of increasing HCl matrix in the determination of precious metals using Sc internal standard method .....	94
<b>Table 5.10:</b> Effects of increasing Na <sup>+</sup> content (EIE's) in the determination of precious metals using the direct calibration method.....	95

---

## List of tables

---

<b>Table 5.11:</b> Effects of increasing Na <sup>+</sup> content (EIE's) in the determination of precious metals using Sc internal standard method .....	95
<b>Table 5.12:</b> Certified concentration values of the precious metals in the CRM bearing Pyroxenite Reference Material-Concentrate at 95 % confidence interval.....	96
<b>Table 5.13:</b> Quantitative results of precious metals using the direct calibration method in the geological CRM after microwave digestion using different mineral acids .....	98
<b>Table 5.14:</b> Quantitative results of precious metals using the Sc internal standard method in the geological CRM after microwave digestion using different mineral acids .....	98
<b>Table 5.15:</b> Quantitative results of precious metals after fusion digestion of the geological CRM with NH <sub>4</sub> HF <sub>2</sub> flux .....	100
<b>Table 5.16:</b> Theoretical excitation and ionization energies of PGM and gold as well as the potential internal standards .....	101
<b>Table 5.17:</b> A combination of the best selected ICP-OES lines for precious metals (bolded) against the selected lines for the internal standards.....	103
<b>Table 5.18:</b> Summary of the precious metals recovery in both CRMs using direct calibration and Sc internal standard methods.....	119
<b>Table 6.1:</b> Measured osmium emission intensities from the calibration standard solutions after every 24 hours using the direct calibration method ....	122
<b>Table 6.2:</b> Osmium percentage recovery obtained from the liquid CRM after every 24 hours using the direct calibration method .....	122
<b>Table 6.3:</b> Measured osmium intensities of the calibration standard solutions of (NH <sub>4</sub> ) <sub>2</sub> [Os(Cl) <sub>6</sub> ] in HF acid matrix using the direct calibration method .....	123
<b>Table 6.4:</b> Measured osmium intensities of the calibration standard solutions of (NH <sub>4</sub> ) <sub>2</sub> [Os(Cl) <sub>6</sub> ] in HCl acid matrix using the direct calibration method .....	123
<b>Table 6.5:</b> Measured osmium intensities of the calibration standard solutions of (NH <sub>4</sub> ) <sub>2</sub> [Os(Cl) <sub>6</sub> ] in HBr acid matrix using the direct calibration method.....	123
<b>Table 6.6:</b> Changes in gradient (sensitivity) of the osmium calibration curves in HF, HCl and HBr acid matrix .....	124
<b>Table 6.7:</b> Measured osmium intensities of the calibration standard solutions of (NH <sub>4</sub> ) <sub>2</sub> [Os(Cl) <sub>6</sub> ] in NaOH acid matrix using the direct calibration method .....	124

<b>Table 6.8:</b> Measured osmium intensities of the calibration standard solutions of $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in KOH acid matrix using the direct calibration method .....	125
<b>Table 6.9:</b> Measured osmium intensities of the calibration standard solutions of $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in $\text{NH}_4\text{OH}$ acid matrix using the direct calibration method ...	125
<b>Table 6.10:</b> Comparison of the changes in the gradients (sensitivity) of the osmium calibration curves in NaOH, KOH and $\text{NH}_4\text{OH}$ base matrix .....	125
<b>Table 6.11:</b> Osmium emission intensities of the calibration standard $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ solutions kept in the open and exposed to the light (Set 1) .....	127
<b>Table 6.12:</b> Osmium emission intensities of the calibration standard $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ solutions kept in the cupboard (dark) (Set 2).....	128
<b>Table 6.13:</b> Osmium emission intensities of the calibration standard $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ solutions at ca. 10 °C and in the absence of sunlight (Set 3) ..	128
<b>Table 6.14:</b> Osmium percentage recovery from the liquid CRM using the direct calibration method with calibration standard $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ solutions kept at ca. 10 °C and in the absence of sunlight .....	129
<b>Table 6.15:</b> Emission intensities of the osmium calibration standard $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ solutions kept at ca. 10 °C and in the absence of sunlight .....	129
<b>Table 6.16:</b> Osmium percentage recovery from the CRM using the Sc internal calibration standard $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ solutions kept at ca. 10 °C and in the absence of sunlight .....	130
<b>Table 6.17:</b> Measured osmium emission intensities of the calibration standard solutions of $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ kept at room temperature and exposed to light using direct calibration.....	133
<b>Table 6.18:</b> Emission intensities of the osmium calibration standard solutions of $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ kept at room temperature and exposed to the light using Sc as internal standard.....	133
<b>Table 6.19:</b> Osmium percentage recovery from the CRM using $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ standard solutions kept at room temperature and exposed to light (direct calibration) .....	134
<b>Table 6.20:</b> Osmium percentage recovery from the CRM using $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ standard solutions kept at room temperature and exposed to the light (using Sc as the internal standard) .....	134

<b>Table 6.21:</b> Measured osmium emission intensities of the calibration standard solutions $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ kept at ca. 10 °C in the absence of light using direct calibration.....	135
<b>Table 6.22:</b> Osmium emission intensities using the $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ calibration standard solutions at ca. 10 °C in the absence of light using Sc as internal standard .....	135
<b>Table 6.23:</b> Osmium percentage recoveries from the CRM using the direct calibration standards ( $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ standards kept at ca. 10 °C and in the absence of sunlight) .....	136
<b>Table 6.24:</b> Osmium percentage recoveries from the CRM using Sc as internal calibration standards ( $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ standards kept at ca.10 °C and in the absence of sunlight) .....	136
<b>Table 6.25:</b> Emission intensities of osmium in the CRM solutions.....	147
<b>Table 6.26:</b> Summary of the quantitative results of osmium obtained using the liquid CRM.....	156
<b>Table 7.1:</b> ICP-OES/MS quantitative determination of iridium in $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ obtained using direct calibration and Sc as internal standard .....	163
<b>Table 7.2:</b> Quantitative results of the iridium in the organometallic compounds using the direct calibration and Sc as internal standard .....	167
<b>Table 7.3:</b> ICP-OES/MS quantitative determination of gold in inorganic salts using the direct calibration and Sc as internal standard .....	168
<b>Table 7.4:</b> Quantitative results of gold in the organometallic compounds using the direct calibration and Sc as internal standard.....	173
<b>Table 7.5:</b> ICP-OES/MS quantitative determination of osmium in $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ using the direct calibration and Sc as internal standard .....	174
<b>Table 7.6:</b> Osmium emission intensities of the calibration standard solutions of $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ kept at room temperature (direct calibration) .....	175
<b>Table 7.7:</b> Osmium percentage recovery from $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ with calibration standard solutions of $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ kept at room temperature (direct calibration).....	176
<b>Table 7.8:</b> Osmium emission intensities of the calibration standard solutions of $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ kept at room temperature (Sc as internal standard).....	176

<b>Table 7.9:</b> Osmium percentage recovery from $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ with calibration standard solutions of $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ kept at room temperature (Sc as internal standard) .....	176
<b>Table 7.10:</b> Quantitative results of the determination of osmium in the organometallic compounds using direct calibration and Sc as internal standard .....	56
<b>Table 7.11:</b> ICP-OES/MS quantitative determination of palladium in inorganic salts using the direct calibration and Sc as internal standard.....	182
<b>Table 7.12:</b> Quantitative results of the palladium in the organometallic compounds using the direct calibration and Sc as internal standard.....	186
<b>Table 7.13:</b> ICP-OES/MS quantitative determination of platinum in inorganic salts using the direct calibration and Sc as internal standard methods .....	187
<b>Table 7.14:</b> ICP-OES/MS quantitative results of the platinum in the organometallic compounds using the direct calibration and Sc as internal standard .....	191
<b>Table 7.15:</b> ICP-OES/MS quantitative determination of rhodium in $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ using the direct calibration and Sc as internal standard .....	192
<b>Table 7.16:</b> ICP-OES/MS quantitative results of the rhodium in the organometallic compounds using direct calibration and Sc as internal standard .....	192
<b>Table 7.17:</b> Quantitative determination of ruthenium in inorganic salts using direct calibration and Sc as internal standard.....	198
<b>Table 7.18:</b> Quantitative results of the ruthenium in the organometallic compounds using direct calibration and Sc as internal standard.....	201
<b>Table 7.19:</b> Quantitative results of the chromitite mineral ore after microwave digestion in <i>aqua regia</i> and hydrochloric acid .....	204
<b>Table 7.20:</b> Quantitative results of chromitite digested using $\text{NH}_4\text{F} \cdot \text{HF}$ flux.....	208
<b>Table 7.21:</b> Quantitative results of chromitite digested using a mixture of $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ flux .....	210
<b>Table 7.22:</b> Quantitative results of the PGM (Ru, Os and Pt) obtained after the fusion of chromitite ore with a flux mixture of $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and the subsequent removal white precipitate .....	212



<b>Table 7.23:</b> Quantitative results of chromitite digested using $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ flux	216
<b>Table 7.24:</b> Comparison of the PGM (Ru, Os and Pt) results obtained after $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ and $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ fusion of the chromitite mineral ore using Sc as internal standard .....	220
<b>Table 7.25:</b> Quantitative results of the Merensky reef ore digested using a mixture of $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ flux .....	221
<b>Table 7.26:</b> Quantitative results of Merensky reef mineral ore digested using $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ flux .....	223
<b>Table 7.27:</b> Comparison of the PGM (Ru, Os, Ir and Pt) results obtained after $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ and $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ fusion of the chromitite mineral ore using Sc as internal standard .....	224
<b>Table 7.28:</b> XRF calibration standards for precious metals determination.....	225
<b>Table 7.29:</b> XRF quantitative results of the metals in the chromitite ore .....	225
<b>Table 7.30:</b> A summary of the results of the determination of PGMs and gold in inorganic compounds using direct calibration and Sc as internal standard ..	227
<b>Table 7.31:</b> A summary of the results of the determination of the PGM and gold in the organometallic compounds using direct calibration and Sc as internal standard .....	228
<b>Table 8.1:</b> Validation of the experimental parameters and results in the determination of precious metals from the liquid CRM using Sc as internal standard .....	233
<b>Table 8.2:</b> Validation of the experimental parameters and results in the determination of osmium from the liquid CRM using Sc as internal standard and $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ calibration solutions kept at ca. 10 °C and in the absence of light.....	234
<b>Table 8.3:</b> Validation of the experimental parameters and in the determination of osmium from the liquid CRM using Sc as internal standard and $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ calibration solutions kept at room temperature and exposed to light .....	235
<b>Table 8.4:</b> Validation of the experimental parameters and results in the determination of osmium from the liquid CRM using Sc as internal standard and $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ calibration solutions kept at ca. 10 °C and in the absence of sunlight.....	235

<b>Table 8.5:</b> Validation of the osmium results from the liquid CRM using the ANOVA test (Sc internal standard).....	236
<b>Table 8.6:</b> Validation of the experimental parameters and results in the determination of precious metals from the geological CRM using Sc as internal standard .....	238
<b>Table 8.7:</b> Validation of the experimental results and parameters in the determination of precious metals from the inorganic compounds using Sc as internal standard .....	239
<b>Table 8.8:</b> Validation of experimental parameters and results in the determination of osmium from the $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ using $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ standards kept at room temperature and in the presence of light (Sc internal standard).....	241
<b>Table 8.9:</b> Validation of osmium results (ANOVA test) of $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ using $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ standards and Sc as internal standard kept at room temperature and in the presence of light.....	241
<b>Table 8.10:</b> Validation of the experimental parameters in the determination of precious metals from the organometallic compounds using Sc as internal standard .....	242
<b>Table 8.11:</b> Validation of the experimental results in the determination of precious metals in various organometallic compounds using Sc as internal standard .....	243
<b>Table 8.12:</b> Validation of the experimental parameters and results in the determination of Ru, Os and Pt in the chromitite mineral ore using Sc as internal standard ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4$ digestion).....	244
<b>Table 8.13:</b> Validation of the experimental parameters and results in the determination of Ru, Os and Pt in the chromitite reef mineral ore using Sc as internal standard ( $(\text{NH}_4)\text{H}_2\text{PO}_4$ digestion).....	245
<b>Table 8.14:</b> Validation of the experimental results (Ru, Os and Pt) obtained after the fusion of the chromitite reef mineral ore with $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}/\text{Na}_2\text{HPO}_4$ and $(\text{NH}_4)\text{H}_2\text{PO}_4$ using Sc as internal standard.....	245
<b>Table 8.15:</b> Validation of the experimental parameters in the determination of Ru, Os, Ir and Pt from the Merensky reef mineral ore using Sc as internal standard ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4$ digestion) .....	246

---

## List of tables

---

<b>Table 8.16:</b> Validation of the experimental parameters in the determination of Ru, Os, Ir and Pt from the Merensky reef mineral ore using Sc as internal standard ((NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub> digestion) .....	247
<b>Table 8.17:</b> Validation of the experimental results (Ru, Os, Ir and Pt) obtained after the fusion of the chromitite reef mineral ore with NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O/Na <sub>2</sub> HPO <sub>4</sub> and (NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub> using Sc as internal standard .....	247
<b>Table 8.18:</b> A summary of the results accepted or rejected using scandium as internal standard .....	249

# List of schemes

---

<b>Scheme 2.1:</b> Selective separation of precious metals from the mineral ore .....	30
<b>Scheme 7.1:</b> Quantitative determination of the precious metals after the microwave digestion of the chromitite ore in <i>conc.</i> HCl and <i>aqua regia</i> .....	207
<b>Scheme 7.2:</b> Quantitative determination of the precious metals after $\text{NH}_4\text{F}\cdot\text{HF}$ fusion with the chromitite mineral ore.....	209
<b>Scheme 7.3:</b> The removal of NaCl from the chromitite analyte solution after digestion with a mixture of $\text{Na}_2\text{HPO}_4$ and $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ flux.....	214
<b>Scheme 7.4:</b> Sample preparation of the chromitite ore using $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ flux and the isolation of chromium.....	217
<b>Scheme 7.5:</b> A schematic presentation showing the selection process between a wet-chemical method and a dry analytical technique.....	226
<b>Scheme 7.6:</b> A summary of the dissolution/digestion procedures for the chromitite mineral ore.....	229

# List of abbreviations

---

## General terms

PGM	Platinum group metals
CRM	Certified reference material
KPM	Kitco precious metals
BIC	Bushveld igneous complex
UG2	Upper Group 2 reef
ISO	Organization for standardization
EIE's	Easily ionized elements
Conc.	Concentration
m.p	Melting point
b.p	Boiling point

## Analytical equipment

AAS	Atomic absorption spectroscopy
XRF	X-ray fluorescence
UV-vis	Ultraviolet–visible absorption spectrometry
ICP-OES	Inductive coupled plasma-optical emission spectroscopy
ICP-MS	Inductive coupled plasma-mass spectrometry

## Ligands

tfaa	1,1,1- trifluoro -2,4 - pentanedione
acac	Acetylacetone
cupf	Cupferron (ammonium salt of N-nitrosophenyl hydroxylamine)
PPh <sub>3</sub>	Triphenylsphosphine

---

## Opsomming

---

Me	Methyl
5-Br-PAPS	2-(5-Bromo-2-pyridylazo)-5-(N-propyl-N-sulphopropylamino) phenol
PAR	4-(2-pyridylazo) resorcinol
EDTA	Ethylenediaminetetraacetic acid

### Units

oz	Ounce
%	Percentage
kg	Kilogram
°C	Degrees Celsius
ppm	Parts per million
ppb	Parts per billion

### Statistical terms

LOD	Limit of detection
LOQ	Limit of quantitation
$r^2$	Linear regression line
s	Standard deviation
RSD	Relative standard deviation
LOL	Limit of linearity
$H_a$	Alternative hypothesis
$H_0$	Null hypothesis
$S_m$	Standard deviation of the slope
$S_b$	The standard deviation of the intercept
$S_c$	Standard deviation for results obtained from the calibration curve
LSD	Least significance difference
ANOVA	Analysis of variance
SSF	The sum of the squares due to the factor
SSE	The sum of the square due to error

# Keywords

---

Precious metals

Platinum group metals

Qualitative and quantitative analysis

Spectrometric analysis

Wavelength

Internal standard

Scandium

Unmatched matrix

Matrices

Chromitite mineral ore

Inorganic and organometallic compounds

# 1 Motivation of this study

---

## 1.1 Background

The platinum group metals (PGM) constitute a family of six chemically similar elements which include platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os) as shown in **Figure 1.1**.

VIIB		VIII		VIII		IB		IIB	
25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn				
43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd				
75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg				
107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn				

**Figure 1.1:** The platinum group metals together with gold and silver form the precious metals

These metals, together with gold (Au), and silver (Ag) are sometimes referred to as the precious or noble metals due to their high economic value, scarcity and chemical inertness. Precious metals are normally coloured and lustrous, exceptionally stable, hard, malleable, electrically resistant and inert to chemical attacks. These metals play a vital role in the chemical and manufacturing industries which include their use as catalysts in the automobile sectors and in large scale industrial processes, jewellery, medical applications and glass production to name a few, due to their corrosive resistance, chemical inertness and high melting points.

South Africa contains the world's largest known PGM (95 % of global resources) and gold deposits (35 % of global resources) and is the principal exporter of these



precious metals, exporting close to 60 % of the world's supply.<sup>1</sup> The majority of PGM in South Africa are mined in the Bushveld Igneous Complex (BIC) and are obtained in trace amounts (10 - 20 ppm) from different mineral ores. The low concentration levels of the PGM in these mineral ores, coupled with the inordinate chemical similarities, complicate any analytical method which involves the determination of PGM and gold.<sup>2</sup>

In the pharmaceutical companies, some of the precious metals e.g. platinum, palladium, ruthenium and gold<sup>3</sup> have widely been used as central atoms in the manufacturing of anti-cancer drugs. Of recent, iridium has been reported to be the key metal in the new development of anti-cancer drugs.<sup>4</sup> Complexes containing iridium as a central atom have attracted attention in this industry as it forms complexes which exhibit high biological stability compared to those of the other precious metal (Pt, Pd, Ru and Au) complexes. Iridium complexes have also been shown to be highly soluble, a property which is desirable in modern drug development for *in vitro* and *in vivo* assays. However, the quantification of iridium at trace levels of these newly synthesized drugs remains a major problem. Recent articles have reported of in-vitro cytotoxic iridium polypyridyl drugs exhibiting IC<sub>50</sub> (IC<sub>50</sub> the measure of the effectiveness of a compound in inhibiting biological or biochemical function) values with low iridium concentration (micro-molar to sub-micro-molar) that causes about 50 % reduction of tumor cell growth.<sup>5</sup> Consequently, analytical methodologies with low detection limits are therefore required for further development of these iridium drugs.

Reports of growing concerns about the effects of automobile catalyst pollution due to its emission of Rh, Pd and Pt into the environment are on the increase.<sup>6,7</sup> The hot

---

<sup>1</sup> J. Matthey, *Platinum 2004*, Matthey Public Limited Company., (2004).

<sup>2</sup> M. Balcerzak, *Japan Society for Analytical Chemistry*., (2002), 18, pp. 737 - 750.

<sup>3</sup> L. Messori, G. Marcon and P. Orioli, *Gold(III) Compounds as New Family of Anticancer Drugs*., (2003), 1, pp. 177 - 187.

<sup>4</sup> Z. Liu, A. Habtemariam, A.M. Pizarro, S.A. Fletcher, A. Kisova, O. Vrana, L. Salassa, P.C. Bruijninx, G.J. Clarkson, V. Brabec and P.J. Sadler, *J. Med. Chem.*, (2011), 54, pp. 3011 - 26.

<sup>5</sup> I. Ott, M. Scharwitz, H. Scheffler, W.S. Sheldric and R. Gust, *Journal of Pharmaceutical and Biomedical Analysis*., (2008), 47, pp. 938 - 942.

<sup>6</sup> C.B. Ojeda and F.S Rojas, *Talanta*., (2007), 71, pp. 1 - 12.

exhaust gases flowing through the converter pipe of the exhaust causes the abrasion of the PGM which lead to the emission of these metals into the environment. The effects of these trace elements in human health and diseases has been reviewed in numerous scientific publications.<sup>8,9,10</sup> Most of these emitted PGM are deposited in the environment and are collected in trace amounts (< 5 ppm) in soil, water and sediment samples.<sup>11,12,13</sup> Therefore, the development of sensitive and reliable analytical methodologies for the determination of these trace amounts of PGM in environmental material is of great importance in the critical evaluation of the possible risks to human health.

Determination of precious metals is mostly hampered by the use of unreliable methods with low limits of detection (LOD), limits of quantification (LOQ) and poor sensitivity and selectivity. Lack of selectivity in these methods makes the determination of PGM and gold susceptible to interferences by other impurities. Other problems associated with PGM and gold quantification includes volatility and instability of some of the products (mainly osmium and ruthenium), lack of certified reference materials (CRM) and interference caused by easily ionized elements (EIE's). These problems also limit the development of new methods due to the lack of CRM which is often used as the benchmark in method development.

The choice of the analytical methods used for PGM and gold determination depends on the level of their concentration and matrix level in the sample. Numerous interferences normally limit the direct application of the spectrometric methods in quantifying PGM and gold in complex matrixes. Relatively new spectrometric methods such as the inductively coupled plasma with either optical emission (ICP-OES) or mass spectrometric (ICP-MS), glow discharge optical emission spectroscopy (GD-OES), X-ray fluorescence (XRF) and atomic absorption

---

<sup>7</sup> J. Fang, Y. Jinng and X. Yan, *Environ. Sci. Technol.*, (2005), 39, pp. 288 - 292.

<sup>8</sup> M. Hambidge, *J. Nutr.*, (2000), 130, p. 1344.

<sup>9</sup> J. Angerer, U. Eweres and M. Wilhelm, *Int. J. Hyg. Environ. Health.*, (2007), 210, p. 201.

<sup>10</sup> C.E. Bryan, S.J Cristopher and B.C Balmer, *Sci. Total Environ.*, (2007), 388, p. 325.

<sup>11</sup> H.P. König, R.F. Hertel, W. Koch and G. Rosner, *Atm. Environ.*, (1992), 26A, p. 741.

<sup>12</sup> M. Moldovan, M.M. Gomez and M.A. Palacios, *J. Anal. Atm. Spectrom.*, (1999), 14, p. 1163.

<sup>13</sup> C. Reimann and P. de Caritat, *Chemical Elements in the Environment*, Springer, Berlin, (1998), pp. 48 - 51.

spectroscopy (AAS) have barely been applied for the simultaneous determination of precious metals due to the similarity in chemistry of these metals which normally requires separation prior to quantification.<sup>14,15</sup> Spectrophotometric methods involving organic reagents are also frequently used in PGM and gold determination due to their ability to form bright coloured complexes. Most of these methods also demand complicated sample preparation prior to analysis and the similarity in chemical properties that exist among these metals makes it difficult to quantify individual elements. These kinds of spectrophotometric methods also lack sensitivity (poor LOD and LOQ), selectivity (similar chemistry), accuracy and are labour intensive, time consuming and are also expensive since most of them require the masking of any interfering compounds. Other problems associated with PGM quantification include signal emission suppression/enhancement caused by an excess of electrons (EIE's) from the matrix and spectral interference (line overlap), acid matrix mismatching, etc.

Different spectrometric methods have been developed to reduce and correct for the numerous matrix effects in these spectrometric analysis. Common methods used to correct for these matrix effects are usually empirical and these includes interactive matrix matching, matrix stripping, standard addition method, mathematical correction by curve fitting to an empirical function, matrix swamping and excitation buffering techniques and finally the use of internal standard addition. The limitations of these methods have been reported by Thompson and Ramsey<sup>16</sup> and will be discussed in **Chapter 3**.

From the above discussion it can be seen that the determination of PGM and gold at trace level is mainly hampered by both techniques and methods that are less sensitive and selective. This research study will therefore be concentrating on the developing of a much more sensitive analytical method for the quantitative determination of PGMs and gold using spectrometric techniques (ICP-OES/MS, GD-OES and XRF) at highly selective lines (wavelengths) or mass/charge ratios using different CRMs, inorganic salts, organometallic compounds and the mineral ores.

---

<sup>14</sup> A.S. Al-Ammar, *Spectrochimica Acta Part B*, (2003), 58, pp. 1391 - 1401.

<sup>15</sup> T.N. Lokhande, M.A. Anuse and M.B. Chavan, *Talanta*, (1998), 47, pp. 823 - 832.

<sup>16</sup> M. Thompson and M. Ramsey, *Analyst*, (1985), 110, p. 1413.

The focus was to establish whether the use of cobalt as an internal standard, which was developed in a previous study,<sup>17,18</sup> is applicable to the quantification of all the PGM and gold or whether an alternative internal standard can be identified and evaluated for the accurate determination of all the PGM and gold. This study will also include a comparison with the traditional direct calibration method as well as with the results obtained using yttrium as internal standard (ISO approved).<sup>19</sup>

The major objectives of this study are summarized below.

### 1.2 Aim of this study

The main objective of this research is to:

- Develop a simple indoor digestion/dissolution procedure for PGM and gold compounds;
- Establish an effective and reliable internal reference element that is compatible with all the PGM and gold;
- Apply the spectrometric analytical method(s) for the determination of PGM and gold in inorganic, organometallic compounds and geological materials;
- Establish measurement traceability in analysing PGM and gold from a certified reference material (CRM);
- Validate the suitability of the newly developed/optimized method in determining PGM and gold from the inorganic, organometallic compounds and geological materials.

---

<sup>17</sup> T.T. Chiweshe, *Quantification of rhodium in series of inorganic and organometallic compounds*, MSc thesis, University of the Free State, Bloemfontein, South Africa, (2010).

<sup>18</sup> T.T. Chiweshe, W. Purcell and J. Venter, *S. Afr. J. Chem.*, (2012), 66, pp. 7 - 16.

<sup>19</sup> International Organization for Standardization: Atomic Absorption. Doc. ISO/WD 11492.

# 2 Overview of PGM and gold

---

## 2.1 History and the discovery of PGM and gold

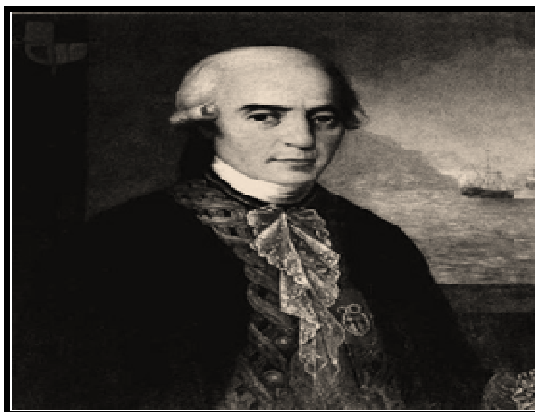
### 2.1.1 Discovery of platinum

The history around platinum discovery is not very well documented and the available literature shows numerous reports with different versions of its discovery.<sup>20</sup> One of the more common versions suggests that platinum was first discovered by the natives of New Granada (Colombia) from the mineral ore as white metal nuggets when they were panning gold. The natives first considered it a '*nuisance metal*' because of its silvery appearance and its interference with their gold mining activities. Some thought that this metal was a sort of unripe gold product and it was sometimes referred to as '*oro blanco*,' or '*juan blanco*' meaning white gold. Reports of the new metal were brought to the notice of European scientists in 1748 after the novel properties of this new metal was recognised (called '*hard metal*') by Julius Caesar Scaliger in 1557.<sup>21</sup> Scaliger described this metal in his book as a strange metal that could not be melted by any means that was available to them. The first complete description of platinum was given by the Spaniard, Antonio de Ulloa (1716 - 1795) (**Figure 2.1**) who was serving in South America as a military leader (1735 - 1748) and he is accredited with the discovery of platinum based on his well documented platinum report.

---

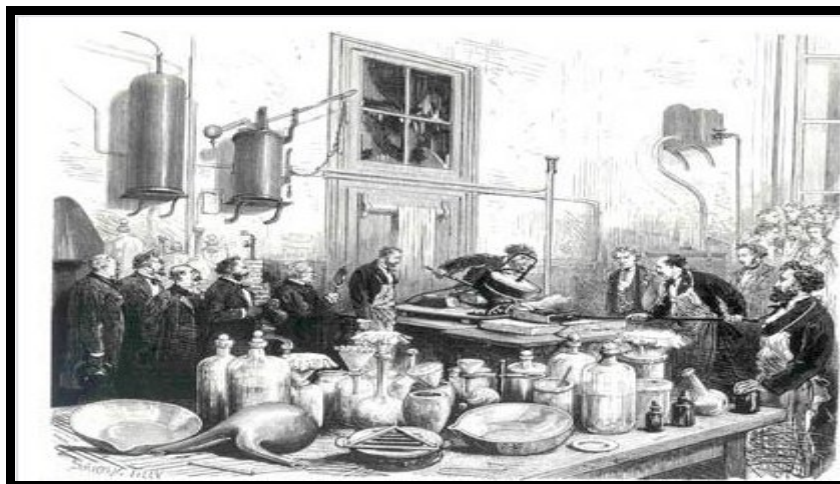
<sup>20</sup> F.R.S. Watson, *Phil. Trans.*, (1749/50), 46, pp. 584 - 596.

<sup>21</sup> <http://www.vanderkrogt.net/elements/element.php?sym=Pt> (accessed on the 09/05/2013).



**Figure 2.1:** Spanish military leader Antonio de Ulloa (1735 - 1748)

This discovery captivated the interest of English, French, German and Swedish scientists,<sup>22</sup> (**Figure 2.2**) who came together to determine the properties of this newly discovered platinum metal. Having tried unsuccessfully to melt the platinum metal, the scientists did not realize that the native platinum ore they were working on also contained other platinum group elements. Joseph Louis Proust, working under the patronage of King Carlos IV in 1799, was the first scientist to recognize that there was a small insoluble black residue that survived the *aqua regia* digestion of the native platinum. Proust described this black residue as '*Nothing less than graphite or plumbago*'.<sup>23</sup>



**Figure 2.2:** The analysis of crude platinum by a group of English, French, German and Swedish scientists.<sup>24</sup>

---

<sup>22</sup> W.A. Smeaton, *Platinum Metals Rev.*, (1963), 7 (3), p.106.

<sup>23</sup> J.L. Proust, *An. Hist. Nat.*, (1799), 1, pp 51 - 84; *Ann. Chim.*, (1801), 38, pp. 146 - 173 and pp. 225 - 247; *Phil. Mag.*, (1802), 11, pp. 44 - 55 and pp. 118 - 128.

<sup>24</sup> J. Foley, *History of Foley's Gold Pens with illustrations*, New York, (1875), pp. 50 - 60.

It was this black residue that greatly intrigued Smithson Tennant shortly after he entered into an unpublicised partnership with William Hyde Wollaston in 1800 (**Figure 2.3**) with the aim of making and selling of malleable platinum. In this partnership, Wollaston was mainly responsible for the chemical and metallurgical innovations for the final production of platinum metal, whilst Tennant was responsible for the establishment of ideas for the marketing of platinum metal.<sup>25</sup> It was soon decided that Wollaston would pursue the study of the *aqua regia* filtrate solution of the native platinum while Tennant would concentrate on the insoluble black residue. Tennant and Wollaston also discovered other PGM (Os, Ir, Pd and Rh) from their respective portions of the native mineral ore they were investigating and which is described in the subsequent sections.



**Figure 2.3:** James Smithson Tennant (1761 - 1815) and William Hyde Wollaston (1766 - 1828).

### 2.1.2 Discovery of osmium

Contrary to Proust's conclusion about the black residue, Smithson Tennant, an English chemist, as the first to discover that the insoluble black residue did not, as was generally believed, consist chiefly of '*plumbago*' (graphite) but contained some unknown metallic compounds. He further proved that the density of the crude residue was too high ( $10.7 \text{ g/cm}^3$ ) for it to be regarded as '*plumbago*'.<sup>26</sup> Tennant took the insoluble black residue that remained after the *aqua regia* digestion of platinum ore,

---

<sup>25</sup> M.C. Usselman, *Platinum Metals Rev.*, (1989), 3, p. 33.

<sup>26</sup> D.L. Proust, *Ann. Chim.*, (1801), 38, p. 160.

heated it with sodium carbonate and isolated a soluble yellow  $[\text{OsO}_4(\text{OH})_2]^{2-}$  compound. On the acidification of the reaction mixture with nitric acid, he observed the formation and liberation of whitish fumes which had a strong penetrating smell that was very distinctive. Tennant then named this metal osmium from the Greek word *osme* (*οσμή*) which means smell, due to this first experience with this metal compound he encountered, which is now known to be the production of osmium tetroxide ( $\text{OsO}_4$ ). From this strong smell of the osmium produced, Tennant recorded the following in his book:

*'it stains the skin of a dark colour which cannot be effaced...(it has) a pungent and penetrating smell...from the extrication of a very volatile metal oxide...this smell is one of its most distinguishing characters, I should on that account incline to call the metal Osmium.'*<sup>27</sup>

### 2.1.3 Discovery of iridium

In his continued quest to completely characterise his black compound, Tennant noticed that there was still some black residue that remained after the white pungent fumes ceased to be liberated from the reaction mixture. He fused this black residue with caustic soda ( $\text{NaOH}$ ) at very high temperature and extracted the melt with hydrochloric acid. The extract gave dark red crystals which was later identified as  $\text{Na}_2[\text{IrCl}_6] \cdot n\text{H}_2\text{O}$ . From this isolated product, Tennant prepared a number of colourful compounds and he decided to call this new metal iridium, which is derived from the Latin word *Iris*, which means rainbow. With this discovery, Tennant wrote in his book:

*...I should incline to call this metal Iridium, from the striking variety of colours which it gives, while dissolving in marine acid*<sup>28</sup> ...

---

<sup>27</sup> S. Tennant, *Phil. Trans.*, (1804), 94, p. 411.

<sup>28</sup> S. Tennant, *Chem. Arts.*, (1805), 10, p. 24.



### 2.1.4 Discovery of palladium

William Hyde Wollaston (1801) an English chemist, first discovered palladium from an acidic filtrate of the crude platinum ore he was assigned to investigate as part of his partnership with Tennant. He first neutralized his filtrate with sodium hydroxide and precipitated the remaining platinum with ammonium chloride. The remaining filtrate from this was again neutralized and then treated with mercuric cyanide ( $\text{Hg}(\text{CN})_2$ ) to give a pale yellow-white precipitate of 'prussiate of palladium' (believed to be  $\text{Pd}(\text{CN})_2$ ) which on ignition gave palladium metal.<sup>29,30</sup> Wollaston first mentioned his discovery in his notebook in 1802 calling the new element 'Pa' <sup>31,32</sup> for palladium but later changed the symbol to Pd. The name palladium was derived from the ancient Greek phrase 'asteroid Pallas', meaning goddess of wisdom.<sup>33</sup>

### 2.1.5 Discovery of rhodium

Soon after the discovery of palladium, Wollaston discovered rhodium<sup>34</sup> in 1803 from the same filtrate solution of the crude platinum ore. Wollaston called his metal '*N-nov<sup>m</sup>*', a Greek word meaning 'rose'<sup>35</sup> due to its distinctive red colour of the rhodium salts<sup>36</sup> that he obtained after the separation and isolation of platinum and palladium from the ore (**Figure 2.4**). The term '*N-nov<sup>m</sup>*' is usually found with the motto '*Dat Rosa Mel Apibus*' a Greek phrase meaning the red rose gives the bees honey. The motto was presumably used by the Rosicrucian's as a reference for the rhodium colour.<sup>37</sup>

---

<sup>29</sup> W.H. Wollaston, *Phil. Trans. Roy. Soc.*, (**1805**), 95, p. 316; *Chem. Arts.*, (**1805**), 10, p. 34.

<sup>30</sup> R. Chenevix, *Phil. Trans. Roy. Soc.*, (**1803**), 93, p. 290.

<sup>31</sup> D. McDonald and L.B. Hunt, *History of Platinum and its Allied Metals*, Johnson Matthey, London, (**1982**).

<sup>32</sup> L.F. Gilbert, *Notes Rec. Roy. Soc. London.*, (**1952**), 9, p. 310.

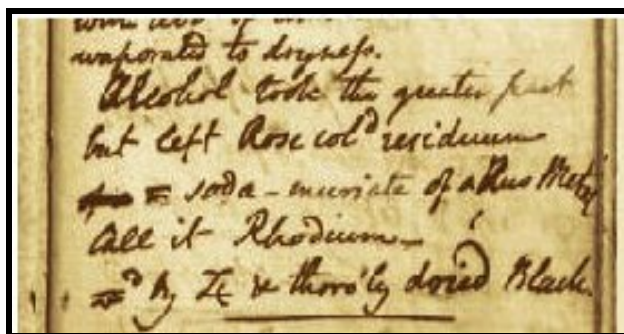
<sup>33</sup> [http://bullion.nwtmint.com/palladium\\_history.php](http://bullion.nwtmint.com/palladium_history.php) (accessed on the 12/07/2012).

<sup>34</sup> N. Greenwood and A. Earnshaw, *Chemistry of the elements*, Pergamon Press, Oxford, (**1984**).

<sup>35</sup> <http://nautilus.fis.uc.pt/st2.5/scenes-e/elem/e04510.html> (accessed on the 05/07/12).

<sup>36</sup> <http://www.vanderkrogt.net/elements/elem/rh.html> (accessed on the 05/07/12).

<sup>37</sup> M. Heindel, *Christian Rosenkreuz and the Order of Rosicrucians*, (**1908 - 1919**).



**Figure 2.4:** A fragment of Wollaston's notebook when he named rhodium in 1803.<sup>38</sup>

Translated, it reads as follows:

*My inquiries having terminated more successfully than I had expected, I design in the present memoir to improve the existence, and to examine the properties, of another metal, hitherto unknown, which may not improperly be distinguished by the name of Rhodium, from the rose-colour of a dilution of the salts containing it.*

The Copley medal (**Figure 2.5**) of the Royal Society was awarded to Wollaston in 1802 and Tennant in 1804 in recognition of their discoveries and isolation of the different platinum group metals. Their incredible discoveries were communicated to the Royal Society and printed in several volumes of the Philosophical Transactions.<sup>39,40</sup> Neither Wollaston nor Tennant acknowledged each other's contribution as part of their unpublicised partnership in their publications. This was by design as they wished to keep their collaboration as part of their business plan.

---

<sup>38</sup> W.H. Wollaston, *Philos. Trans. R. Soc. London*, (**1804**), 94, p. 419.

<sup>39</sup> S. Tennant, *Phil. Trans.*, (**1804**), 94, pp. 411 - 418.

D. McDonald, *Platinum Metals Rev.*, (**1961**), 5, pp. 146 - 148.

<sup>40</sup> [http://www.encyclopedia.com/topic/William\\_Hyde\\_Wollaston.aspx](http://www.encyclopedia.com/topic/William_Hyde_Wollaston.aspx) (accessed on the 04/08/2012).



**Figure 2.5:** William Hyde Wollaston's Copley Medal by the Royal Society <sup>41</sup> and the 250<sup>th</sup> anniversary medal made in recognition of Smithson Tennant's work.<sup>42</sup>

#### 2.1.6 Discovery of ruthenium

The last platinum group metal to be discovered was ruthenium. As was the case with osmium, it was extracted from the insoluble residue of the crude platinum ore after the *aqua regia* treatment. Karl Karlovitch Klaus discovered ruthenium in 1844 when he was trying to confirm the presence of the previously found metals (Ir, Pd, and Rh) by Tennant and Wollaston in platinum ore. His objective was not to discover any new metals from the native platinum mineral ore, but to re-affirm these discoveries. Klaus recorded in his book that:

*'My aim was not to discover ... new bodies, but to prepare the compounds. By the way, I accidentally found out the presence of a new body, but I could not separate it at first.'* <sup>43</sup>

Klaus also found that on treating the chloride salts of this new compound with hydrogen sulphide a 'dense sapphire-blue colour' was formed. He noted that, '*neither iridium nor rhodium nor any other metal...*' had the ability to react in such a

---

<sup>41</sup> D. McDonald and L.B. Hunt, *A History of Platinum and its Allied Metals*, Johnson Matthey, London, (1982), pp.147 - 152.

<sup>42</sup> R.N. Perutz, *Platinum Metals Rev.*, (2012), 3, p. 56.

<sup>43</sup> K. Klaus, *Gorn. Zh.*, (1845), 7 (3), pp. 157 - 163.

way.<sup>44</sup> He named the new metal, ruthenium, in honour of his motherland, *Ruthenia*, the Latin name for Russia.

### **2.1.7 Discovery of gold**

Gold was first discovered (as far back as 3100 BC) as shining yellow nuggets and is undoubtedly the first pure metal known to early civilizations. Because of its widely dispersion throughout the geologic world, its discovery occurred in many different places and time. Archeological digs suggest gold was first used in the Middle East where the first known civilizations developed. Experts in the study of fossils have observed that pieces of natural gold were found in Spanish caves used by Paleolithic Man in about 40 000 BC while the oldest pieces of gold jewellery were discovered in the tombs of Queen Zer of Egypt and Queen Pu-abu of Ur in Sumeria and date from the third millennium BC.<sup>45</sup>

Gold's name originated from the Latin word '*aurum*', which is related to the goddess of dawn, Aurora. Early civilizations equated gold with gods and rulers, and gold was sought in their name and dedicated to their glorification.<sup>46</sup> Gold has always been associated with wealth, and has been a tool for trading in the early 1900's amongst the European countries and the United States. During this period, their currencies were backed by the amount of gold they had in the bank and this was known as the gold standard. Under the gold standard, any country that wanted to print more money had to buy gold to back their money.

## **2.2 Distribution of PGM and gold**

### **2.2.1 Occurrence of PGM in the world**

Most of the world's known deposits for PGM are found in South Africa which accounts for nearly 87.7 % of the world's supply followed by Russia (8.3 %), the

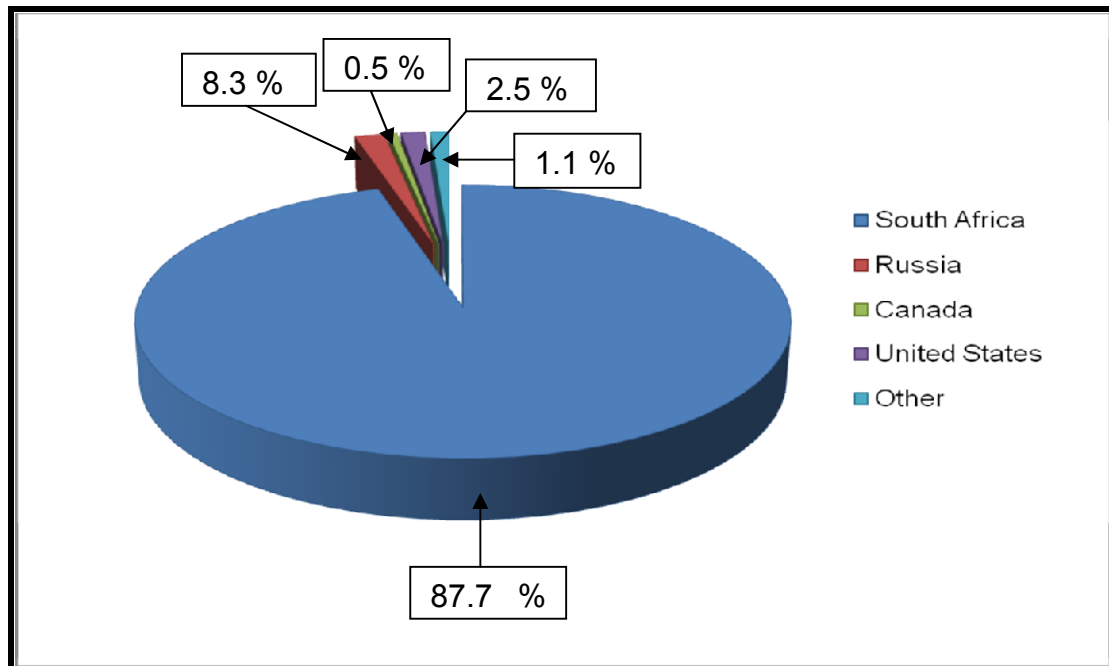
---

<sup>44</sup> V.N. Pitchkov, *Platinum Metals Rev.*, (1996), 4, p. 40.

<sup>45</sup> [http://bullion.nwtmint.com/gold\\_history.php](http://bullion.nwtmint.com/gold_history.php) (accessed on the 15/06/2012).

<sup>46</sup> ISBN: 978-3-527-32029-5

United States of America (2.5 %), Canada (0.5 %) and other countries 1.1 % (**Figure 2.6**).<sup>47</sup> Most of the PGM supplied by these countries are commonly recovered as either PGM deposits or by-products of nickel and copper recovery or from secondary (recycled) resources.

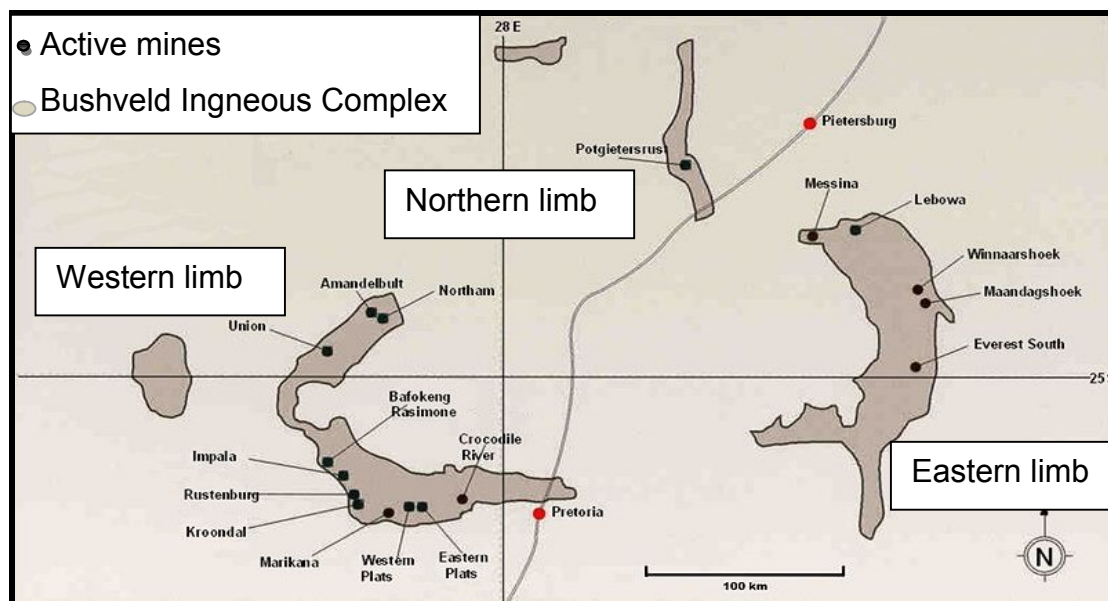


**Figure 2.6:** World PGM reserves

In South Africa, PGM mineral ore deposits are mainly found in the three layered suits of the Bushveld Igneous Complex (BIC) and encompasses the Limpopo and part of the North West Province. The BIC covers an estimated total area of about 66 000 km<sup>2</sup> and is sub-divided into the Western, Northern and Eastern limbs as shown in **Figure 2.7**.

---

<sup>47</sup> [http://en.wikipedia.org/wiki/Platinum\\_group](http://en.wikipedia.org/wiki/Platinum_group) (accessed on the 05/07/12).



**Figure 2.7:** The Bushveld Igneous Complex of South Africa.<sup>48</sup>

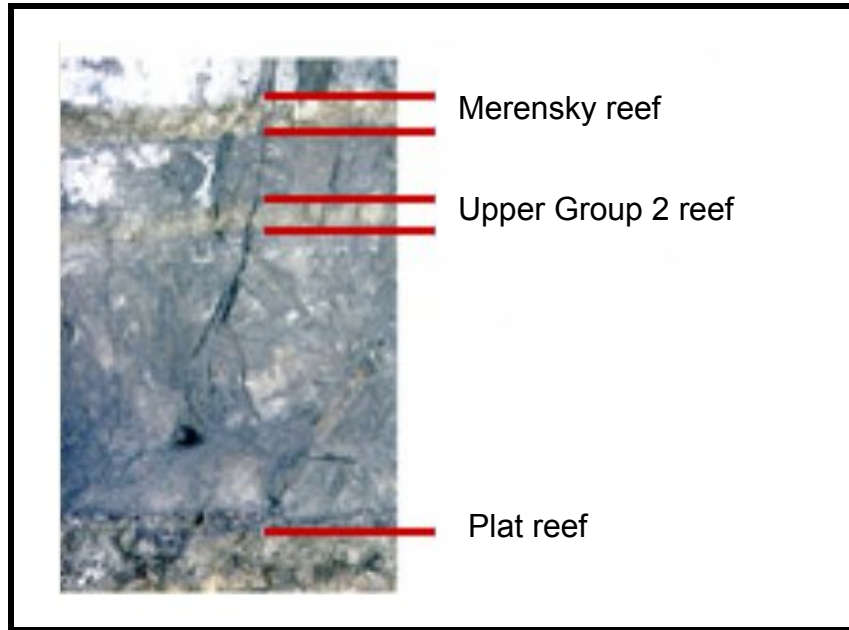
The PGM are mainly produced by six privately owned companies which operate both underground and opencast mines on the Merensky reef and UG2 chromitite layer in the BIC. The Merensky reef (near Rustenburg on the Western Limb) was first mined in 1926 and today has more than twelve operating mines producing 4.5 million ounces of platinum annually. Upper Group 2 (UG2) ores (**Figure 2.8**) were first processed in the 1980's and the PGM recovery from these remains an ongoing challenge because of the very high chromium and base metal content present in the chromite layer.

The BIC complex is the world's largest mafic-ultramafic layered (volcanic) intrusion in the earth's crust that was formed when the molten rock solidified in layers before reaching the earth's surface. These intrusions were brought near or on the earth's surface through erosion to form what appears as the edge of a great geological basin.<sup>49</sup> These three layered suites are (i) the Merensky reef (0.3 - 0.9 m in thickness) and consist mostly of pyroxenite rocks (ii) the UG2 reef (18 - 36 m) which consist mainly of chromitite and (iii) the Plat reef (10 - 400 m) which consist mainly of pyroxenite.<sup>50</sup>

<sup>48</sup> [http://en.wikipedia.org/wiki/Bushveld\\_Igneous\\_Complex](http://en.wikipedia.org/wiki/Bushveld_Igneous_Complex) (accessed on the 27/08/12).

<sup>49</sup> <http://geosphere.geoscienceworld.org/cgi/content/extract/2/7/352> (accessed on the 17/09/12).

<sup>50</sup> D.A. Holwell and I. McDonald, *Miner. Deposita.*, (2006), 41, (6), p. 575.



**Figure 2.8:** Cross-section through the Bushveld Igneous Complex (BIC).

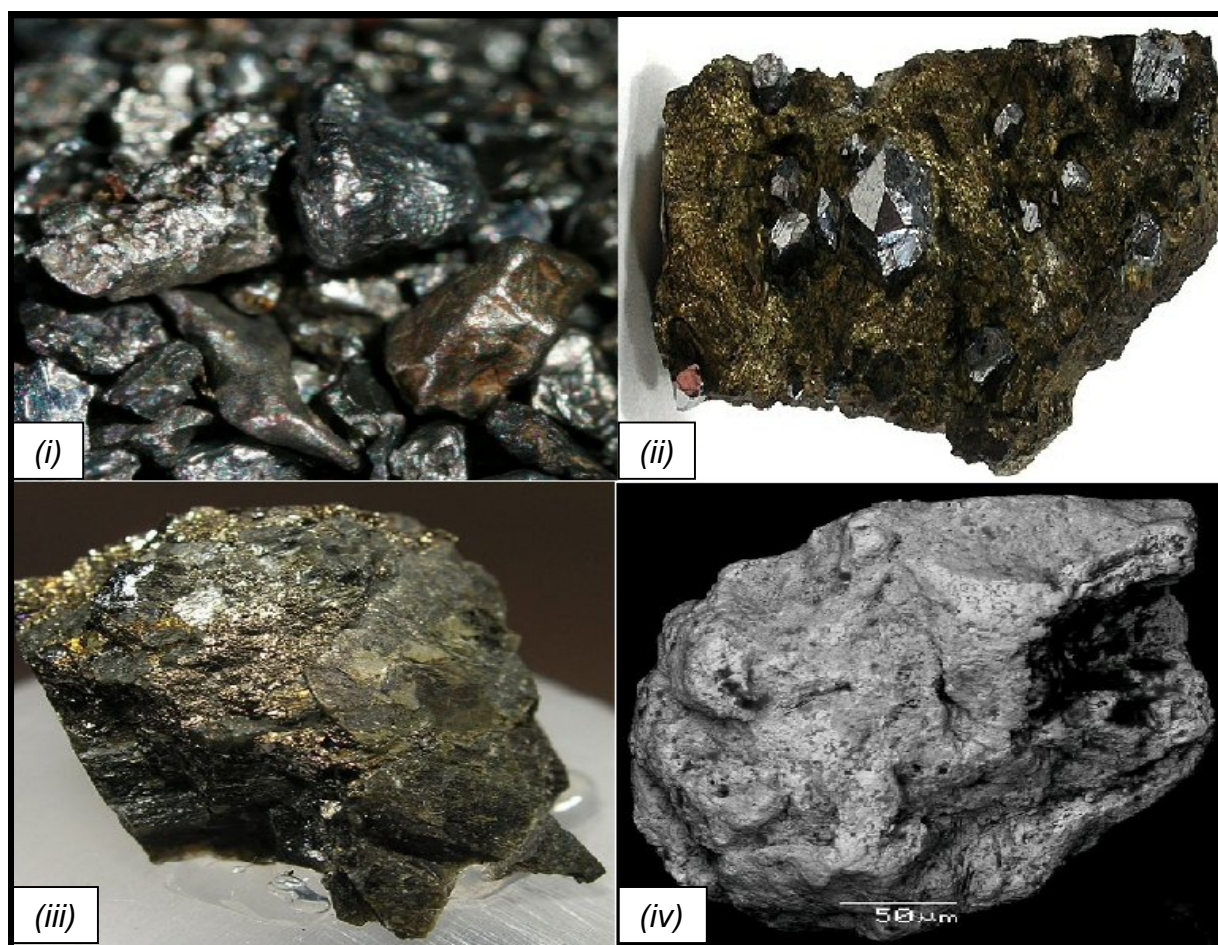
The importance of the Merensky and the UG2 reefs is underlined by the fact that they contain approximately (90 %) of the world's PGM reserves. Intensive mining activities are currently taking place in these layers as a result of the proximity of the PGM mineral ore to the earth's surface ( $<0.9$  m) as shown in **Figure 2.9**. The Merensky reef has been the source of most of South Africa's PGM for the past 5 years and is estimated to still contain about 17 000 tons of PGM reserves.



**Figure 2.9:** Cross-section of the Merensky reef showing PGM deposits in an open pit mine.



The PGM mineral ore within the BIC are mainly of sperrylite origin<sup>51</sup> and contains up to 43.5 % of the chromite (UG2) and varying proportions of sulfur and arsenides. Examples of the mineral ores found in the BIC includes osmoiridium (Os, Ir), plumbopalladinite (Pd), hollingworthite (Rh, Pt),<sup>52</sup> sperrylite (Pt),<sup>53</sup> platarsite (Pt, Rh, Ir),<sup>54</sup> laurite (Ru), merenskyite (Pd, Pt) and irarsite (Ir, Ru, Rh and Pt) and a few mineral samples are shown in **Figure 2.10**. A summary of the PGM content in these mineral ores is given in **Table 2.1**.



**Figure 2.10:** Types of PGM mineral ores (i) Osmoeridium mineral ore (Os and Ir), (ii) Sperrylite (Pt), (iii) Plumbopalladinite (Pd) and (iv) Irarsite (Ir, Ru, Rh and Pt)

---

<sup>51</sup> T.L. Grokhovskaya, V.V. Distler, A.A. Zakharov and S.F. Klyunin, I.P. Laputina, *Dokl Akad Nauk.*, (1989), 306, pp. 430 - 434.

<sup>52</sup> A.E. Boudreau, E.A. Mathez and I.S. McCallum, *J. Petrol.*, (1986), 27, pp. 967 - 986.

<sup>53</sup> I.S. McCallum, *J. Petrol.*, (1989), 102, pp. 138 - 153.

<sup>54</sup> V.S. Dokuchaeva, A.A. Zhangurov and Z.A. Fedotov, *Dokl Akad Nauk.*, (1982), 265, pp. 1231 - 1234.



**Table 2.1:** Characteristics of Bushveld Igneous Complex PGM ore types<sup>55</sup>

Characteristic	Merensky Reef	UG2 Reef	Plat Reef
<b>Thickness of PGM deposit</b> (m)	0.3 - 0.9	18 - 36	10 - 400
<b>Grade PGM</b> (g/t)	5 - 9	6 - 7	3 - 4
<b>Gangue minerals</b>	50 - 80 % pyroxene 20 - 40 % plagioclase 3 - 5 % chromite 0.5 - 5 % talc	60 - 90 % chromite 5 - 25 % pyroxene 5 - 15 % plagioclase 1 - 5 % talc	80 - 90 % pyroxene 10 - 20 % plagioclase 3 - 5 % chromite 0.5 - 3 % talc
<b>PGM grain size</b> (microns)	20 - 150	40 - 200	3 - 10
<b>Examples of PGM minerals</b>	Hollingworthite (Rh, Pt) Plumbopalladinite (Pd) Merenskyite (Pd, Pt) Sperrylite (Pt) Isoferroplatinum (Pt, Au)	Laurite (Ru) Braggite (Pt, Pd) Isoferroplatinum (Pt) Sperrylite (Pt) Irarsite (Ir, Ru, Rh, Pt)	Moncheite (Pt, Pd) Merenskyite (Pd, Pt) Sperrylite (Pt) Isoferroplatinum (Pt, Au) Braggite (Pt, Pd)
<b>PGM analysis</b>			
Pt (%)	59	41	42
Pd (%)	25	34	46
Rh (%)	3	9	3
Ru (%)	8	12	4
Ir (%)	1	1.9	0.8
Os (%)	0.8	1.7	0.6
Au (%)	2.5	0.4	3.4

### 2.2.2 Distribution of gold in the world

South Africa is one of the largest producers of gold in the world accounting approximately 7.7 % of the world supply with China (11.8 %) Australia (8.6 %), United States (8.1 %), Russia (7.7 %)<sup>56</sup> also topping the list. Most of the gold in South Africa comes from the Witwatersrand basin which when translated means 'White Water Ridge' (Wits basin). The basin was formed between 2.6 and 3.0 billion years ago and stretches from the east of Johannesburg to the northern Free State. The

---

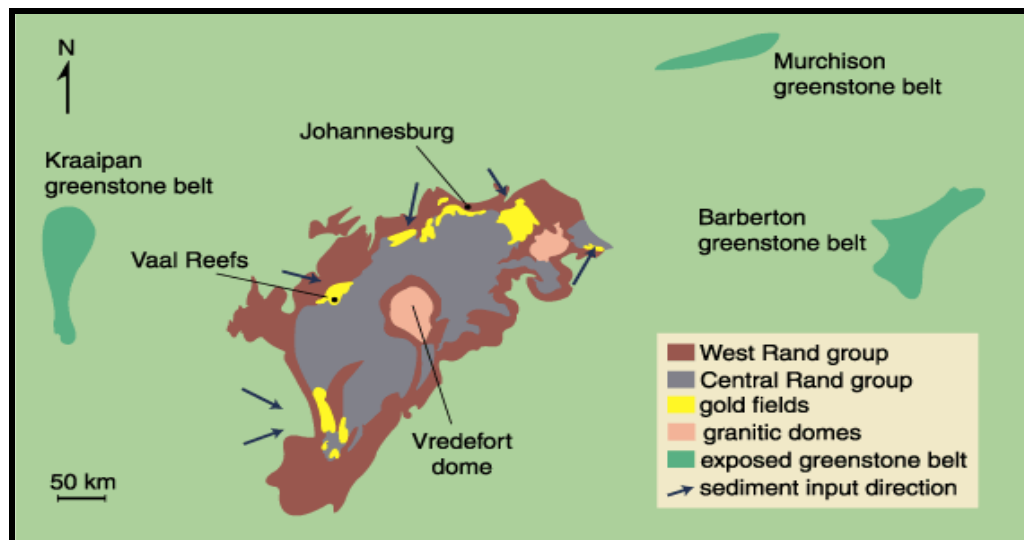
<sup>55</sup> [http://www.northam.co.za/business/merensky\\_ug2\\_reef.htm](http://www.northam.co.za/business/merensky_ug2_reef.htm) (accessed on the 27/08/12).

<sup>56</sup> <http://www.globalresearch.ca/geopolitics-and-the-world-s-gold-holdings/24462> (accessed on the 08/05/2012)

Witwatersrand basin is elliptical in shape with gold deposits of up to 3 kilometers (km) deep and covers an area of approximately 18 000 km<sup>2</sup> (**Figure 2.11 and 2.12**).



**Figure 2.11:** Witwatersrand basin, which contains nearly half the world's gold reserves.<sup>57</sup>



**Figure 2.12:** Features within the gold-bearing conglomerates in the Witwatersrand basin.<sup>58</sup>

Geologists believe that several braided rivers flowed into a huge inland sea that extended across this area at this time. These rivers carried eroded materials that

---

<sup>57</sup><http://www.americanscientist.org/issues/issue.aspx?id=907&y=0&no=&content=true&page=2&css=print> (accessed on the 13/09/2012).

<sup>58</sup><http://www.americanscientist.org/issues/issue.aspx?id=907&y=0&no=&content=true&page=2&css=print> (accessed on the 15/09/2012).

hold small grains of gold from the surrounding highlands and deposited them in alluvial deltas around this sea, at their respective entry points.<sup>59</sup> The deposited materials were transformed into conglomerate rocks (**Figure 2.13**) which are being mined today as the primary gold source.



**Figure 2.13:** Witwatersrand gold conglomerate<sup>60</sup>

### 2.3 Economic values of PGM and gold

PGM and gold are extremely expensive metals due to their demand and supply constraint in the world market. Except for rhodium, their prices have been steadily increasing since 2008, with gold topping the list according to the metal dealer Kitco Precious Metals (KPM)<sup>61</sup> (see **Figure 2.14 and 2.15**). Rhodium price has dropped significantly possibly due to the motor industry opting for other cheaper platinum group metals e.g. Pd and Pt to be used as catalytic converters in exhaust systems of new cars.

---

<sup>59</sup> <http://www.witsgold.com/our-business/geology-of-the-wits-basin> (accessed on the 19/09/2012).

<sup>60</sup> <http://conglomerate.usegrid.net/> (accessed on the 19/09/2012).

<sup>61</sup> <http://www.kitco.com/> (accessed on the 22/02/2013).

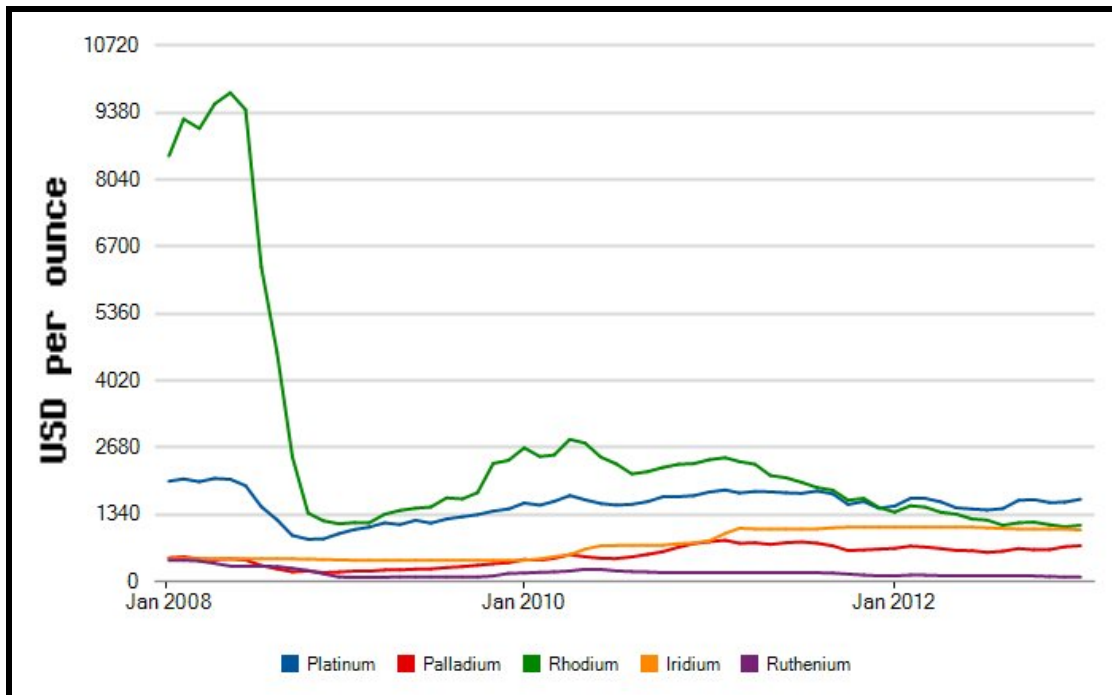


Figure 2.14: Monthly average prices of PGM for the last few years (2008 - 2012)<sup>62</sup>



Figure 2.15: The increase in gold price over the past 5 years (2008 - 2012)<sup>63</sup>

In a five-year span beginning from 2008, the average price of PGM and gold had been increasing steadily since March (2008) to September (2012) and these metals

<sup>62</sup> <http://www.platinum.matthey.com/prices/price-charts> (accessed on the 04/12/2012)

<sup>63</sup> [www.kitco.com](http://www.kitco.com) (accessed on the 04/12/2012).

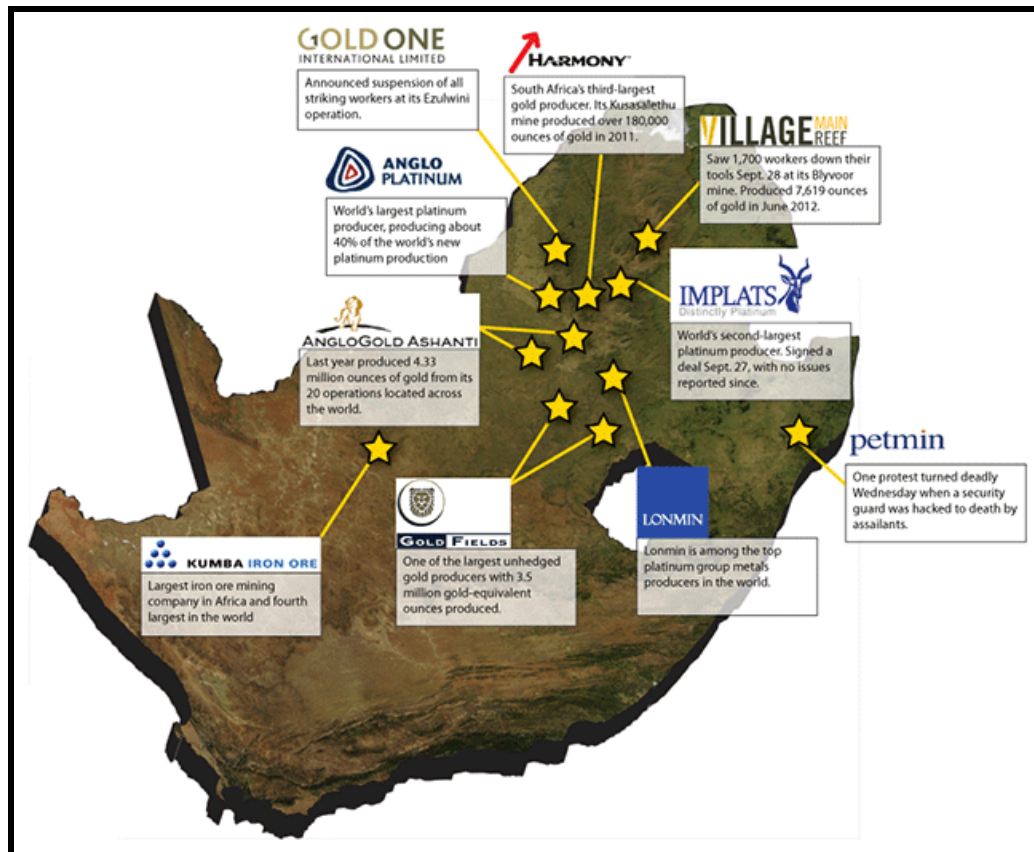
are currently trading at the average price per ounce of \$1 540.77 for platinum, \$515.94 for palladium, \$2 656.76 for rhodium, \$738.38 for iridium, \$171.69 for ruthenium and \$1 576.30 for gold as on 04/12/2012 <sup>62</sup> with projections indicating further increases in the prices of these commodities in future. Expectations are that the price increase of PGM and gold will be driven by demand from the automobile industry where PGM are used for the manufacture of catalytic converters as well as in the jewellery industry. Johnson Matthey<sup>64</sup> predicts that South Africa has the potential to benefit much more from the ever skyrocketing prices of PGM and gold on condition that the right legislation pertaining labour laws is put in place.

The reductions in PGM supply due to the labour unrest have been reported to cause an increase in the prices of PGM and gold, according to an online analyst.<sup>65</sup> Mining strife in South Africa between the year 2011 and 2014 (**Figure 2.16**) has resulted in a new level of uncertainty around the supply of PGM and gold as the cost escalation related to labour has become a continuing trend. The situation was reported to have triggered a reduction in PGM and gold supply and forced the commodity prices higher and threatened the country's capacity to increase its PGM and gold output as these disruptions and subsequent rationalisation seemed to have been on the increase.<sup>65</sup>

---

<sup>64</sup> <http://www.matthey.com/> (accessed on the 30/08/2013).

<sup>65</sup> <http://www.platinum.matthey.com/media/1393537/outlook.pdf> (accessed on the 21/02/2013).



**Figure 2.16:** Companies affected by the recent labor strife in South Africa between the year 2011 and 2014<sup>66</sup>

The economic driver for PGM growth demand has largely come from the automotive industry where these metals are mostly used as automotive exhaust catalysts. Several factors within this industry have contributed to this growing demand in PGM supply. Some of these factors include the growing rate of the automobile sales worldwide and the passed legislation in some countries governing the mitigation of the emission of air pollution by automobiles.<sup>67</sup> Under this legislation, automobiles are compelled to be equipped with advanced catalytic converters, which require higher loadings of PGM. This legislation has seen an increase in recycled PGM of up to 15 % in 2011 in European countries.

<sup>66</sup> <http://www.forbes.com/sites/kitconews/2012/10/08/recap-of-the-major-mines-impacted-by-the-south-african-mine-strikes/> (accessed on the 20/08/2012).

## 2.4 Physical and chemical properties of PGM and gold

PGM and gold belong to the transition metals of Groups VIII - X and XI respectively on the periodic table. PGM are coloured and lustrous, hard, malleable, electrically resistant and exceptionally stable. These metals are sometimes subdivided into two groups according to their densities with the first group called the heavier triad and consist of platinum, iridium and osmium. The second group, the lighter triad consists of palladium, rhodium and ruthenium. The heavier triad elements have higher melting points and densities (ca. 22 g/cm<sup>3</sup>) than the lighter triad (ca. 12 g/cm<sup>3</sup>) as shown in **Table 2.2**.

**Table 2.2:** Physical properties of PGM and gold

Chemical symbol	Pt	Ir	Os	Pd	Rh	Ru	Au
Groups	Heavier triad			Lighter triad			
Atomic no.	<b>78</b>	<b>77</b>	<b>76</b>	<i>46</i>	<i>45</i>	<i>44</i>	79
Atomic weight (g/mol)	<b>195.09</b>	<b>192.22</b>	<b>190.20</b>	<i>106.40</i>	<i>102.91</i>	<i>101.07</i>	196.97
Density (g/cm <sup>3</sup> )	<b>21.45</b>	<b>22.65</b>	<b>22.61</b>	<i>12.02</i>	<i>12.41</i>	<i>12.45</i>	19.3
Melting point (°C)	<b>1 769</b>	<b>2 443</b>	<b>3 050</b>	<i>1 554</i>	<i>1 960</i>	<i>2 310</i>	1 064
Boiling point (°C)	<b>3 827</b>	<b>4 500</b>	<b>5 500</b>	<i>2 900</i>	<i>3 700</i>	<i>4 080</i>	2 856
Electrical resistivity (microhm.cm at 0°C)	<b>9.85</b>	<b>4.71</b>	<b>8.12</b>	<i>9.93</i>	<i>4.33</i>	<i>6.80</i>	2.4
Thermal conductivity (watts/meter/°C)	<b>73</b>	<b>148</b>	<b>87</b>	<i>76</i>	<i>150</i>	<i>105</i>	293
Crystal structure*	<b>FCC</b>	<b>FCC</b>	<b>HCP</b>	<i>FCC</i>	<i>FCC</i>	<i>HCP</i>	FCC
Crustal abundance (ppm)	<b>0.01</b>	<b>0.001</b>	<b>0.005</b>	<i>0.01</i>	<i>0.005</i>	<i>0.005</i>	0.0031

\*FCC - Face centered cubic and HCP - Hexagonal close - packed

Bolded - Heavier triad

Italicized - Lighter triad

<sup>67</sup> J. Tollefson. *Nature.*, (2007), 450, pp. 334 - 335.

Gold on the other hand, is a soft, shiny, yellow, dense, malleable, ductile (trivalent and univalent) transition metal. Pure gold is too soft for ordinary use and is hardened by alloying with silver, copper, and other metals. Because of its high electrical conductivity and resistance to corrosion and other desirable combinations of physical and chemical properties, gold has also emerged as an essential industrial metal.

### 2.4.1 Chloride chemistry of PGM and gold

The most important chemical properties of PGM and gold are their similarity in chemical reactions especially in the formation of chlorido-complexes. These complexes are mostly formed through substitution reactions between the aqua and the chlorido species *via* a dissociative ( $S_N1$ ) mechanism<sup>68</sup> of the form  $[M(H_2O)_{6-x}Cl_x]^{(3-x)+}$  (where M= metal) as indicated in **Table 2.3** below.

**Table 2.3:** Common properties PGM and gold in chlorido complexes<sup>69,70</sup>

Metal	Oxidation state	Complex	Thermal stability
Pt	IV	$[PtCl_6]^{2-}$	Very stable
Pt	II	$[PtCl_4]^{2-}$	
Pd	IV	$[PdCl_6]^{2-}$	Unstable
Pd	II	$[PdCl_4]^{2-}$	
Ir	IV	$[IrCl_6]^{2-}$	
Ir	III	$[IrCl_6]^{3-}$	
Rh	III	$[RhCl_6]^{3-}$	Unstable
Ru	IV	$[RuCl_6]^{2-}$	unstable
Au	III	$[AuCl_4]^{3-}$	

---

<sup>68</sup> S.I. Ginzberg, *Analytical Chemistry of the Platinum Metals*. Wiley, New York., (1975), pp. 102 - 106 and pp. 434 - 458.

<sup>69</sup> W.C. Wolsey, C.A. Reynolds and J. Kleinberg, *Inorg. Chem.*, (1963), 2, p. 463.

<sup>70</sup> S.I. Ginzberg, *Analytical Chemistry of the Platinum Metals*. Wiley, New York., (1975), pp. 102 - 106 and pp. 434 - 458.



The relative substitution rates of the aqua ligands indicate the lability or inertness of the aqua ligand to undergo chlorido substitution, with the small value indicating inertness and larger value lability to substitutions.

**Table 2.4:** Relative substitution kinetics of the precious metal chlorido-complexes

Ruthenium	Rhodium	Palladium	Gold
Ru(III) $10^{-3}$ - $10^{-4}$ Ru(IV) $10^{-5}$ - $10^{-6}$	Rh(III) $10^{-3}$ - $10^{-4}$	Pd(II) 1	Au(III) $10^1$ - $10^{-1}$
Osmium	Iridium	Platinum	
Os(III) $10^{-7}$ - $10^{-9}$ Os(IV) $10^{-10}$ - $10^{-12}$	Ir(III) $10^{-4}$ - $10^{-6}$ Ir(IV) $10^{-8}$ - $10^{-10}$	Pt(II) $10^{-3}$ - $10^{-5}$ Pt(IV) $10^{-10}$ - $10^{-12}$	

These substitutions are reported to be generally slower than those of the base metals and normally follow the following sequence starting with the most easily dissociated ions Pd(II) > Pt(II) > Ru(III) > Ir(III) > Os(III) > Ir(IV) and Pt(IV). This difference in substitution rates is sometimes used in the separation process of PGM and gold from the base metals using gravimetric techniques. The extent of these substitution reactions also depends strongly on the chloride concentration, temperature, time after preparation and the pH of the solution.

## 2.4.2 PGM and gold oxides

### 2.4.2.1 Ruthenium and osmium oxides

The oxides of ruthenium and osmium are isomorphous with both having the same tetroxide structure, RuO<sub>4</sub> and OsO<sub>4</sub>. Both oxides are very volatile, light sensitive, toxic, forms yellow crystals, have low melting points (m.p) of ca. 25.4 °C (RuO<sub>4</sub>) and 40.46 °C (OsO<sub>4</sub>) and different boiling points (b.p) of ca. 40 °C (RuO<sub>4</sub>) and 130 °C (OsO<sub>4</sub>). Although both oxides are generally the same, their stability indicates that RuO<sub>4</sub> is much more unstable than OsO<sub>4</sub> and decomposes when exposed to heat to form RuO<sub>2</sub> which is more stable than RuO<sub>4</sub>. The reduced stability of RuO<sub>4</sub> therefore makes it a stronger oxidizing agent than OsO<sub>4</sub>.<sup>71</sup>

---

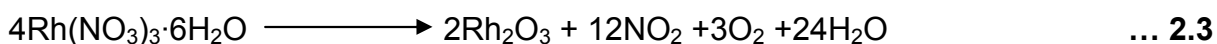
<sup>71</sup> W.P. Griffith, *Chem. Soc.Rev.*, (1992), 21, p.179.

OsO<sub>4</sub> is obtained by oxidizing any osmium compound or by its direct synthesis at 300 - 800 °C from elemental osmium (**Equation 2.1**). RuO<sub>4</sub> is also prepared in the same manner as OsO<sub>4</sub>, but the process needs to contain a strong oxidizing agent such as NaIO<sub>4</sub> (**Equation 2.2**). The products are very volatile (RuO<sub>4</sub> and OsO<sub>4</sub>) and are mostly released as fumes of unpleasant vapours which are very poisonous. Upon the action of reducing agents, both RuO<sub>4</sub> and OsO<sub>4</sub> are converted to the lower oxides RuO<sub>2</sub> and OsO<sub>2</sub> which are more stable. Further reduction produces the metallic state.



#### 2.4.2.2 Iridium and rhodium oxides

Rhodium and iridium form common oxides of the form M<sub>2</sub>O<sub>3</sub> and MO<sub>2</sub>.<sup>72</sup> The most common rhodium oxide is the brown Rh<sub>2</sub>O<sub>3</sub> and is prepared by heating rhodium metal at 300 - 1 000 °C in air or oxygen or by heating rhodium nitrate at 730 °C as shown in **Equation 2.3**. The structure of RhO<sub>2</sub> is isomorphous to IrO<sub>2</sub> and both have a rutile structure. RhO<sub>2</sub> is prepared by heating the rhodium metal or Rh<sub>2</sub>O<sub>3</sub> at 400 - 900 °C under oxygen and pressure of up to 3 500 atm (**Equation 2.4**). The other known stable rhodium oxides include RhO<sub>2</sub>·xH<sub>2</sub>O, Na<sub>2</sub>RhO<sub>3</sub>, Sr<sub>3</sub>LiRhO<sub>6</sub> and Sr<sub>3</sub>NaRhO<sub>6</sub>.



IrO<sub>2</sub> is prepared by heating the iridium metal in an oxygen atmosphere to produce a black solid product as shown in **Equation 2.5**. The other iridium oxide, Ir<sub>2</sub>O<sub>3</sub>, is not thermally stable at temperatures exceeding 500 °C and it decomposes to form IrO<sub>2</sub>

---

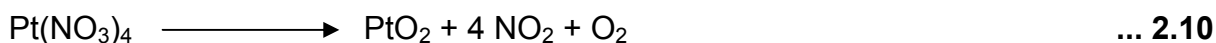
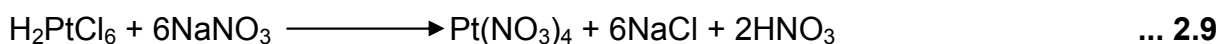
<sup>72</sup> J.H.M. Biesterbos and J. Hornstra, *J. Less Common Metals*, (1973), 30, p. 121.

which on further heating above 1 100 °C produces a pure metal as shown in **Equation 2.6 and 2.7**.



#### **2.4.2.3 Platinum and palladium oxides**

Platinum and palladium form oxides that are similar to each other, for example the brown PtO<sub>2</sub> and the black PdO<sub>2</sub> which have both rutile structures. The most common oxide for palladium is PdO which is also black in appearance and is prepared by the heating of palladium metal in oxygen (**Equation 2.8**) or by heating PdCl<sub>2</sub> in NaNO<sub>3</sub> melt at 520 °C. The obtained PdO is then heated with KClO<sub>3</sub> under pressure at 950 °C and rapidly cooled at room temperature to produce PdO<sub>2</sub>. PtO<sub>2</sub>, generally called the Adam's catalyst, is made as its hydrated form by the hydrolysis reaction with NaNO<sub>3</sub> in boiling PtCl<sub>6</sub><sup>2-</sup> solution as shown in **Equation 2.9 and 2.10**.



#### **2.4.2.4 Gold oxides**

Amongst the precious metals, gold shows the smallest tendency to form metal oxides. Gold(III) oxide (Au<sub>2</sub>O<sub>3</sub>) is prepared by heating gold metal in a sealed quartz vessel with perchloric acid and an alkali metal perchlorate at a temperature of 250 °C and pressure of 30 MPa. Au<sub>2</sub>O<sub>3</sub> is the most stable oxide amongst the known gold oxides and is red-brown in appearance. It is thermally unstable at temperatures above 160 °C as shown in **Equation 2.11** below.



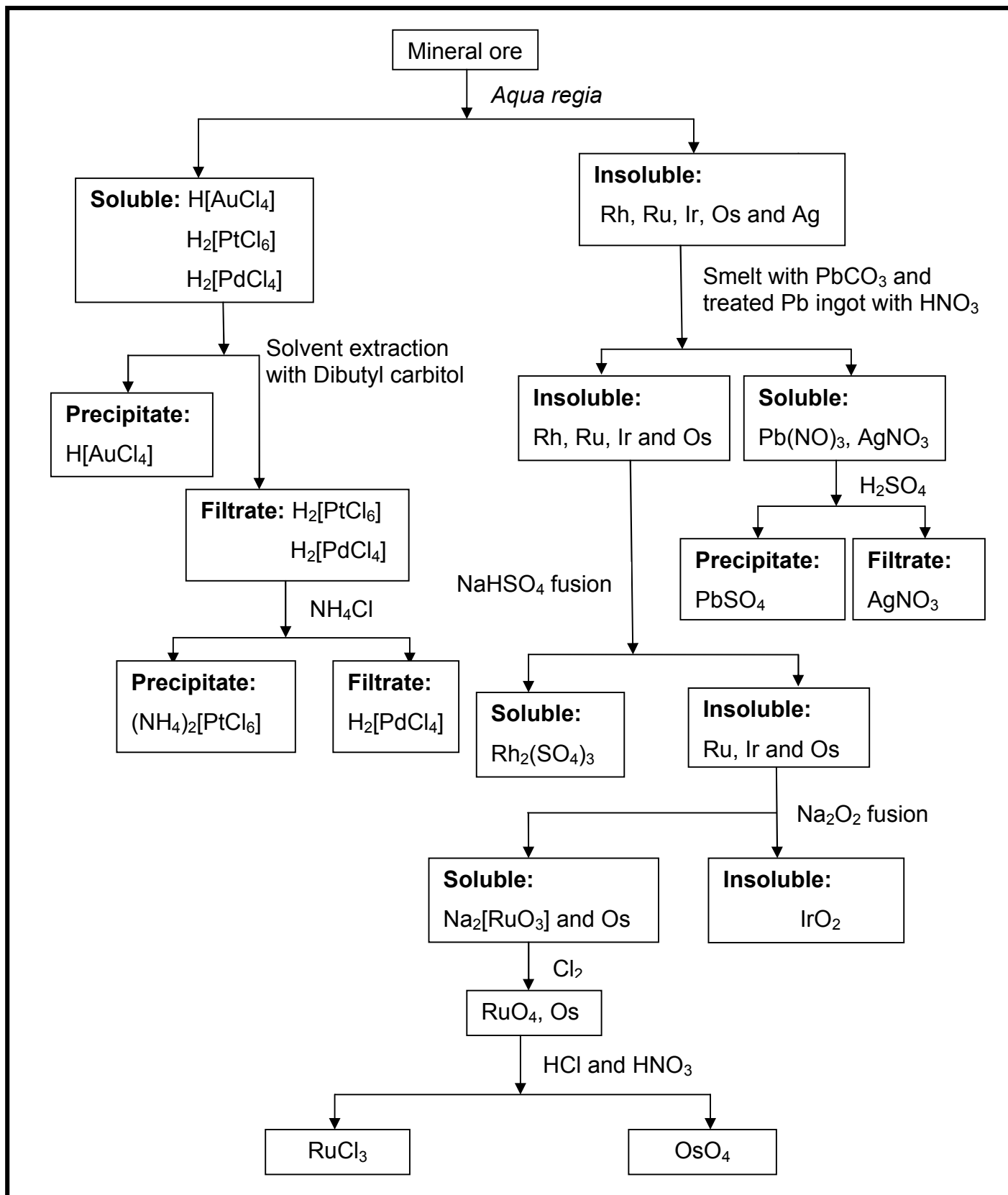
The most common and stable PGM and gold oxides are summarized in **Table 2.5** below.

**Table 2.5:** Common oxidation states of PGM and gold

Charge number	Ru	Rh	Pd	Os	Ir	Pt	Au
+2			PdO				
+3		Rh <sub>2</sub> O <sub>3</sub>					Au <sub>2</sub> O <sub>3</sub>
+4	RuO <sub>2</sub>	RhO <sub>2</sub>		OsO <sub>2</sub>	IrO <sub>2</sub>	PtO <sub>2</sub>	
+8	RuO <sub>4</sub>			OsO <sub>4</sub>			

## 2.5 Separation of PGM and gold from the mineral ore

The PGM and gold generally occur in nature and is associated with the major base metals such as iron, copper, nickel and cobalt and a wide range of other minor elements such as lead, tellurium, selenium and arsenic. In the technical and commercial processes, it is highly recommended that the individual PGM and gold be separated from the other metal impurities and from each other prior to quantitative analysis. This separation enables the accurate determination of PGM and gold of high purity to be quantified without any interference from other elements. The chloride system provides the most effective separation medium for PGM and gold from other metal impurities due to the differences in chemical reactions with the chlorides. PGM and gold complexes are generally much more stable than the equivalent base metal complexes and this allows PGM and gold to be separated from the base metals using their solubility e.g. for gold, platinum and palladium as shown in **Scheme 2.1**.



**Scheme 2.1:** Selective separation of precious metals from the mineral ore<sup>73</sup>

<sup>73</sup> F.R. Hartley, *Chemistry of the Platinum group metals*, Elsevier science publishers, (1991), 11, pp. 13 - 20.

## **2.6 Uses of PGM and gold**

PGM and gold are widely used due to their unique catalytic properties, chemical inertness, relative thermal stability, hardness, high melting points, electrical conductivity and aesthetic appearance. Uses of PGM and gold include chemical catalysts and coatings, dental alloys, electronic components and computer hard discs, fuel cells<sup>74</sup> for power generation, glassmaking equipment, investment coinage, jewellery, medicines and petroleum catalysts for gasoline refining.

The automobile industry is the major consumer of PGM of which Pd, Pt and Rh are the main active components used in the vehicle catalysts for controlling vehicle exhaust gas pollution. These metals promote the oxidation (Pt and/or Pd for CO and unburnt HC) and reduction (Rh for NO<sub>x</sub>) of the gases emitted from vehicle exhausts (**Figure 2.17**) and converts them to more environmental friendly H<sub>2</sub>O, CO<sub>2</sub> and N<sub>2</sub> gases.<sup>75</sup> An automobile catalytic converter typically contains 0.08 % Pt, 0.04 % Pd and between 0.005 - 0.007 % Rh supported on a base.<sup>76</sup> Iridium has recently been introduced as a new entrant in the automobile catalytic converter with Mitsubishi of Japan now opting for the iridium-containing catalytic converters in their engines.<sup>77</sup>

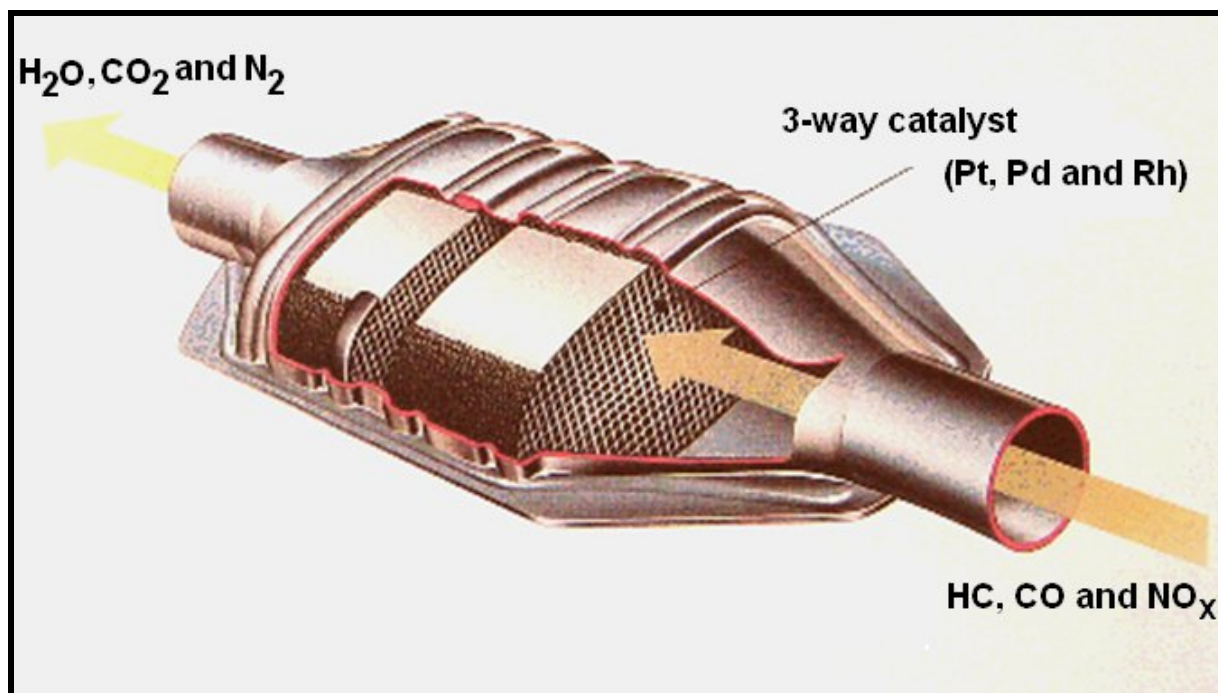
---

<sup>74</sup> T.H. Shin, Y. Okamoto, S. Ida and T. Ishihara, *Chem. Eur. J.*, **(2012)**, 18, (37), pp. 11695 - 11702.

<sup>75</sup> M. Motelica-Heino, S. Rauch, G.M. Morrison and O.F.X. Donard, *Analytica Chimica Acta.*, **(2001)**, 436, pp. 233 - 244.

<sup>76</sup> B. Gilmour, *Metals Miner. Annu. Rev.*, **(1998)**, pp. 29 and 169 - 247.

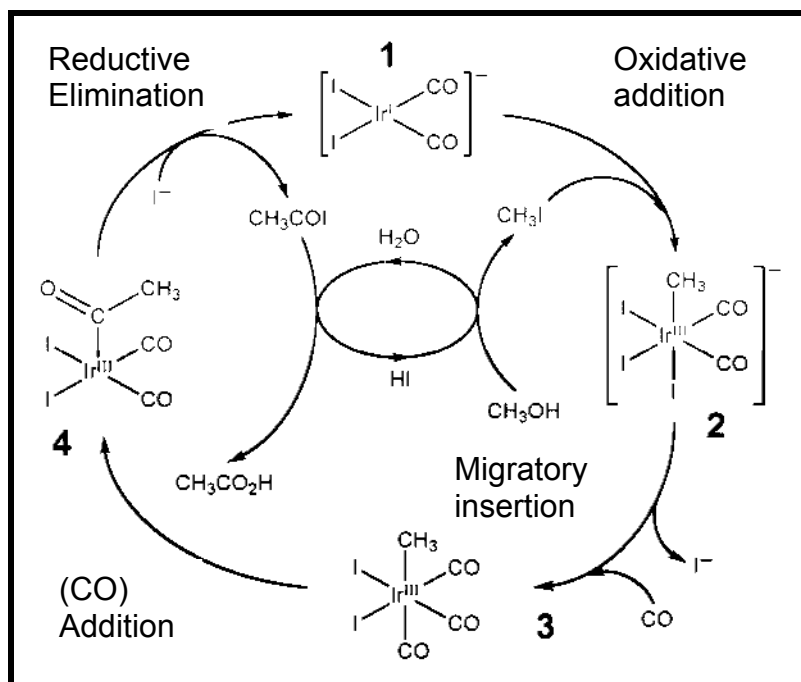
<sup>77</sup> C.R.M. Rao and G.S. Reddi, *Trends in analytical chemistry*, **(2000)**, 19, p. 9.



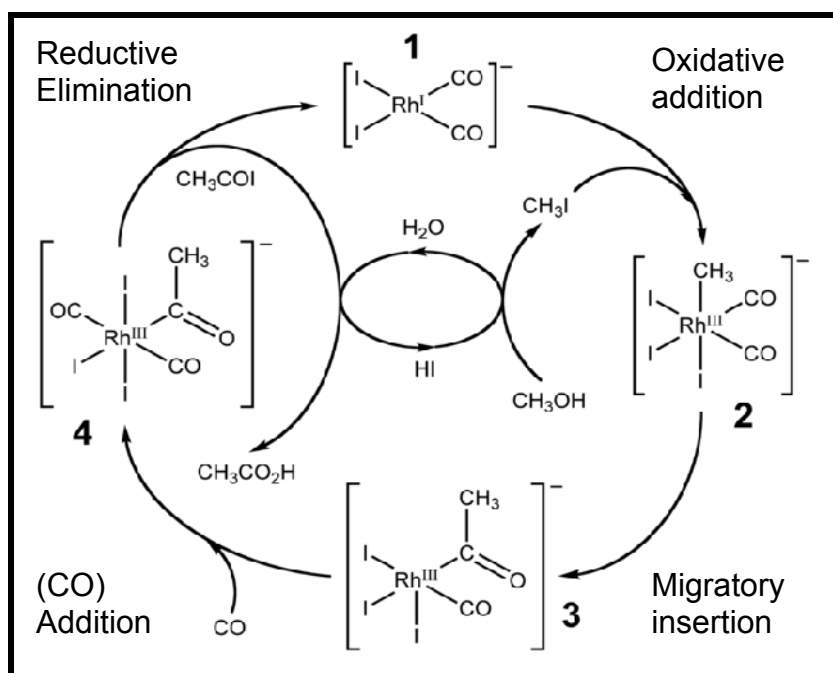
**Figure 2.17:** A section through a catalytic converter<sup>78</sup>

In the chemical industry, iridium and rhodium have been widely used in the Cativa and Monsanto processes respectively as catalysts in the manufacture of acetic acid from methanol (**Figure 2.18** and **2.19** respectively). In these two processes, methanol is converted to acetic acid *via* a four step pathway catalysed by the active metal *cis*-[M(CO)<sub>2</sub>I<sub>2</sub>]<sup>−</sup> anion (M = Rh/Ir). The first step is the oxidative addition of methyl iodide to *cis*-[M(CO)<sub>2</sub>I<sub>2</sub>]<sup>−</sup> to form the hexacoordinate M(III) species [(CH<sub>3</sub>)M(CO)<sub>2</sub>I<sub>3</sub>]<sup>−</sup>. This anion rapidly transforms, *via* the migration of a methyl group to the carbonyl ligand, affording the pentacoordinate acetyl M(III) complex [(CH<sub>3</sub>CO)Rh(CO)I<sub>3</sub>]<sup>−</sup> and [(CH<sub>3</sub>CO)Ir(CO)I<sub>3</sub>]. The five-coordinate complex then reacts with carbon monoxide to form a six coordinate dicarbonyl complex which decomposes by reductive elimination to form acetyl iodide compound (CH<sub>3</sub>COI) and also regenerate the active form of the M(I) catalyst. Acetyl iodide is then hydrolyzed to acetic acid in the last phase of the process.

<sup>78</sup> <http://www.precisionautosales.com/exhaust.php> (accessed on the 19/02/2013).



**Figure 2.18:** Use of iridium in the Cativa process

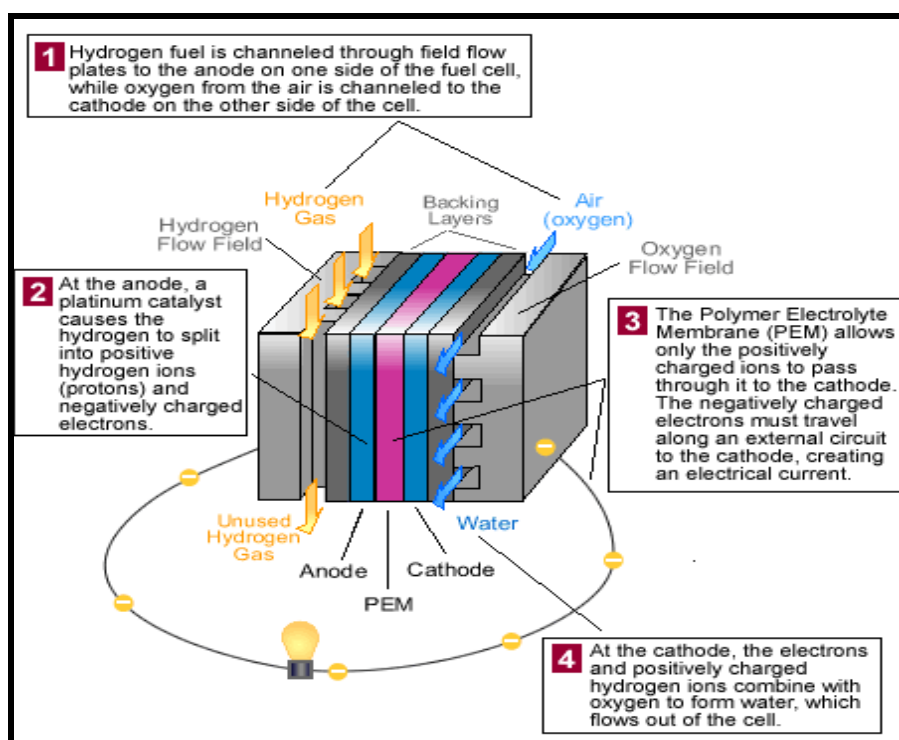


**Figure 2.19:** Use of rhodium in the Monsanto process

In the electrical sector, platinum has been used in the manufacture of fuel cells (**Figure 2:20**). By definition a fuel cell is an electrochemical mechanism that combines hydrogen and oxygen to produce heat, electricity and water. The electrodes used in this new pollution free technology are platinum-coated and this technology is expected to be a major player in the automobile field and hence will



boost platinum demand in the years to come.<sup>79</sup> The use of hydrogen fuel cells using platinum catalysts have so far been applied in South Africa at Anglo Platinum mine at a small scale as means of producing alternative clean, efficient, versatile, reliable and cost-effective source of electricity. This technology was also approved at the Conference of the Parties (COP 17) in Durban 2011 during which platinum based hydrogen fuel cells plant (150 kilowatts) was launched at the Greyville Racecourse by the Anglo American Platinum limited company. This kind of fuel cells were described to offer a clean source of energy with zero-emission electricity and also had a potential of easing the unemployment rate in South Africa through the mining of platinum which is a major component in the system.<sup>80</sup> In this respect, South Africa has taken the initiative in funding relevant research into the design of fuel cells as part of its strategy to curb electricity shortages for the country's domestic consumption.



**Figure 2.20:** A section through a platinum-coated fuel cell.<sup>81</sup>

---

<sup>79</sup> C.R.M. Rao and G.S. Reddi, *Trends in analytical chemistry*, (2000), 19, p. 9.

<sup>80</sup> M. Creamer, *Mining Weekly's print magazine*, 16th December (2011).

<sup>81</sup> <http://www.eetimes.com/electronics-news/4205844/Fuel-cell-breakthrough-aims-at-commercialization> (accessed on the 19/02/2013).

In the medical and biomedical sectors, platinum complexes e.g. the *cis*-diamminedichloridoplatinum(II), or cisplatin has widely been used (in half of all chemotherapeutic schemes) as an anticancer drug against a wide range of tumours that includes ovarian, testicular, lung and bladder cancers, as well as lymphomas, myelomas and melanoma. Although this platinum drug is effective against a handful of tumourigenic diseases, its continued use is greatly limited by severe dose limiting side effects and intrinsic or acquired drug resistance.<sup>82</sup> Some compounds based on ruthenium have lately been developed and tested against cancer cells and have shown to have less side effects compared to the platinum drugs. Sun, *et al.*<sup>83</sup> reported on the developments of new ruthenium(II), ruthenium(III) and ruthenium(IV) complexes alongside with gold as anticancer and anti-HIV agents. Iridium-192 has also been applied in radiotherapy as a source of gamma radiation for the treatment of cancer using brachytherapy (a form of radiation source which is placed inside or next to the area requiring treatment).

PGM also have aesthetic qualities and permanent luster and for this reason they are often used in the manufacture of jewellery and for decorative purposes. A wide range of PGM alloy compositions are currently used in electronic applications such as low voltage and low-energy contacts, thermocouples, furnace components and electrodes owing to their corrosion-resistant nature. Osmium being the hardest and having the highest melting point amongst the PGM, is difficult to work with and has to date limited applications in the industrial sectors. A summary of the consumption of PGM in the year 2012 is shown in **Table 2.6**.

---

<sup>82</sup> N.J. Wheate, S. Walker, G.E. Craig and R. Oun, *Dalton Trans.*, (2010), 39, pp. 8113 - 8127.

<sup>83</sup> R.W.Y. Sun, D.L. Ma, E.L.M. Wong and C.M. Chen, *Dalton Trans.*, (2007), 43, p. 4884.

**Table 2.6:** PGM consumption (in million troy ounces) in different sectors in the year 2012<sup>84</sup>

Use	Pt	Pd	Rh	Ru	Ir
<b>Auto-catalysts</b>	3.125	5.450	0.724	-	-
<b>Chemical</b>	0.445	0.395	0.068	0.100	0.018
<b>Dental</b>	-	0.580	-	-	-
<b>Electrical</b>	0.220	1.410	0.004	0.754	0.194
<b>Glass</b>	0.345	-	0.057	-	-
<b>Investment</b>	0.650	1.085	-	-	-
<b>Jewellery</b>	2.415	0.620	-	-	-
<b>Medical and Biomedical</b>	0.255	-	-	-	-
<b>Petroleum</b>	0.170	-	-	-	-
<b>Electrochemical</b>	-	-	-	0.132	0.082
<b>Other</b>	0.255	0.085	0.020	0.043	0.040
<b>Total Gross Demand</b>	7.880	9.625	0.873	1.029	0.334

Data in million troy ounce (oz t = 31.103 g)

## 2.7 Conclusion

It can be concluded that since the discovery of the precious metals their unique properties such as their outstanding appearances, catalytic properties, corrosion resistance only to name a few, has been the center of interest across the world. These metals have been shown to be in great demand in almost every sector (industrial, pharmaceutical, jewellery, petroleum, etc.). The growth in demand as witnessed over the past few years has even triggered price increases on the market which prompted the industry in reacting to these high prices to initiate the development of new techniques and methods to recover the precious metals. Since the main sources of precious metals are currently obtained from mineral ore processing, recycling of these metals from the used catalyst, inorganic and organometallic compounds can possibly contribute to the easing of demand and prices of the PGM and gold on the international market.

---

<sup>84</sup> Platinum group metals, Polinares Consortium, (2012), pp. 1 - 16.

# 3 Literature review

---

## 3.1 Introduction

The extraordinary properties of platinum, such as its high melting point and resistance to chemical manipulations, aroused the interest of the European scientists soon after its discovery in the 17<sup>th</sup> century. In the 18<sup>th</sup> century platinum was regarded as a tough chemical challenge to the European scientific establishment who tried to understand and characterize its chemistry as it was so different from the other metals they were familiar with. The challenges they encounter was the very properties which make platinum so ideally suitable for many applications, such as its high melting point and its great resistance to corrosion. During this period, platinum was mainly used for decoration purposes due to its shiny properties, the coating of porcelain as well as the making of laboratory ware and ornaments. Platinum ornaments were used as a symbol of wealth and for trading due to its novelty in appearance to prospective customers as it was commonly called white gold (see **Chapter 2, Section 2.1.1**). The economic differences that existed between this perceived 'white gold' and the real gold prompted the search methods for separation, extraction and quantification of all the precious metals to determine their market values. Most of the developed techniques and methods were centered around the determination of the precious metals based on spectrophotometric, chromatographic, gravimetric and titrimetric techniques as shown in **Table 3.1**. These techniques were very helpful at that stage, but due to the limited knowledge of the precious metals chemistry, researchers were unable to establish reliable methods for the accurate determination of these metals.

**Table 3.1:** Previously used analytical techniques for the determination of precious metals

Technique	Concentration range				
	Sub - ppb	ppb	ppm	0.1 %	Above 0.1 %
<b>Spectrophotometry</b>	-	-	yes	yes	yes
<b>Chromatography</b>	-	-	yes	yes	yes
<b>Gravimetric and titrimetric methods</b>	-	-	-	yes	yes

In order to develop new methods for the accurate determination of the precious metals, it is crucial that sufficient information of the old and current techniques be studied in order to recognize the possible opportunities for improvement. In this chapter, a general overview of the previous research that has been done on the quantification and determination of PGM and gold in different samples will be discussed. The selection of an analytical technique(s) for both the quantification and dissolution of the precious metals will also be discussed in more detail.

## 3.2 A preview of the methods used for the determination of precious metals

### 3.2.1 Spectrophotometric techniques

UV-vis spectrophotometry was historically the first instrumental technique used for the quantification of small amounts (< ppm) of precious metals in various geological and environmental materials. This technique was supposedly adopted from the visibly distinguished colours for the different platinum group elements which were observed during the discovery of these metals.<sup>85</sup> Since then, many organic reagents were synthesized and used in the spectrophotometric determination of precious metals. These include chromogenic reagents such as N,N-dimethyl-p-nitrosoaniline,<sup>86</sup> p-nitrosodiphenylamine,<sup>87</sup> dimethylglyoxime, thiourea,<sup>88</sup> 7-amino-1-

<sup>85</sup> L.B. Hunt, *Platinum Metals Review.*, (1987), 31, pp. 32 - 41.

<sup>86</sup>F.E. Beamish and W.A.E. McBryde, *Analytical chemistry of Platinum Metals*, Pergamon Press, London (1966).

<sup>87</sup> J.H. Yoe and L.G. Overholser, *J. Am. Chem. Soc.*, (1939), 61, p. 2058.

naphthol-3,6-disulfonic acid,<sup>89</sup> leucocrystal violet,<sup>90</sup> *p*-nitrosodimethylaniline,<sup>91</sup> 1-(2-pyridylazo)-2-naphthol,<sup>92</sup> etc. Studies done by Boltz and Mellon<sup>93</sup> showed that the spectrophotometric determinations of precious metals such as iridium using various complexing reagents, were affected by the presence of different transition metals and even in the presence of other PGM as shown in **Table 3.2**.

**Table 3.2:** Effects of transition metals and PGM in the determination of iridium (3.86 ppm)<sup>94</sup>

Added metal ion (0.4 ppm)	Iridium found (ppm)	Error (%)
<b>Ni(II)</b> as NiCl <sub>2</sub>	3.92	+1.6
<b>Co(II)</b> as CoCl <sub>3</sub>	4.03	+4.2
<b>Fe(II)</b> as Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>	3.77	-2.3
<b>Pt(IV)</b> as PtCl <sub>4</sub>	3.92	+1.6
<b>Os(III)</b> as OsCl <sub>3</sub>	4.07	+5.4
<b>Rh(III)</b> as Rh(NO <sub>3</sub> ) <sub>3</sub>	4.27	+11
<b>Ru(III)</b> as RuCl <sub>3</sub>	4.69	+21

In 1974, Boltz and Mellon reported<sup>9</sup> that the direct application of UV-vis spectrophotometry on PGM and gold determination was limited due to the chemical similarity of these metals. They concluded that separation of the precious metals prior to quantification is highly recommended to prevent the spectral interference by the respective elements and also to improve the selectivity and accuracy during the chemical analysis as shown in **Table 3.3**.

<sup>88</sup> S. Kalyanaraman and S.M. Khopkar, *Anal. Chim. Acta.*, (1975), 78, p. 231.

<sup>89</sup> B.V. Agarwala and A.K. Ghose, *Talanta.*, (1973), 20, p. 129.

<sup>90</sup> G.H. Ayres and W.T. Bolleter, *Anal. Chem.*, (1957), 29, p. 72.

<sup>91</sup> R.B. Wilson and W.D. Jacobs, *Anal. Chem.*, (1961), 33, p. 1654.

<sup>92</sup> A.I. Busev, V.M. Ivanov, N.N. Gorbunova and V.G. Cresl, *Tr. Kom. Anal. Khim., Akad. Nauk. SSSR.*, (1969), 17, p. 360.

<sup>93</sup> D.F. Boltz and M.G. Mellon, *Anal. Chem.*, (1974), 46, p. 233R; (1972), 44, p. 330R; (1970), 42, p. 152R; (1968), 40, p. 255R; (1966), 38, p. 317R; (1964), 36, p. 256R; (1962), 34, p. 232R.

<sup>94</sup> D.W. Fink and W.E. Ohnesorge, *Anal. Chem.*, (1969), 41, p. 39.

**Table 3.3:** Separation of precious metals prior to analysis

Sample mixture	Reagents	Remarks
<b>Rh, Au, Ir, Pd and Pt</b>	Pd: $\alpha$ - furildioxime <sup>95</sup>	Pd: extraction in $\text{CHCl}_3$
	Au: rhodamine B	Au: extraction in isopropanol
	Pt: rubeanic acid	Pt: extraction in $\text{Bu}_3\text{PO}_4$
	Rh: $\text{SnCl}_2$	Rh: extraction in $\text{Bu}_3\text{PO}_4$
<b>Rh, Os and Pd</b>	Thiotropolone <sup>96</sup>	Pd: extracted in cold water
		Rh and Os: heated and separated in a boiling water bath

Improvements in technology over the years have shown that in spite of selectivity problems, promising ligands such as 5-(2-pyridylazo)-*p*-cresol,<sup>97</sup> rhodamine 6G,<sup>98</sup> diphenylcarbazide<sup>99</sup> and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP)<sup>100</sup> had been developed in order to circumvent this problem. Regardless of the tremendous efforts in developing these ligands, which have led to improved recoveries and accuracy, other factors such as time, pH and temperature were also found to affect the selectivity and also the sensitivity of these UV-vis techniques. Research indicates that methods which used these ligands required sufficient time for the full colour development<sup>101</sup> and conditions such as pH and temperature which enhance this development. These setbacks have led to renewed interest in the accurate determination of precious metals. A number of researchers have investigated these limitations to try and establish the best experimental conditions necessary for PGM and gold quantification in the presence of these synthesized ligands.

Makino *et al.*<sup>102</sup> synthesized one of the most selective bidentate ligands towards PGM determination, 2-(5-bromo-2-pyridylazo)-5-(N-propyl-N-

<sup>95</sup> K. Brajter, U. Kozicka, *Chem. Anal.*, (1981), 26, p. 989.

<sup>96</sup> J.L. Sharma, B.S. Garg, J.N. Srivastava, R.P. Singh, *J. Indian Chem. Soc.*, (1977), 54, p. 407.

<sup>97</sup> G.G. Goroshko, Y.M. Dedkov and A.N. Errnakov, *Zh. Anal. Khim.*, (1978), 33, p. 1114.

<sup>98</sup> K. Kalinowski and Z. Marczenko, *Mikrochim. Acta.*, (1985), 1, p. 167.

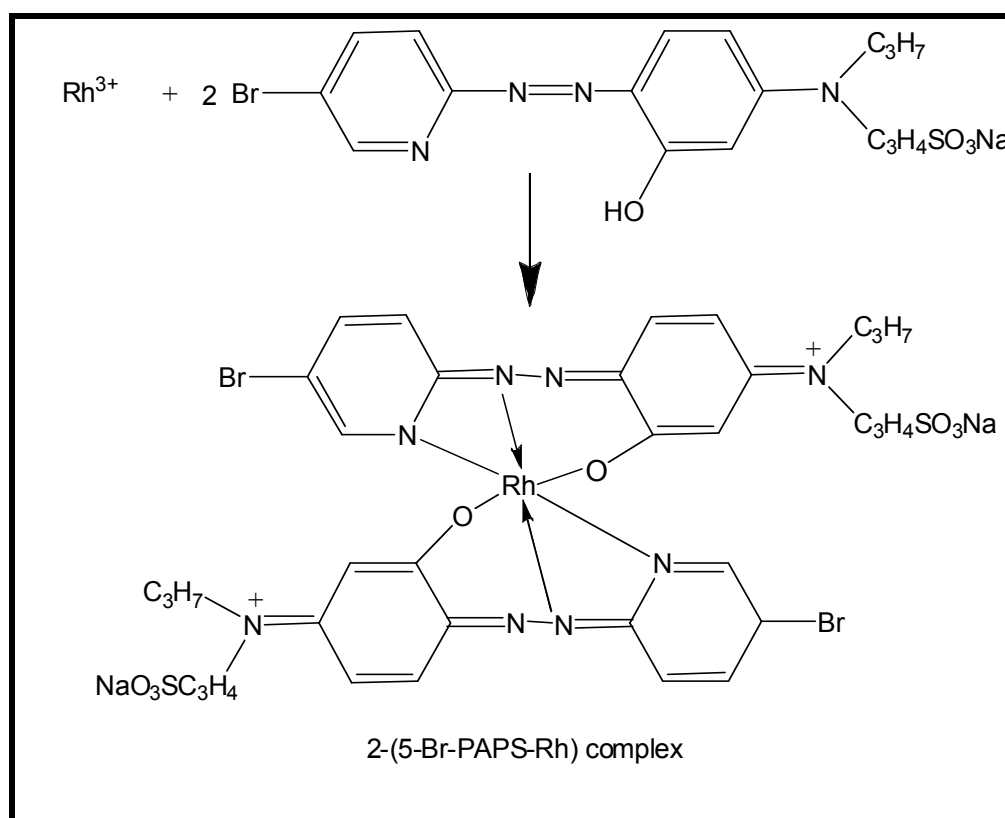
<sup>99</sup> K. Sarmah and H.K. Das, *J. Indian Chem. Soc.*, (1985), 62, p. 631.

<sup>100</sup> J.P. Pancras and B.K. Puri, *Analytical Sciences.*, (1999), 15, pp. 575 - 580.

<sup>101</sup> J.C. Sternberg, H.S. Stillo and R.H. Schwendeman. *Anal. Chem.*, (1960), 32, p. 84.

<sup>102</sup> T. Makino, M. Saito, D. Horiguchi and K. Kina, *Clin.Chim. Acta.*, (1982), 120, p.127.

sulphopropylamino)phenol (5-Br-PAPS) towards PGM determination. This ligand was found to react selectively with rhodium(III) in the ratio 1:2 (metal:ligand) (**Figure 3.1**) at 95 °C to form a water-soluble complex which had a molar absorptivity of  $1.09 \times 10^5 \text{ mol}^{-1} \text{ cm}^{-1}$  at 600 nm. Their research results showed that the rhodium(III)-5-Br-PAPS complex formation was specific under the above conditions and this product was stabilized by the addition of a masking agent such as ethylenediaminetetraacetic acid (EDTA). The 5-Br-PAPS chelating agent has since attracted the attention of many researchers<sup>103,104,105,106</sup> and a number of derivatives (**Figure 3.2**) has been developed over the years which are currently being used in the selective determination PGM and gold.



**Figure 3.1:** Complexation of Rh(III) with 5-Br-PAPS

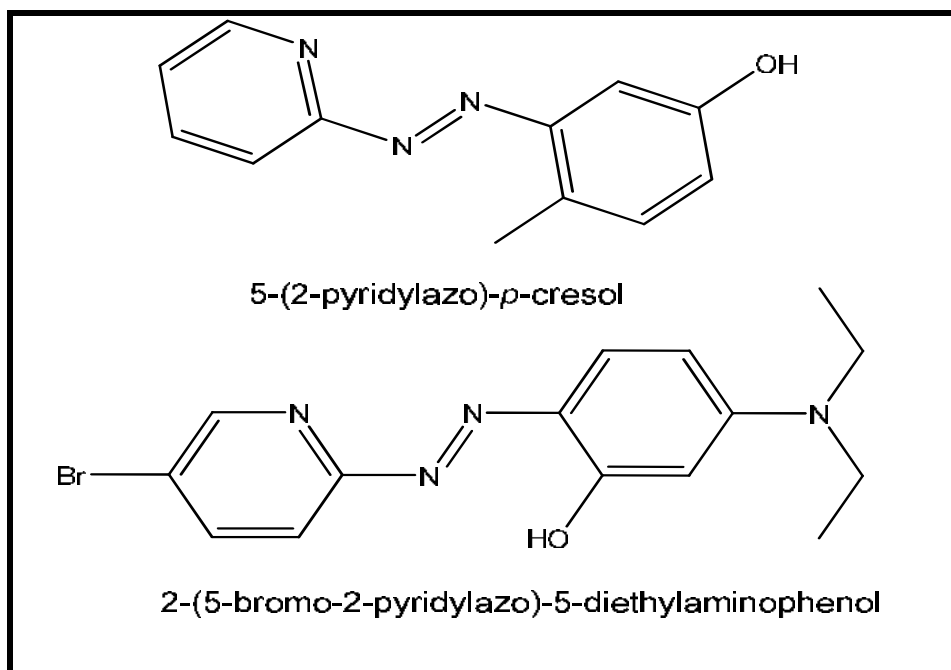
<sup>103</sup> Y. Shijo, K. Nakaji and T. Shimizu, *Analyst*, (**1988**), 113, pp. 519 - 521.

<sup>104</sup> X. Zhang, H. Yang and G. Liu, *Anal. Lett.*, (**2001**), 34, p. 2159.

<sup>105</sup> B. Wang, S. Ruan, S. Qin and M. Zhang, *Ziran Kexueban*, (**2001**), 24, p. 286.

<sup>106</sup> C.B. Ojeda and F.S. Rojas, *Talanta.*, (**2005**), 67, pp. 1 - 19.





**Figure 3.2:** Different 5-Br-PAPS derivatives used for the selective determination of PGM and gold

### 3.2.2 Chromatographic techniques

Chromatographic techniques such as cation exchange have also been used in the separation and isolation of precious metals. Studies done by Jarvis *et al.*<sup>107</sup> showed that the application of cation exchange chromatography to precious metals was limited due to the chemical similarity of these metals as well as the interference caused by other interfering metal ions. Their approach was to try to eliminate all possible interferences by separating the PGM and gold initially from other interfering metal ions followed by the quantification of the isolated precious metals. The biggest disadvantage of this approach was the difficulty in obtaining a quantitative elution from the resin column which could be measured by either spectrophotometric or titrimetric techniques. Jarvis *et al.* and Sen Gupta<sup>108</sup> demonstrated the feasibility of using the strongly acidic cation-exchange resin Dowex 50 or its higher purity equivalent (AG-50) for the separation of the precious metals from geological materials using matrix absorption. Their results using an AG-50 resin were generally satisfactory, (**Table 3.4**) but the total recovery was still not acceptable.

<sup>107</sup> I. Jarvis, M.M. Totland and K.E. Jarvis, *Chemical Geology.*, (1997), 143, pp. 27 - 42.

<sup>108</sup> J.G. Sen Gupta, *Talanta.*, (1989), 36, pp. 651 - 656.

**Table 3.4:** Percentage recoveries of PGM and gold after elution by HCl from an AG 50W-X8 column<sup>24</sup>

Element	Average recoveries (%)
Ru	93 ± 3
Rh	97 ± 3
Pd	98 ± 2
Ir	94 ± 4
Pt	96 ± 1
Au	91 ± 1

### 3.2.3 Gravimetric and titrimetric techniques

Gravimetric and titrimetric methods were initially amongst the preferred methods used in the determination of precious metals because of its high precision and reproducibility of the PGM and gold recoveries. However, the biggest drawback of these techniques was that they are time consuming, labour intensive and involves a number of stages such as sample digestion, separation, pre-concentration, *etc.* during the precious metals determination. Previous studies in gravimetric and titrimetric methods of precious metals have showed that these techniques were mostly used in cases when other techniques and methods did not give the desired precision.<sup>109,110,111</sup> The determination of PGM and gold using gravimetric and titrimetric methods have been used mostly on samples with PGM and gold concentration levels of 0.1 % or higher due to its poor detection limits. Recent studies by Singh<sup>112</sup> showed that the determination of gold by gravimetric analysis was improved by the addition of reducing agents such as oxalic acid, hydroquinone, sulphur dioxide, ferrous sulphate, 2,4,6-triphenylpyrylium chloride and sodium borohydride. These reducing agents were shown to promote the maximum

<sup>109</sup> Y.A. Zolotov, G.M. Varshal and V.M. Ivanov, *Analytical Chemistry of Platinum Group Metals*, URSS: Moscow., (2003).

<sup>110</sup> S.I. Ginzburg, N.A. Ezerskaya and I.V. Prokof'eva, *Analytical Chemistry of Platinum Metals*, Moscow: Nauka., (1972).

<sup>111</sup> F.F. Beamish, *The Analytical Chemistry of Noble Metals*, Oxford: Pergamon, (1966).

<sup>112</sup> N. Singh, *SpringerPlus.*, (2012), 1, p. 14.

precipitation of gold to yield satisfactory recoveries of between 85 - 95 %, depending on the type of the reducing agent used. According to El-Shahawi and Farag,<sup>113</sup> the main source of error in gravimetric determination of PGM and gold was mostly caused by losses occurring during the precipitation, purification and drying of the formed residues. A summary of the advantages and disadvantages of these and spectrophotometric methods previously used in the determination of precious metals are tabulated in **Table 3.5**.

**Table 3.5:** Assessment of the previously used analytical techniques in the determination of precious metals

Techniques	Advantages	Disadvantages
<b>Spectrometric analysis</b>	Accuracy, Reproducibility, Wide concentration range, Availability, Simplicity and Rapidly	Narrow pH range, Interference by many metal ions, Instability of complex, Low molar absorptivity and photosensitivity, high operational and maintenance cost
<b>Gravimetric and titrimetric analysis</b>	Efficiency, Accuracy, Reproducibility and Stability	Labour intense and a Great summary error of analysis

### 3.2.4 Spectrometric techniques

In the late 1990's scientific and technological progress gathered momentum and numerous analytical techniques for the determination of PGM and gold were developed. In the 20<sup>th</sup> century traditional labour intensive techniques were replaced by the development of numerous automated techniques such as the inductive coupled plasma (ICP) with both the optical emission (ICP-OES)<sup>114,115,116</sup> and mass

---

<sup>113</sup> M.S. El-Shahawi and A.B. Farag, *Analytica chimica Acta.*, (1995), 307, pp. 139 - 144.

<sup>114</sup> R.A. Conte, J.M. Mermet, J.D.A. Rodrigues and J.L. Martino, *J. Anal. Atomic Spectrometry.*, (1997), 12, pp. 1215 - 1220.

<sup>115</sup> O.N. Grebneva, I.V. Kubrakova, T.F. Kudinova and N.M. Kuz'min, *Spectrochimica Acta Part B.*, (1997), 52, pp. 1151 - 1159.

spectrometry (ICP-MS),<sup>117,118</sup> atomic absorption spectrometry (AAS)<sup>119,120,121</sup> and X-ray fluorescence (XRF).<sup>122,123</sup> These techniques have been found to be much faster, efficient and reliable than the previously used techniques and had low detection limits in ppm - sub-ppb range (**Table 3.6**).

**Table 3.6:** Spectrometric techniques for the determination of PGM and gold

Technique	Concentration range				
	Sub - ppb	ppb	ppm	0.1 %	Above 0.1 %
<b>F-AAS</b>	-	-	yes	yes	yes
<b>ET-AAS</b>	yes	yes	-	-	-
<b>ICP-OES</b>	-	-	yes	yes	-
<b>ICP-MS</b>	yes	yes	yes	-	-
<b>XRF</b>	-	-	yes	yes	yes

Since the commercial introduction of ICP in the late 1970's, this technique has increasingly attracted the interest of analytical chemists and has since been widely used for routine elemental analysis. The popularity of the ICP technique has been largely attributed to its excellent analytical characteristics such as high precision, long-term stability, high selectivity and sensitivity as well as low detection limits and large linear dynamic range ( $10^5$ - $10^6$  orders of magnitude). Wendt and Fassel<sup>124</sup> and

<sup>116</sup> R. K. Winge, V. A. Fassel, V.J. Peterson and M.A. Floyd, *Inductively Coupled Plasma Atomic Emission Spectroscopy. An Atlas of Spectral Information*, Elsevier, Amsterdam., (1993).

<sup>117</sup> C. Qing, T. Shibata, K. Shinotsuka, M. Yoshikawa and Y. Tatsumi, *Frontier research on earth evolution*, (2003), 1, pp. 357 - 362.

<sup>118</sup> L. Bencs, K. Ravindra and R. Van Grieken, *Spectrochim. Acta B.*, (2003), 58, p. 1723.

<sup>119</sup> J.M. Scarborough, *Anal. Chem.*, (1969), 41, p. 250.

<sup>120</sup> R.C. Mallett, D.C.G. Pearton, E.J. King and T.W. Steele, *J. S. Afr. Anal. Chem.*, (1976), 48, pp. 142 - 174.

<sup>121</sup> K.W. Jackson and S. Lu, *Anal. Chem.*, (1998), 70, pp. 363 - 367.

<sup>122</sup> V. John, I.C. Gilfrich, T.C. Noyan, D.K. Huang, K. Smith, *Advances in X-Ray Analysis.*, (1995), 39, p. 137.

<sup>123</sup> R. Jenkins, *X-Ray Fluorescence Spectrometry.*, (1988), pp. 465 - 487.

<sup>124</sup> R.H. Wendt and V.A. Fassel, *Anal. Chem.*, (1965), 37, p. 920.

Greenfield *et al.*<sup>125</sup> were among the first researchers to highlight the advantages of the uses of ICP for analytical purposes as fast and effective in the determination of trace elements. In recent years, the use of ICP as an analytical technique has increasingly been used as the method of choice for the qualitative and quantitative determination of major (above 0.1 %), minor (ppm - 0.1 %) and trace (ppm - sub ppb) metals including precious metals.<sup>126</sup>

Despite the improvement in techniques used for the determination of PGM and gold, accurate determination of these metals still remains a difficult task due to spectral and chemical interferences, instrumental drifts and different matrices (acid, EIE's matrix) (see **Chapter 4**). Thompson and Ramsey<sup>127</sup> discovered that EIE's and acid matrix had an effect of suppressing or enhancing the intensities of the ICP-OES or ICP-MS emission signals thereby causing a decrease in the percentage recoveries. Their discovery was shown to be consistent with the results we obtained in our previous study<sup>128</sup> for the determination of rhodium in the inorganic salt ( $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ). In this study different increments of EIE's (Na, K and Rb) and acid ( $\text{HNO}_3$ , HCl and HBr) concentrations were added to the  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  samples and determined for the rhodium content as shown in **Figure 3.3** and **3.4** respectively. Results obtained revealed that the percentage recoveries of rhodium in these matrix samples decreased with the increase in EIE's and acid concentrations. The decrease in the percentage of rhodium recovery from these samples was attributed to the suppression of the ICP-OES rhodium emission intensities and also an increase in the relative standard deviation (RSD).

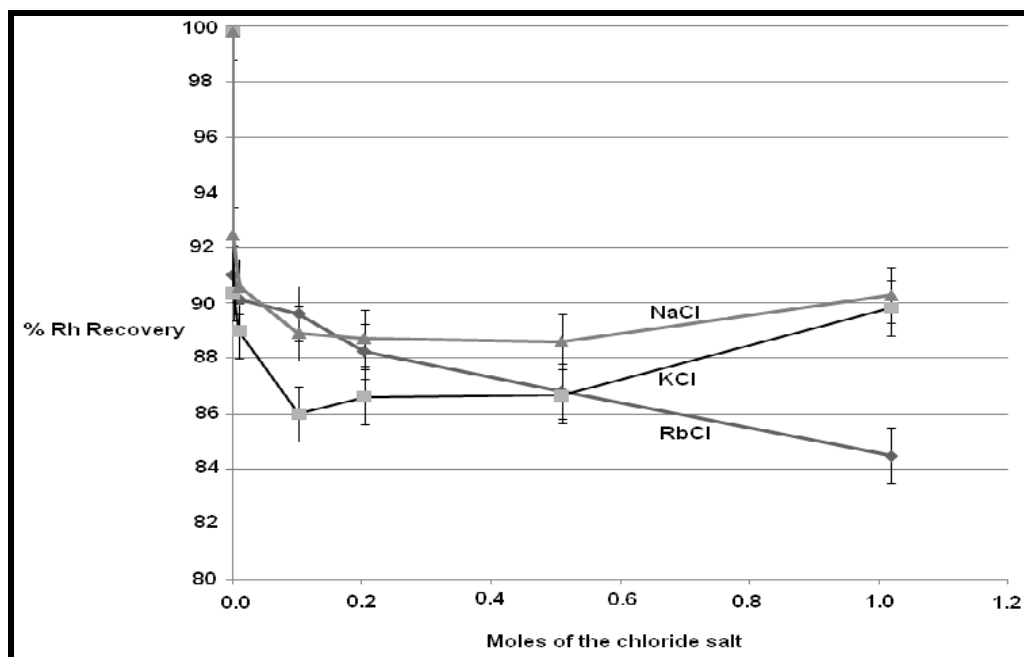
---

<sup>125</sup> S. Greenfield, I.L. Jones and C.T. Berry, *Analyst.*, (1964), 89, p. 713.

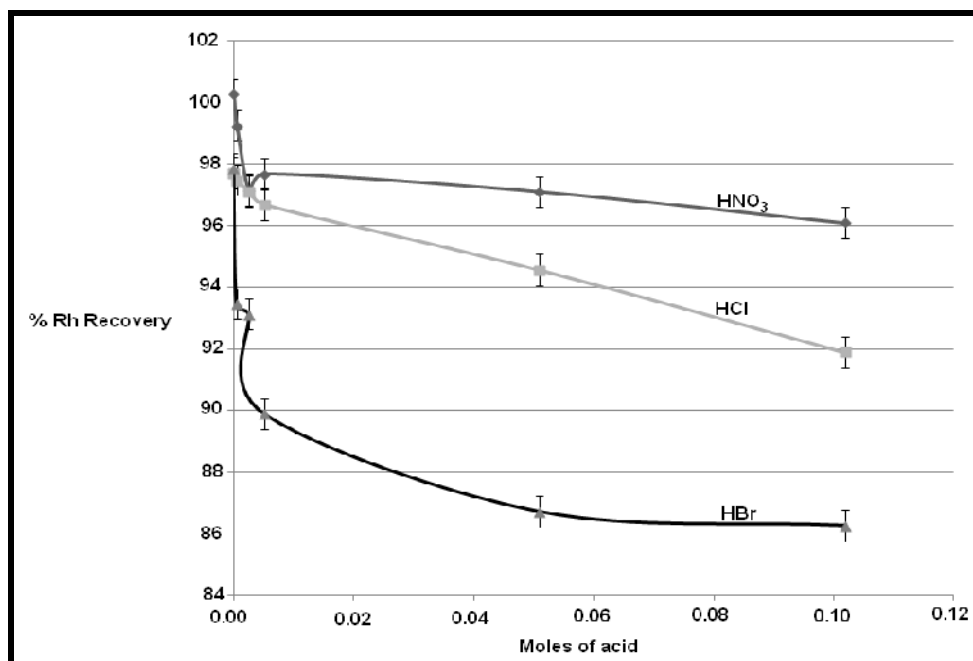
<sup>126</sup> J. Todolí, S. Maestre, J. Mora, A. Canals and V. Hernandis, *Fresenius. J. Anal Chem.*, (2000), 368, pp. 773 - 779.

<sup>127</sup> M. Thompson and M. Ramsey, *Analyst.*, (1985), 110, p. 1413.

<sup>128</sup> T.T. Chiweshe, W. Purcell and J. Venter, *S. Afr. J. Chem.*, (2012), 66, pp. 7 - 16.



**Figure 3.3:** Effects of EIE's in rhodium recovery from  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  in different chloride salt solutions



**Figure 3.4:** Effects of acid matrix in rhodium recovery from  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  in different acidified solutions

Different spectrometric methods have been developed in the past few years in an attempt to reduce or correct for these numerous matrix effects in spectrometric analysis. Common methods used in spectrometric techniques for correcting matrices

are usually empirical and these methods includes interactive matrix matching, matrix stripping, standard addition method, mathematical correction by curve fitting to an empirical function, matrix swamping, excitation buffering techniques and finally the use of internal standard addition. Recent studies done by Z. Li and Y. Feng<sup>129</sup> in determining PGM in geological samples by ICP-MS showed that good percentage recoveries (**Table 3.7**) of these metals were obtained when acid matrices were matched and determined under robust conditions. The success of this method was attributed to the use of robust conditions, matrix matching and the application of mathematical models in correcting for the numerous matrix effects.

**Table 3.7:** Recoveries of PGM using ICP-MS in peridotite igneous rock<sup>44</sup>

	<b>Ru</b>	<b>Rh</b>	<b>Pd</b>	<b>Os</b>	<b>Ir</b>	<b>Pt</b>
<b>Certified values (ppb)</b>	15±3	1.3±0.3	4.6±0.6	10±2	4.3±0.5	6.4±0.9
<b>Experimental values (ppb)</b>	14.2±0.6	1.2±0.1	4.5±0.3	10.1±0.5	4.4±0.3	6.1±0.4

Among the common matrix correcting methods used, the internal standard addition method has been the most preferred method of matrix correction. This preference is due to its ability to effectively improve the precision and accuracy of results in spectrometric techniques. Its application in PGM and gold determination is not very common due to the unavailability of suitable internal standard elements, complicated precious metal chemistry in aqueous solution, undefined sample matrix, instrumental drifts and interference caused by other metal impurities. Studies to determine an ideal internal standard for precious metal determination have been investigated by several researchers and will be discussed in **Chapter 4**.<sup>130,131,132,133</sup>

---

<sup>129</sup> Z. Li and Y. Feng, *J. Anal. At. Spectrom.*, (2006), 21, pp. 90 - 93.

<sup>130</sup> X. Chen and R.S. Houk, *J. Anal. At. Spectrom.*, (1995), 10, pp. 837 - 841.

<sup>131</sup> J.J. Thompson and R.S. Houk, *Appl. Spectrosc.*, (1987), 41, pp. 801 - 806.

<sup>132</sup> C. Sartoros and E.D. Salin, *Spectrochim. Acta Part B.*, (1999), 54B, pp. 1557 - 1571.

<sup>133</sup> F. Vanhaecke, H. Vanhoe, R. Dams and C. Vandecasteele, *Talanta.*, (1992), 39, pp. 737 - 742.

### **3.2.5 Calibration methods**

Different calibration methods such as the direct calibration, internal standard addition and the standard addition are widely used in spectrometric determination of precious metals at trace levels. The internal standard and the standard addition methods are the most commonly used methods in correcting the different matrix problems and instrumental drifts and also to improve the accuracy and precision of the results. The use of a direct calibration curve in the determination of precious metals is mostly considered unreliable due to the interference by other PGM and transition metals (see **Chapter 2, Section 2.4.1**). The application of the standard addition method has also been less preferred due to large volumes of standards required during the sample preparation. Recent studies by Steharnik *et al.*<sup>134</sup> showed that satisfactory gold recoveries (90 - 115 %) were obtained from a gold alloy using the standard addition method. However, the method was shown to require prior knowledge of the gold analyte concentration prior to sample preparation in order to determine the small increments of standard solutions (spikes) of either 2x or 3x, *etc.* (where x is the standard concentration) to be added to the analyte samples.

Internal standard calibration has been the mostly preferred method of matrix correcting because of its cost effectiveness compared to the standard addition. Indium and yttrium are amongst the highly recommended internal standard elements by the International Organisation for Standards (ISO) for the determination of precious metals.<sup>135</sup> However, the major disadvantage of using indium and yttrium internal standards has been their presence in many of the geological and environmental samples. This problem has prompted more research into establishing other internal standard elements that are compatible with the simultaneous determination of precious metals. Several studies have been attempted to establish protocols for the selection of a suitable internal standard for the determination PGM

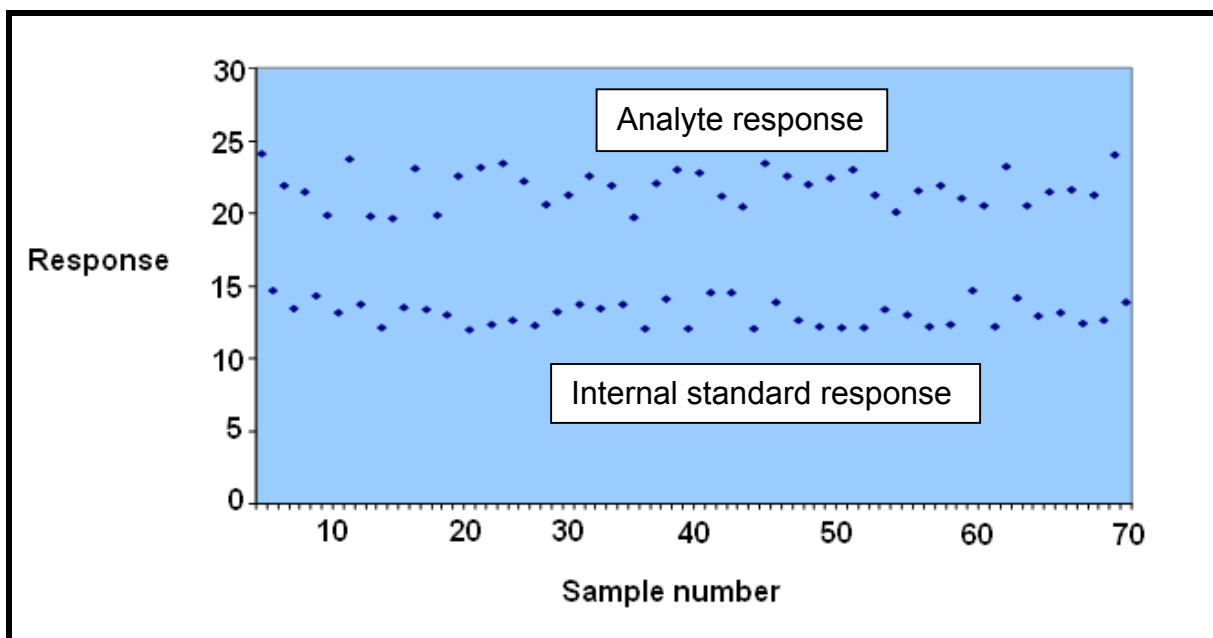
---

<sup>134</sup> M. Steharnik, M. Todorovic, D. Manojlovic, D. Stankovic, J. Mutic and V. Trujic, *J. Serb. Chem. Soc.* (**2013**), 78 (4) pp. 565 - 577.

<sup>135</sup> International Organization for Standardization, Determination of platinum in platinum jewellery alloys-method using inductively coupled plasma emission spectroscopy on a solution with yttrium as internal standard. Doc. ISO/DIS 11494.2.



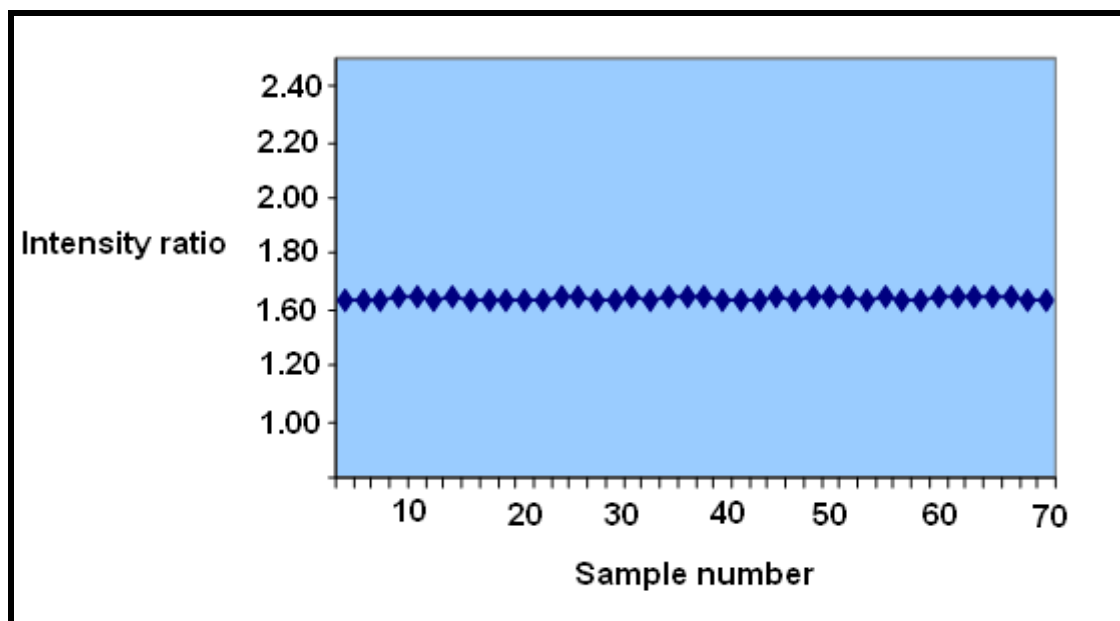
and gold. Finley-Jones *et al.*<sup>136</sup> described the behaviour patterns of an 'ideal' internal standard for any given analyte as one whose intensity changes is directly proportional to that of the analyte intensity as illustrated in **Figure 3.5**.



**Figure 3.5:** The direct proportion between the analyte and the internal standard intensities<sup>52</sup>

In a same study,<sup>136</sup> Finley-Jones *et al.* also discovered that the intensity ratios between the analyte and internal standard intensities had an advantage of correcting any imprecision caused by different matrices such as background noise, instrumental drifts, acid matrix, *etc.* They also reported that for an effective matrix correction to be achieved, the intensity ratios at constant concentration should remain constant regardless of all the changes in the sample composition and the fluctuations in the instrumental performance. Thus, a small percentage RSD was shown to represent a good analyte-internal standard pair (**Figure 3.6**).

<sup>136</sup> H.J. Finley-Jones, J.L. Molloyx and J.A. Holcombe, *J. Anal. At. Spectrom.*, (2008), 23, pp. 1214 - 1222.



**Figure 3.6:** Analyte to internal standard intensity ratio<sup>136</sup>

Thompson *et al.*<sup>137</sup> and Vanhaecke *et al.*<sup>138</sup> reported that similarities in atomic masses and the first ionization potential between the internal standard and the analyte were the major dominating factors in choosing an ideal internal standard. Their idea was further confirmed by Barnett *et al.*<sup>139</sup> who proposed a systematic procedure for choosing an ideal internal standard for a particular analyte element at a specific analytical line or wavelength ( $\lambda$ ). Their procedure was based on the comparison of the ionization energy, excitation energy and volatilization rate of the analyte element with that of the internal standard. Results obtained by Beamish *et al.*<sup>140</sup> using the same concept showed that the determination of precious metal using ICP-OES as an analytical technique and yttrium (371.02 nm) as internal standard at very specific emission lines for Au (267.6 nm), Pt (265.9 nm), Pd (340.5 nm), gave reproducible results with exceptional precision of at least 0.01 %.

<sup>137</sup> J.J. Thompson and R.S. Houk, *Appl. Spectrosc.*, (1987), 41, pp. 801 - 806.

<sup>138</sup> F. Vanhaecke, H. Vanhoe, R. Dams and C. Vandecasteele, *Talanta.*, (1992), 39, pp. 737 - 742.

<sup>139</sup> W.B. Barnett, V.A. Fassel and R.N. Kniseley, *Spectrochim. Acta, Part B.*, (1968), 23, pp. 643 - 664; *Spectrochim. Acta, Part B*, (1970), 25, pp. 139 - 161.

<sup>140</sup> F.E. Beamish, J.C. Van Loon and C.L. Lewis, '*Analysis of Noble Metals: Overview and Selected Methods*', Academic Press, New York, USA., (1977).

Mokgalaka *et al.*<sup>141</sup> also applied the same method as Barnett *et al.* and used ICP-OES to determine the precious metal content in a converter matte. In this study they used tin (Sn) however as an internal standard. The results obtained during this study were compared with that of the conventional direct calibration method as shown in **Table 3.8**. The results obtained by using an internal standard were closer to the actual values and a small percentage RSD values compared to the direct calibration method were obtained. The direct calibration method was also much easier affected by matrices compared to the internal standard addition method.

**Table 3.8:** Comparison of the results obtained using the conventional method and internal standard in the determination of precious metals<sup>56</sup>

Element line (Å/nm)	Direct calibration method (ppm)	Internal standard method (ppm)
<b>Au I (267.596)</b>	85 ± 2	109 ± 3
<b>Ir II (212.681)</b>	Results were out of the calibration range by ca. 12 %	113 ± 3
<b>Pd I (360.955)</b>	101 ± 14	100 ± 6
<b>Pt II (214.423)</b>	112 ± 24	102 ± 2
<b>Rh I (343.489)</b>	106 ± 7	100 ± 3
<b>Ru II (349.894)</b>	114 ± 13	97 ± 5

In an attempt to optimize the percentage recovery of rhodium, Romero *et al.*<sup>142</sup> and Dubuisson *et al.*<sup>143</sup> suggested the possibility of using an internal standard method under robust ICP conditions (high power of 1.0 kW and a low carrier gas flow rate of 0.61 min<sup>-1</sup> or 0.41 min<sup>-1</sup> with a 2 mm or 1.5 mm diameter injector respectively) to improve the efficiency, accuracy and precision of the results. Results obtained from this study indicated that an internal standard addition method can be used to effectively compensate for the fluctuations in the aerosol production, analyte transport into the nebulizer and sodium (EIE's) matrix using these robust conditions. Their results also showed that the effectiveness of an internal standard addition

---

<sup>141</sup> N.S. Mokgalaka, T. Wondimu and R.I. McCrindle, *J. Anal. At. Spectrom.*, (2004), 19, pp. 1493 - 1497.

<sup>142</sup> X. Romero, E. Poussel and J.M. Mermet, *Spectrochim. Acta, Part B.*, (1997), 52, pp. 487 - 493.

<sup>143</sup> C. Dubuisson, E. Poussel, J.L. Todoli, J.M. Mermet, *J. Anal. At. Spectrom.*, (1998), 13, p. 63.

method can be improved under these robust conditions with the radial viewing ICP-OES plasma. Better detection limits and sensitivity were obtained with radial viewing compared to using axial viewing plasma.

### **3.2.6 Sample preparation**

The success of the wet chemical analysis in precious metal determination depends critically upon the complete dissolution of the analyte sample. The determination of precious metals by spectrometric methods therefore requires its quantitative transformation into water soluble species which then form the basis of the analysis. The selection of the most appropriate digestion methods for precious metals remains a fundamental problem in spite of a huge amount of work done in developing accurate techniques and methods for their determination in various materials. The major challenge is the high resistance of PGM such as Ru, Os and Ir to acid attack, even with the widely used acid mixture, *aqua regia*. The incomplete digestion/dissolution of analyte samples using mineral acids generally limit the use of direct wet digestion procedures of these metals. Dissolution, separation and pre-concentration of samples are sometimes vital steps in precious metals analysis, owing to the very low concentration of these metals in many samples and the complexity of the matrix.

#### **3.2.6.1 Acid dissolution**

Acid dissolution of precious metals has been widely used during the sample preparation prior to the determination of precious metals. Tresl *et al.*<sup>144</sup> together with Nowinski and Suchanek<sup>145</sup> reported about the extensive incomplete dissolution of PGM after acid dissolution of mineral ores. Their results showed a 20 - 40 % recovery of Pt, Rh and Os and 1 - 10 % of Ir from a mineral ore. They also found 55 - 87 % of Pt recovery from the soil sample digested in *aqua regia* or by using a combination of different acid mixtures e.g. HF/HClO<sub>4</sub>. Improved average recoveries were obtained by using microwave assisted digestion in *aqua regia*. Recoveries of 46 - 55 % Pt, 61 - 78 % Au, 61 - 88 % Pd, 73 - 94 % Rh, 30 % Ru and 44 % Ir were obtained using ICP-MS. Incomplete sample dissolution and increased acid

---

<sup>144</sup> I. Tresl, O. Mestek and M. Suchanek, *Collect. Czech. Chem. Commun.* (2000), 65, p. 1875.

<sup>145</sup> P. Nowinski and V. Hodge, *At. Spectrosc.*, (1994), 15, p. 109.

concentrations (acid matrix) in the analyte solutions were found to be the main cause of the low percentage recovery of precious metals. Increasing acid concentrations was shown to cause a greater depression of the analyte emission signals during the spectrometric determination of precious metals which eventually led to the low precious metals recovery (see **Chapter 4**). From our previous study,<sup>146</sup> the use of mineral acids (HCl, *aqua regia*, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>) during the open beaker digestion of a certified reference material (CRM) ERM<sup>®</sup>-504 containing rhodium was characterised by low percentage recovery of the rhodium content using the ICP-OES. However, increased recoveries of rhodium were obtained using the direct calibration and microwave digesting method at high temperature (240 °C) and pressure (60 bar) for 3 hours. These results showed that the digestion of samples using mineral acids at higher temperatures and pressure was much more effective than the open beaker digestion method.

**Table 3.9:** Rhodium determination from a CRM after acid digestion using open beaker and microwave digestion<sup>61</sup>

Sample	Mineral acid used	% Rh recovery after open beaker digestion	% Rh recovery after microwave
CRM 1	HCl	62.30	89.39
CRM 2	<i>Aqua regia</i>	46.15	80.73
CRM 3	HNO <sub>3</sub>	33.83	44.40
CRM 4	H <sub>2</sub> SO <sub>4</sub>	23.39	31.28

#### 3.2.6.2 Fusion digestion

Sample decomposition through salt or flux fusion has also been employed in sample preparations of PGM which were difficult to dissolve in mineral acids. These samples include soils, sludges, silicates and some metal oxides containing samples. Fusion of these samples were mostly accomplished by heating an appropriate salt (flux) such as Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, Na<sub>2</sub>CO<sub>3</sub>, Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, KOH, *etc* with an appropriate amount of the analyte sample. The biggest drawback using this technique was the high amount of

<sup>146</sup> T.T. Chiweshe, *Quantification of rhodium in series of inorganic and organometallic compounds*, MSc thesis, University of the Free State, Bloemfontein, South Africa, (2010).

EIE's that was introduced as the flux in the analyte solutions. Li *et al.*<sup>147</sup> determined the effectiveness of the fusion method by digesting a CRM containing precious metals using Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> flux for 4 hours at 650 °C. A complete digestion of the CRM was accomplished but the quantitative results of the precious metals were affected to different degrees by the high concentration of sodium (EIE's) which was introduced by the flux as shown in **Figure 3.10**.

**Table 3.10:** Influence of EIE's (Na) on PGM and gold recovery from the CRM (GBW 07291)<sup>63</sup>

	<b>Ru</b>	<b>Rh</b>	<b>Pd</b>	<b>Ir</b>	<b>Pt</b>	<b>Au</b>
<b>CRM values (ppb)</b>	2.4±0.4	4.7±0.9	60±6	4.6±0.9	58±4	4.3±0.3
<b>Experimental result (ppb)</b>	3.0±0.4	4.6±0.3	62±4	5.2±0.7	51±3	5.0±0.4

### 3.2.7 Conclusion

This literature review clearly emphasize that considerable amount of work has been done by several researchers in an attempt to establish accurate methods for the determination of precious metals. History shows that the determinations of these metals have improved over the years with the introduction of much faster and reliable automated techniques. The use of calibration methods in spectrometric techniques for the accurate determination of precious metals have been widely reported to be affected by different matrices. Different methods for matrix reduction have been investigated and amongst these methods internal standard addition was shown to yield the better results. The major challenge however of using this method was shown to be the selection of an 'ideal' internal standard element compatible with all the precious metals. The knowledge regarding the best or optimal experimental conditions needed for these spectrometric techniques which are required for the accurate determination of precious metals in different samples are also still unclear. The other critical factor which was shown to cause reduced recoveries in the determination of precious metals was the dependence of the spectrometric methods

---

<sup>147</sup> C. Li, C. Chai, X. Li and X. Mao, *Journal of Geostandards and Geoanalysis.*, (1998), 22, pp. 195 - 197.

on the efficiency of the sample preparation method. Incomplete sample digestion or dissolution, acid matrix and the introduction of EIE's from the flux salts and during the sample preparation was shown to affect the percentage recovery of the precious metals. These numerous challenges and limitations were shown to be the most common difficulties associated with the determination of PGM and gold using the calibration methods.

# 4 Selection of methods for precious metals determination

---

## 4.1 Introduction

Precious metals still remains the most poorly studied group of metals despite the introduction of automated analytical techniques such as the ICP-OES/ MS, XRF, AA, etc.<sup>148</sup> The challenge is mainly due to the analytical difficulties involved in generating accurate and reliable methods for their quantitative determination. The commonly used methods (traditional methods) in spectrometric analysis (see **Chapter 3, Section 3.2.4**) have been shown to be affected by spectral interferences, acid matrix, instrumental drifts and interferences caused by EIE's. These problems were reported to affect the accurate determination of precious metals and have recently triggered a lot of research into the development of new analytical methods for their accurate determination. Errors in spectrometric analysis, such as systematic and random errors during sample preparation and measurement have also been reported to cause loss of accuracy and precision in the determination of precious metals. A comprehensive literature study to determine the appropriate techniques and methods for the accurate determination of precious metals was carried out and the results are reported in this chapter. The best technique(s) and method(s) to be used in this study was selected on the basis of the availability of the equipment, running cost, lower detection limits, accuracy, reproducibility and the method(s) ability to correct for matrix effects and instrumental drifts. Principles and guidelines relating to method validation using ISO 17025 as the bench mark, will be highlighted in order to determine whether the newly developed method is fit for its intended use.

---

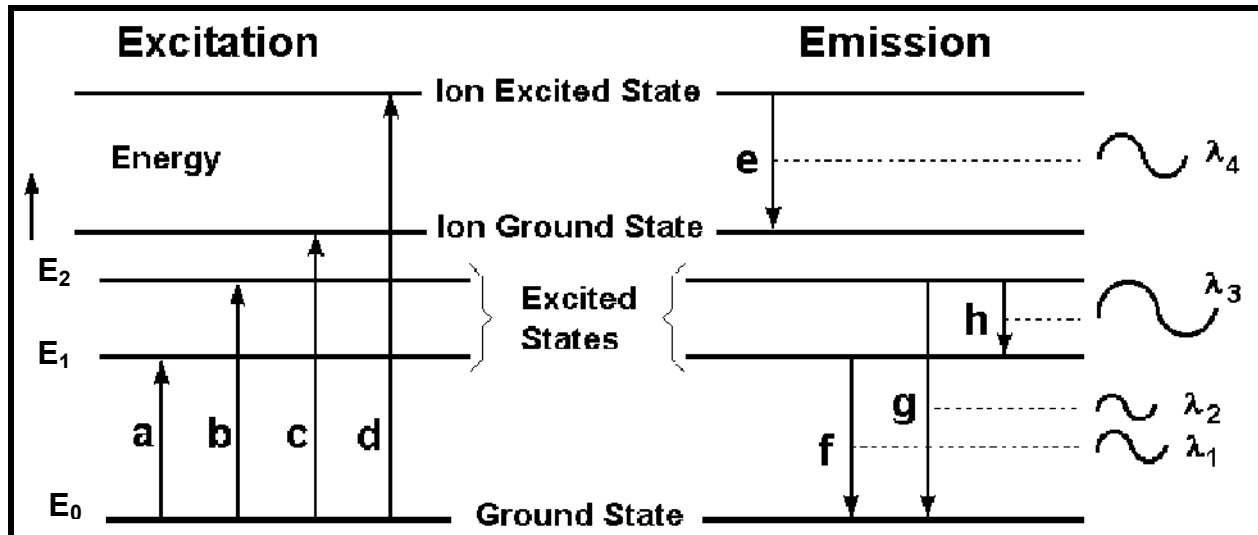
<sup>148</sup> R.R. Barefoot and J.C. Van Loon, *Talanta*, (1999), 49, pp. 1 - 14.



## 4.2 Calibration methods in spectrometric analysis

### 4.2.1 Principles of spectral origin and measurements

Spectrometric techniques such as ICP-OES/MS begins with the volatilization of the analyte sample into a fine mist/aerosol, at elevated temperatures of approximately 6 000 °C and higher. The energy absorbed by the analyte atoms excites most of the ground state ( $E_0$ ) electrons to orbitals of higher energy levels (excited state,  $E_n$ ) as shown in **Figure 4.1**. These atoms are less stable in this excited state and will therefore decay back to the ground state by losing energy through either collisions with other particles or by the emission of electromagnetic radiation, known as photons. As a result of this energy loss, the electrons return back to orbitals closer to the nucleus. An emission line ( $\lambda_n$  where  $n = 1, 2, 3...$ ) is generated as a result of this ( $E_n \rightarrow E_{n-1}$ ) transition process from an excited energy level ( $E_n$ ) to a lower energy state ( $E_{n-1}$  or  $E_0$ ).



**Figure 4.1:** Energy level diagram showing energy transitions where (a) and (b) represents excitation, (c) is ionization, (d) is ionization/excitation, (e) is ion emission (ionic line), and (f, g and h) are atom emission (atomic lines).<sup>149</sup>

<sup>149</sup> C.B. Boss and K.J. Fredeen, *Concepts of Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry.*, (2004).

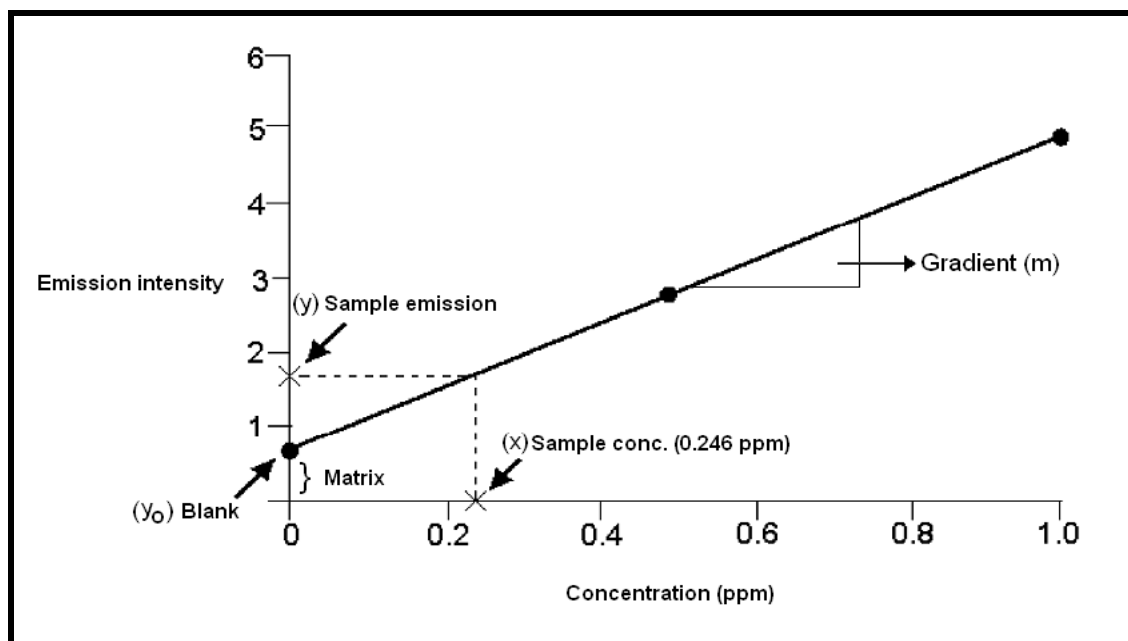
The emitted electromagnetic radiation is then used to identify (unique emission lines for all elements) and quantify (concentration is directly proportional to the emitted radiation) the concentration of the different elements present in a sample. Quantitative information is related to the amount of electromagnetic radiation that is emitted, whilst qualitative information is related to the wavelength at which the radiation was absorbed or emitted.

#### **4.2.2 Direct calibration method**

The direct calibration method is a commonly used method and is sometimes referred to as the traditional method. The direct calibration method involves the direct measurement of the analyte emission intensities or response as a function of its concentration. High-quality standards are often used in the construction of calibration plots to avoid possible matrix effects and as a means of improving accuracy and precision. A calibration plot is constructed using the least square method<sup>150</sup> and the best calibration curve has a linear regression coefficient,  $R^2$  (dimensionless) of close to a unity (1). The data points on the calibration curve are made to fit into a straight line using linear regression analysis which is described by the equation  $y = mx + y_0$ , where (y) is the instrument response, (m) is the gradient depicting the sensitivity of the method and ( $y_0$ ) is a constant that describes the background noise or the blank matrix. The analyte concentration (x) of unknown samples may either be calculated from this equation or can be extrapolated from the curve as illustrated in **Figure 4.2**.

---

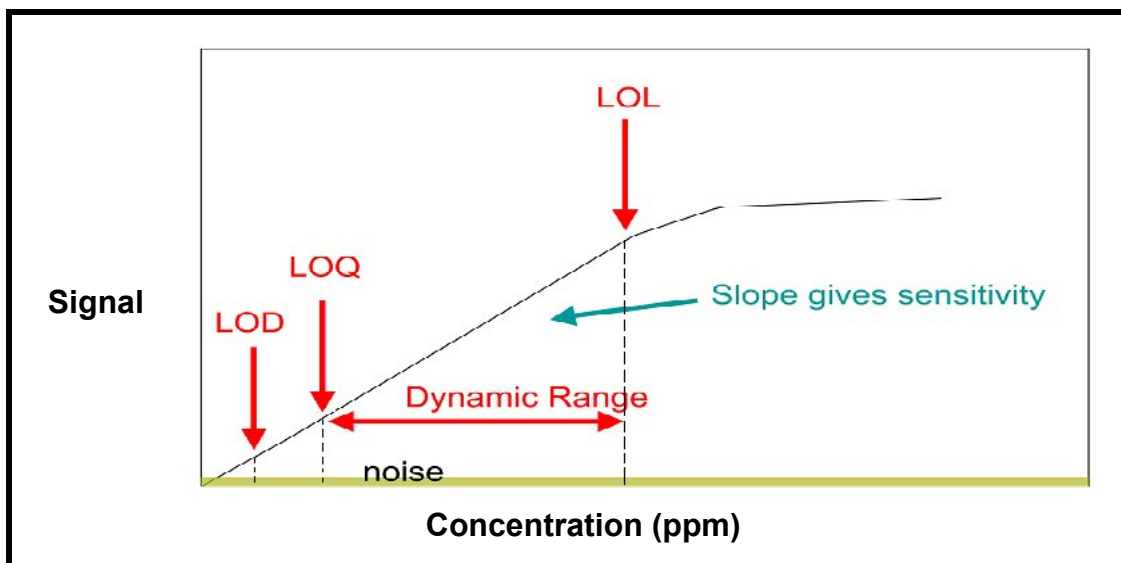
<sup>150</sup> [http://bcs.whfreeman.com/qca/cat\\_080/ch05.pdf](http://bcs.whfreeman.com/qca/cat_080/ch05.pdf) (accessed on the 24-07-2013)



**Figure 4.2:** The direct calibration curve

The direct calibration method has the advantage of being easy to construct and use for the determination of the percentage recovery of the analyte samples since it doesn't involve demanding calculations. The biggest drawback however, is that the results obtained using this method can easily be influenced by spectral interference, acid matrix, instrumental drifts and chemical interferences. Furthermore, the uncertainty (standard deviation) values obtained from the quantitative measurements can be very high as a result of the uncorrected matrix effects and drifts.

In quantitative analysis, it is important to know the lowest concentration (limit of detection (LOD)) of the analyte that can be detected by this method. Frequently the detection of the analyte does not simply cease at a threshold level, but tends to 'fade' from a predictable signal/concentration ratio gradually to an indiscernible response. For quantitative measurements, there is likely to be a concentration threshold level on which specificity becomes unreliable (limit of linearity (LOL)). The threshold may vary if the experiment is repeated at another time with different reagents, fortification, spiking materials, etc. The limit of quantitation (LOQ) is the smallest concentration of analyte that can be determined with an acceptable level of repeatability, precision and trueness as illustrated in **Figure 4.3**. The dynamic/working range of the calibration curve refers to the range in which the analyte solutions can be measured with high degree of accuracy.



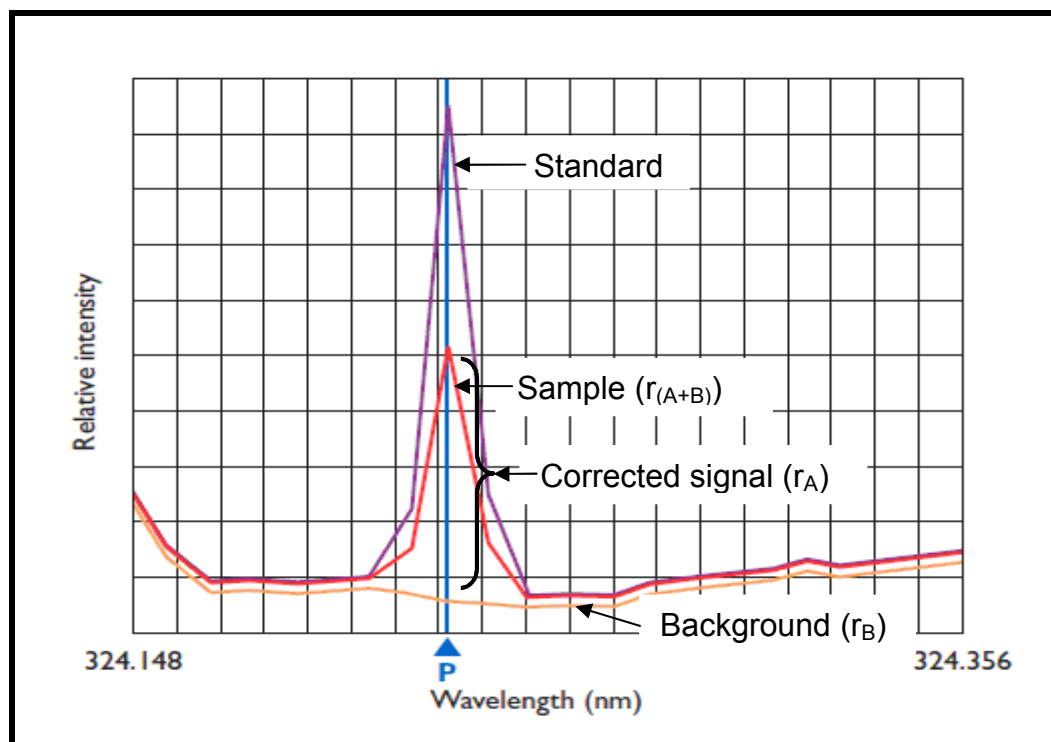
**Figure 4.3:** A calibration curve plot showing limit of detection (LOD), limit of quantitation (LOQ), dynamic range and limit of linearity (LOL).<sup>151</sup>

During the quantitative analysis using the direct calibration method, the corrected analyte signal ( $r_A$ ) is determined as the difference between the total signal ( $r_{A+B}$ ) and the background signal/noise ( $r_B$ ) as illustrated in **Equation 4.1** and **Figure 4.4** on a specific line (P).

$$r_A = (r_{A+B}) - r_B$$

... 4.1

<sup>151</sup> [http://en.wikipedia.org/wiki/Calibration\\_curve](http://en.wikipedia.org/wiki/Calibration_curve) (cited 17/10/09).

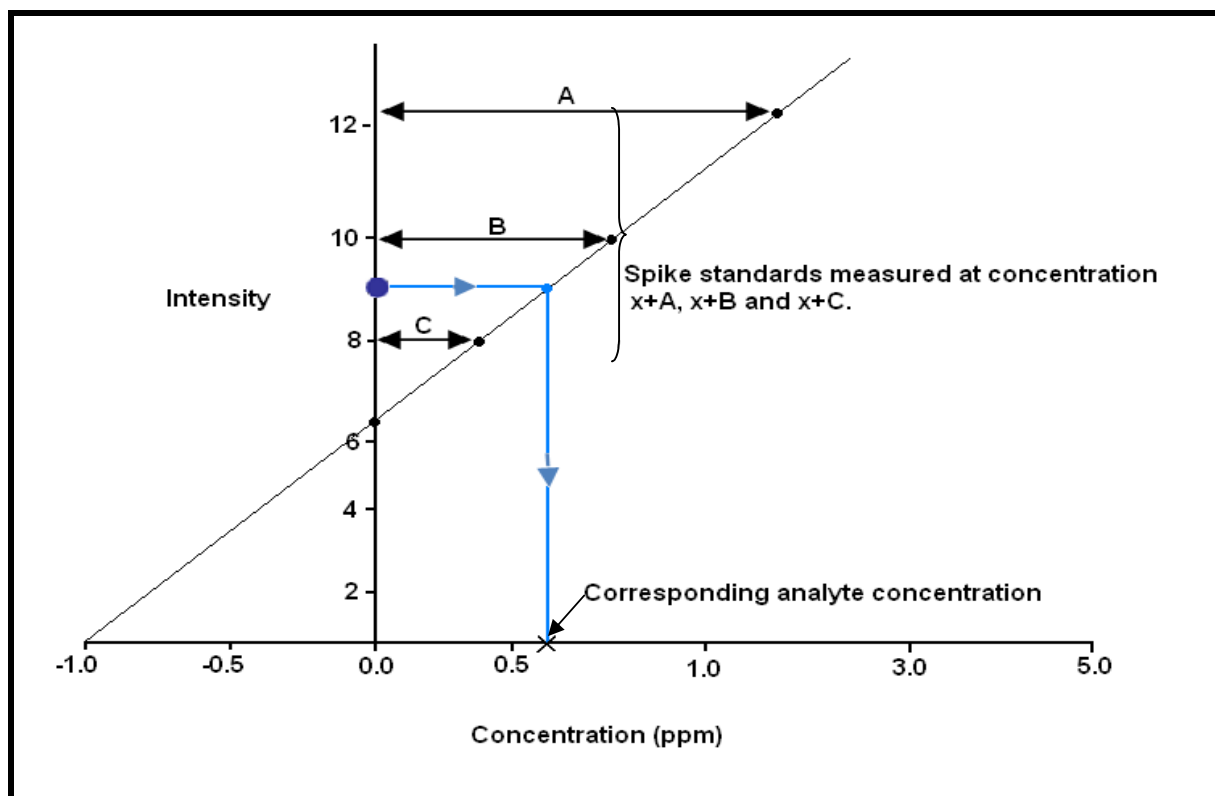


**Figure 4.4:** Comparison of the analyte signal to the standard signal<sup>152</sup>

#### 4.2.3 Standard addition method

The standard addition method is mostly used when samples with unknown matrix composition cannot be ideally matched with the matrix of the calibration standards. This method is especially important in correcting for the matrix present in the sample solution. Some of the species present in the matrices may interact with the analyte to alter the analyte instrumental response which will consequently result in poor recoveries. In the standard addition method, small increments of standard solutions (spikes) (see **Chapter 3, Section 3.2.5**) are added to the analyte samples. Unlike in the direct calibration method, the impurities in the sample are accounted for within the calibration curve shown in **Figure 4.5**. The concentration of the analyte solution is determined either by extrapolation of the calibration curve or from the equation of the curve.

<sup>152</sup> T.J. Manning and W.R. Grow, *Inductively Coupled Plasma-Atomic Emission Spectrometry*, (1997), 2, pp. 1 - 19.



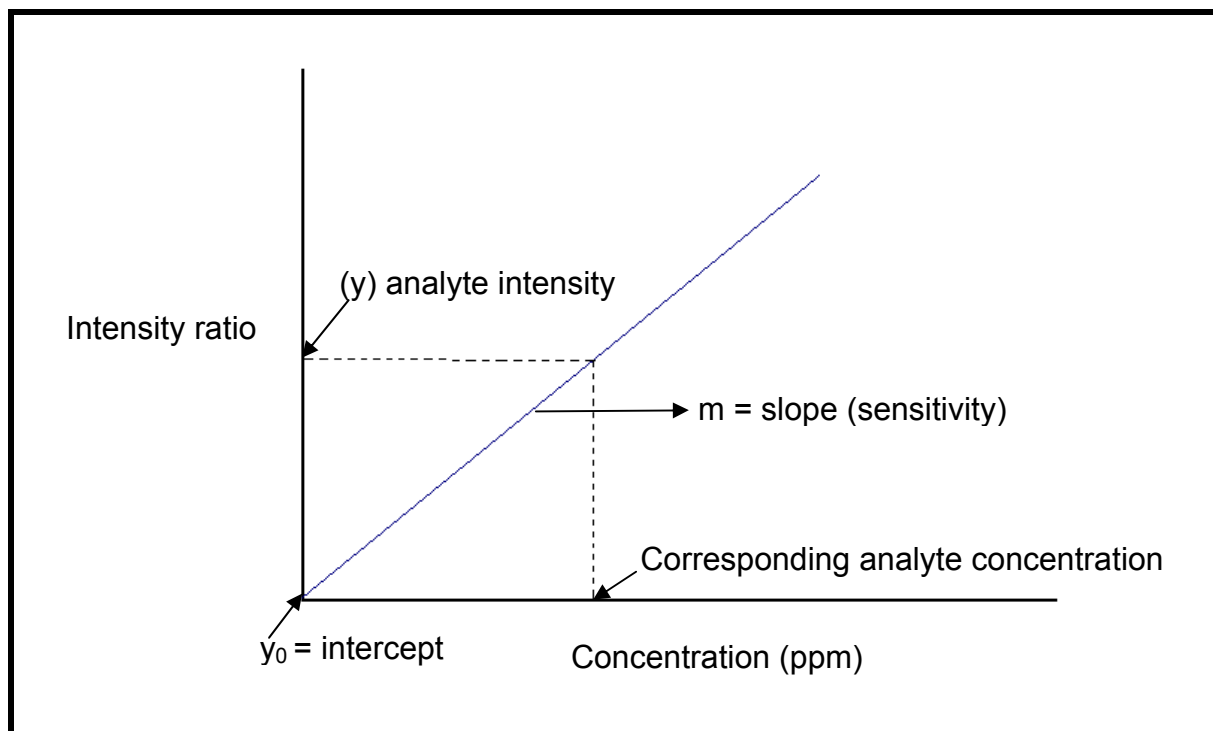
**Figure 4.5:** Standard addition calibration curve

The standard addition method has the advantage of correcting for spectral interferences caused by other minor elements in the analyte sample by enhancing the analyte signal. The ability of this method to minimize the effects of impurities by enhancing the analyte signal has been much preferred than the direct calibration method where response signals are not compensated for. The drawback of this method is that it requires relatively large volumes of standard solution (at least 100 mL, preferably 250 mL) for analysis and is also easily affected by instrumental drifts and the presence of EIE's.

#### 4.2.4 Internal standard addition method

The internal standard addition method involves the selection of a suitable internal standard element which is added in equal volumes to both the calibration standards and the analyte solution(s). The internal standard method assumes that any unknown source of error will affect both the internal standard and the analyte emission intensities equally. The measured analyte emission intensity of the standard solution is weighed against that of the internal standard to give an emission

intensity ratio. This corrected response (emission intensity ratio) has the advantage of correcting for the imprecision caused by instrumental drifts, background noise and other matrix-induced signal variations caused by the sample. However, the internal standard method involves more work and calculations than the direct calibration method but has better precision and accuracy than both the direct calibration and the standard addition methods. The internal standard calibration curve is constructed by plotting the corrected emission intensity ratios against the corresponding standard concentration, (**Figure 4.6**). A linear equation similar to that in the direct calibration curve,  $y = mx + y_0$  is obtained and is used to determine the analyte concentration by either extrapolating the analyte intensity ratio or by calculating the value of (x) from the linear equation.

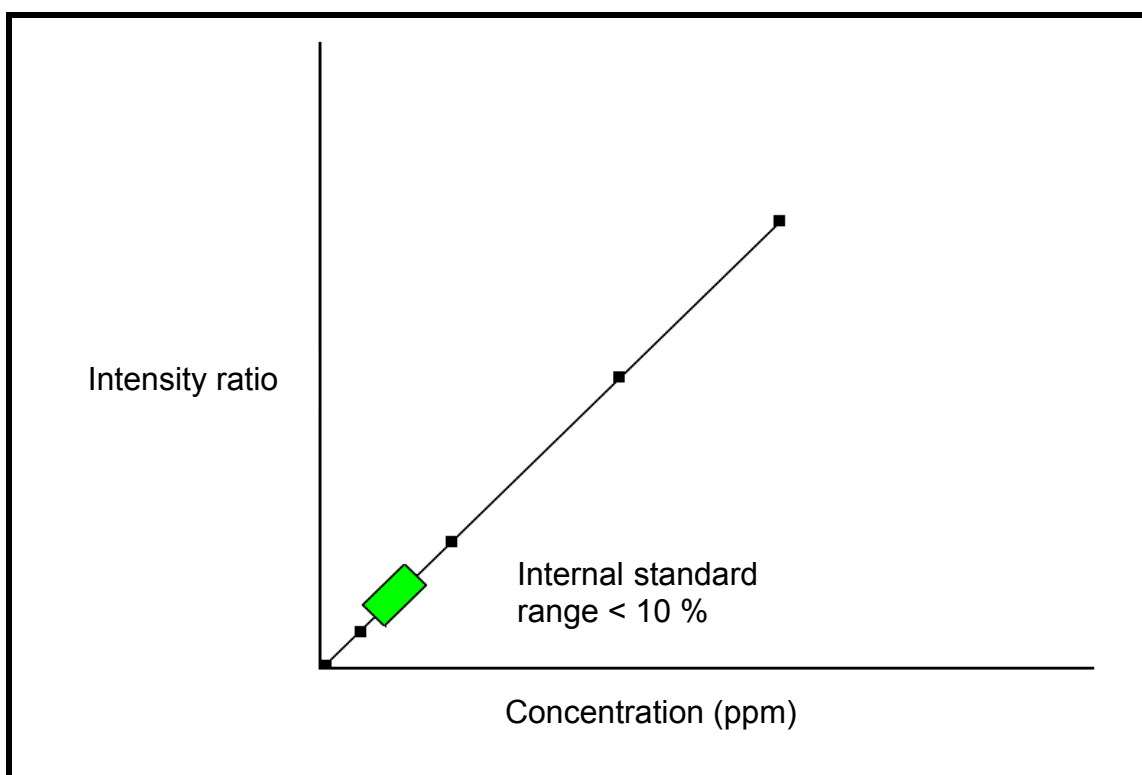


**Figure 4.6:** The internal standard calibration curve

#### **4.2.4.1 Selection of an internal standard**

The choice of a suitable internal standard is critical for the successful use of this method. All the quantitative measurements are dependent on the internal standard's performance and its ability to mimic the behaviour patterns of the analyte as was discussed in **Chapter 3, Section 3.2.5**. It is highly recommended that the selected

element to be used as an internal standard should be completely absent from the analyte sample to ensure that the measurement is only the result of the changes in the analyte solution. Furthermore, the emission intensities of an internal standard itself must be free from interferences from other ions present in the sample. Any interference will affect the signal by either suppressing or enhancing the emission intensities of the internal standard. It is therefore recommended that the concentration levels of the chosen internal standard must be less than 10 % of the calibration range to avoid any interference with the analyte metals (**Figure 4.7**).



**Figure 4.7:** Concentration range of an internal standard solution

The fundamental requirement in using this method is that both the analyte and the internal standard signals should be enhanced or suppressed to similar degrees. This will result in signal ratios (of the analyte/internal standard element) to remain constant regardless of the instrumental drifts or any other matrix induced changes. Different approaches have been used to select a suitable internal standard(s) in the determination of precious metals. Methods that target specifically the physical properties such as metal stability, first ionization and excitation energies are commonly used to select possible internal standards. These methods seek to



identify an internal standard element which has the potential to behave in a similar manner as the analyte under prevailing experimental conditions.

The use of principal component analysis which involves the statistical determination of a suitable internal standard using the atomic and ionic emission lines has also been applied. This method has been reported to promote the use of the most sensitive atomic or ionic lines in the quantitative analysis since these lines are less affected by matrices. According to this procedure, preliminary sets of measurement are performed during the determination of a suitable internal standard and the results of this analysis (score plot) are grouped according to their empirical behaviour. The closer the analyte to the reference lines in the score plot, the higher is their similarity and compatibility in compensating for the matrix-induced signal variations.<sup>153</sup> However, this method has led to widespread speculation on whether atomic lines or ionic lines between pairs of internal standards and an analyte samples can be used or a combination of both during the quantitative analysis of metals.<sup>154</sup> Attempts to substantiate these differences are relatively scarce in literature with few researchers recommending the same use of either atomic/ionic line for both the internal standard and the analyte sample.

#### **4.2.4.2 Factors affecting the internal standard method**

##### *4.2.4.2.1 Effects of acid matrix in internal standard addition method*

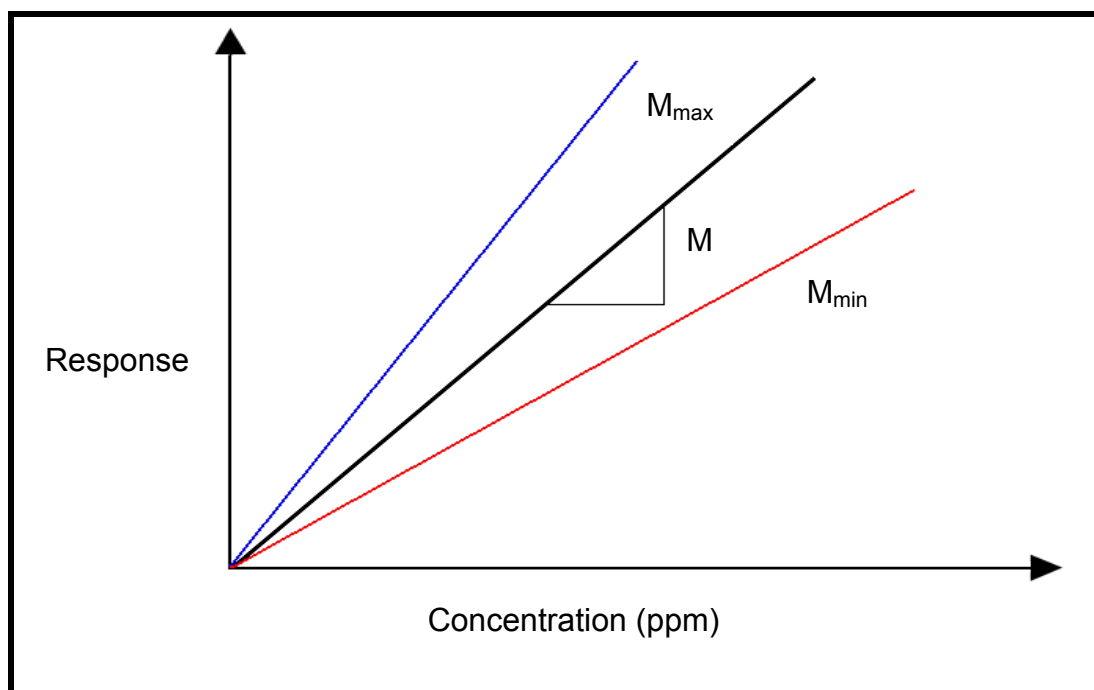
Analytical procedures involving metal species mostly include the use of concentrated acids or acid mixtures for sample digestion/dissolution or stabilization. Increasing acid concentrations in analyte samples have been reported to cause (i) a decrease in the uptake rate of the analyte solution as a result of increased viscosity, (ii) a change in the primary and tertiary aerosol drop size distribution, (iii) a reduction in the aerosol transport efficiency because of a change in aerosol density, (iv) an aerosol ionic

---

<sup>153</sup> M. Grotti, E. Magi and R. Leardi, *J. Anal. At. Spectrom.*, (2003), 18, pp. 274 - 281.

<sup>154</sup> M. Brill and P. Cassagne, *European Winter Conference on Plasma Spectrochemistry, Dortmund*, (1991).

redistribution in the spray chamber (which mostly affects the sensitivity, **Figure 4.8**) and (v) a change in the ICP-OES/MS atomization and excitation conditions.<sup>155,156</sup>



**Figure 4.8:** Sensitivity error ( $M_{\max}$  and  $M_{\min}$ ) as a result of acid matrix

These changes have been reported to cause a suppression of the analyte emission signals which eventually reduces the percentage recoveries of the analyte element.<sup>157</sup> The degree of suppression has also been found to vary depending on the type of acid used in the sample preparation. Acids such as  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  give rise to coarser primary aerosol size by increasing the viscosity of the solutions, whereas acids such as  $\text{HNO}_3$ ,  $\text{HClO}_4$  and  $\text{HCl}$  affect the plasma excitation conditions. Amongst these commonly used acids, the emission depressions were reported to decrease according to the series *aqua regia* <  $\text{HCl}$  <  $\text{HNO}_3$  <  $\text{HClO}_4$  <  $\text{H}_3\text{PO}_4$  <  $\text{H}_2\text{SO}_4$ .<sup>158</sup>

<sup>155</sup> R.F. Browner, *Fundamental aspects of aerosol and transport*, in: P.W. Boumans (Ed.), *Inductively Coupled Plasma Emission Spectrometry, Part II: Applications and Fundamentals*, Wiley-Interscience, New York, (1987), pp. 244 - 288.

<sup>156</sup> J. De Boer and M. Velterop, *J. Anal. Chem.*, (1996), 356, p. 362.

<sup>157</sup> Z. Mester and R. Sturgeon, *Comprehensive Analytical Chemistry*, Wilson & Wilson's, Elsevier, Amsterdam., (2003), p. 41.

<sup>158</sup> E.G. Chudinov, I.I. Ostroukhova and G.V. Varvanina, *Fresenius. Z. Anal. Chem.*, (1989), 335, pp. 25 - 33.

#### *4.2.4.2.2 Effects of EIE's and instrumental drifts in internal standard addition method*

The most common form of matrix interference observed within the plasma is ionization interference. It is also known as easily ionized element (EIE's) interference. Ionization interferences due to the presence of high concentrations of EIE's in samples such as the alkali and the alkaline earth elements. These elements have low ionization energies and are easily ionized at high plasma temperatures to generate a rich electron density environment. This increase in electron density as a result of EIE's, commonly results in either the enhancement or suppression of the analyte emission signals which eventually leads to either false-high (positive error) or false-low (negative error) percentage recoveries.

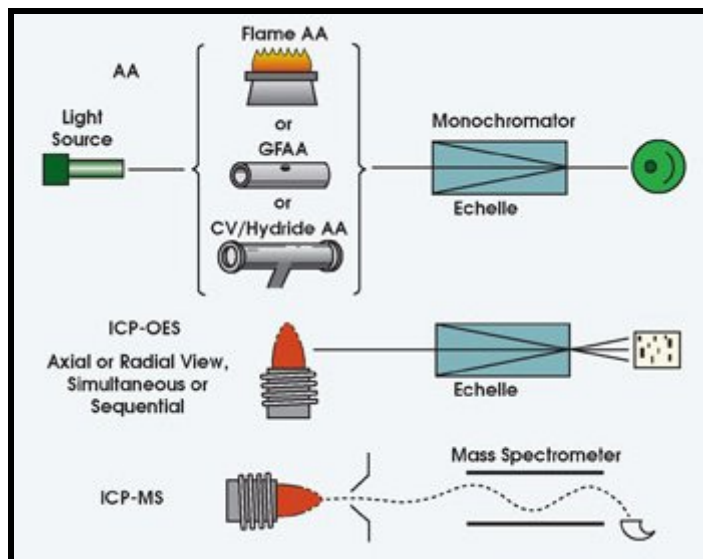
The varying degree of signal enhancement or suppression caused by these EIE's makes it difficult to select a suitable internal standard. The use of Cs as an ionization buffer in spectrometric techniques has been reported to significantly reduce ionization interference effects.<sup>159</sup> Cs itself is classified as an EIE, but its presence in analyte solutions has been shown to negate (buffers) the effects of the other EIE's that may be relatively present in samples. Its effects on the ICP-OES and ICP-MS flame and on the analyte signal has been reported to be relatively weak and incapable of causing spectral interferences compared to the other alkali metals. The advantages of using Cs as a buffer has been greatly attributed to its availability in pure form and low cost, compared to the additional cost involved in argon usage when robust conditions are used.

One of the most common and troublesome sources of instrumental drifts is the one derived from samples with high total dissolved solids (TDS) including EIE's. Poor instrumental stability lowers the precision and the accuracy of the measurements. The main cause of sample induced drift in ICP-MS is the deposition of sample material on the interface cones found between the interface region and the ion optics. During the sample measurement using AA and ICP-OES, the light emitted by the analyte enters the spectrometer whilst in ICP-MS the sample actually enters the measuring device (**Figure 4.9**). This makes the ICP-MS technique vulnerable to drifts

---

<sup>159</sup> <http://www.referanskimya.com/pdfs/hps/06>.(accessed on the 15/05/2013).

due to the deposition of the solid materials on the interface cones which will eventually affects the accuracy of the results.

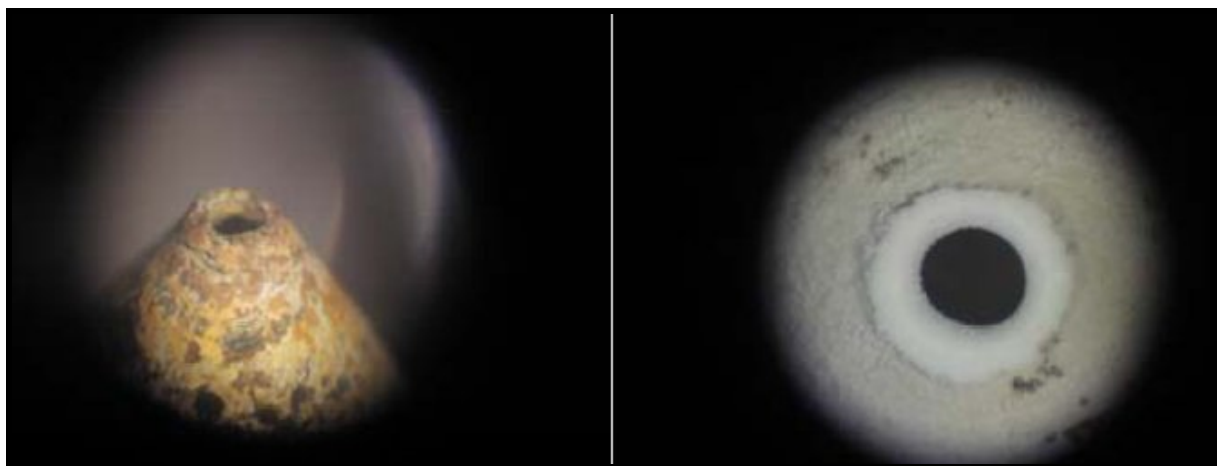


**Figure 4.9:** AA, ICP-OES and ICP-MS measuring devices<sup>160</sup>

Geological materials with moderate to high TDS contents and EIE's have also the potential to deposit salts on the cone orifices of the ICP-MS (**Figure 4.10**). This deposition of salts action has been reported to cause instrumental drifts which ultimately affect the accuracy of the results. Carbon formation in the plasma has also been reported to affect the ICP-MS measurements in several ways when it is deposited on the cooled sampling orifice of the MS ultimately resulting in cone clogging. The presence of carbon from the decomposition of organometallic compounds has been shown to cause polyatomic interferences, e.g.  $^{40}\text{Ar}^{12}\text{C}^+$  on  $^{52}\text{Cr}^+$  and  $^{12}\text{C}^{14}\text{N}^+$  on  $^{26}\text{Mg}^+$ , when low-resolution ICP-MS instruments are used. This plating action on the cones was shown to decrease the sensitivity of the detector over time and degradation of signal stability. Instrumental responses due to these depositional processes are mostly non-linear with respect to time. Cheatham *et al.*<sup>161</sup> reported that these drifts will eventually lead to lower percentage recoveries if not corrected.

<sup>160</sup> <http://www.photonics.com/Article.aspx?AID=18132> (accessed on 12/06/2013).

<sup>161</sup> M.M. Cheatham, W.F. Sangrey, W.M. White, *Spectrochim. Acta B.*, (1993), 48, pp. 487 - 506.



**Figure 4.10:** Skimmer cone with salt (EIE's) build up<sup>162</sup>

The effect of EIE's in ICP-OES/MS analysis has been investigated and reported by several researchers. The main aim of these studies were to minimize or eliminate the effects of EIE's in analytical results by using robust conditions on a radially-viewed ICP-OES.<sup>163</sup> This robust condition which involves reducing the nebulizer pressure and increasing the radio frequency (RF) power, has been shown to reduce ionization interference on a radially-viewed ICP-OES.<sup>164</sup> The most successful method to reduce the influence of EIE's when analyzing samples that contain high levels of EIE's is to ensure that all standards have similar or identical levels of EIE's as the analyte samples (matrix matching) so as to maintain equivalent ionisation and transport characteristics in the plasma.

#### **4.2.4.3 Optimization of the internal standard method**

Matrix matching and the use of robust conditions have been reported to maximize the performance of the internal standardization method. This procedure has been highly recommended to allow uniform ionization and emissions in the ICP-OES/MS plasma.<sup>165,166</sup> Robustness refers to the ability of the plasma to resist plasma changes as a result of the changes in the plasma conditions due to composition of the sample

---

<sup>162</sup> [www.SpectronUS.com](http://www.SpectronUS.com) (accessed 03-06-2012).

<sup>163</sup> I.B. Brenner, A. Zander, M. Cole, and A. Wiseman, *J. Anal. At. Spec.*, (1997), 12, pp. 897 - 906.

<sup>164</sup> C. Dubuisson, E. Poussel and J.M. Mermet, *J. Anal. At. Spec.*, (1997), 12, pp. 281 - 286.

<sup>165</sup> A. Marucco, *Nucl. Instr. Meth. Phys. Res B.* (2004), 213, p. 14.

<sup>166</sup> C. Dubuisson, E. Poussel, J.L. Todoli and J.M. Mermet, *J. Anal. At. Spectrom.* (1998), 13, p. 63.

matrix. Internal standardization has been shown to be more efficient under robust conditions than in non-robust conditions.<sup>167</sup> In these studies, the internal standard method was reported to effectively correct for the matrix interference caused by the changes within the plasma, sample transport process, background emissions and energy transfers between the plasma and the analyte sample.

Research also indicates that the use of ionic lines in ICP-OES under robust conditions has an added advantage towards the reduction of interferences.<sup>168</sup> Results indicated that at a particular location in the plasma flame, called the 'cross-over point', the matrix elements in a sample solution appear to have a minimal effect on the analyte signal. However, the location of this cross-over point was described as dependent on the selected ionic analyte line. The ionic lines were mostly preferred on the basis of their greater sensitivity and their ability to resist changes under robust conditions compared to atomic lines.

### **4.3 Sample preparation methods of PGM and gold**

Complete sample digestion is always a prerequisite for achieving accurate and reproducible results in wet chemical analysis. Many digestion/dissolution techniques have been developed and studied by many researchers and these techniques includes the use of open-beaker, microwave and fusion digestion steps.

#### **4.3.1 Open beaker acid digestion/dissolution**

The digestion of various precious metal samples involving wet acid treatment has widely been studied by different researchers. This method has been described to be fast, simple to use and inexpensive compared to other methods. Mineral acid and mixtures such as HF, HCl, HNO<sub>3</sub>, HClO<sub>4</sub> and *aqua regia* were most commonly used in these dissolution steps. Incomplete dissolution of samples or occlusion of the analyte within the grains of the remaining sample particles can result in a non-

---

<sup>167</sup> X. Romero, E. Poussel, J.M. Mermet, *Spectrochim. Acta Part B* 52., (1997), pp. 487 - 493.

<sup>168</sup> G.C.Y. Chan and G.M. Hieftje, *J. Anal. At. Spectrom.* , (2009), 24, pp. 439 - 450.

quantitative recovery of the analyte metals. The purity of the acids used in the digestion/dissolution of samples should also be assessed so as to avoid any contamination of the samples. Hydrofluoric acid is widely used for the digestion of geological and various environmental materials, e.g. soils and sediments. It is one of the main acids that succeed in breaking the silicate phases (Si-O bond) which then facilitate the liberation of the analyte metals. However, the use of HF is highly unpopular because of its extremely corrosive and toxic property which causes safety concerns.

The maximum digestion temperatures for open beaker acid digestion are limited by the ambient pressure and the boiling point of the acid or acid mixtures used, e.g. the boiling point of 32 % HCl is ca. 84 °C and *aqua regia* is ca. 108 °C at room temperature. Furthermore, this technique requires long reaction times before complete digestion/dissolution is achieved. This method also suffers from increased contamination risks due to the usage of large amount acids.

#### **4.3.2 Microwave dissolution**

Many analytical samples, especially samples of geological and environmental origin such as felsic, ultramafic rocks, sediments and soils, contain mineral phases that are resistant to acid attack. In these cases high-pressure acid digestion (close-vessel digestions) for multi-element analyses is employed to dissolve the minerals. Microwave digestion with open or closed vessels has been reported<sup>169</sup> to dissolve a wide range of materials within shorter dissolution times. However, the microwave technique is limited by both the particle size and the amount of sample to be digested. Powdered samples are easily digested, compared to coarse particles, whilst the amounts of the sample to be digested have to be small (mostly 0.2 - 2 g) depending on the equipment.<sup>170</sup> Despite these challenges, the microwave technology has improved over the past few years with the introduction of the more efficient automated machines. These microwave reactors allows for longer digestion times of up to 3 hours at high temperatures (240 °C) and pressures (60 bar).

---

<sup>169</sup> M. Balcerzak, *Analytical Sciences*, (2002), 18, pp. 737 - 750.

<sup>170</sup> L.Kotz, G. Kaiser, P. Tschopel and G. Tolg, *Z. Anal. Chem.*, (1972), 260, pp. 207 - 209.

The major advantage of using microwave for digestion purposes is that the digestion is normally performed in closed vessels which allow for higher temperatures to be reached which increase the success of complete dissolution. Conventional closed acid digestion vessels consist of polytetrafluoroethylene (PTFE) tubes which can withstand very high pressures (above 60 bar) at relatively high temperatures of up to 250 °C. These robust experimental conditions can significantly shorten sample decomposition times and also allows for the complete digestion of many geological materials. The drawback of using a microwave digestion/dissolution method is that it involves tedious operating procedures and is expensive to maintain due to the high cost of the vessel jackets.

#### **4.3.3 Fusion digestion**

Another dissolution method which is often applied to highly inert geological materials and inorganic compounds is flux or molten salt fusion. Flux fusions with acidic or basic salts are mostly a preferred alternative method to mineral acid dissolution. Flux fusion involves the mixing of a sample with an excess of an appropriate flux salt. The resultant mixture is then heated to a temperature above the melting point of the salt with the aim to produce a soluble melt which can then be easily dissolved with water (see **Chapter 3, Section 3.2.6.2**).<sup>171,172</sup> The most common fluxes used in sample digestion are tabulated in **Table 4.1**.

---

<sup>171</sup> G.D. Christian, *Analytical Chemistry 5<sup>th</sup> ed.*, (1994), p. 670.

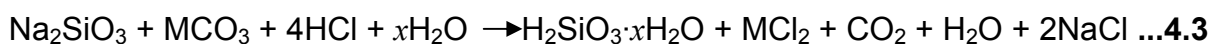
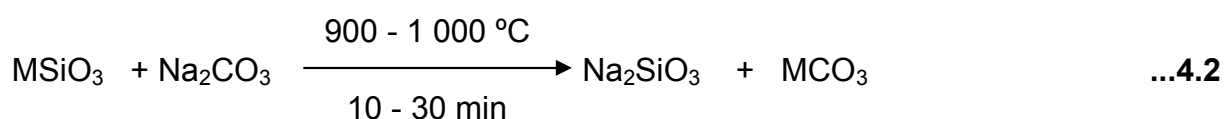
<sup>172</sup> J. Bassette, R.C. Denney, G.H. Jeffery, J. Mendham, *Vogel's Textbook of Quantitative Inorganic Analysis. 4<sup>th</sup> ed.*, (1978), pp.105 - 106.



**Table 4.1:** The most commonly used fluxes in various PGM and gold mineral ores

FLUX	SAMPLE TYPE
<b>Sodium carbonate</b>	Silicates, refractory oxides, quartz, insoluble phosphates and sulphates.
<b>Sodium pyrosulphate or potassium pyrosulphate</b>	Basic materials, insoluble oxides and oxide-containing samples.
<b>Sodium hydroxide or potassium hydroxide</b>	Acidic materials, silicates, oxides, phosphates, and fluorides.
<b>Lithium metaborate</b>	Acidic oxides such as silica and TiO <sub>2</sub> and nearly all minerals.
<b>Lithium tetraborate</b>	Basic oxides and some resistant silicates.
<b>Sodium peroxide</b>	Sulfides, acid-insoluble alloys of precious and base metals.

This molten salt reaction converts the chemical components within the sample into more soluble compounds. A typical example is the use of sodium carbonate as flux that reacts with some metal silicates which converts the silicates into a form that is soluble in hydrochloric acid as indicated in **Equations 4.2** and **4.3**.



Where M = metal

Precious metals on the other hand are readily attacked by alkaline hydroxides in the presence of an oxidizing agent such as metal peroxides or nitrates. Sodium hydroxide mixed with sodium peroxide or sodium peroxide is often used as flux in the precious metal digestion. This type of fusion is normally performed at temperatures between 450 - 600 °C for 15 - 60 min. The melt obtained from this fusion process is dissolved in water and acidified with hydrochloric acid to convert all the precious

metals into chlorido-complexes, which serve as the basis of most separation and quantification methods (see **Chapter 2, Section 2.4.1**). The big drawback of this method is the limited amount of sample usually between 0.5 - 5 g that can be digested at a time depending on the size of the sample crucible used. Furthermore, the large amount of flux salt introduced to the sample together with possible contamination by the crucible complicates the accurate quantitative analysis of the targeted metals.

## **4.4 Validation parameters**

The purpose of method validation is to demonstrate that the established or newly developed method is fit for its intended purpose. Much of the method validation and development are performed in an iterative manner with adjustments or improvements on the method parameters such as temperature (laboratory and spray chamber), concentration of reagents and equipment parameters such as RF power, nebulizer, spray chamber, as well as torch design and torch height. This is done with the aim of assessing the precision/reproducibility, accuracy, linearity, specificity/selectivity, limit of detection, limit of quantitation and robustness/ruggedness of the developed method.<sup>173</sup>

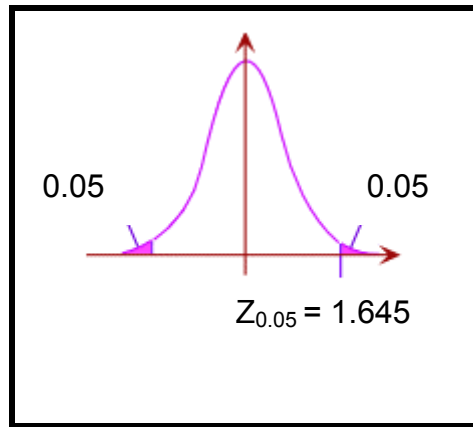
Regression analysis is normally applied to measure the uncertainties associated with the response measurement of the analyte samples or of the data points of the calibration curve. This uncertainty can be evaluated by specifying the percentage confidence interval (mostly 95 %) under stipulated degrees of freedom to which the outcome can be accepted or rejected using the hypothesis test.<sup>174</sup> In the hypothesis test there are two contradictory outcomes that influence the decision on whether to accept or reject the outcome. The first outcome can be regarded as a null hypothesis  $H_0$ , which states that the outcome  $\mu$  is statistically not different from the known value  $\mu_0$  (i.e.  $\mu = \mu_0$ ) at a certain confidence level. The second test is called the alternative hypothesis  $H_a$  which can be stated in several ways. The  $H_0$  can be rejected in favour

---

<sup>173</sup> T.T. Chiweshe, *Quantification of rhodium in series of inorganic and organometallic compounds*, MSc thesis, University of the Free State, Bloemfontein, South Africa, (2010), pp. 65 - 70.

<sup>174</sup> D.A. Skoog, F.J. Holler and T.A. Nieman, *Principles of Instrumental Analysis*, Saunders College Publishing, USA, 5<sup>th</sup> ed., (1998), pp. 149 - 153.

of the  $H_a$  if  $\mu$  is proved to be statistically different from  $\mu_0$  (i.e.  $\mu \neq \mu_0$ ). For tests with a larger number of experimental replicates ( $> 20$ ) such that the standard deviation ( $s$ ) of the outcome values is a good estimate of the population standard deviation ( $\delta$ ), a z-statistic is used, and in the case where ( $s$ ) is not known or is not a good estimate of  $\delta$ , a t-statistic is used. The rejection region for the z-statistic at 95 % percentage confidence level is shown in **Figure 4.11**.



**Figure 4.11:** The normal distribution for the z-statistic at 95 % confidence interval<sup>175</sup>

The alternative hypothesis ( $H_a$ ) for  $\mu > \mu_0$  is rejected when  $z$  is greater than 1.64 ( $z_{crit}$ ) and for  $H_a: \mu < \mu_0$ ,  $z$  values less than -1.64 ( $z_{crit}$ ) are rejected. The  $z$  values are calculated as shown in **Equation 4.4** where  $\bar{x}$  is the mean of the outcomes and  $N$  is the sample size.

$$z = \frac{\bar{x} - \mu_0}{\left( \frac{s}{\sqrt{N}} \right)} \quad \dots 4.4$$

Possible outliers can be detected by Dixon's or Grubbs' test at 95 % confidence level. It should be noted that before rejecting the experimental values dependent on whether enough samples replicates were measured (at least 4) to avoid bias in rejecting or accepting of the results. Dixon's test is a useful method to investigate the data for outliers. The test can be performed by using different values of data as shown in **Equation 4.5**.

---

<sup>175</sup> C. Dougherty, *Introduction to Econometrics*, Oxford University Press, Oxford (2<sup>nd</sup> ed), (2002), pp. 1 - 4.

$$Q = \frac{|\text{Suspect} - \text{nearest}|}{\text{Largest} - \text{smallest}} \quad \dots 4.5$$

If  $Q > Q_{critical}$  (from the tables)<sup>176</sup> then the suspect value can be classified as an outlier, and be rejected. In Grubbs' test a single suspected value ( $X_s$ ) value within a set of measurements is determined and compared to the mean and divided by the standard deviation ( $s$ ) as shown in **Equation 4.6**.

$$G = \frac{|X_s - \bar{X}|}{s} \quad \dots 4.6$$

If  $G > G_{critical}$  (from the tables)<sup>176</sup> then the suspect value can be classified as an outlier, and be rejected. This method is most commonly used and recommended by ISO test for the determination of outliers since it is iterated until no outliers are detected.<sup>177</sup>

## 4.5 Conclusion

It can be concluded that the key point in circumventing the matrix effects is in a way dependent on a thorough understanding of the nature of the matrix containing in the analyte. The majority of the interferences as were shown in this chapter to mostly be derived from the analyte solution. This suggested that samples with complicated or undefined matrices are much more difficult to analyse compared to those with simple matrices. Although the internal standardization was found to be the best method of correcting these sample matrices, the use of robust experimental conditions and matrix matching were also found to optimise the percentage recoveries. The standard addition method was also shown to be an effective alternative method for eliminating matrices in quantitative analysis. However, this method was considered to be very costly in terms of the volumes of standards that have to be used as spikes in order to avoid the matrix effects. Amongst the sample preparation methods used for sample

---

<sup>176</sup> C. Dougherty, *Introduction to Econometrics*, Oxford University Press, Oxford (2<sup>nd</sup> ed), (2002), pp. 1 - 4.

<sup>177</sup> W. Horwitz, *Pure and Appl. Chem.*, (1995), 67, pp. 331 - 343.

digestion/dissolution, open beaker and microwave digestion techniques were shown to be the suitable methods for compounds which do not contain silica and oxides such as simple inorganic salts and organometallic compounds. Flux fusion on the other hand is mostly preferred in samples containing silica and oxides such as the geological and inorganic compounds. Its ability to break the silicate bonds has made it the ideal method for complete digestion of the geological samples. However, the use of a high flux content containing the EIE's give rise to matrix problems during the quantitative analysis, which was shown to adversely affect the internal standardization method. Therefore, methods which seek to minimize the effects of EIE's have to be developed or alternatively a different flux salt has to be used, which can achieve a complete digestion of the precious metals without introducing EIE's into the analyte solution.

# 5 Method development for the determination of precious metals

---

## 5.1 Introduction

In the process of developing a new analytical method, it is essential to validate the performance of the method using a certified reference material (CRM) which has been completely and accurately characterized by different stakeholders. Traceability of experimental results is very crucial in method development as it provides a platform where qualitative or quantitative results can be compared at a certain level. CRMs for precious metals are relatively scarce and the few available do not contain all the elements (Ru, Rh, Pd, Pt, Os, Ir and Au) and those CRMs that do contain all the elements only contain them at very low concentration levels (ppm - bbp) which makes the development of analytical methods for precious metals a challenging task. As part of the method development for precious metals, it was first decided to establish a suitable method using a liquid CRM which contained all the precious metals at appreciable concentration levels (ppm) as reported by the accompanying certificate (see **Appendix**). The newly developed method was further evaluated using a commercially available PGM CRM (pyroxenite reference material concentrate (IA-MIM C2)).<sup>178</sup> The final accepted method was then used to determine the precious metals in geological mineral ores as well as inorganic and organometallic compounds (see **Chapter 7**). The validation of all experimental results will be reported in **Chapter 8**. A detailed outline of the experimental procedures and guidelines followed during the method development process for the determination of precious metals will be discussed in this chapter. Experimental results obtained in this study will also be discussed as part of the assessment of the method towards the establishment of the accurate determination of precious metals in a large number of different types of samples.

---

<sup>178</sup> [www.industrialanalytical.co.za](http://www.industrialanalytical.co.za) (accessed on the 26/08/2013).

## **5.2 Reagents and glassware**

### **5.2.1 Chemicals and glassware**

The CRM (PGM bearing Pyroxenite Reference) was purchased from Mintek while the different inorganic salts {HAuCl<sub>3</sub>·2H<sub>2</sub>O (99 %), IrCl<sub>3</sub>·3H<sub>2</sub>O (98 %), RhCl<sub>3</sub>·3H<sub>2</sub>O (99 %), RuI<sub>3</sub>·3H<sub>2</sub>O (99 %), OsCl<sub>3</sub>·3H<sub>2</sub>O (99 %), PdCl<sub>2</sub> (99 %) and PtCl<sub>2</sub> (98 %)} and separate precious metals calibration standards (1 000 ppm each) were purchased from Inorganic Ventures. The liquid CRM (100 mL, 10.00 ppm) containing all the precious metals in (3 % v/v HCl) used in this study was also purchased from Inorganic Ventures. Organometallic compounds with known purity such as chlorido(1,5-cyclooctadiene)iridium(I) dimer (97 %), [Ru(cod)(Cl)<sub>2</sub>] (97 %), [Pt(cod)(Cl)<sub>2</sub>] (99 %) were purchased from Sigma Aldrich. Disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>) (99 %) and sodium dihydrogen phosphate monohydrate (NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O), ammonium hydrogen difluoride (NH<sub>4</sub>·HF<sub>2</sub>) (98 %), ammonium hydrogen phosphate (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) (99 %) and the mineral acids {HF (48 %), HCl (32 %), HBr (48 %) and HNO<sub>3</sub> (65 %)} were purchased from Merck. The glassware used for all the metal analysis in this study was of Schott Duran, grade (A) type. The average values of the experimental results are reported together with the standard deviation indicating the uncertainty in measurement.

### **5.2.2 Preparation of double distilled and deionised water**

Double distilled water (DDW) and deionised water (ultra-pure) were both used for all the analytical solution preparations. DDW was prepared in the laboratory from an electronic distillatory vessel (Fisons w/FF9/4) whilst deionised water was prepared using a commercial reverse osmosis (RO) system (J-11,500 series) which uses pressure driven membranes to remove the TDS from water. The electrical resistivity of this water was determined as 18 MΩ.cm at 25 °C. Qualitative analyses of this purified water were further conducted to determine any remaining trace metal impurities using ICP-OES. The qualitative results showed no metal impurities present in both the DDW and the deionised water.

### **5.2.3 House keeping**

The equipment used in this research study was constantly monitored to ensure consistence in measurements while the purity of all chemicals and solvents were first determined and the expiry date inspected before used. Appropriate handling of chemicals, reagents, standards and solutions were strictly adhered to in order to avoid cross contamination and also to ensure quality assurance of all analytical results. Contamination of glassware, digestion vessels and storage bottles was avoided by soaking them in freshly prepared 10 % v/v HNO<sub>3</sub> for at least 48 hrs and finally washed them with double distilled water (DDW) prior to use.

## **5.3 Equipment**

### **5.3.1 Weighing**

Samples (triplicate) and reagents were accurately weighed to 0.1 mg at room temperature on a Scaltec (SBA 33) electronic balance, tested and calibrated in compliance to ISO 9001. A much more sensitive balance, Sartorius CP Series, Model CPA26P (**Figure 5.1**) was also used to accurately measure masses less than 0.1 g (accurate to 0.01 mg). All the balances were equipped with a self-calibration system which automatically performs an internal calibration and adjustments at regular intervals to correct for the temperature fluctuations with consistently high accuracy. Analytical samples and reagents used in this study were all weighed by adding a sample to a pre-weighed vial.





**Figure 5.1:** Scaltec (SBA 33) and Sartorius (CPA26P Series) electronic balances

### 5.3.2 Microwave digestion

An Anton Paar Perkin-Elmer Multiwave 3000 microwave (**Figure 5.2**) digestion system equipped with an 8SXF 100 rotor and eight polytetrafluoroethylene (PTFE) reaction vessels was used for the acid digestion of the certified reference material (CRM) and the mineral ore samples. An internal program for the digestion of the platinum group metals (PGM XF100-8) was selected with conditions as set in **Table 5.1**.



**Figure 5.2:** Anton Paar Perkin-Elmer Multiwave 3000 microwave

**Table 5.1:** Microwave optimum conditions for the PGM and gold mineral ore digestion (PGM XF100-8)

Parameter	Condition (Mode PGM XF100-8)
Power	1 400 Watts
Ramp	15 min
Hold	15, 45 and 60 min
Pressure rate	0.5 bar·sec <sup>-1</sup>
Temperature	240 °C
Pressure	60 bar
Weight	0.5 g
Volume of the acid	10.0 mL
Acid matrix	HCl (32 %), <i>aqua regia</i> and HNO <sub>3</sub> (65 %)

### 5.3.3 Fusion digestion

Fusion of the solid CRM and the mineral ore samples (triplicate) were achieved by using a Barnstead Thermolyne furnace (**Figure 5.3**) with temperature ranging from 25 to 1 300 °C. The furnace consists of a heating chamber and a digital controller. The temperature is thermocouple controlled and reported on a digital display. The CRM and the mineral ore samples were first weighed on the Scaltec electronic balance, then mixed thoroughly with an excess amount of flux in a known ratio and then quantitatively transferred to a platinum crucible. The mixtures were transferred to the oven and heated for at least an hour. The resultant melt was dissolved, either by the addition of acids or water, depending on the nature of the flux and the mineral ore used as discussed in **Section 5.8.1.1** and **Chapter 7**.



**Figure 5.3:** Barnstead Thermolyne furnace

#### **5.3.4 Inductive coupled plasma-optical emission spectrometry and mass spectrometry (ICP-OES/MS)**

A Shimadzu ICPS-7510 ICP-OES (**Figure 5.4**) and ICPM-8500 ICP-MS (**Figure 5.5**) were used for the wet chemical analysis in this study. The ICP-OES with the torch vertically oriented (radial viewing plasma) and ICP-MS with the torch horizontally oriented (axial viewing plasma) were chosen for all experimental measurements on the basis of their high sensitivity, good detection limits, *etc.* The emission intensity and the mass/charge ratio measurements of the two ICPs were made using optimum conditions as showed in **Table 5.2** and **Table 5.3**.



**Figure 5.4:** Shimadzu ICPS-7510 ICP-OES



**Figure 5.5:** Shimadzu ICPM-8500 ICP-MS

**Table 5.2:** ICP-OES optimum operating conditions for PGM and gold analysis

Parameter	Condition
RF power	1.2 kW
Coolant gas flow rate	14.0 L·min <sup>-1</sup>
Plasma gas flow rate	1.2 L·min <sup>-1</sup>
Carrier gas flow rate	0.7 L·min <sup>-1</sup>
Sample uptake method	Peristaltic pump
Type of spray chamber	Glass cyclonic
Type of nebulizer	Concentric
Injector tube diameter	3.0 mm

**Table 5.3:** ICP-MS optimum operating conditions for PGM and gold analysis

Parameter	Condition
RF power	1.2 kW
Sampling depth	5.0 mm
Coolant gas flow rate	7.0 L·min <sup>-1</sup>
Plasma gas flow rate	1.5 L·min <sup>-1</sup>
Carrier gas flow rate	0.6 L·min <sup>-1</sup>
Sample uptake method	Peristaltic pump
Type of spray chamber	Scott double pass type
Type of nebulizer	Concentric

### 5.3.5 UV-vis spectrophotometer

A Varian Cary UV-vis spectrophotometer (**Figure 5.6**) was used for the spectrophotometric determination of Os at a pre-selected/determined wavelength. High precision cuvettes made in Germany in compliance to ISO 9001 and certified by the Physikalisch Technische Bundesanstalt (PTB) and National Institute of Standards and Technology (NIST) were used for the absorbance measurements of the coloured osmium solutions.





**Figure 5.6:** Varian Cary UV-vis spectrophotometer

### 5.3.6 Infrared (IR) spectroscopy

Characterization of inorganic and organometallic compounds as well as other solid products was done on a Digilab (FTS 2000) IR spectrometer (**Figure 5.7**). The IR was first calibrated by running a background scan (10 scans) before analyzing the samples. The sample (spatula tip) was mounted on a crystal plate using an adjustable pressure clamp. Sample spectrum was collected from 32 repetition scans and the resultant scan was base line corrected and the final peaks of the sample integrated.



**Figure 5.7:** A Digilab (FTS 2000) spectrometer

## **5.4 Qualitative analysis and the determination of limits of detection and quantitation (LOD and LOQ) of precious metals in the CRM**

### **5.4.1 Description of the CRM**

The liquid CRM used in this study was purchased from Inorganic Ventures. According to the certificate the CRM was prepared from mixing of highly pure PGM and gold inorganic salts into an analytical solution and stabilized in hydrochloric acid matrix (3 % v/v). The concentration of the precious metals and the uncertainty measurement of the CRM (10.00 ppm) were verified using ICP-OES and ICP-MS as shown on the certificate (see **Appendix**). All the calculations were performed at 95 % confidence interval.

### **5.4.2 Qualitative analysis of the CRM and the selection of the precious metals and the internal standards wavelength**

The wavelength selection in the quantitative analysis of precious metals and the internal standards (Sc, Co, Y, In and La) was made using the ICP-OES profile function or the Win-image.<sup>179</sup> These programmes allow for a rapid semi-quantitative analysis for a multiple wavelength analysis and they function basically the same. The methods involve the recording of the number of background scans against that of the analyte solution. The spectra of the background and analyte are then superimposed upon each other and the resultant spectrum clearly shows the presence or absence of possible interferences on the selected lines for all the elements present in the sample (**Table 5.4**).

---

<sup>179</sup> <http://www.horiba.com/fileadmin/uploads/Scientific/Documents/Emission/ICP31.pdf> (accessed on the 26/08/2013)

**Table 5.4:** Selected ICP-OES ionic wavelengths for the internal standards

Element	Status (atomic/ionic)	Wavelength (nm)
<b>Sc*</b>	Ionic	361.384
<b>Co*</b>	Ionic	238.892
<b>Y*</b>	Ionic	371.030
<b>In</b>	Ionic	230.606
<b>La*</b>	Ionic	333.749

\*Element does not possess atomic lines

The results obtained from this 'Win image' selection procedure indicated that the best wavelengths for the precious metals are ionic lines ( $\lambda$ ) for Ir, Os, Ru and Pt and atomic lines for Au, Rh and Pd as shown in **Table 5.5**. Qualitative determination of other elements in the CRM showed the presence of trace amounts (< 1 ppm) of 8 elements which includes Na, Mg, Ca, Fe, Al, Ni, Cu and Ag.

**Table 5.5:** Selected ICP-OES atomic and ionic wavelengths for PGM and gold determination

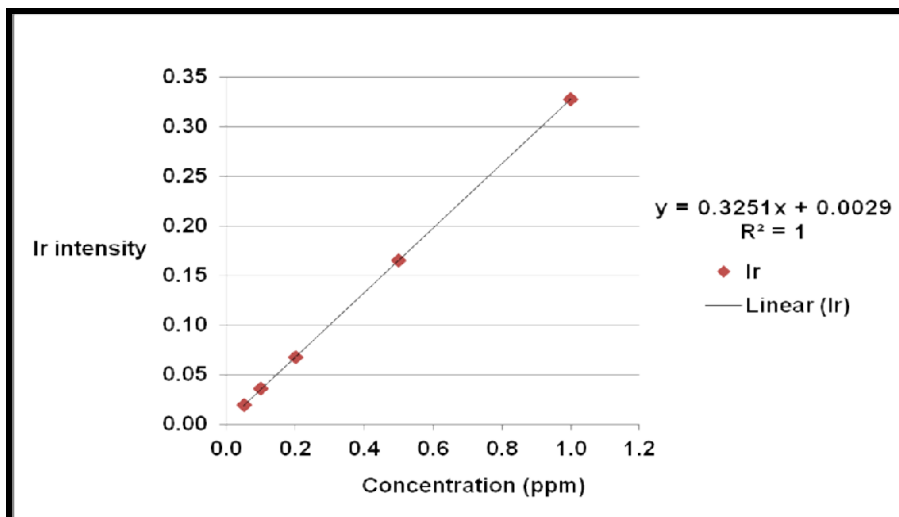
Element	Status (atomic/ionic)	Wavelength (nm)
<b>Ir</b>	ionic	224.268
<b>Au</b>	atomic	267.595
<b>Os</b>	ionic	228.226
<b>Rh</b>	atomic	343.489
<b>Ru</b>	ionic	240.272
<b>Pd</b>	atomic	340.458
<b>Pt</b>	ionic	203.646

#### 5.4.3 Determination of LOD and LOQ of precious metals

Precious metal calibration standards were prepared from the original standard solutions (1 000.00 ppm). Standard with concentrations of 0.0 (blank), 0.05, 0.1, 0.2, 0.5 and 1.0 ppm were prepared in 100.0 volumetric flasks using a 'Transferpette' micro-pipette. Hydrochloric acid (5.0 mL; 32 %) was added and the flasks were filled up to the mark using double distilled water. The solutions were mixed uniformly to obtain homogenized solutions and left to stabilize for an hour before used. The calibration curves (see **Appendix**) were obtained by plotting the measured e.g. iridium response from the



above selected wavelength (224.268 nm) against the corresponding concentrations of the standards as shown in **Figure 5.8**.



**Figure 5.8:** Iridium calibration curve obtained using the direct calibration method

Limits of detection of the remaining precious metals were determined at their respective selected ICP-OES atomic and ionic lines using the same procedure as that of iridium. The LOD of the elements were calculated according to **Equation 5.1** using their different calibration curves.

$$\text{LOD} = 3 \times s_{\text{blank}} / m \quad \dots 5.1$$

Where  $s_{\text{blank}}$  is the standard deviation of the blank and  $m$  is the gradient of the calibration curve. The LOQ which is the smallest analyte concentration that can be measured with an acceptable level of repeatability, precision and accuracy is calculated as 10 times the limit of detection as shown in **Equation 5.2**.

$$\text{LOQ} = 10 \times \text{LOD} \quad \dots 5.2$$

The experimentally determined LOD/LOQ for the different precious metals are reported in **Table 5.6**.

**Table 5.6:** Experimentally determined LOD and LOQ for PGM and gold

Element	LOD (ppm)	LOQ (ppm)
Au	0.000314	0.00314
Ir	0.000240	0.00240
Os	0.000150	0.00150
Pd	0.000177	0.00177
Pt	0.000124	0.00124
Rh	0.000253	0.00253
Ru	0.000154	0.00154

## 5.5 Experimental determination of PGM and gold (Method development)

### 5.5.1 Determination of a suitable internal standard for precious metals using a CRM

#### 5.5.1.1 Preparation of the internal standards stock solutions

The Co, Y, Sc, La and In internal standard stock solutions (1 000 ppm) were prepared in separate volumetric flasks (100.0 mL) from the original standard solution (1 000 ppm). The flasks were acidified using HCl (5.0 mL; 32 %) and filled up to the mark using double distilled water. The solutions were homogenized and left to stabilize for an hour before it was used.

#### 5.5.1.2 Preparation of the precious metals calibration standards (direct calibration method)

The calibration standards for the precious metals were prepared from the original PGM and gold stock solutions (1 000 ppm) to concentrations of 0.0 (blank), 0.1, 0.2, 0.5 and 1.0 ppm in different 100.0 mL volumetric flasks using a 'Transferpette' micro-pipette. Hydrochloric acid (5.0 mL; 32 %) was added to each flask and filled up to the mark using double distilled water. The solutions were mixed to ensure homogeneity and left to stabilize for an hour before it was used.

#### ***5.5.1.3 Preparation of the precious metals calibration standards (internal standard method)***

The calibration standards for the precious metals were prepared from the original PGM and gold stock solutions (1 000 ppm) to concentrations of 0.0 (blank), 0.1, 0.2, 0.5 and 1.0 ppm in different 100.0 mL volumetric flasks using a 'Transferpette' micro-pipette. To each standard solution, aliquots (0.2 mL; 1 000 ppm) of the prepared internal standard solutions (**Section 5.5.1.1**) and HCl (5.0 mL; 32 %) were added and the volumetric flasks were filled up to the mark using double distilled water. The solutions were mixed to ensure homogeneity and left to stabilize for an hour before it was used.

#### ***5.5.1.4 Wavelength and internal standard selection***

CRM solutions (0.7 ppm) in triplicate were prepared by pipetting aliquots of the original CRM solution (7.0 mL; 10.00 ppm) into 100.0 mL volumetric flasks. To each flask, equal volumes of the internal standard (0.2 mL; 1 000 ppm) (**Section 5.5.2.1**) were added. The solutions were acidified with HCl (5.0 mL; 32 %) and the volumetric flasks were filled up to the mark using double distilled water. The solutions were homogenized and left to stabilize for an hour before determined for the precious metals content using standards prepared in **Section 5.5.1.2** (direct calibration method) and **5.5.1.3** (internal standard method). Experimental results of the precious metals obtained after each successive analysis are graphically presented in **Figure 5.10, Section 5.7.2** and the average results recovery are reported in **Table 5.7**.

**Table 5.7:** Average percentage recoveries of the precious metals from the liquid CRM

Average	Ru	Rh	Pd	Os	Ir	Pt	Au
<b>Direct calibration</b>	97(2)	92(6)	95(3)	83 (6)	94(5)	93(1)	98(3)
<b>Sc</b>	<b>100.3(8)</b>	<b>100.0(9)</b>	<b>100.0(6)</b>	<b>89(9)</b>	<b>101(1)</b>	<b>99.4(3)</b>	<b>101.2(5)</b>
<b>Co</b>	102(2)	100.6(9)	100(2)	86(11)	100(6)	99(2)	103(4)
<b>Y</b>	105(4)	99(10)	102(6)	88(12)	101.7(7)	102(2)	105(3)
<b>In</b>	110(3)	104(9)	107(5)	91(18)	111(5)	106(1)	85(45)
<b>La</b>	106(5)	101(11)	88(20)	89(19)	103.9(9)	103(5)	91(30)

Bolded results = highlight overall recoveries of Sc as preferred internal standard

## 5.5.2 Robustness of the selected scandium internal standard method towards acids and EIE's

### 5.5.2.1 Preparation of the scandium internal standards

The calibration standards for the precious metals using scandium as an internal standard was prepared from the original PGM and gold stock solutions (1 000 ppm) to concentrations of 0.0 (blank), 0.1, 0.2, 0.5 and 1.0 ppm in different 100.0 mL volumetric flasks. To each standard solution, equal volumes (0.2 mL; 1 000 ppm) of the prepared scandium internal standard solutions (**Section 5.5.1.1**) and HCl (5.0 mL; 32 %) were added after which the volumetric flasks were filled up to the mark using double distilled water. The solutions were thoroughly mixed to ensure homogeneity and were left to stabilize for an hour before it was used.

### 5.5.2.2 Effects of the acid matrix on the scandium internal standard method

Five CRM solutions (7.0 mL; 10.00 ppm) were prepared from the original stock solution in different 100.0 mL volumetric flasks. Increasing volumes of HCl acid (0.0; 1.0; 3.0; 8.0 and 10.0 mL; 32 %) respectively were added to these CRM solutions. Equal volumes of the Sc internal standard aliquots (0.2 mL; 1 000 ppm) prepared in **Section 5.5.2.1** were added and the volumetric flasks were filled up to the mark using double distilled water. The solutions were homogenized and stabilized for an hour before determined for the precious metals content by the direct calibration and the Sc internal standard methods using the standards prepared in **Section 5.5.1.2** and **5.5.1.3** respectively. The results obtained using these two methods are reported in **Table 5.8**

and **5.9** respectively and are graphically represented in **Figure 5.13** and **5.14** respectively in **Section 5.7.3.1**.

**Table 5.8:** Effects of increasing HCl matrix in the determination of precious metals using the direct calibration method

% HCl increase	Au	Ru	Rh	Pd	Ir	Pt
<b>0</b>	95.4(3)	95.7(0)	93.2(8)	93.9(1)	105.4(6)	92.3(7)
<b>10</b>	94.0(3)	95.8(9)	93.8(3)	92.2(1)	104.7(4)	91.7(0)
<b>30</b>	92.8(2)	94.2(4)	92.1(0)	88.7(7)	102.8(3)	91.0(4)
<b>80</b>	88.7(8)	90.6(4)	92.0(1)	86.4(0)	99.6(2)	88.5(5)
<b>100</b>	88.8(9)	90.2(6)	89.8(1)	85.6(0)	98.8(6)	86.3(2)

**Table 5.9:** Effects of increasing HCl matrix in the determination of precious metals using Sc internal standard method

% HCl increase	Au	Ru	Rh	Pd	Ir	Pt
<b>0</b>	<b>99.7(1)</b>	<b>99.8(5)</b>	<b>100.3(3)</b>	<b>99.8(9)</b>	<b>99.7(8)</b>	<b>99.9(2)</b>
<b>10</b>	99.7(3)	101.7(3)	100.5(7)	100.1(8)	99.0(9)	97.5(6)
<b>30</b>	102.1(2)	101.2(2)	101.0(4)	95.2(4)	96.0(8)	96.9(8)
<b>80</b>	96.2(7)	99.8(5)	103.4(2)	95.0(3)	93.4(6)	95.9(1)
<b>100</b>	99.6(5)	100.1(4)	102.6(9)	93.9(0)	93.3(7)	94.7(7)

Bolded results = optimum level of HCl matrix for precious metals determination

### 5.5.2.3 Preparation of the NaCl stock solution

A sodium chloride stock solution (1 000.00 ppm) was prepared by dissolving 0.1 g of the salt in a 100.0 volumetric flask ( $[\text{Na}^+] = 393.4$  ppm) with double distilled water. The solution was homogenized and left to stabilize for an hour before it was used.

### 5.5.2.4 Effects of increasing sodium content (EIE's) in the determination of precious metal from the CRM

Five CRM solutions (7.0 mL; 10.00 ppm) were prepared from the original stock solution. Increasing  $\text{Na}^+$  concentrations 0.0, 3.9, 11.8, 31.5 and 39.3 ppm respectively were added to these CRM solutions. Equal volumes (0.2 mL; 1 000 ppm) of the Sc internal standard were added and the volumetric flasks were filled up to the mark using double

distilled water. The solutions were homogenized and stabilized for an hour before determined for the precious metals content by the direct calibration and the Sc internal standard methods using the standards prepared in **Section 5.5.1.2** and **5.5.1.3** respectively. The results obtained using these methods are reported in **Table 5.10** and **5.11** respectively and the results are graphically presented in **Figure 5.16** and **5.17** in **Section 5.7.3.2**.

**Table 5.10:** Effects of increasing Na<sup>+</sup> content (EIE's) in the determination of precious metals using the direct calibration method

Added Na <sup>+</sup> concentration (ppm)	Au	Ru	Rh	Pd	Ir	Pt
<b>0.0</b>	95.4(3)	95.7(0)	93.2(8)	93.9(1)	105.4(6)	92.3(7)
<b>3.9</b>	85.2(1)	222.0(0)	65.4(2)	82.8(2)	84.6(2)	73.3(3)
<b>11.8</b>	52.5(3)	213.3(4)	52.5(2)	77.0(4)	66.2(5)	63.6(5)
<b>31.5</b>	35.6(4)	100.8(2)	29.5(8)	47.1(8)	41.9(4)	37.8(5)
<b>39.3</b>	32.3(4)	55.5(9)	26.7(3)	26.2(1)	21.8(4)	17.8(5)

**Table 5.11:** Effects of increasing Na<sup>+</sup> content (EIE's) in the determination of precious metals using Sc internal standard method

Added Na <sup>+</sup> concentration (ppm)	Au	Ru	Rh	Pd	Ir	Pt
<b>0.0</b>	<b>99.2(1)</b>	<b>99.8(5)</b>	<b>100.3(3)</b>	<b>99.0(5)</b>	<b>99.0(0)</b>	<b>99.2(9)</b>
<b>3.9</b>	100.6(0)	100.0(2)	104.9(0)	114.7(8)	97.5(4)	82.9(1)
<b>11.8</b>	113.8(5)	121.7(3)	77.3(9)	117.7(4)	118.4(5)	92.4(3)
<b>31.5</b>	73.0(5)	116.2(6)	149.5(9)	145.9(6)	114.9(9)	120.0(7)
<b>39.3</b>	213.6(7)	88.4(6)	301.7(2)	91.7(1)	365.9(1)	329.4(6)

Bolded results = optimum level of the Na<sup>+</sup> ion concentration of the Sc internal standard method

## **5.6 Determination of precious metals in the geological certified reference material (CRM)**

### **5.6.1 Description of the geological CRM**

The geological CRM used in this study was the PGM bearing Pyroxenite Reference Material-Concentrate (IA-MIM C2). The material is composed of pyroxene, plagioclase,

olivine and serpentine materials originated from the Mimosa Mining Company and Zimasco Holdings. According to the certificate, the material was prepared under standard conditions by the Mimosa Mining Company. The concentrate was obtained after flotation separation. The homogeneity of the stock was measured with respect to its chromium values and was confirmed by the supplier of the material. The material was then further homogenized and separated before bottling by a certified independent laboratory. All the calculations were performed at 95 % confidence interval using a coverage factor of  $k = 2$ . All the reported values were traceable to NIST and the values were obtained by independent methods (see the certificate in the **Appendix**). The certified and the standard deviation values of the precious metals excluding osmium are given in **Table 5.12**.

**Table 5.12:** Certified concentration values of the precious metals in the CRM bearing Pyroxenite Reference Material-Concentrate at 95 % confidence interval

<b>PGM bearing Pyroxenite Reference Material Concentrate</b>		
<b>Constituent</b>	<b>Certified value</b>	<b>STD (95 %)</b>
<b>Cu</b>	3.31 (%)	0.12
<b>Co</b>	0.12 (%)	0.01
<b>Ni</b>	4.28 (%)	0.14
<b>Au</b>	4.90 (µg/g)	0.47
<b>Pt</b>	44.5 (µg/g)	1.68
<b>Pd</b>	33.4 (µg/g)	2.06
<b>Rh</b>	4.01 (µg/g)	0.29
<b>Ru</b>	3.76 (µg/g)	0.51
<b>Ir</b>	2.18 (µg/g)	0.07
<b>Ag</b>	(5.5) (µg/g)	(Not applicable)

### 5.6.2 Digestion of the CRM

CRM samples were first dried at 110 °C in an oven for 48 hours to remove all the traces of moisture. All the coarse solid particles were grounded to a fine powder using a mortar and pestle in order to increase the surface area. The theoretical concentrations in µg/g (ppm) of the precious metals in a 0.5 g CRM sample were 0.049 Au, 0.445 Pt, 0.334 Pd, 0.0401 Rh, 0.0376 Ru and 0.0218 Ir in a 50.0 mL volumetric flask and were found to be well above the LOD's for the different elements (see **Table 5.5**) which

facilitated the continuation of this investigation using Sc as internal standard. All the qualitative and quantitative measurements for the CRM samples were done using ICP-OES which is able to handle increased TDS from the CRM (see **Chapter 4, Section 4.2.4.2.2**).

#### ***5.6.2.1 Preparation of the precious metals calibration standards (direct calibration method)***

The calibration standards for the precious metals were prepared from the original PGM and gold stock solutions (1 000 ppm) to concentrations of 0.0 (blank), 0.01, 0.05, 0.1, 0.2 and 1.0 ppm in different 100.0 mL volumetric flasks using a 'Transferpette' micro-pipette. Hydrochloric acid (5.0 mL; 32 %) was added to each flask and filled up to the mark using double distilled water. The solutions were mixed to ensure homogeneity and left to stabilize for an hour before it was used.

#### ***5.6.2.2 Preparation of the precious metals calibration standards (internal standard method)***

The calibration standards for the precious metals were prepared from the original PGM and gold stock solutions (1 000.00 ppm) to concentrations of 0.0 (blank), 0.01, 0.05, 0.1, 0.2 and 1.0 ppm in different 100.0 mL volumetric flasks using a 'Transferpette' micro-pipette. To each standard solution, aliquots (0.2 mL; 1 000.00 ppm) of the prepared internal standard solutions (**Section 5.5.1.1**) and HCl (5.0 mL; 32 %) were added to the solutions after which the volumetric flasks were filled up to the mark using double distilled water. The solutions were mixed to ensure homogeneity and left to stabilize for an hour before it was used.

#### ***5.6.2.3 Acid assisted microwave digestion of the geological CRM***

Three solid CRM samples (ca. 0.5 g) were dried at 110 °C for 48 hours, accurately weighed and quantitatively transferred to microwave polytetrafluoroethylene (PTFE) vessels. Equal volumes of either HCl (10.0 mL; 32 %), HNO<sub>3</sub> (10.0 mL; 65 %) or *aqua regia* (10.0 mL) was added to each of the PTFE vessels and the mixtures were digested under the microwave conditions specified in **Section 4.2.3, Table 4.1**. The resultant



mixtures were filtered to separate the soluble product from any possible insoluble residue remaining in the reaction mixture after microwave digestion. The filtrates were heated to reduce the acid volume to yield a final volume of approximately 2 mL. Hydrochloric acid (5.0 mL; 32 %) was added to each filtrate solution to match the acid matrix to those of the standard solutions. The analyte solutions were then quantitatively transferred to 50.0 mL volumetric flasks and Sc internal standard (0.2 mL; 1 000 ppm) was added and the volumetric flasks filled up to the mark using double distilled water. The samples were left to stabilize for an hour before determined for the precious metals content using the direct calibration and the Sc internal standard methods with the calibration standards prepared in **Section 5.6.2.1** and **5.6.2.2** respectively. Quantitative results of the precious metals using the direct calibration method are reported in **Table 5.13** and **5.14** respectively and the results are graphically presented in **Figure 5.20** and **5.21** in **Section 5.8.1**.

**Table 5.13:** Quantitative results of precious metals using the direct calibration method in the geological CRM after microwave digestion using different mineral acids

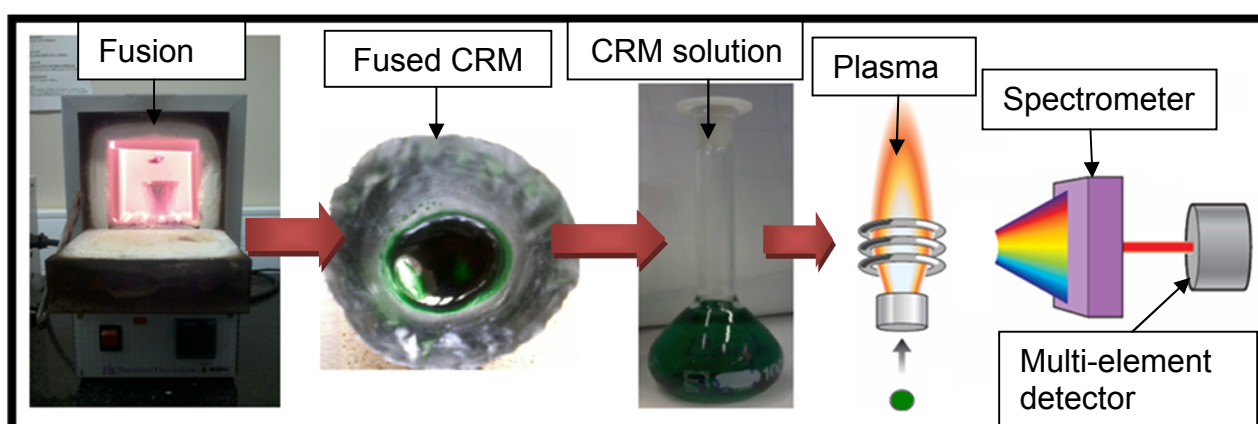
Mineral acid	Ru	Rh	Pd	Ir	Pt	Au
<i>Aqua regia</i>	68.3(7)	77.4(7)	85.7(6)	75.2(1)	89.4(3)	81.4(6)
HCl (32 %)	35.1(4)	58.9(5)	71.0(7)	51.7(9)	42.6(1)	45.0(7)
HNO <sub>3</sub> (65 %)	9.4(9)	26.6(4)	37.3(8)	30.1(6)	25.5(4)	15.8(6)

**Table 5.14:** Quantitative results of precious metals using the Sc internal standard method in the geological CRM after microwave digestion using different mineral acids

Mineral acid	Ru	Rh	Pd	Ir	Pt	Au
<i>Aqua regia</i>	93.2(0)	79.8(1)	88.6(6)	81.7(8)	91.3(9)	83.8(1)
HCl (32 %)	59.1(4)	60.7(0)	73.5(8)	55.6(8)	43.7(6)	52.6(4)
HNO <sub>3</sub> (65 %)	32.4(2)	28.0(6)	41.1(0)	37.1(2)	26.3(5)	23.7(2)

#### 5.6.2.4 Ammonium hydrogen difluoride ( $\text{NH}_4\text{F}\cdot\text{HF}$ ) flux fusion of the geological CRM

Three solid CRM samples (ca. 0.5 g) were thoroughly mixed in a 1:20 ratio with  $\text{NH}_4\text{F}\cdot\text{HF}$ . The mixtures were quantitatively transferred to a platinum crucible and further homogenized before heated in an oven. The sample mixture was heated for an hour whilst gently increasing the temperature (optimum temperature 250 °C) until a homogeneous melt was formed. The resultant melt was cooled at room temperature until a glassy melt was formed. The melt was completely dissolved by the addition of distilled water (20 mL) and stirred until a green solution was obtained. *Aqua regia* (10 mL) was added to the resultant solution and heated until the final volume was approximately 5 mL. A clear green solution was obtained and was quantitatively transferred into a 50.0 mL volumetric flask. Equal volumes of HCl (5.0 mL; 32 %) and Sc internal standard (0.2 mL; 1 000 ppm) were added and the volumetric flasks were filled up to the mark using double distilled water. The solutions were homogenized and left to stabilize before analyzed for PGM and gold content using the direct and the Sc internal standard methods with the calibration standards prepared in **Section 5.6.2.1** and **5.6.2.2** respectively. A summary of the experimental procedure of the CRM analysis is given in **Figure 5.9** and the quantitative results of the determination of the precious metals are given in **Table 5.15**.



**Figure 5.9:** Experimental procedure for the determination of PGM and gold in the CRM using the fusion method

**Table 5.15:** Quantitative results of precious metals after fusion digestion of the geological CRM with  $\text{NH}_4\text{F}\cdot\text{HF}$  flux

Method	Ru	Rh	Pd	Ir	Pt	Au
Direct calibration (%)	98 (7)	97 (7)	98 (3)	96 (2)	72(4)	97 (8)
Sc internal standard (%)	<b>101(7)</b>	<b>100.4 (6)</b>	<b>99 (7)</b>	<b>100 (5)</b>	<b>102 (4)</b>	<b>100.9 (8)</b>

The bolded results = best possible method for the accurate determination of all precious metals in the geological CRM

## 5.7 Discussion of results

### 5.7.1 Selection of an internal standard element

The internal standard calibration method was described in the previous chapters (see **Chapter 3, Section 3.2.4.1** and **Chapter 4, Section 4.2.4**) as the preferred method for the quantification of precious metals. One of the most distinctive attributes of this method is its ability to correct for small matrix differences and instrumental drifts during spectrometric analysis. Different selection criteria for the best possible internal standard element were employed in this study in an attempt to establish the most suitable internal standard that can be used to accurately quantify all the precious metals individually or simultaneously (mineral ore). These selection criteria included those discussed in **Chapter 3, Section 3.2.5** with similar first ionization potentials, excitation energies and volatilization rates with the precious metals and absence from PGM ores. Prior to the selection of the most suitable internal standard element, efforts were made to evaluate the most commonly used internal standard in the determination of precious metals. Cobalt was also selected as a potential internal standard element for precious metals determination based on its ability to accurately quantify rhodium as was shown in our previous study.<sup>180</sup> Yttrium on the other hand is highly recommended by ISO<sup>181</sup> in the determination of PGM from re-cycled materials and was also considered as a potential internal standard for the determination of precious metals. Other elements which were chosen include scandium and lanthanum which are all members of rare earth metals

<sup>180</sup> T.T. Chiweshe, *Quantification of rhodium in series of inorganic and organometallic compounds*, MSc thesis, University of the Free State, Bloemfontein, South Africa, (2010).

<sup>181</sup> R. Kovacevic, M. Todorovic, D. Manojlovic and J. Mutic, *J. Iran. Chem. Soc.*, (2008), 5 (2), pp. 336 - 341.

(REE). Indium was also included as a potential internal standard on the basis that it is seldom found in naturally occurring PGM and gold mineral ores. Additionally, these metals are widely employed in spectrometric analysis as internal standards in the quantitative determination of base metals (Ni, Zn, Cr, Mn, *etc*).<sup>182,183</sup> A thorough qualitative analysis was performed on all the samples prior to the selection of the suitable internal standard to ensure that the chosen internal standard element was completely absent from the analyte solutions.

The ionization and excitation energies (**Table 5.16**) of the selected elements (Co, Y, Sc, La and In) were also examined and compared to the PGM in an effort to identify possible candidates to be used as internal standards for precious metals quantification. Previous reports and literature<sup>184</sup> suggests that this is a convenient method to identify possible internal standards for certain metals or metal groups.

**Table 5.16:** Theoretical excitation and ionization energies of PGM and gold as well as the potential internal standards

Elements	Excitation energy (kJ·mol <sup>-1</sup> )	1 <sup>st</sup> Ionisation energy (kJ·mol <sup>-1</sup> )
Rh	449	720
Ru	441	711
Pd	470	805
Os	740	840
Ir	757	880
Pt	790	870
Au	970	890
<b>Possible internal standards</b>		
Sc	216	631
Co	297	758
Y	379	616
In	488	558
La	501	538

<sup>182</sup> I.B. Brenner, A.E. Watson, G. M. Russell and M. Goncalves, *Chem. Geo.*, (**1980**), 28, p. 321.

<sup>183</sup> A.E. Watson, *ICP Inf. Newslett*, (**1980**), 5, p. 533.

<sup>184</sup> F.E. Beamish, J.C. Van Loon and C.L. Lewis, "*Analysis of Noble Metals: Overview and Selected Methods*", Academic Press, New York, USA. (**1977**).

The comparison of the excitation energy values of Sc, Co and Y to those of the precious metals clearly shows no similarity in energy values and are in fact much lower than that of any of the precious metals. The excitation energy of In and La on the other hand appears to be closer to the excitation energy of some of the PGM in an appreciable range (441 - 470 kJ·mol<sup>-1</sup>). This similarity in the excitation energies suggest the possibility that In and La might be used as suitable internal standards for the quantification of Rh, Ru and Pd. However, this selection method for the determination of the most suitable internal standard using the excitation/ionization energies was found to be unsuccessful as the experimental results obtained using this method (see **Section 5.7.2**) were either too high or low compared to the expected theoretical values.

The difference between the 1<sup>st</sup> ionization energies of the internal standards and that of the precious metals also appears to be too large (e.g. between La and Au the difference is 352 kJ·mol<sup>-1</sup>) with no obvious candidate to be used as internal standard from this selection process possible. It is only Co that possesses a 1<sup>st</sup> ionization energy that are in the precious metal ionization range range (710 - 810 kJ·mol<sup>-1</sup>) and appears to be a suitable internal standard for Rh, Ru and Pd. From our previous study, this similarity in the 1<sup>st</sup> ionization energy between the Co internal standard and Rh analyte was assumed to have been the reason behind the rhodium total recovery (100 %) from the CRM, inorganic salts and different organometallic compounds.<sup>185</sup> The success of this selection method towards the Rh recovery was largely attributed to the comparison of the 1<sup>st</sup> ionization energies of a single internal standard (Co) to a single analyte (Rh) in a 1:1 ratio respectively.

An alternative criterion based on the selection of an emission line(s) or mass/charge (m/z) ratio(s) of both the internal standards and the precious metals was considered. This criterion seeks to select the most stable, un-interfered and sensitive atomic or ionic line(s) and m/z ratio(s) which is not easily affected during the measurement process (see **Chapter 4, Section 4.2.4.3**). The controversy behind the use of ionic-ionic, ionic-atomic or atomic-atomic lines between the internal standard element and the precious metals was also considered and was experimentally examined as outlined in **Section 5.4.2** to determine the best combination of lines between the internal standard and the

---

<sup>185</sup> T.T. Chiweshe, W. Purcell and J. Venter, *S. Afr. J. Chem.*, (2012), 66, pp. 7 - 16.

precious metals (**Table 5.17**). The results of this investigation are discussed in detail in **Section 5.7.2**. From this investigation it was concluded that different line combinations *i.e.* ionic-ionic, ionic-atomic or atomic-atomic between the internal standard and the analyte species can be used in the determination of precious metals on condition that these lines are not interfered with and are sensitive enough to mimic the behaviour of the analyte species.

**Table 5.17:** A combination of the best selected ICP-OES lines for precious metals (bolded) against the selected lines for the internal standards

Elements	Rh	Ru	Pd	Os	Ir	Pt	Au
<b>Sc*</b>	ionic- <b>atomic</b> (361.384 - <b>343.489</b> )	ionic- <b>ionic</b> (361.384 - <b>240.272</b> )	ionic- <b>atomic</b> (361.384 - <b>340.458</b> )	ionic- <b>ionic</b> (361.384 - <b>228.226</b> )	ionic- <b>ionic</b> (361.384 - <b>224.268</b> )	ionic- <b>ionic</b> (361.384 - <b>203.646</b> )	ionic- <b>atomic</b> (361.384 - <b>267.595</b> )
<b>Co*</b>	ionic- <b>atomic</b> (238.892 - <b>343.489</b> )	ionic- <b>ionic</b> (238.892 - <b>240.272</b> )	ionic- <b>atomic</b> (238.892 - <b>340.458</b> )	ionic- <b>ionic</b> (238.892 - <b>228.226</b> )	ionic- <b>ionic</b> (238.892 - <b>224.268</b> )	ionic- <b>ionic</b> (238.892 - <b>203.646</b> )	ionic- <b>atomic</b> (238.892 - <b>267.595</b> )
<b>Y*</b>	ionic- <b>atomic</b> (371.030 - <b>343.489</b> )	ionic- <b>ionic</b> (371.030 - <b>240.272</b> )	ionic- <b>atomic</b> (371.030 - <b>340.458</b> )	ionic- <b>ionic</b> (371.030 - <b>228.226</b> )	ionic- <b>ionic</b> (371.030 - <b>224.268</b> )	ionic- <b>ionic</b> (371.030 - <b>203.646</b> )	ionic- <b>atomic</b> (371.030 - <b>267.595</b> )
<b>In</b>	ionic- <b>atomic</b> (230.606 - <b>343.489</b> )	ionic- <b>ionic</b> (230.606 - <b>240.272</b> )	ionic- <b>atomic</b> (230.606 - <b>340.458</b> )	ionic- <b>ionic</b> (230.606 - <b>228.226</b> )	ionic- <b>ionic</b> (230.606 - <b>224.268</b> )	ionic- <b>ionic</b> (230.606 - <b>203.646</b> )	ionic- <b>atomic</b> (230.606 - <b>267.595</b> )
<b>La*</b>	ionic- <b>atomic</b> (333.749 - <b>343.489</b> )	ionic- <b>ionic</b> (333.749 - <b>240.272</b> )	ionic- <b>atomic</b> (333.749 - <b>340.458</b> )	ionic- <b>ionic</b> (333.749 - <b>228.226</b> )	ionic- <b>ionic</b> (333.749 - <b>224.268</b> )	ionic- <b>ionic</b> (333.749 - <b>203.646</b> )	ionic- <b>atomic</b> (333.749 - <b>267.595</b> )

\*Element does not possess atomic lines

From the above discussion it can be clearly seen that the commonly used criteria of selecting the internal standard based on the excitation and 1<sup>st</sup> ionization energies could not be applied in this research study. These selection procedures were reported to be mostly centred on the similarities between the excitation and the 1<sup>st</sup> ionization energies of a single internal standard to single analyte specie in a ratio of 1:1 respectively. The use of this selection method was found to be inapplicable to the selection of a suitable internal standard for all the precious metals. Therefore the identification and selection of the most appropriate internal standard in this investigation is based on the best analytical results obtained from using the optimum analytical line combinations of the internal standard and the precious metals. The final internal standard was selected based on the quantitative results which showed high accuracy (recovery), repeatability and the low uncertainty (standard deviations) obtained for the different internal standards using a CRM to ensure measurement traceability.

<sup>186</sup> R.K. Winge, V.A. Fassel, V.J. Peterson and M.A. Floyd, *Inductively coupled plasma-atomic emission spectroscopy*, Elsevier science publishers B.V, (1985).

### 5.7.2 Determination of the suitable internal standard for the quantification of precious metals in the CRM

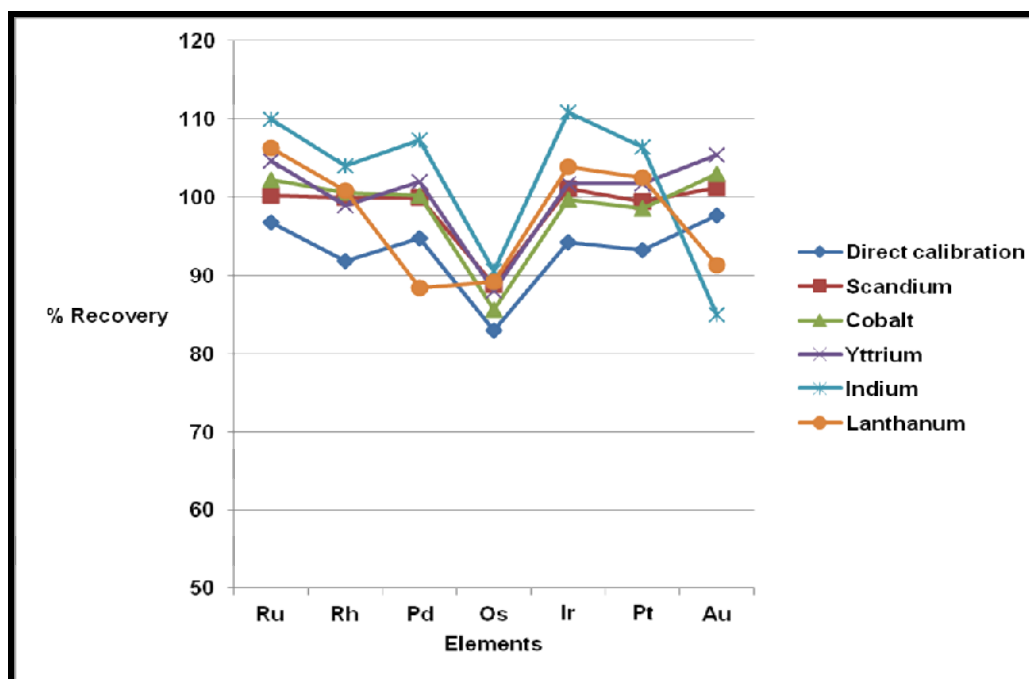
The average percentage recoveries obtained using the direct calibration method showed that Ru and Au had the highest percentage recovery (ca. 98 %) with the remaining metals (Rh, Pd, Ir and Pt) in the range 92 - 95 % except for Os (83 %) (see **Table 5.7, Section 5.5.1.4**). These low percentage recoveries obtained for most of the elements using the direct calibration method indicate that this method is most probably sensitive to the interferences by the large number of elements present (7 PGM) in the analyte solution. Other possibilities to account for these low percentage recoveries using this method include the effects of background emissions, acid matrices and instrumental drifts which were previously reported to limit this method (see **Chapter 4, Section 4.2.2**).

The average results obtained from the preliminary investigation of the most suitable internal standard showed excellent overall recovery (99 % +) of the precious metals except for Os (ca. 89 %) using Sc internal standard (see **Table 5.7** and **Figure 5.10**). Quantitative results obtained using In and La as internal standards fluctuated below (< 92 % for Au, Pd and Os) and above (max. 111 % for Ru, Rh, Ir and Pt) the expected theoretical values. This fluctuation suggests the instabilities of these internal standards' emission intensities or their inability to mimic the behavioural patterns of the precious metals during the sample measurement. Experimental results obtained from using Y as internal standard showed an average total recovery (100 % plus) of Ru, Pd, Ir, Pt and Au with an average percentage recovery of Rh and Os below the expected values. Average quantitative results obtained using Co as internal standard showed a remarkable total recovery (ca. 99 % +) of Ru, Rh, Pd, Ir, Pt and Au except for Pt and Os (ca. 86 %). Percentage recoveries obtained using both Co and Y internal standards for rhodium determination were both in agreement with the results obtained from a previous study.<sup>187</sup> From this study by Chiweshe it was found that the recovery of Rh was affected by the presence of interfering ions such as transition and alkaline metals (above 10 ppm) in the presence of Y as an internal standard. The quantitative results

---

<sup>187</sup> T.T. Chiweshe, *Quantification of rhodium in series of inorganic and organometallic compounds*, MSc thesis, University of the Free State, Bloemfontein, South Africa, (2010).

obtained using this internal standard were found to be either false-high or false-low depending on the concentration of the interfering ions.



**Figure 5.10:** Average percentage recovery of precious metals from the liquid CRM in the determination of the best internal standard

The quantitative results obtained using Sc, Co, Y, In and La indicates that these metals can be divided into two groups (see **Table 5.7, Section 5.**), namely those recovering generally above 100 % (Y, In and La) and those recovering almost 100 % (Sc and Co). The direct calibration method was found to yield percentage recoveries lower than the expected theoretical values. The over-estimation of results as shown from the use of Y, In and La is commonly associated with the differences in the physical behavioural properties such as ionization and emission intensities between the internal standard and the analyte.<sup>188</sup> On the other hand, the under-estimation of the quantitative results of the precious metals as shown for Os, Pd and Au using both In and La is mostly a result of the suppression of the analyte or internal standard's emission intensities.<sup>189</sup>

The experimental results obtained for the determination of a suitable internal standard for precious metals clearly shows no correlation between this selection criteria of using

<sup>188</sup> S.A. Rabb and J.W. Olesik, *Spectrochimica Acta Part B*, (2008), 63, pp. 244 - 256.

<sup>189</sup> G.J. Schmidt, W. Slavin, *Anal. Chem.*, (1982), 54, pp. 2491 - 2495.



the excitation/ionization energies and the percentage recoveries. A typical example in this case was that of the selection of In and La metals using the 1<sup>st</sup> ionization energies as the most probable internal standards for the quantification of Ru, Rh and Pd. The quantitative approach method revealed higher percentages recoveries for Rh, Ru and Pd (+ 105 %) with standard deviations of approximately  $\pm 9$  using In as internal standard. On the other hand, fluctuating percentage recoveries using La were obtained with higher percentage recoveries of Ru and Rh (+ 101 %) with standard deviations of approximately  $\pm 8$  accompanied by a lower recovery of Pd (88 %) with a standard deviation of approximately  $\pm 20$ . This selection criterion was found to be unsuitable in this study and instead an alternative method based on the selection of an internal standard based on the emission lines was investigated and will be discussed in the next Section.

Also notable from this study is that all the internal standards recover Os at lower than expected values, suggesting either their inability to correct for Os emission line fluctuations or the incompatibility (instability or volatilisation) of the Os of the applied chemical environment. The overall percentage recovery of Os was found to be decreasing using both the direct and the internal standard addition methods. This decrease in the percentage of Os recovery was found to be in the range of *ca.*  $\pm 15$  %. However, excellent percentage recoveries of Os were obtained in a preliminary investigation using Sc and Co (*ca.* 99 + and 98 % respectively) as internal standards. These results suggested that total recovery of Os can be achieved within a few hours of having prepared either the standards or the analyte solutions. This decrease in the Os percentage recovery was initially attributed either to precipitation or the vaporization of Os within the solution. This uncertainty in the Os percentage recovery prompted a further investigation into the Os chemistry to determine the optimum conditions for Os quantification (see **Chapter 6**).

Overall, the quantitative results obtained using Sc internal standard showed small standard deviations of approximately  $\pm 0.9$  % (excellent precision) compared to the other evaluated internal standards. Although Co has showed promise as internal standard for most of the precious metals in solution, the overall results showed less precision with standard deviations of  $\pm 6$  %. Furthermore, the use of Sc as an internal standard was seen as a step closer in establishing an effective and reliable internal

reference element (excellent recovery and small standard deviations) for the majority of PGM and gold, as was indicated as one of the objective of this research project (see **Chapter 1, Section 1.2**).

The experimental results obtained using the Sc internal standard method also clearly showed that total recoveries of Ir, Pt and Ru were obtained using ionic-ionic (**Table 5.17**) lines whilst Rh, Pd and Au were obtained using ionic-atomic lines. The use of different combinations of lines such as atomic-atomic or ionic-ionic lines as discussed in **Chapter 4, Section 4.2.4.3** was found not to have a notable effect on the quantitation of the precious metals using the Sc internal standard. The success of this line pair selection required that care is taken in choosing lines that are not interfered by other species in the solution and are also sensitive enough to mimic the emission patterns of the analyte signals. Further investigations using this method under the current experimental conditions were used to determine the limitations (robustness) of this method in different acid and EIE's (un-matched) matrices.

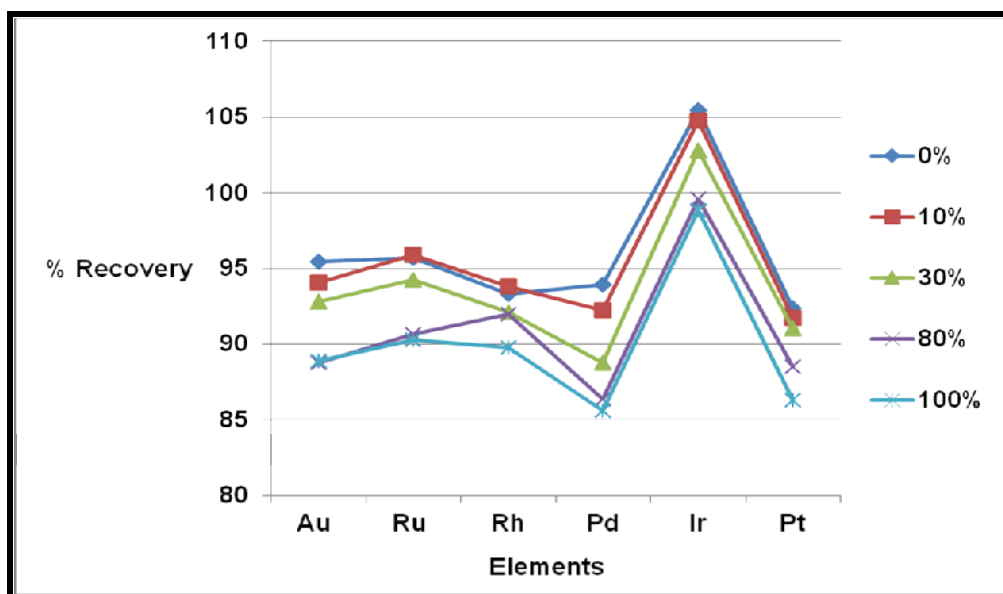
### **5.7.3 Robustness of the selected scandium internal standard method towards acids and EIE's**

The effects of EIE's and the use of an unmatched acid matrix in precious metals determination were also investigated in order to determine the limitations and the robustness of the developed Sc internal standard method. These tests were necessary in order to establish the highest level of interference permissible to this method. The effects of EIE's and the acid matrix on Os as element were excluded since its optimum conditions for its accurate determination were still not established. The most commonly used acid (HCl) in sample preparation and stabilization of PGM and gold standards and analyte solutions was used to determine the effects of the unmatched acid matrix. Optimum ICP-OES conditions which were employed in the previous experimental determination were used in this part of the study.

#### **5.7.3.1 Effects of the acid matrix on the scandium internal standard method**

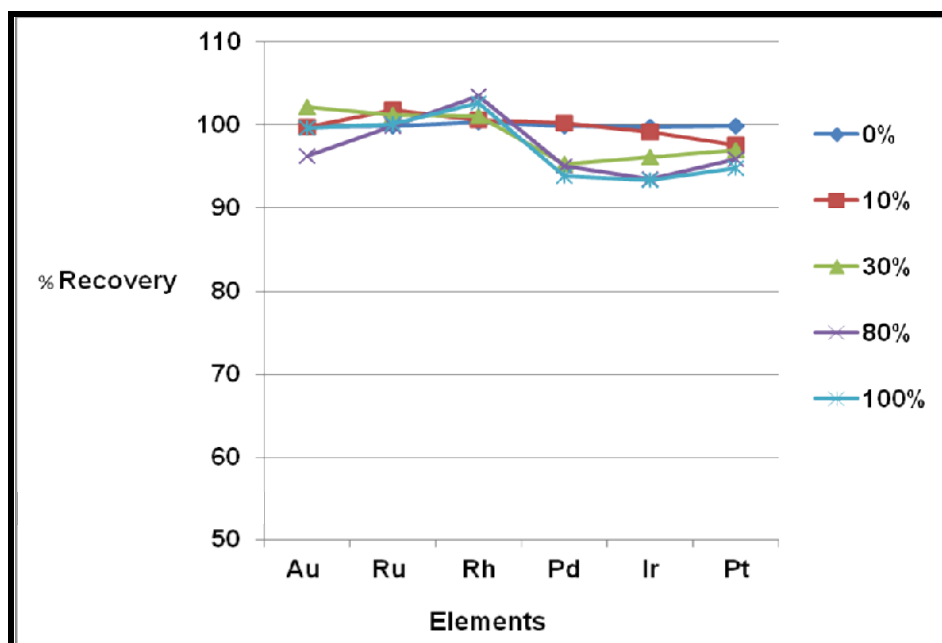
Quantitative results obtained from this investigation revealed that the increase in HCl matrix in the CRM solutions had a profound effect on the total recovery of the precious

metals. Both the direct calibration and Sc internal standard methods were shown to be affected by this increment in HCl concentrations (unmatched HCl matrix). Results obtained using the direct calibration method showed that the addition of extra HCl decreases the percentage recovery of precious metals compared to acid matched solutions except for Ir, as shown in **Figure 5.11**.



**Figure 5.11:** Effects of unmatched HCl acid matrix in the determination of precious metals using the direct calibration curve

The effects of unmatched HCl matrix were found to decrease the percentage recovery of Au, Ru, Rh, Pd and Pt from approximately 95 to 85 % with the increase in HCl content using the direct calibration. Iridium on the other hand was found to yield higher than expected percentage recovery from approximately 93 to 105 % with the increase in HCl matrix. Total percentage recoveries of the precious metals on the other hand were also obtained from solutions with matched HCl matrices. These results indicated that Sc is only effective as internal standard which succeeds in the accurate recovery of the PGM when matrix matching was applied to the reaction mixture (**Figure 5.14**). Quantitative results (**Figure 5.12**) clearly shows that an increase of 10 % in HCl concentration had only a small effect on the PGM recovery as indicated by the good percentage recoveries of + 98 % for all the precious metals. (see **Table 5.9, Section 5.5.2.2**). The percentage recoveries of precious metals were shown to fluctuate above (Ru and Rh) and below (Au, Pd, Ir and Pt) as the HCl matrix was increased from 10 to 100 %.

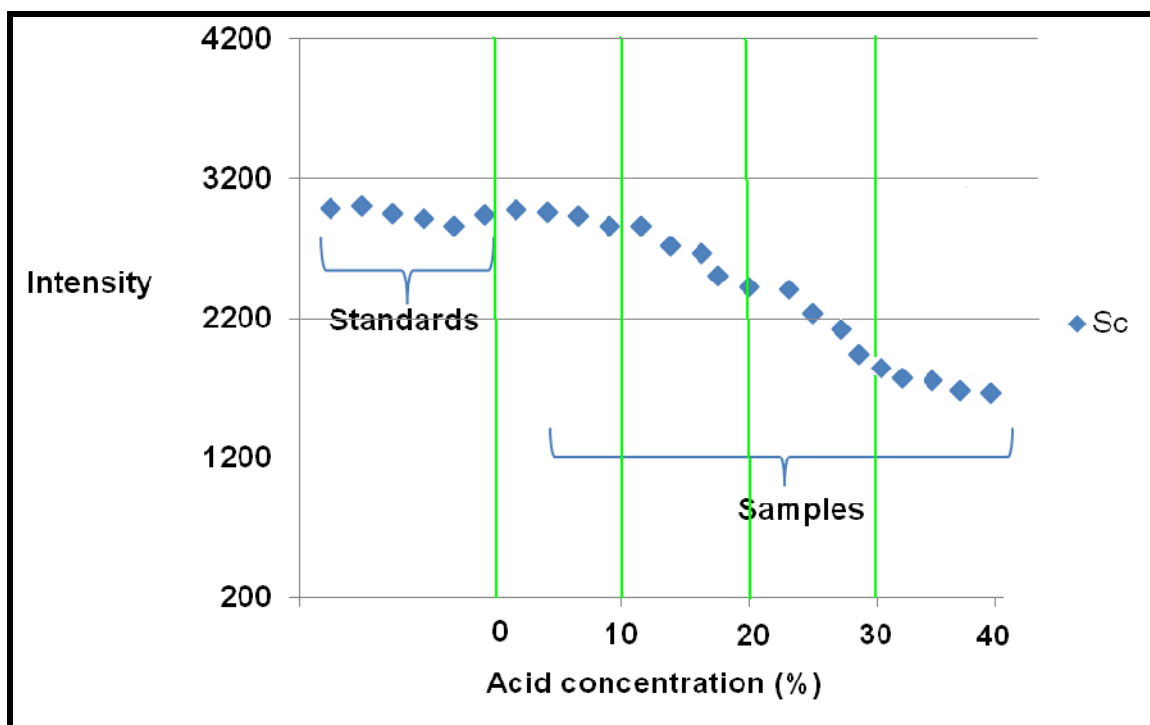


**Figure 5.12:** Effects of unmatched HCl acid matrix in the determination of precious metals using the Sc internal standard

The decrease in the precious metals percentage recovery may have been the result of factors such as viscosity and mobility changes of the CRM solutions compared to those of the calibration standards. Less viscous solutions are easily volatilized compared to highly viscous solutions and this difference has the potential to affect the migration of the analyte solution to reach the nebulizer. These changes in the viscosity of the CRM solutions lower the concentration levels of precious metals contained in a droplet size. This phenomenon was shown to be in agreement with the decrease in most of the percentage recoveries of precious metals using both the internal standard and the Sc internal standard method.

The emission intensities of Sc and precious metals were monitored to determine the extent at which increasing in the HCl matrix affected these emission signals. Both the emission intensities of the Sc and the precious metals were found to be decreasing as the HCl concentration was increased as shown for Sc in **Figure 5.13**. The Sc emission signals obtained in CRM solutions containing below 10 % HCl matrix were shown to be unaffected by this difference. It was assumed that the suppressed of precious metals emission intensities when the HCl matrix is below 10 % were able to be compensated for, since the emission intensities of Sc were not affected under this percentage range.

This ability to resist the suppression of the Sc emission intensities due to the increase of the HCl matrix (below 10 %) was found to be consistence with the total percentage recovery (+ 100 %) obtained for Au, Rh, Ru, Pd and Ir except for Pt *ca.* 98 %.

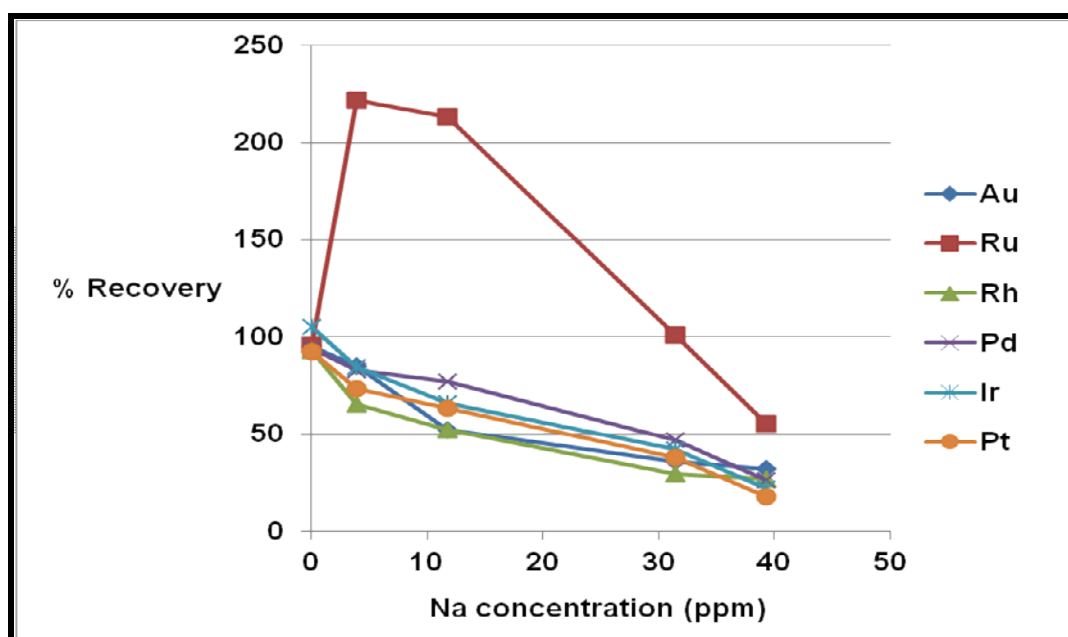


**Figure 5.13:** The effects of increasing HCl acid matrices on the Sc emission intensities

#### **5.7.3.2 Effects of increasing sodium content (EIE's) on the scandium internal standard method**

Sample preparation of geological samples commonly involves fusion with a salt (flux) in a known ratio. This digestion procedure has been reported to convert the solid particles to a liquid analyte solution which forms the basis of quantitative analysis in wet chemistry as discussed in **Chapter 4, Section 4.3.3**. However, fusion methods have a major drawback of introducing EIE's into the analyte solutions which have the potential to affect the quantification of precious metals. The majority of the fluxes used in precious metals digestion were discussed in **Chapter 4, Table 4.1** and most of these fluxes contain  $\text{Na}^+$  as cation which is one of the members of the so-called EIE's. An investigation was conducted to determine the effects of  $\text{Na}^+$  ion concentration on the recovery of the precious metals using both the direct calibration and the Sc internal standard method.

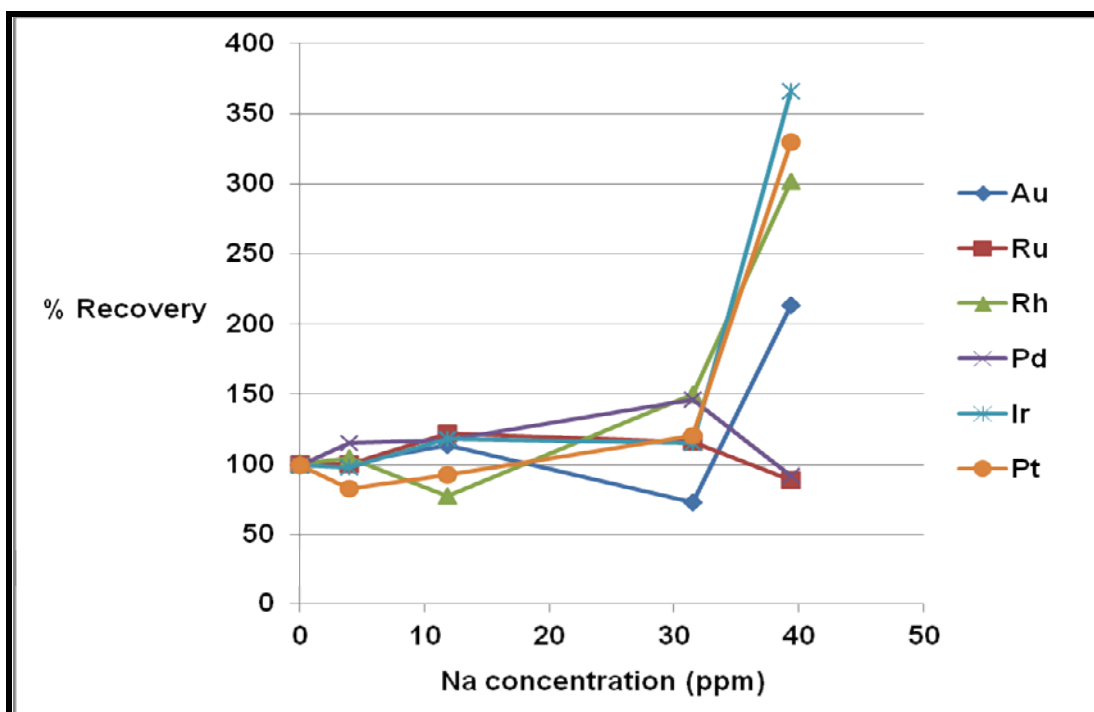
Quantitative results obtained from this part of the investigation clearly showed that the effect of  $\text{Na}^+$  ion concentration in both the direct calibration and the Sc internal standard were different (see **Table 5.10**). Results obtained using the direct calibration method showed a decrease in the percentage recoveries of Au, Rh, Pd, Ir and Pt except for Ru with an increase in the  $\text{Na}^+$  concentrations in the CRM solutions (**Figure 5.14**). This decrease in the percentage recovery of the precious metals is believed to be due to the suppression of the emission signals of Au, Rh, Pd, Ir and Pt. On the other hand, the increase in the Ru percentage increase was also believed to have been the result of the Ru signal enhancement. These uncorrected emission intensities from the direct calibration method (**Chapter 4, Section 4.2.2**) were found to yield incorrect (false-low and false-high) measurements which made this method unreliable when working with samples at high or un-matched EIE's.



**Figure 5.14:** Effects of increasing Na ions concentrations (EIE's) in the determination of precious metals using the direct calibration method

The results obtained using Sc as internal standard showed total percentage recoveries (100 %) of all the precious metals in matched CRM solutions (zero  $\text{Na}^+$  ions, EIE's) (see **Table 5.9 and 5.11**). At high  $\text{Na}^+$  ions (EIE's) concentration level (above 5 ppm) the quantitative results of precious metals were found to fluctuate inconsistently below and above the theoretical values (**Figure 5.15**). Large deviations in the percentage

recoveries of precious metals were observed after the addition of 30 ppm of the  $\text{Na}^+$  ions to the samples solutions.



**Figure 5.15:** Effects of Na content (EIE's) in PGM and gold recovery using the Sc internal standard method

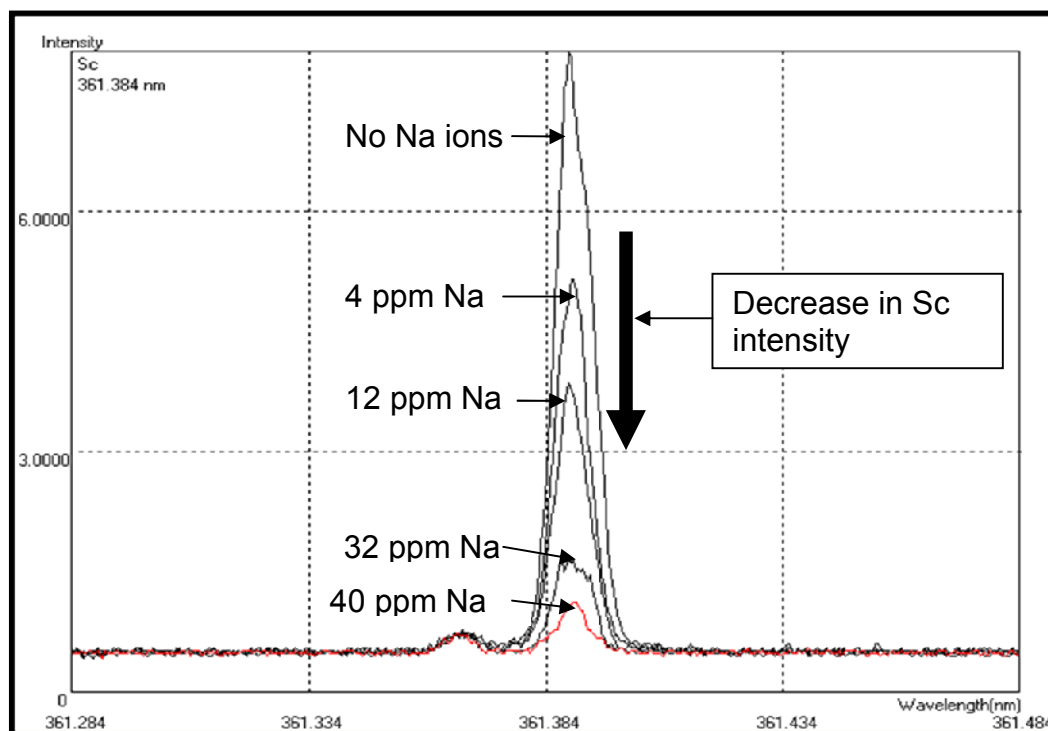
The influence of the addition of  $\text{Na}^+$  ions on precious metals recovery was again different for the different elements. False-low recoveries were obtained for Ru (88 %) and Pd (92 %) and false-high recoveries for Au (214 %), Rh (302 %), Ir (366 %) and Pt (329 %) using Sc as internal standard method. These fluctuations were assumed to have been the result of either the suppression or enhancement (above 5 ppm addition of  $\text{Na}^+$  ions) of the Sc or the precious metals emission intensities to yield these poor percentage recoveries.

The experimental results obtained for the precious metals using Sc as internal standard (see **Table 5.11**) revealed that this method was very sensitive to slight increments in  $\text{Na}^+$  ion concentration (above 5 ppm). The percentage recovery of Rh and Pd obtained after a slight increase of above 5 ppm of  $\text{Na}^+$  ion concentration showed a higher percentage recovery (above 104 %) of these metals using Sc as internal standard. Furthermore, the percentage recovery of Ir and Pt were also found to be decreasing from initial recovery of 100 to 98 % and 100 to 83 % respectively at the same level of  $\text{Na}^+$  ion

concentration. However, total recoveries of 100 % for Au and Ru were obtained suggesting that the Sc internal standard method was able to resist the effects of  $\text{Na}^+$  ions at this level (ca. 5 ppm) for these metals. Quantitative results of the precious metals obtained at high  $\text{Na}^+$  ion concentration above 30 ppm were shown to deviate considerably from the true values (theoretical values) indicating the loss of accuracy and also precision as shown by the high standard deviation ca.  $\pm 9$  in both methods. Overall, the determination of precious metals using both the direct calibration and the Sc internal standard method was found to be affected by the increase in  $\text{Na}^+$  ions (EIE's) in solution. The effect of EIE's were reported in **Chapter 4, Section 4.2.4.2.2** to increase the electron density of the ICP-OES/MS plasma which commonly results in the suppression of either the internal standard or analyte emission signals or both.

The effect of  $\text{Na}^+$  ions (EIE's) on Sc emission intensities using the ICP-OES profile function for precious metals determination was experimentally investigated. Results obtained from this separate qualitative investigation indicated the degree of suppression of the selected Sc emission line with an increase in  $\text{Na}^+$  ion concentration. This effect of increasing the  $\text{Na}^+$  ions in the analyte solutions was also assumed to affect the precious metals emission intensities in almost the same manner. More emphasis was put on the Sc since its emission intensities possessed the ability to compensate for the fluctuations in the precious metals signals. This observed decrease in Sc emission intensity is believed to be part of the source that contributes to the error of element recovery which is observed at high  $\text{Na}^+$  concentrations (**Figure 5.16**).





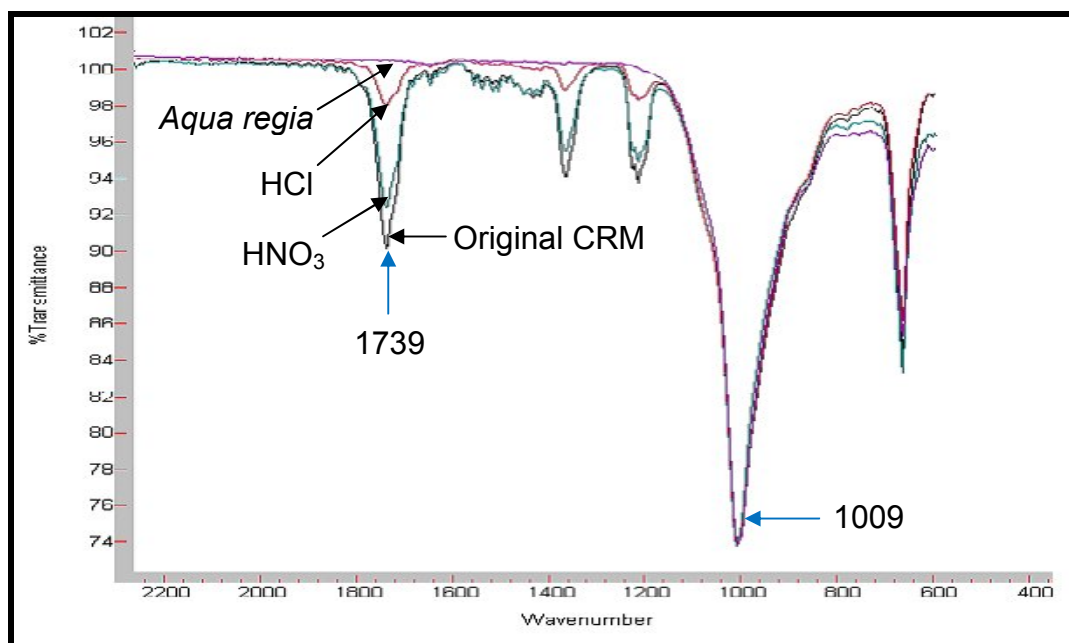
**Figure 5.16:** Effects of increasing Na content (EIE's) on the Sc internal standard in the determination of precious metals using the ICP-OES at 361.384 nm

## 5.8 Determination of precious metals in the geological certified reference material (CRM)

### 5.8.1 Determination of precious metals in the geological CRM after microwave digestion

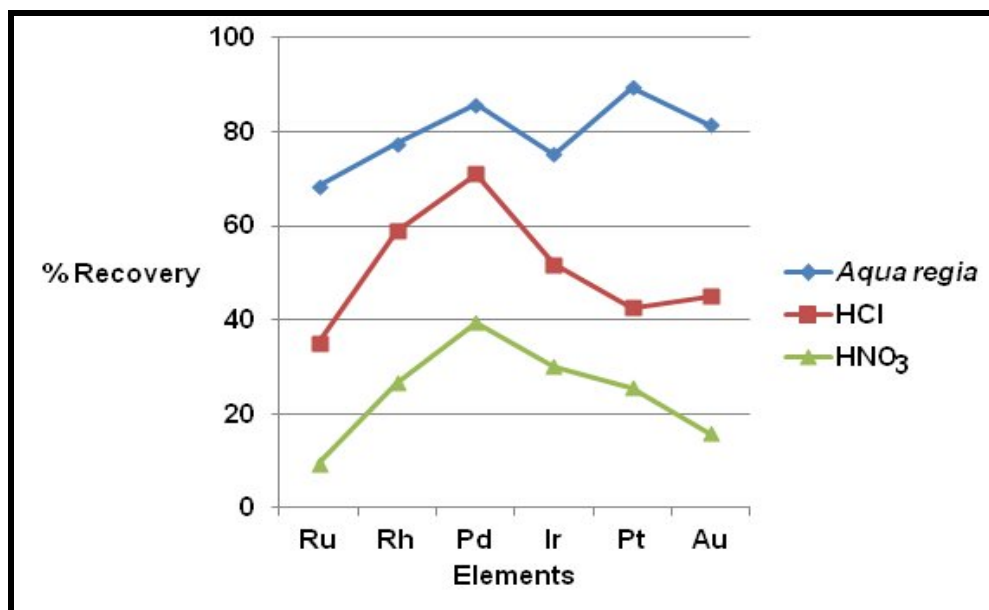
Microwave digestion of the CRM using microwave was shown to yield an incomplete digestion which was evidenced by the insoluble residue that remained in the digestion vessels. Fairly high percentage recoveries of precious metals (see **Table 5.13** and **5.14**) were obtained using *aqua regia* in above mentioned digestion and *ca.* 68 % for the direct calibration and above *ca.* 80 % for the Sc internal standard method were obtained. The order of the precious metals percentage recoveries in both methods were shown to increase in the order  $\text{HNO}_3 < \text{HCl} < \text{aqua regia}$ . The colour of the collected residue obtained from the three mineral acids used (*aqua regia*, HCl and  $\text{HNO}_3$ ) also differed considerably. The residue remaining after  $\text{HNO}_3$  dissolution was almost the same as that of the original CRM (grey) suggesting no dissolution of the CRM whilst the residues obtained after HCl and *aqua regia* dissolution were brown and

light yellow respectively signifying an incomplete dissolution of the CRM. These differences in colour intensities gave a good insight of the changes that might have occurred in the CRM sample during the digestion process. Apart from the colour differences, no significant differences in the final masses (after drying) between the residues and the original CRM samples were observed. Further characterization of the residue was carried out using IR to quantify the chemical changes that occurred in the CRM during the digestion process (**Figure 5.17**).



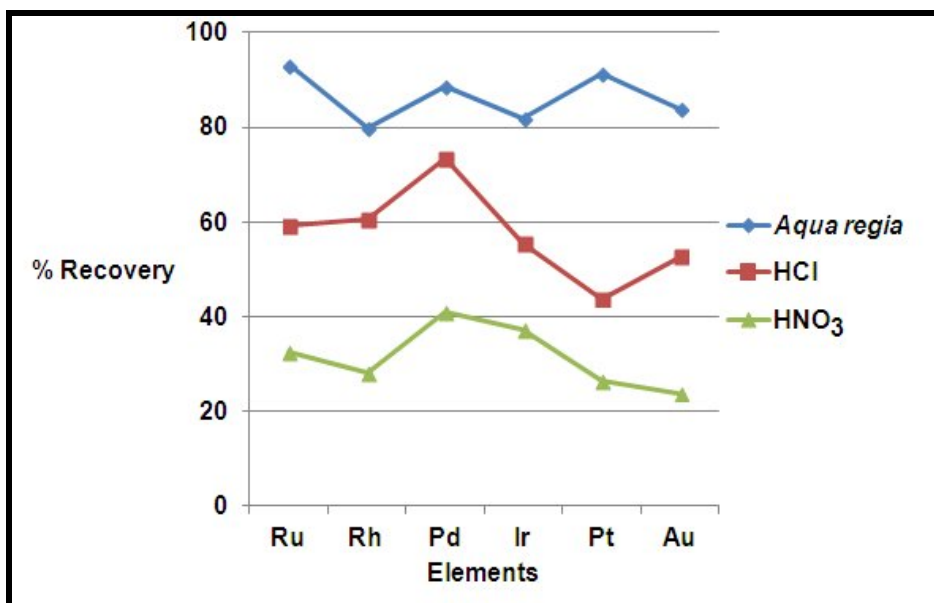
**Figure 5.17:** Infrared spectrum of the digested CRM residues in different mineral acids

The IR spectra showed significant changes of the stretching frequency in the region of  $1\,739\text{ cm}^{-1}$  which signify a change in the chemical composition between the original CRM and the resultant solids after digestion. The decrease in the stretching frequency at  $1\,739\text{ cm}^{-1}$  was characterized by an increase in the percentage recovery of precious metals as shown by the results in **Figure 5.18**. Due to this incomplete digestion of the geological CRM, low percentage recoveries of the precious metals were obtained using both the direct and the Sc internal standard method.



**Figure 5.18:** Quantitative results of the CRM digested using the direct calibration method after microwave digestion in *aqua regia*, HCl and HNO<sub>3</sub>

The increase in the percentage recoveries of precious metals were found to be in the opposite order of the peak strength (see **Figure 5.17**) CRM > HNO<sub>3</sub> > HCl > *aqua regia* at 1 739 cm<sup>-1</sup> using both the direct and Sc internal standard methods (**Figure 5.19**). The unchanged stretching frequencies in the region of 600 – 1 000 cm<sup>-1</sup> were assumed to represent the undissolved precious metals and other elements trapped possibly in silica (SiO<sub>2</sub>) matrix which is highly inert in the acids that were used in this study. This incomplete dissolution of the geological CRM using this technique clearly confirmed the weakness associated with this digestion method towards samples containing silica (see **Chapter 4, Section 4.3.2**).

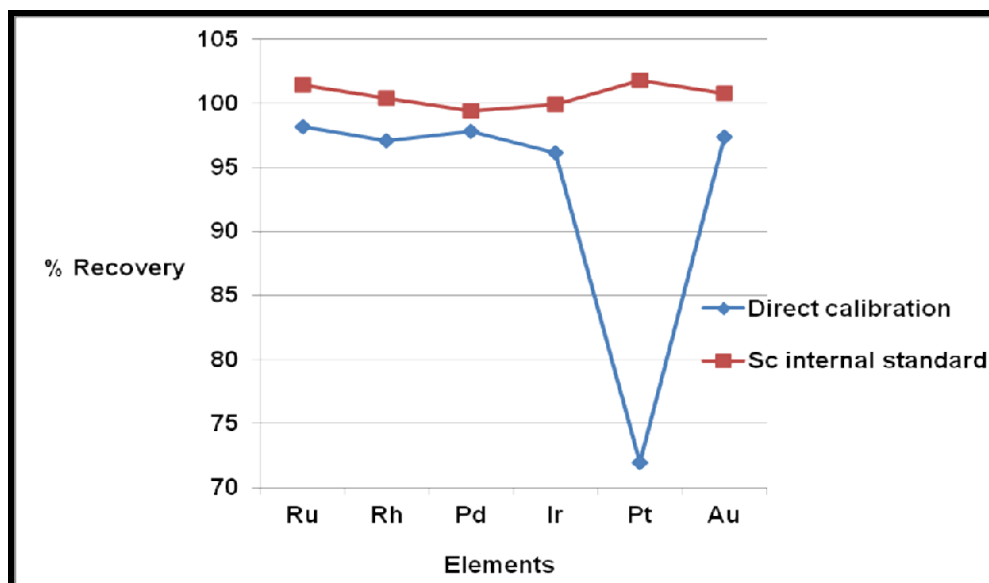


**Figure 5.19:** Quantitative results of the CRM acid digested using the Sc internal standard method after microwave digestion

#### **5.8.1.1 Determination of precious metals in the geological CRM after ammonium hydrogen difluoride ( $\text{NH}_4\text{F}\cdot\text{HF}$ ) flux fusion**

Complete digestion of the CRM was accomplished by fusing the CRM samples with  $\text{NH}_4\text{F}\cdot\text{HF}$  (flux) in a 1: 20 ratio at 250 °C. Qualitative determination of the CRM revealed the presence of 17 other elements (excluding the precious metals) which consist mainly of the alkaline and transition metals in the 10 - 100 ppm range and included Mg, Al, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Sr, Ba, Ag, Tl and Pb.

These elements all had the potential of causing spectral interference with that of Sc and the precious metals in the solution. The selected lines for the precious metals and the Sc internal standard were inspected to ensure that the emission lines of these additional elements do not interfere with the previously selected wavelengths. Total percentage recoveries (+ 99 %) of precious metals were obtained for all the precious metals using the Sc as internal standard (see **Table 5.15**). Low percentage recoveries (below 98 %) of precious metals were obtained using the direct calibration method (**Figure 5.20**).



**Figure 5.20:** Quantitative results of CRM digested using  $\text{NH}_4\text{F}\cdot\text{HF}$  flux

The decrease in the Pt percentage recovery (72 %) using the direct calibration method was mostly attributed to the choice of the method. The direct calibration method was reported in the **Chapter 4, Section 4.2.2** to be susceptible to any changes during the measurement process such as instrumental drifts or clogging of the nebulizer. These changes were assumed to have the potential to yield inconsistent recoveries during the quantitative determination of precious metals.

## 5.9 Conclusion

The Sc internal addition method was found to be the most appropriate method for the quantification of the precious metals based on its ability to yield total recovery of precious metals in both CRMs used in this study. The use of either atomic-atomic or atomic-ionic lines combination between the Sc internal standard and the precious metals was shown not to have any negative effects towards the determination of precious metals as long as the chosen line was not interfered with any of the elements present in solution. The developed Sc internal standard method was shown to be affected by unmatched HCl and  $\text{Na}^+$  ion concentrations (EIE's) of more than 10 % and 10 ppm respectively. The osmium determination was found to be affected by either the instability of the Os standards or the analyte samples which prompted a further investigation into the osmium chemistry. The developed Sc internal standard method was therefore adopted as the best method for the determination of precious metals in

geological samples, inorganic salts and organometallic compounds. A summary of the quantitative results obtained using the direct calibration and the Sc internal standard are shown in **Table 5.18**.

**Table 5.18:** Summary of the precious metals recovery (%) in both CRMs using direct calibration and Sc internal standard methods

Sample	Method	Ru	Rh	Pd	Os	Ir	Pt	Au
<b>Liquid CRM</b>	Direct cal.	97(2)	92(6)	95(3)	83 (6)	94(5)	93(1)	98(3)
	<b>Sc</b>	<b>100.3(8)</b>	<b>100.0(9)</b>	<b>100.0(6)</b>	<b>89(9)</b>	<b>101(1)</b>	<b>99.4(3)</b>	<b>101.2(5)</b>
<b>Liquid CRM (Acid matrix test)</b>	Direct cal.	95.4(3)	95.7(0)	93.2(8)	-	93.9(1)	105.4(6)	92.3(7)
	<b>Sc</b>	<b>99.7(1)</b>	<b>99.8(5)</b>	<b>100.3(3)</b>	-	<b>99.8(9)</b>	<b>99.7(8)</b>	<b>99.9(2)</b>
<b>Liquid CRM (EIE's test)</b>	Direct cal.	95.4(3)	95.7(0)	93.2(8)	-	93.9(1)	105.4(6)	92.3(7)
	<b>Sc</b>	<b>99.2(1)</b>	<b>99.8(5)</b>	<b>100.3(3)</b>	-	<b>99.0(5)</b>	<b>99.0(0)</b>	<b>99.2(9)</b>
<b>Geological CRM</b>	Direct cal	98 (7)	97 (7)	98 (3)	-	96 (2)	72(4)	97 (8)
	<b>Sc</b>	<b>101(7)</b>	<b>100.4 (6)</b>	<b>99 (7)</b>	-	<b>100 (5)</b>	<b>102 (4)</b>	<b>100.9 (8)</b>

# 6 Quantification of osmium (method development)

---

## 6.1 Introduction

Quantitative determination of osmium from the liquid CRM solutions was characterized by a continual decrease in osmium recovery after every successive analysis of the same CRM solutions (see **Chapter 5, Section 5.7.2**). This decrease in osmium percentage recovery was shown to be consistent in both the direct calibration and the internal standard methods. It was this decrease in osmium percentage recovery that prompted further investigation into possible optimum conditions for osmium quantification using the ICP-OES. The main objective of this chapter is to determine the optimum conditions or alternative ways of quantifying osmium preferably using the scandium internal standard method. The preference to keep the scandium internal standard was to enable the quantification of precious metals using a single internal standard as highlighted in **Chapter 1, Section 1.2** as part of the main objectives in this study. The first part of this investigation is aimed at identifying the sources of errors or interferences associated with the decrease in osmium recovery using the direct calibration method. The focus is then to use alternative methods and reagents to rectify these problems. All the experimental quantitative results obtained in this chapter will be validated in **Chapter 8**.

## 6.2 Reagents and glassware

Osmium calibration standards  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  (1 000 ppm) was purchased from Inorganic Ventures. CsCl (99 %), NaOH pellets (97 %), KOH flakes (90 %) and  $\text{NH}_4\text{OH}$  (25 %) as well as all the halide mineral acids, HF (48 %), HCl (32 %) and HBr (48 %) were purchase from Merck Chemicals.  $\text{OsO}_4$  (99 %), NaCN (97 %) and the glass cuvettes were purchased from Sigma Aldrich. All the glassware used for the metal analysis in this study was of Schott Duran, grade (A) type.

## **6.3 Equipment**

Equipment used in this part of the study include ICP-OES, Varian Cary UV-vis spectrophotometer and Infrared spectrometer which have been described in **Chapter 5, Section 5.3**.

## **6.4 Experimental procedures**

### **6.4.1 Preliminary determination of the optimum conditions for osmium analysis**

#### **6.4.1.1 Preparation of the osmium calibration standards (direct calibration method)**

Osmium calibration standards were prepared from the original  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  standard solution (1 000 ppm) to concentrations with a working range of 0.1 - 1.0 ppm in separate 100.0 mL volumetric flasks. The solutions were acidified with HCl (5.0 mL; 32 %) and the volumetric flasks were filled up to the mark using double distilled water. The solutions were homogenized and allowed to stabilize for a few minutes to prevent substantial changes for longer periods before it was used.

#### **6.4.1.2 Quantitative determination of osmium in the CRM solutions**

Freshly prepared CRM (triplicate) solutions as described in **Chapter 5, Section 5.5.1.2** as well as freshly prepared Os standards,  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ , as described in **Section 6.2.1.1** were used to quantify Os. The Os emission intensities of the calibration standards were continuously monitored during this study for a period of up to 4 days using the ICP-OES at the ionic line of 225.585 nm (see **Chapter 5, Section 5.4.2**). The corresponding percentage recoveries of Os from the CRM were recorded after every 24 hours and the experimental results are reported in **Table 6.1** and **6.2** respectively. Graphical presentations of these quantitative results are given in **Section 6.5.1** and the ANOVA test for the Os results obtained using the CRM are shown in **Chapter 8**.



**Table 6.1:** Measured osmium emission intensities from the calibration standard solutions after every 24 hours using the direct calibration method

Os standards concentrations (ppm)	Measured emission intensities				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
0.5	0.1581	0.1816	0.2005	0.2338	0.24000
1.0	0.2679	0.3300	0.4055	0.5190	0.56250
2.0	0.4784	0.5590	0.7459	1.0477	1.18902
5.0	1.0716	1.2655	1.9788	2.9024	3.28402
10.0	1.9711	2.4966	4.1851	6.2889	7.06792

**Table 6.2:** Osmium percentage recovery obtained from the liquid CRM after every 24 hours using the direct calibration method

CRM replicates (n)	Osmium recovery (%)				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
CRM 1	98.28	87.48	78.82	76.52	75.12
CRM 2	98.64	89.09	78.95	75.03	73.15
CRM 3	97.51	88.03	78.24	75.46	76.34
Average	<b>98.1(6)</b>	<b>88.2(8)</b>	<b>78.7(4)</b>	<b>75.7 (8)</b>	<b>75 (2)</b>

Bolded results = average percentage recovery of osmium

#### 6.4.2 Stability test of the Os standard, $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ , in different acidic mediums (HX where X = F, Cl and Br)

##### 6.4.2.1 Preparation of the osmium calibration standards (direct calibration method)

Three sets of osmium calibration standards were prepared from the original  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  standard solution (1 000 ppm) to yield concentrations with a working range of 0.5 - 10.0 ppm in different 100.0 mL volumetric flasks. Different acids (5.0 mL) which included HF (48 %), HCl (32 %) and HBr (48 %) were added to each set of the standards and the volumetric flasks were filled up to the mark using double distilled water. The solutions were homogenized and allowed to stabilize for a few minutes to prevent potential changes in intensity (due to decomposition or any other chemical reaction) for longer periods before it was used. The measured Os emission intensities are reported in **Table 6.3 - 6.5**. The influence of time on the slope ( $m$ ) of

the calibration curves is reported in **Table 6.6** while the graphical presentations of these results are shown in **Section 6.5.2**.

**Table 6.3:** Measured osmium intensities of the calibration standard solutions of  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  in HF acid matrix using the direct calibration method

Os standards concentrations (ppm)	Measured emission intensities				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
0.5	0.1581	0.1816	0.2005	0.2338	0.2400
1.0	0.2679	0.3300	0.4055	0.5190	0.5625
2.0	0.4784	0.5590	0.7459	1.0477	1.1890
5.0	1.0716	1.2655	1.9788	2.9024	3.2840
10.0	1.9711	2.4966	4.1851	6.2889	7.0679

**Table 6.4:** Measured osmium intensities of the calibration standard solutions of  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  in HCl acid matrix using the direct calibration method

Os standards concentrations (ppm)	Measured emission intensities				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
0.5	0.1794	0.2062	0.2347	0.2546	0.2739
1.0	0.3063	0.3387	0.3954	0.4428	0.4783
2.0	0.5080	0.5430	0.6517	0.7909	0.8933
5.0	1.0408	1.1205	1.4273	1.9388	2.2944
10.0	1.8940	2.0540	2.7086	3.9223	4.7850

**Table 6.5:** Measured osmium intensities of the calibration standard solutions of  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  in HBr acid matrix using the direct calibration method

Os standards concentrations (ppm)	Measured emission intensities				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
0.5	0.0898	0.0945	0.0979	0.0991	0.0982
1.0	0.1785	0.1836	0.1885	0.1970	0.1985
2.0	0.3488	0.3540	0.3676	0.3816	0.3877
5.0	0.9997	1.1040	1.5618	2.1550	2.4368
10.0	1.8811	2.1571	3.6913	5.7063	6.7270

**Table 6.6:** Changes in gradient (sensitivity) of the osmium calibration curves in HF, HCl and HBr acid matrix

Time (Hours)	Calibration gradients		
	HF	HCl	HBr
0	0.1904	0.1783	0.1907
24	0.2419	0.1926	0.2205
48	0.4196	0.2588	0.3857
72	0.6386	0.3863	0.6028
96	0.7199	0.4764	0.7126

#### 6.4.3 Stability test of osmium standards $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in different basic mediums (NaOH, KOH and $\text{NH}_4\text{OH}$ )

##### 6.4.3.1 Preparation of the osmium calibration standards (direct calibration method)

Three sets of osmium calibration standards were prepared from the original  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  standard solution (1 000 ppm) to yield concentrations with a working range of 0.5 - 10.0 ppm in different 100 mL volumetric flasks. Different bases (5.0 mL) which included NaOH, KOH and  $\text{NH}_4\text{OH}$  (1.0 M each) were added to each set of the standards and the volumetric flasks were filled up to the mark using double distilled water. The solutions were homogenized and allowed to stabilize for a few minutes to prevent substantial changes for longer periods before it was used. The measured Os emission intensities are reported in **Table 6.7 - 6.9**. The influence of time on the slope ( $m$ ) of the calibration curves is reported in **Table 6.10** while the graphical presentations of these results are shown in **Section 6.5.3**.

**Table 6.7:** Measured osmium intensities of the calibration standard solutions of  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  in NaOH acid matrix using the direct calibration method

Os standards concentrations (ppm)	Measured emission intensities				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
0.5	0.1114	0.0241	0.0241	0.0241	-0.0550
1.0	0.4333	0.0699	0.0699	0.0699	-0.0096
2.0	1.3298	0.0988	0.0988	0.0988	0.0295
5.0	3.8786	0.3275	0.3275	0.3275	0.2048
10.0	8.7376	1.4775	1.4775	1.4775	0.4911

**Table 6.8:** Measured osmium intensities of the calibration standard solutions of  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  in KOH acid matrix using the direct calibration method

Os standards concentrations (ppm)	Measured emission intensities				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
0.5	0.1050	0.0249	0.0183	0.0196	-0.0560
1.0	0.5084	0.0664	0.0585	0.0617	-0.0071
2.0	1.0811	0.0973	0.0906	0.0891	0.0275
5.0	3.7810	0.3175	0.2296	0.2283	0.2068
10.0	8.6554	1.4295	0.4458	0.4320	0.4973

**Table 6.9:** Measured osmium intensities of the calibration standard solutions of  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  in  $\text{NH}_4\text{OH}$  acid matrix using the direct calibration method

Os standards concentrations (ppm)	Measured emission intensities				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
0.5	0.1045	0.0250	0.0194	0.0194	0.0193
1.0	0.6091	0.0683	0.0590	0.0590	0.0621
2.0	1.4879	0.0979	0.0901	0.0901	0.0893
5.0	3.9842	0.5186	0.2346	0.2346	0.2317
10.0	8.4529	1.4489	0.4429	0.4429	0.4304

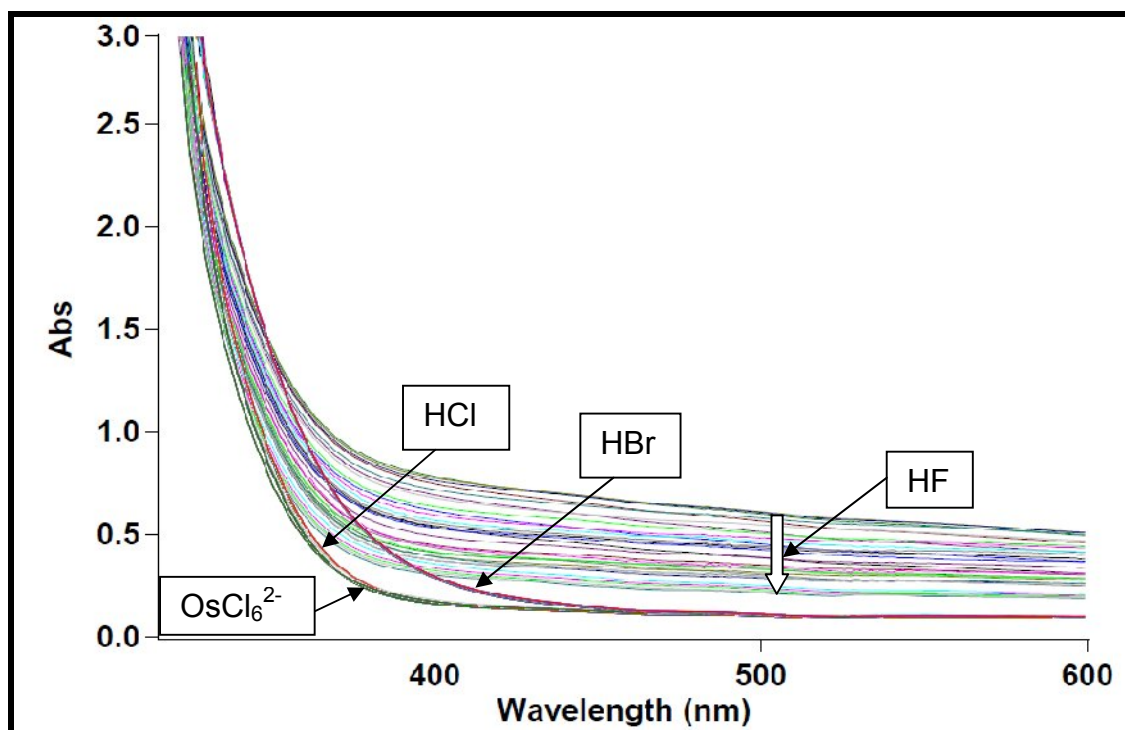
**Table 6.10:** Comparison of the changes in the gradients (sensitivity) of the osmium calibration curves in NaOH, KOH and  $\text{NH}_4\text{OH}$  base matrix

Time (Hours)	Calibration gradients		
	NaOH	KOH	$\text{NH}_4\text{OH}$
0	0.9110	0.9045	0.8726
24	0.1505	0.1455	0.1516
48	0.0444	0.0443	0.0440
72	0.0426	0.0427	0.0440
96	0.0568	0.0575	0.0426

#### 6.4.4 UV-vis analysis of the Os standards $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in acidic medium (HF, HCl and HBr)

Aliquots of the prepared Os standard stock solution  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  (1.0 mL; 1 000 ppm) were transferred into glass cuvettes. Aliquots (3 mL) of HF (48 %), HCl (32 %) and HBr (48 %) were added to the different Os standard (1.0 mL; 1 000 ppm) solutions. These reactions were monitored for spectral changes in the absorbance

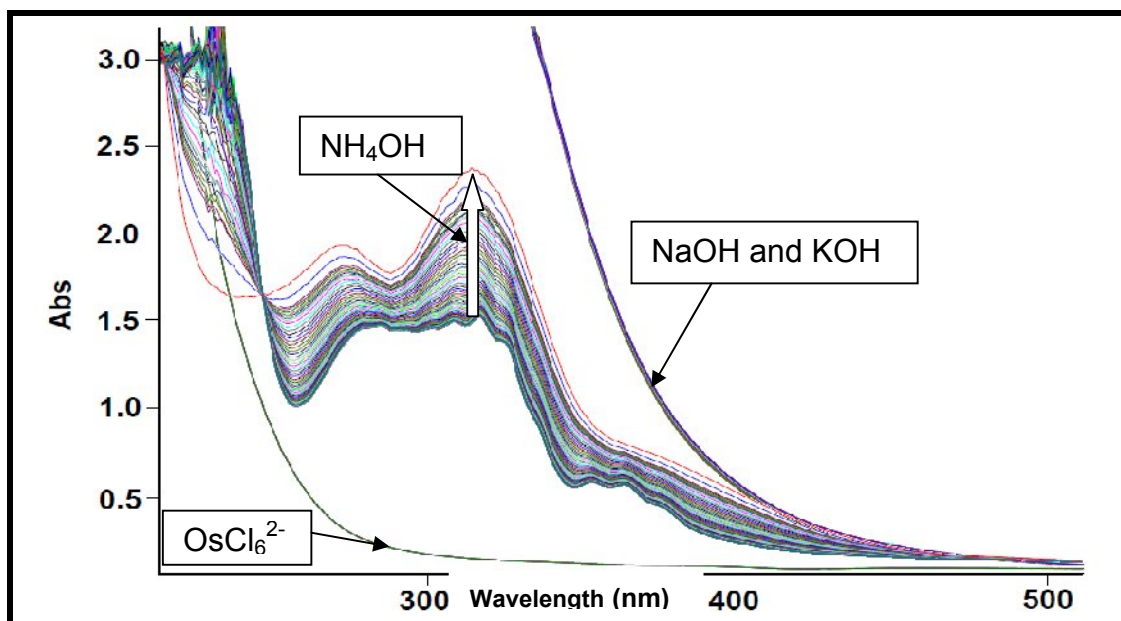
range of 200 - 600 nm at time intervals of 5 minutes for  $\pm 24$  hours. The results of the analysis are shown in **Figure 6.1**.



**Figure 6.1:** UV-vis determination of the stability of osmium standard,  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ , in acidic medium (HF, HCl and HBr)

#### 6.4.5 UV-vis analysis of the Os standards $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in basic medium (NaOH, KOH and $\text{NH}_4\text{OH}$ )

Aliquots (3 mL) of NaOH, KOH and  $\text{NH}_4\text{OH}$  (1.0 M) more than enough to neutralize the acid contained in the Os standard  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  solution (1.0 mL; 1 000 ppm) were added into the separate glass cuvettes. The resultant reaction mixtures were monitored for spectral changes in the absorbance range of 200 - 500 nm at time intervals of 5 minutes for  $\pm 24$  hours. The results of the analysis are shown in **Figure 6.2**.



**Figure 6.2:** Spectrophotometric determination of the stability of Os standard  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  in basic medium ( $\text{NH}_4\text{OH}$ ,  $\text{NaOH}$  and  $\text{KOH}$ )

#### 6.4.5.1 Stability test of the osmium standards $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in HCl matrix in different storage conditions using direct calibration

Three different sets of Os standards  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  solutions were prepared in HCl as described in **Section 6.4.2.1** and each set was placed in a different environment. The 1<sup>st</sup> set was kept at room temperature in the open and exposed to the sunlight at all times whilst the 2<sup>nd</sup> set was kept at room temperature in the cupboard (dark) at all times while the 3<sup>rd</sup> set was kept at ca. 10 °C and in the absence of sunlight at all times. The measured Os emissions intensities of these standards were monitored for stability every 24 hours and the results are reported in **Table 6.11 - 6.13**.

**Table 6.11:** Osmium emission intensities of the calibration standard  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  solutions kept in the open and exposed to the light (Set 1)

Os standards concentrations (ppm)	Measured emission intensities				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
0.5	0.0881	0.1082	0.1009	0.1269	0.1035
1.0	0.1615	0.1938	0.1978	0.1931	0.1911
2.0	0.3170	0.3622	0.3604	0.3865	0.3703
5.0	0.7689	0.8154	0.8087	0.8734	0.8697
10.0	1.4641	1.5856	1.5908	1.6600	1.6755

**Table 6.12:** Osmium emission intensities of the calibration standard  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  solutions kept in the cupboard (dark) (Set 2)

Os standards concentrations (ppm)	Measured emission intensities				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
0.5	0.0874	0.0916	0.0973	0.0993	0.1148
1.0	0.1607	0.1691	0.1754	0.1822	0.1947
2.0	0.3049	0.3123	0.3209	0.3349	0.3719
5.0	0.7266	0.7717	0.7655	0.7905	0.8529
10.0	1.4130	1.5014	1.5063	1.5481	1.6308

**Table 6.13:** Osmium emission intensities of the calibration standard  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  solutions at ca. 10 °C and in the absence of sunlight (Set 3)

Os standards concentrations (ppm)	Measured emission intensities				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
0.5	0.0917	0.0970	0.0885	0.0932	0.1047
1.0	0.1715	0.1781	0.1676	0.1731	0.1892
2.0	0.3230	0.3344	0.3282	0.3251	0.3491
5.0	0.7953	0.8020	0.7798	0.7779	0.8127
10.0	1.5362	1.5665	1.5394	1.5464	1.5791

#### 6.4.5.2 Determination of osmium in the CRM using $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ standards at ca. 10 °C in the absence of sunlight (direct calibration method)

CRM solutions in triplicate were prepared by pipetting aliquots of the original CRM solution (7.0 mL; 100.0 ppm) into 100.0 mL volumetric flasks. The solutions were acidified with HCl (5.0 mL; 32 %) and the volumetric flasks were filled up to the mark using double distilled water. The CRM solutions were homogenized and left to stabilize for an hour before analyzing the Os content using the prepared standards in **Section 6.4.5.2** which were kept at ca. 10 °C (Set 3) and in the absence of sunlight. The CRM solutions were kept under the same storage conditions as the calibration standards solutions for the duration of the experimental analysis. The Os calibration standards and the CRM solutions were simultaneously removed from the dark cool environment for a maximum time of  $\pm 15$  min for the duration of the experimental analysis. Experimental results of the Os emission intensities and percentage recovery are reported in **Table 6.14** and the ANOVA test results for the Os recovery obtained using the CRM are shown in **Chapter 8**.

**Table 6.14:** Osmium percentage recovery from the liquid CRM using the direct calibration method with calibration standard  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  solutions kept at ca. 10 °C and in the absence of sunlight

CRM replicates (n)	Osmium recovery (%)				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
CRM 1	98.18	98.48	97.72	86.52	81.12
CRM 2	98.56	98.19	98.95	85.03	80.25
CRM 3	97.43	98.13	97.24	85.46	81.34
Average	98.1(6)	98.3(2)	98.0 (9)	85.7(8)	80.9(6)

#### 6.4.6 Application of the scandium internal standard in osmium determination

##### 6.4.6.1 Stability test of the osmium standards $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ using the scandium as internal standard at ca. 10 °C in the absence of sunlight

Osmium calibration standards were prepared from the original  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  standard solution (1 000 ppm) to concentrations with a working range of 0.1 - 1.0 ppm in 100.0 mL volumetric flasks. The solutions were acidified with HCl acid (5.0 mL; 32 %) and Sc internal standard (0.2 mL; 1 000 ppm) were added to the volumetric flasks and were filled up to the mark using double distilled water. The solutions were homogenized and allowed to stabilize for few minutes to prevent substantial changes for longer periods before it was used. The standard solutions were stored at ca. 10 °C and in the absence of sunlight for the duration of the experimental analysis and analyzed every 24 hours. The measured emission intensities are reported in **Table 6.15** and the graphical presentation of these results are shown in **Section 6.5.5, Figure 11**.

**Table 6.15:** Emission intensities of the osmium calibration standard  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  solutions kept at ca. 10 °C and in the absence of sunlight

Os standards concentrations (ppm)	Measured emission intensities				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
0.5	0.0917	0.0970	0.0885	0.0932	0.1047
1.0	0.1715	0.1781	0.1676	0.1731	0.1892
2.0	0.3230	0.3344	0.3282	0.3251	0.3491
5.0	0.7953	0.8020	0.7798	0.7779	0.8127
10.0	1.5362	1.5665	1.5394	1.5464	1.5791



#### 6.4.6.2 Determination of osmium in the CRM using the calibration standards $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ and Sc as internal standard at ca. 10 °C in the absence of sunlight

CRM solutions in triplicate were prepared by pipetting aliquots of the original CRM solution (7.0 mL; 100.00 ppm) into 100.0 mL volumetric flasks. Equal volumes of the internal standard (0.2 mL; 1 000 ppm) were added to each flask. The solutions were acidified with HCl (5.0 mL; 32 %) and the volumetric flasks were filled up to the mark using double distilled water. The CRM solutions were homogenized and left to stabilize for an hour before determined for the osmium content using standards prepared in **Section 6.4.6.1**. The CRM solutions were kept under the same storage conditions as the calibration standard solutions for the duration of the experimental analysis. Experimental percentage recoveries of Os from the CRM are reported in **Table 6.16** and the ANOVA test results are shown in **Chapter 8**.

**Table 6.16:** Osmium percentage recovery from the CRM using the Sc internal calibration standard  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  solutions kept at ca. 10 °C and in the absence of sunlight

CRM replicates (n)	Osmium recovery (%)				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
CRM 1	100.76	101.22	100.23	99.22	98.00
CRM 2	100.86	101.37	100.31	99.37	97.36
CRM 3	100.35	100.02	98.60	98.28	96.85
<b>Average</b>	<b>100.7(3)</b>	<b>100.9(7)</b>	<b>100(1)</b>	<b>99.0(6)</b>	<b>97.4(6)</b>

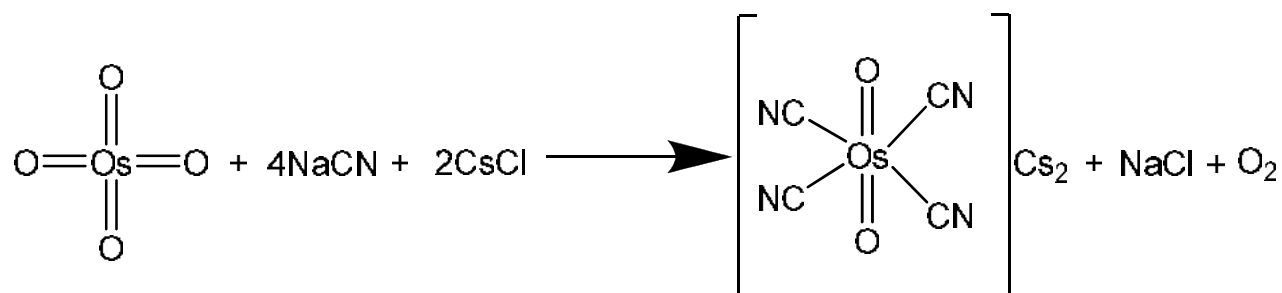
Bolded results = average percentage recovery of osmium

#### 6.4.7 Selection of an alternative osmium standard

The reactivity/instability of the commercially sourced Os standard in both acid and basic conditions was illustrated in the previous paragraphs. This uncertainty in Os recovery necessitated the need to find an alternative Os standard to accurately quantify in different samples. Minimum requirements of such a 'new' standard include improved stability over longer periods, preferably at room temperature and in the presence of light that will allow total recovery of Os. A study conducted by

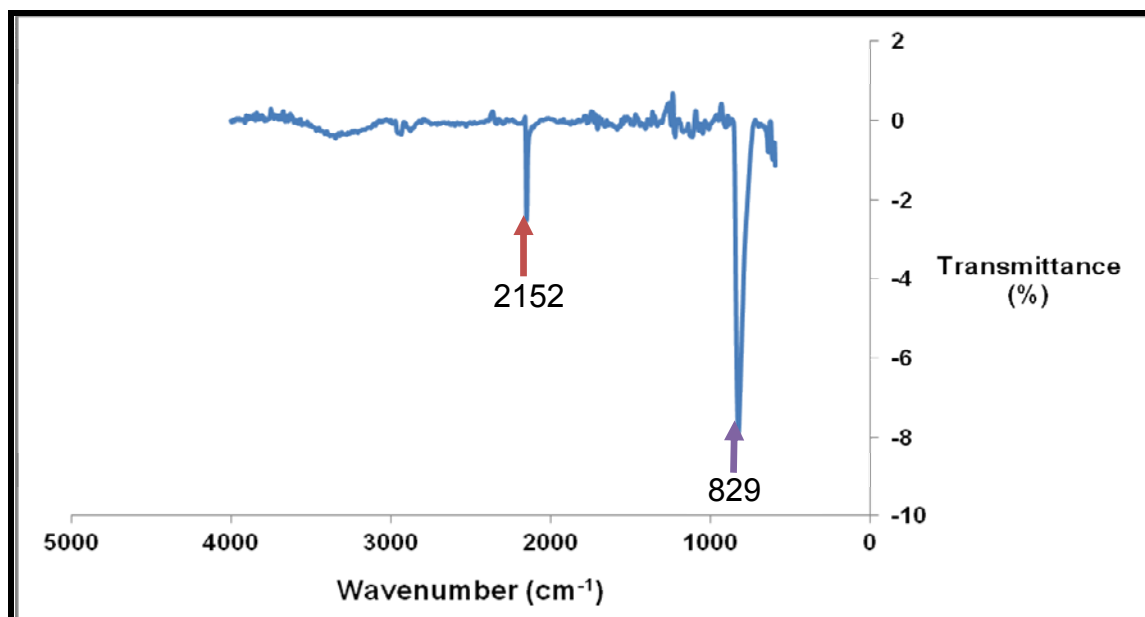
Purcell *et al.*<sup>190</sup> showed the excellent stability of  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  in both aqueous and strong acidic medium and this osmium complex was investigated as potential osmium standard. A detailed description of this compound and its stability properties will be discussed in **Section 6.5.6.1**.

#### 6.4.7.1 Synthesis of $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$



$\text{OsO}_4$  (0.1 g; 0.4 mmol) crystals were dissolved in distilled water (5 mL) and stirred at room temperature. A portion of NaCN (201 mg; 4.1 mmol) was added to the solution whilst gently stirring and heating for 30 min. A solution of CsCl (260 mg; 1.5 mmol) in 1.0 mL of water was added and the resultant solution was heated until the final volume of the reaction mixture was approximately 2 mL. The reaction mixture was left for 36 hours during which orange-red crystals of  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  crystallized. Yield 70 %, IR data:  $\nu_{(\text{Os}=\text{O})}$   $829\text{ cm}^{-1}$ ;  $\nu_{(\text{CN})}$   $2152\text{ cm}^{-1}$  (**Figure 6.3**).

<sup>190</sup> W. Purcell, A. Roodt, S.S. Basson and J.G. Leipoldt, *Transition Met. Chem.*, (1991), 16, pp. 60 - 61.



**Figure 6.3:** Infrared spectrum of  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$

#### 6.4.7.2 Preparation of the $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ stock solution

$\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  (25 mg; 0.4 mmol) stock solution was prepared by dissolving the compound in double distilled water. Hydrochloric acid (5.0 mL; 32 %) was added and the resultant homogeneous solution was quantitatively transferred to a 100.0 mL volumetric flask and was filled up to the mark using double distilled water. The final osmium solution (803.17 ppm) was homogenized and left to stabilize for an hour before it was used.

#### 6.4.7.3 Preparation of the $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ calibration standard solutions kept at room temperature and exposed to the sunlight (direct calibration method)

Two sets of Os calibration standards were prepared from the  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  compound to yield Os concentrations with a working range of 0.5 - 10.0 ppm in different volumetric flasks (100.0 mL). In the first set (using Sc as internal standard) equal volumes of Sc standard (0.2 mL; 1 000 ppm) and HCl (5.0 mL; 32 %) was added. In the second set (direct calibration) HCl (5.0 mL; 32 %) was added to the volumetric flasks and were all filled up to the mark using double distilled water. The solutions were homogenized and allowed to stabilize for an hour before it was used.

The calibration standards were stored at room temperature and exposed to sunlight for the duration of the experimental analysis. The Os emission intensities were measured every 24 hours and reported in **Table 6.17 and 6.18** together with the gradients (sensitivities) of the obtained calibration curves. The graphical presentations of these results are shown in **Section 6.5.6.2** and the ANOVA test results for the calibration gradients ( $m$ ) are shown in **Chapter 8**.

**Table 6.17:** Measured osmium emission intensities of the calibration standard solutions of  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  kept at room temperature and exposed to light using direct calibration

Os standards concentrations (ppm)	Measured Os emission intensities				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
0.5	0.0828	0.0634	0.0867	0.0864	0.0864
1.0	0.1705	0.1557	0.1710	0.1761	0.1718
2.0	0.3359	0.3392	0.3459	0.3486	0.3435
5.0	0.8254	0.8945	0.8849	0.8598	0.8813
10.0	1.6507	1.7841	1.7737	1.7201	1.7925
Calibration gradients (sensitivity)	0.1647	0.1813	0.1780	0.1717	0.1784

**Table 6.18:** Emission intensities of the osmium calibration standard solutions of  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  kept at room temperature and exposed to the light using Sc as internal standard

Os standards concentrations (ppm)	Measured emission intensities				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
0.5	0.0784	0.0858	0.0901	0.0950	0.0915
1.0	0.1499	0.1573	0.1631	0.1693	0.1743
2.0	0.2795	0.2938	0.2920	0.3043	0.3142
5.0	0.6985	0.7138	0.7029	0.7227	0.7192
10.0	1.3764	1.3790	1.3671	1.3946	1.4049
Calibration gradients (sensitivity)	0.1367	0.1362	0.1343	0.1367	0.1373

#### **6.4.7.4 Determination of osmium in the CRM using $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ calibration standards kept at room temperature and exposed to sunlight**

CRM solutions in triplicate were prepared by pipetting aliquots of the original CRM solution (7.0 mL; 100.00 ppm) into 100.0 mL volumetric flasks. All the standards

solutions were acidified with HCl (5.0 mL; 32 %) and the volumetric flasks were filled up to the mark using double distilled water. The CRM solutions were homogenized and left to stabilize for an hour before determined for the osmium content using the direct calibration and Sc as internal standard with the standards prepared in **Section 6.4.7.3**. Experimental results of the osmium percentage recovery using the direct calibration method and the Sc internal standard are reported in **Table 6.19** and **6.20** respectively and the ANOVA test results for the Os recoveries from the CRM are shown in **Chapter 8**.

**Table 6.19:** Osmium percentage recovery from the CRM using  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  standard solutions kept at room temperature and exposed to light (direct calibration)

CRM replicates (n)	Osmium recovery (%)				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
CRM 1	87.56	102.86	104.24	103.92	103.79
CRM 2	88.29	99.40	100.24	97.89	99.89
CRM 3	88.30	99.06	100.22	103.00	102.66
<b>Average</b>	<b>88.1(4)</b>	<b>100(2)</b>	<b>102(2)</b>	<b>103(3)</b>	<b>102(2)</b>

Bolded results = average percentage recovery of osmium

**Table 6.20:** Osmium percentage recovery from the CRM using  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  standard solutions kept at room temperature and exposed to the light (using Sc as the internal standard)

CRM replicates (n)	Osmium recovery (%)				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
CRM 1	99.19	99.10	100.44	100.10	99.98
CRM 2	100.01	100.64	101.52	99.14	101.18
CRM 3	100.02	97.65	98.80	101.53	101.21
<b>Average</b>	<b>99.7(5)</b>	<b>99(2)</b>	<b>100(1)</b>	<b>100(1)</b>	<b>100.8(7)</b>

Bolded results = average percentage recovery of osmium

#### **6.4.7.5 Preparation of the $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ calibration standards kept at ca. 10 °C and in the absence of sunlight (direct calibration method)**

Two sets of Os calibration standards were prepared from the  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  compound to yield Os concentrations with a working range of 0.5 - 10.0 ppm in

different volumetric flasks (100.0 mL). In the first set (using Sc as internal standard) equal volumes of Sc standard (0.2 mL; 1 000 ppm) and HCl (5.0 mL; 32 %) was added. In the second set (direct calibration) HCl (5.0 mL; 32 %) was added to the volumetric flasks and were all filled up to the mark using double distilled water. The solutions were homogenized and allowed to stabilize for an hour before it was used. The standard solutions were stored at *ca.* 10 °C in the absence of sunlight for the duration of the experimental analysis. The Os emission intensities were measured every 24 hours and reported in **Table 6.21** and **6.22** together with the gradients (sensitivities) of the obtained calibration curves. The graphical presentations of these results are shown in **Section 6.3.6.2** and the ANOVA test results for the calibration curve gradients (*m*) are shown in **Chapter 8**.

**Table 6.21:** Measured osmium emission intensities of the calibration standard solutions  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  kept at *ca.* 10 °C in the absence of light using direct calibration

Os standards concentrations (ppm)	Measured Os emission intensities				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
0.5	0.1021	0.0858	0.0999	0.0970	0.0828
1.0	0.1812	0.1769	0.1817	0.1752	0.1705
2.0	0.3478	0.3433	0.3500	0.3393	0.3359
5.0	0.8542	0.8295	0.8514	0.8178	0.8254
10.0	1.6604	1.6628	1.6520	1.6186	1.6507
Calibration gradients (sensitivity)	0.1645	0.1653	0.1636	0.1602	0.1647

**Table 6.22:** Osmium emission intensities using the  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  calibration standard solutions at *ca.* 10 °C in the absence of light using Sc as internal standard

Os standards concentrations (ppm)	Measured Os emission intensity ratios				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
0.5	0.0065	0.0050	0.0068	0.0068	0.0068
1.0	0.0133	0.0121	0.0133	0.0137	0.0134
2.0	0.0253	0.0256	0.0261	0.0263	0.0259
5.0	0.0620	0.0671	0.0664	0.0645	0.0662
10.0	0.1268	0.1370	0.1362	0.1321	0.1377
Calibration gradients (sensitivity)	0.0126	0.0139	0.0136	0.0132	0.0138

#### 6.4.7.6 Determination of osmium in the CRM using the prepared $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ calibration standards at ca. 10 °C and in the absence of sunlight

Two sets of CRM solutions in triplicate were prepared by pipetting aliquots of the original CRM solution (7.0 mL; 100.00 ppm) into 100.0 mL volumetric flasks. Equal volumes of the internal standard (0.2 mL; 1 000 ppm) were added to each set of standards. All the standard solutions were acidified with HCl (5.0 mL; 32 %) and the volumetric flasks were filled up to the mark using double distilled water. The CRM solutions were homogenized and left to stabilize for an hour before determined for the osmium content using both the direct calibration and the Sc internal standard methods with the standards prepared in **Section 6.4.7.5** and **6.2.6.1**. Experimental results of the osmium percentage recovery using the direct calibration method and the Sc internal standard are reported in **Table 6.21** and **6.22** respectively and the ANOVA test results for the Os recoveries from the CRM are shown in **Chapter 8**.

**Table 6.23:** Osmium percentage recoveries from the CRM using the direct calibration standards ( $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  standards kept at ca. 10 °C and in the absence of sunlight)

CRM replicates (n)	Osmium recovery (%)				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
CRM 1	73.32	93.96	81.53	75.31	83.08
CRM 2	74.11	92.97	81.69	73.91	83.74
CRM 3	72.16	95.06	81.10	74.85	85.10
<b>Average</b>	<b>73 (1)</b>	<b>94 (1)</b>	<b>81.4(3)</b>	<b>74.7 (7)</b>	<b>84 (1)</b>

Bolded results = average percentage recovery of osmium

**Table 6.24:** Osmium percentage recoveries from the CRM using Sc as internal calibration standards ( $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  standards kept at ca.10 °C and in the absence of sunlight)

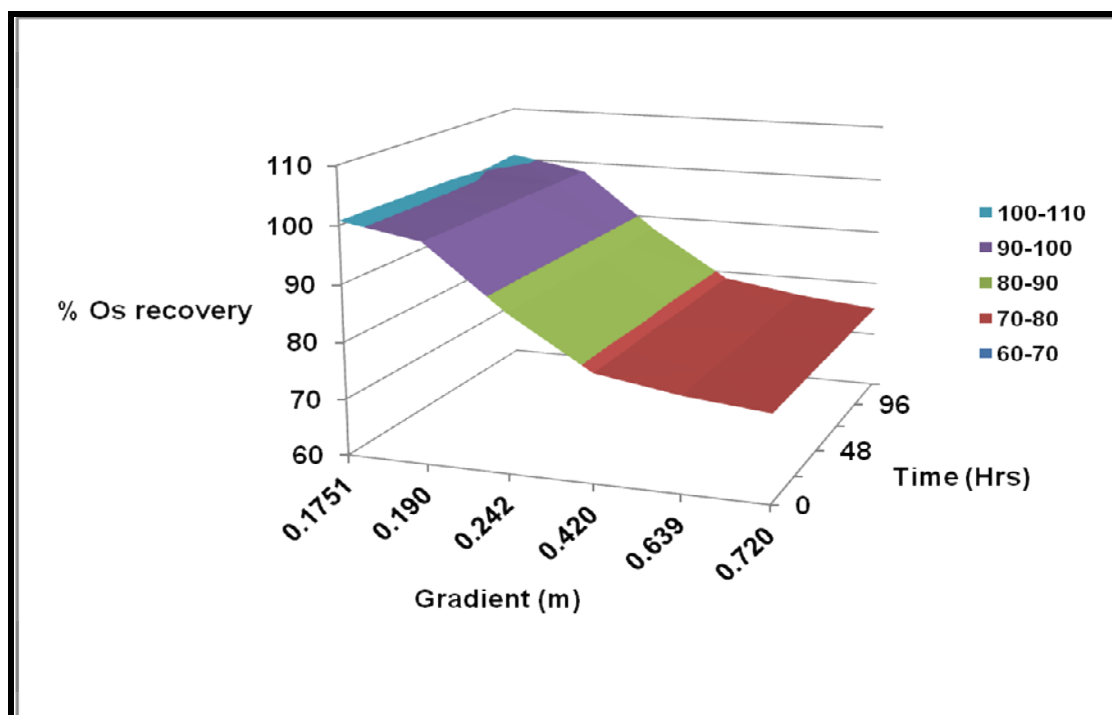
CRM replicates (n)	Osmium recovery (%)				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
CRM 1	100.05	100.97	101.14	101.19	98.61
CRM 2	101.07	99.68	101.36	99.37	99.47
CRM 3	98.53	102.40	100.57	100.59	101.26
<b>Average</b>	<b>100 (1)</b>	<b>101 (1)</b>	<b>101.0 (4)</b>	<b>100.4 (9)</b>	<b>100 (1)</b>

Bolded results = average percentage recovery of osmium

## 6.5 Discussion of the experimental results

### 6.5.1 Preliminary determination of the optimum conditions for osmium analysis

The preliminary investigation to find the optimum conditions for the accurate quantification of Os was conducted using the direct calibration method. This analysis was aimed to try and isolate the chemical variables that interfere with the Os recoveries in the liquid CRM (see **Table 6.2** and **Figure 6.4**).



**Figure 6.4:** Decrease in osmium percentage recovery from the liquid CRM using the direct calibration method with  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  as calibration standard

The results in **Figure 6.4** using the direct calibration method clearly indicate initial good percentage recovery (98 %) of Os in the liquid CRM using the freshly prepared osmium calibration standards and the CRM analyte solutions. The Os percentage recovery then decrease rapidly from 98 - 79 % within a period of 0 - 48 hours. This percentage decrease in the Os recovery continued but at a slower rate after 48 hours to reach a maximum recovery of only 75 % after 96 hours. Os percentage recovery

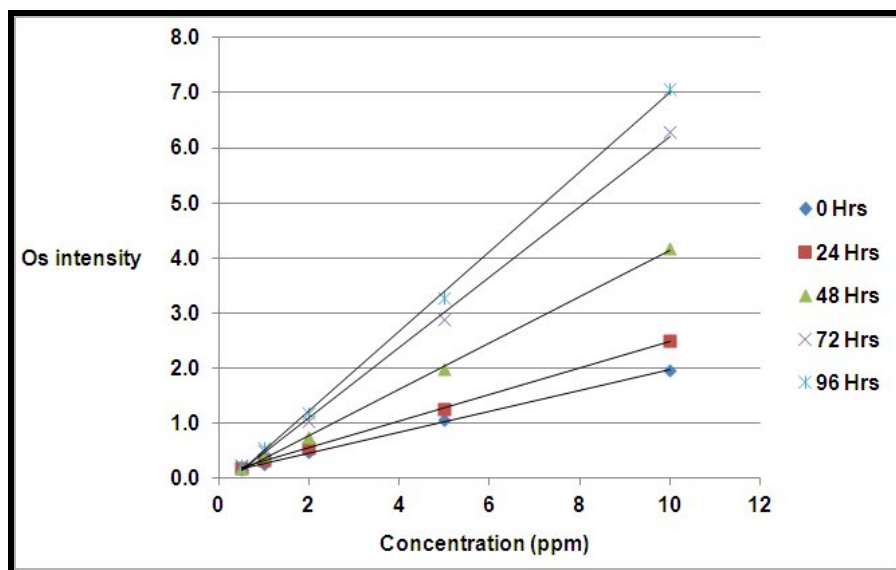


was shown to decrease exponentially from the onset of the experiment ( $t_{\text{initial}} = 0$  Hrs) to the end of the experiment ( $t_{\text{final}} = 96$  Hrs).

At this stage of the study it was mostly believed that the decrease in Os percentage recovery was the result of factors such as the instrumental drift or possibly precipitation or volatilisation of Os in the analyte solution. However, inspection of the Os calibration standard solutions indicated no traces of precipitation in both the Os calibration standards and the CRM analyte solutions. This observation more or less ruled out any possibilities of precipitation in both solutions as was initially assumed. The formation of yellow-black stains on the plastic stoppers gave the first indications of the chemistry of the Os in solution which may account for the instability of the calibration curves using  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  standard as Os source (discussion of chemistry, see **Section 6.5.6**).

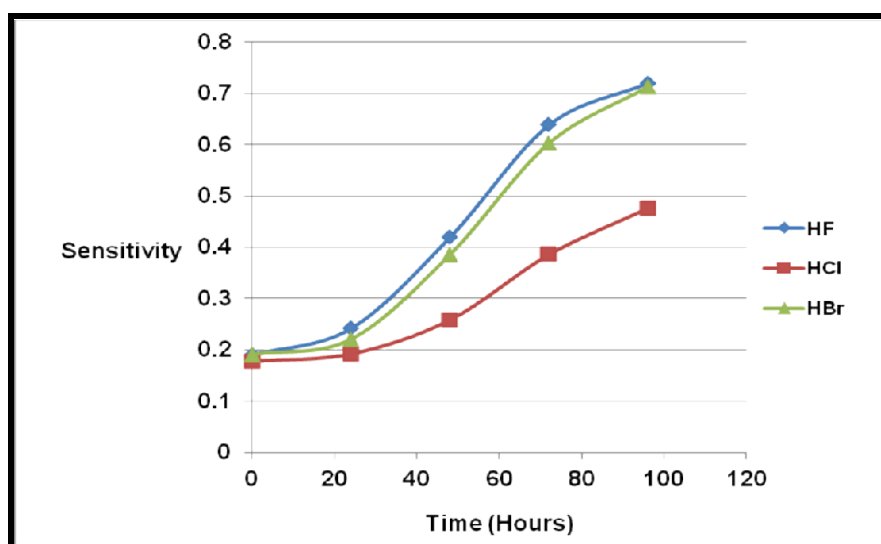
### **6.5.2 Stability test of the Os standards $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in acidic medium (HF, HCl and HBr)**

The next step in this investigation was to determine the influence of different halide acids (HF, HCl and HBr) on the calibration stability. The results obtained from this investigation (see **Table 6.4 - 6.6**) clearly show an increase in Os emission intensities with increase in time as shown in **Figure 6.5**. The magnitude of this shift in the Os calibration curves were assessed using the calibration gradients (sensitivity). This increase in the sensitivity or slope of the calibration curves account well for the decrease in Os recovery that was experienced throughout the quantification of the precious metals as shown in **Chapter 5, Section 5.5.1.4**. The increase in slope with time as shown in **Figure 6.5** results in Os concentration decrease which ultimately leads to poor Os recoveries.



**Figure 6.5:** Influence of time on the slope of the Os calibration curves of  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  in HCl matrix using the direct calibration method

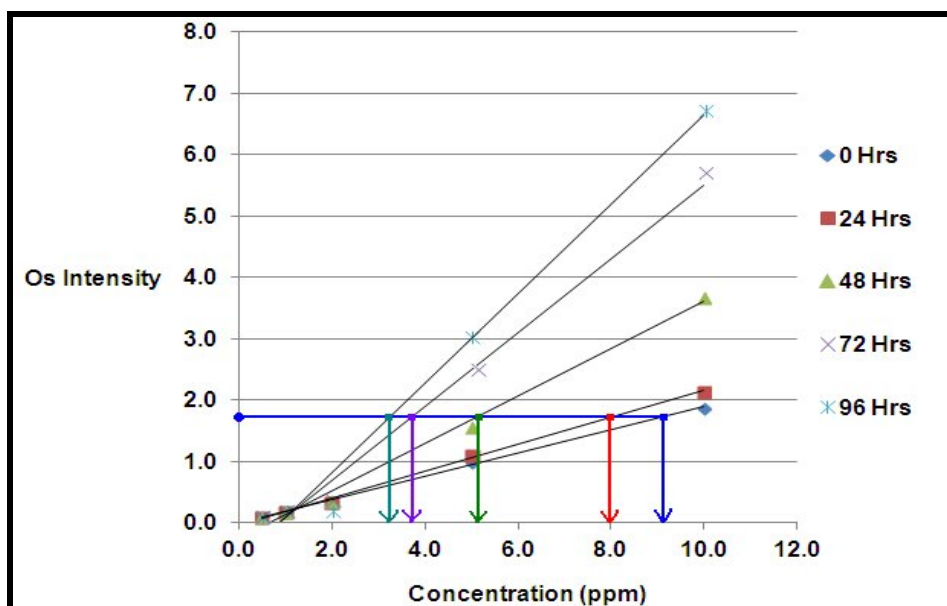
This change in sensitivity increased in the order  $\text{HCl} < \text{HBr} < \text{HF}$  (**Figure 6.6**) suggesting the percentage recovery of Os to be dependent also on the acid type used in its quantification (discussion of chemistry, see **Section 6.5.6**).



**Figure 6.6:** Change in calibration curve sensitivity with time using different halide acids HX (X= F, Cl and Br) and the direct calibration

The increase in sensitivity is much larger for HF and HBr compared to the standards in HCl matrix. The increase in sensitivity using HF and HBr is almost the same, predicting similar influence on the physical properties of osmium complex in solution. However, significant sensitivity differences between the calibrations for these two

acids compared to that obtained for HCl acid is observed. Calibration standards in HCl matrix is increasing in sensitivity at a slower rate compared to those in HF and HBr. An increase in sensitivity for all the acids is observed after 24 hours of having prepared the Os standards. This gain in sensitivity clearly collaborate the decrease in Os percentage recovery as shown in **Section 6.3.1** and **Figure 6.7**.



**Figure 6.7:** Influence of Os recovery concentration as a function of time in HCl matrix

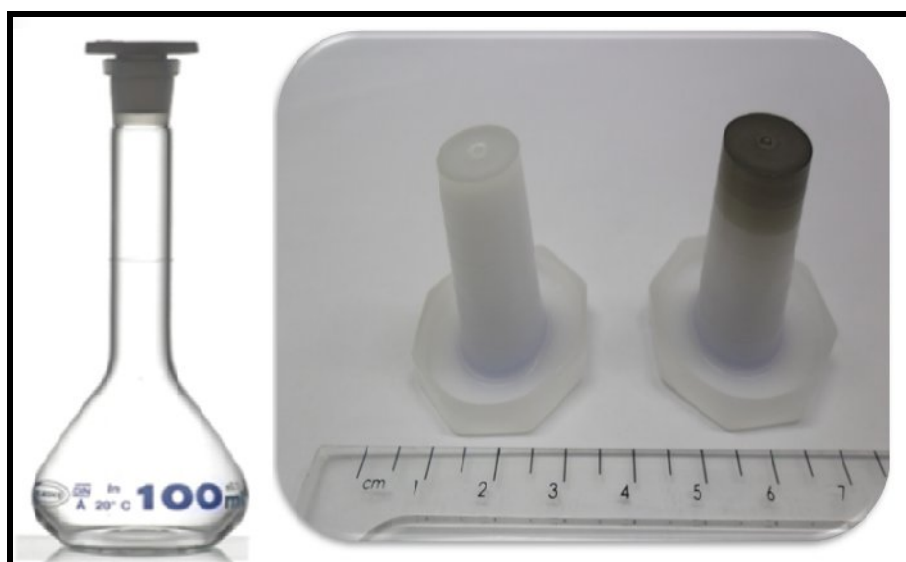
The decrease in Os percentage recovery was also consistent with the results obtained with a variation of the acid type, using Sc as internal standard (see **Chapter 5, Section 5.5.1.4**). The quantitative results of Os are decreasing after every analysis of the same CRM solutions.

From these results it was therefore concluded that satisfactory Os recoveries can only be obtained from freshly prepared standards and on condition that the analysis is quickly performed after the preparation of both standards and the analyte solutions. These results also clearly confirmed the use of HCl to acidify the solutions (amongst the acid halides) due to the lower rate at which the intensity increases (change in chemical preparation of the Os in solution).

Further investigations were conducted in order to establish the source of the error or the shift in the Os calibration curves. Although instrumental drifts were not completely ruled out, the magnitude of the shift observed was not consistent (random

error) to be only attributed to instrumental drifts. Further information to substantiate the influence of instrumental drifts was explained by Kola and Peramaki.<sup>191</sup> These authors reported that long or short instrumental drifts often results in systematic errors which are predictable and their description was contrary to the results obtained in this part of the investigation.

On further examination of the Os calibration standards solutions it was again found that a yellow-black stain was formed on all the lids of the volumetric flasks (**Figure 6.8**) containing osmium standards. This yellow-black stain strongly adhered to these volumetric flasks tops and could not be removed by washing with either water or any organic solvents such as acetone and ethanol (discussion of chemistry, see **Section 6.5.6**).



**Figure 6.8:** A yellow-black coating observed on the volumetric flask stoppers containing the osmium calibration standards

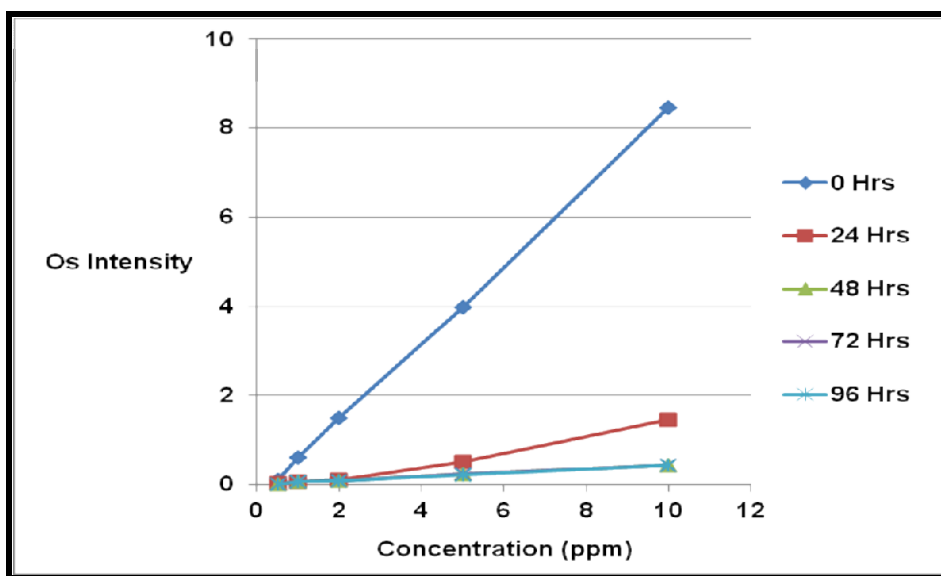
### **6.5.3 Stability of osmium standards $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in basic medium (NaOH, KOH and $\text{NH}_4\text{OH}$ )**

In this part of the study the stability of the Os standards were evaluated in basic medium to try and prevent the possible monitored ‘decomposition’ of the Os complex as was observed from the yellow-black colour of the plastic tops in the acidic

---

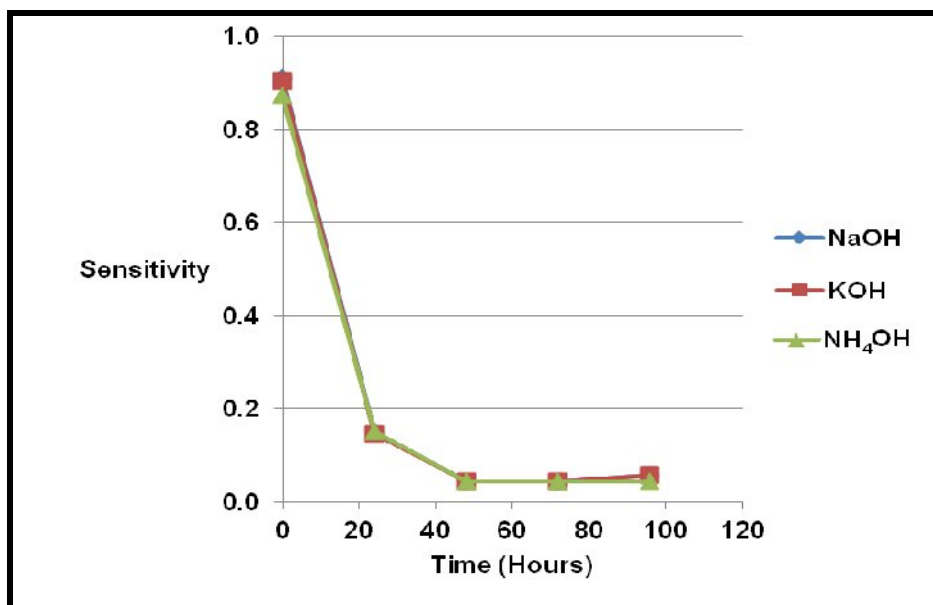
<sup>191</sup> H. Kola and P. Peramaki, *Spec. Chim. Acta Part B*, (2004), 59, pp. 231 - 242.

medium. Os calibration standards  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  were prepared in basic medium (NaOH, KOH and  $\text{NH}_4\text{OH}$ ) and the emission intensities of Os in these solutions were monitored every 24 hours. The experimental results shown in **Section 6.3.3**, **Tables 6.7 - 6.9** and **Figure 6.9** clearly show a decrease in the slopes of the calibration curves, contrary to the previously observed results obtained in the acid matrices.



**Figure 6.9:** Osmium calibration curves in the basic medium ( $\text{NH}_4\text{OH}$ ) as a function of time (48 and 72 Hrs are superimposed)

Results obtained in this part of the study also clearly showed that this decrease in sensitivity with time does not lead to the production of the yellow-brown ( $\text{OsO}_2$  or  $\text{OsO}_4$ ) coating on the volumetric flasks lids. The decrease in the sensitivity (**Figure 6.10**) is also much faster in the first 24 hours but became nearly constant after 48 hours. These results clearly indicate the Os standard  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  is not very stable in either basic or acidic medium and deteriorated rapidly within the first 48 hours.



**Figure 6.10:** Comparison of sensitivity of the osmium calibration curves in NaOH, KOH and NH<sub>4</sub>OH base matrix

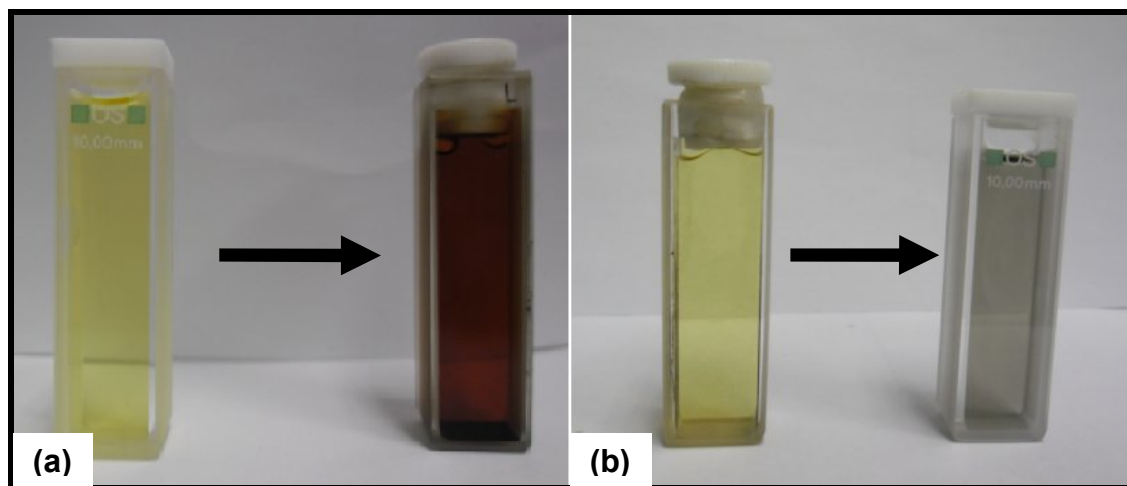
The differences in the emission intensities coupled by the shift in the calibration curves suggested different reactions (as expected) would occur between the Os standards in the acidic and basic medium. It was these differences in sensitivity and chemical reactivity using standards in acidic or basic medium that prompted further characterization of the chemical behaviour associated with (NH<sub>4</sub>)<sub>2</sub>[Os(Cl)<sub>6</sub>] in the basic and acidic medium (discussion of chemistry, see **Section 6.5.6**)

#### 6.5.4 UV-vis determination of Os standard (NH<sub>4</sub>)<sub>2</sub>[Os(Cl)<sub>6</sub>] in basic and acidic medium

A UV-vis study was carried out to investigate the chemical behaviour of the Os standard (NH<sub>4</sub>)<sub>2</sub>[Os(Cl)<sub>6</sub>] in both the acidic and basic medium. The spectrophotometric evaluation of Os standard in basic medium showed different kind of reactions compared to those observed in the acidic medium (see **Figure 6.2**). The reaction in the presence of NH<sub>4</sub>OH, NaOH and KOH clearly showed a steady decrease in absorbance in the region of 250 - 450 nm with the formation of an isosbestic point at 245 nm indicating the formation of one product.

The absorption spectra completely changes with the addition of NaOH and KOH and showed a rapid and large absorption increase from 400 nm with the formation of

absorption peaks with large extinction coefficients in the special area below 400 nm. These spectral changes is accompanied by a colour change from yellow to deep brown for  $\text{NH}_4\text{OH}$  addition while the colour change from yellow to brown-black after the addition of  $\text{NaOH}$  and  $\text{KOH}$  (**Figure 6.11**).



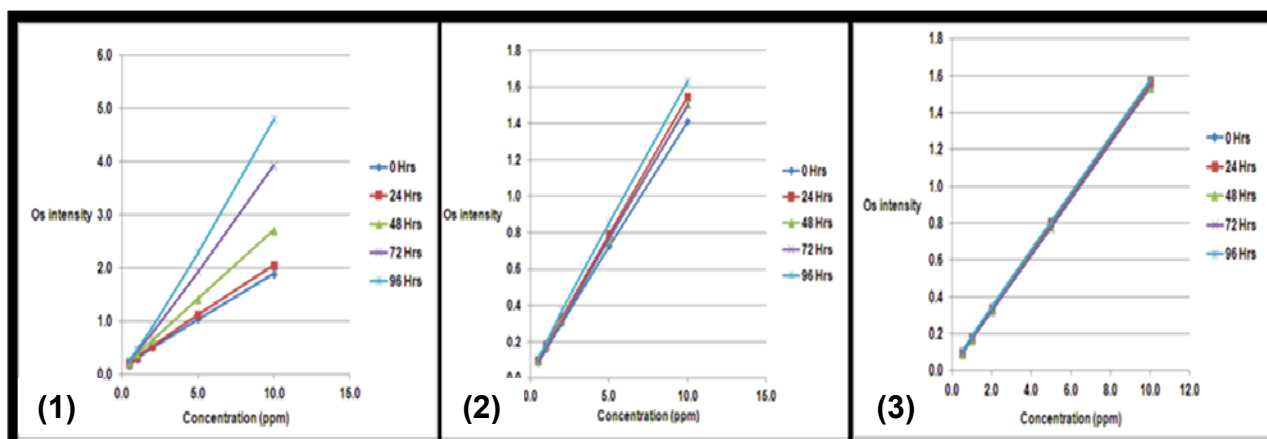
**Figure 6.11:** Spectrophotometric analysis of  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  in basic medium **(a)**  $\text{NH}_4\text{OH}$  and **(b)**  $\text{NaOH}$  and  $\text{KOH}$

No observable colour change or drastic changes in the absorbancies were observed after the addition of the different acids. However, the addition of  $\text{HF}$  led to a slow decrease in absorption in the region of 300 - 600 nm (discussion of chemistry, see **Section 6.5.6**).

#### 6.5.5 Stability of the Os standards $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ in $\text{HCl}$ in different storage conditions

The study was further expanded to determine the optimum storage and handling conditions of the Os calibration standards in  $\text{HCl}$  matrix which showed to be the preferred acid for the Os stabilization (as shown by the smallest sensitivity change). The influence of temperature and exposure to light were assessed to establish the optimum storage conditions that could minimize the decomposition of  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  in solution. It is well known that these factors may have the potential to enhance the decomposition of chemical changes during the hydrolysis reactions of  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ . Experimental results obtained in this investigation (see **Tables 6.11 - 6.13** and **Figure 6.12**) showed that the sensitivity of Os calibration curves of the

standards solution kept in the dark to increase much slower than those exposed to light. The calibration curves of the standards which were kept in the refrigerator (ca. 10 °C) were found to be constant (stable) for 4 days (see **Chapter 8** for the ANOVA test). After this period the calibration curves gradually shifted upwards as indicated by the increase in Os emission intensities.



**Figure 6.12:** Os calibration standards solutions stored in different conditions: **(1)** kept left exposed to the light, **(2)** kept in the cupboard (dark) and **(3)** kept at ca. 10 °C

These result clearly suggested that both light and temperature have an effect on the stability or lack of it on the Os standard  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ . Standards kept in the cupboard suggested that heat also had an effect on the stability of Os standards. This instability was shown to be less compared to those exposed to the light. It is therefore concluded that the optimum conditions for storing the Os standard  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  in HCl matrix is at ca. 10 °C and in the absence of light based on the ability of these standards to remain constant (discussion of chemistry, see **Section 6.5.6**).

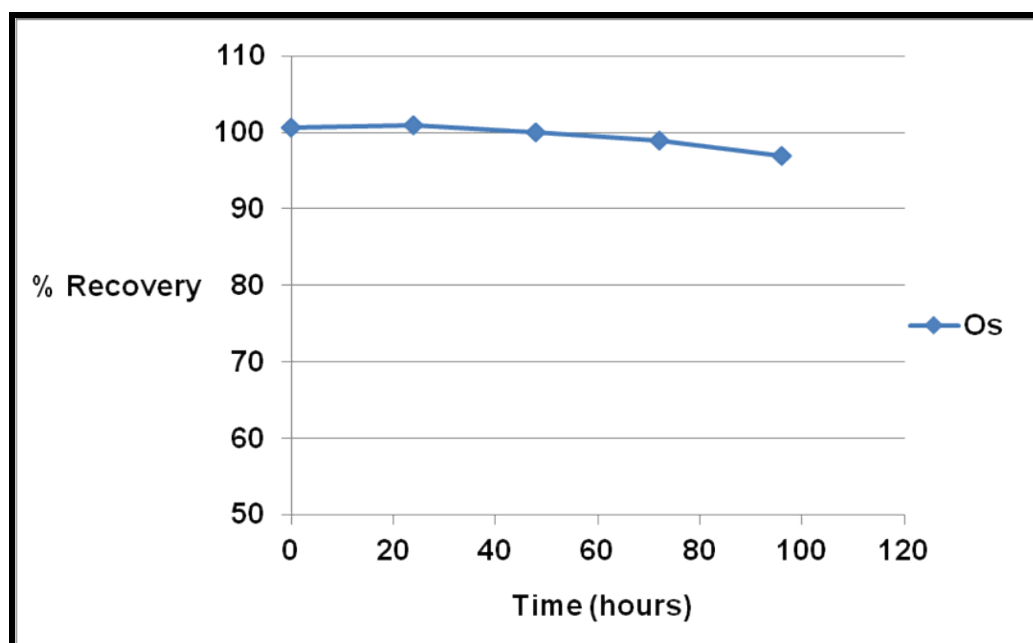
#### **6.5.5.1 Evaluation of osmium recovery in the CRM using the osmium standards kept at ca. 10 °C**

The quantification of Os in the liquid CRM, using the direct calibration method, see **Section 6.2.5.2** showed recoveries of Os (98 %) with freshly prepared standards from the onset. This inability to obtain total recovery of the osmium using the direct calibration method was mostly attributed to background emissions errors and the



possible influence by the numerous elements in the CRM (see **Chapter 5, Section 5.4.2**).

Total recovery (100 %) of the Os was obtained using Sc as internal standard for at least the first 96 hours using the prepared calibration standards which were kept at *ca.* 10 °C (see **Table 6.16** and **Figure 6.13**)



**Figure 6.13:** Determination of Os content in liquid CRM using  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  calibration standards kept at 10 °C in the absence of light

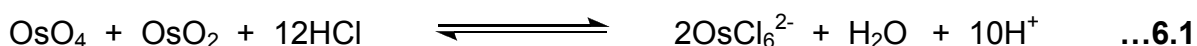
After 96 hours the Os content decreased as a result of the increase in the emission values of the standards solutions which indicates an upward shift in the calibration curve as previously determined. Based on these results, it became apparent that this instability of the Os standards was specifically confined to the Os calibration standard  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  and not the CRM solution. Inspection of the emission intensities of the (Table 6.25) CRM showed that these emissions were almost the same throughout the measurement process which indicated the stability of the CRM solutions. The instability of the  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  standards prompted the search for an alternative Os calibration standard that is stable in acidic medium.

**Table 6.25:** Emission intensities of osmium in the CRM solutions

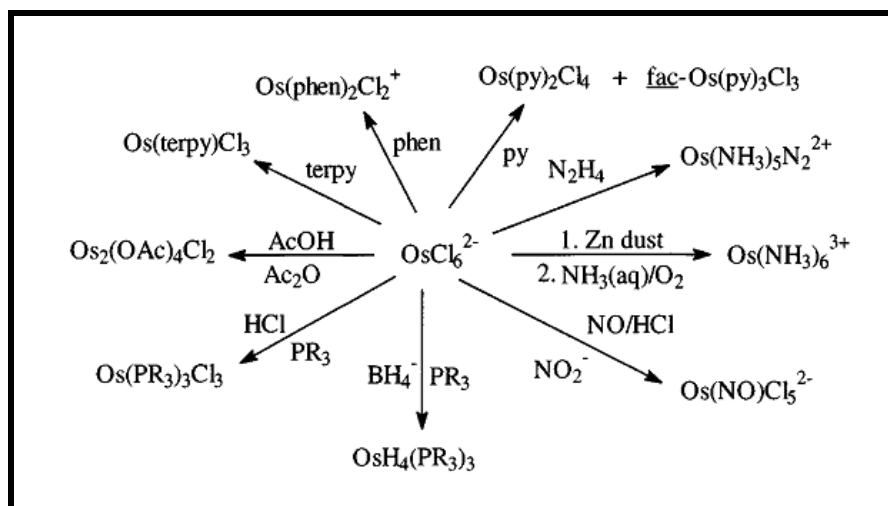
CRM replicates (n)	Osmium emission intensities				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
CRM 1	1.0953	1.0966	1.0882	1.0975	1.0962
CRM 2	1.0928	1.0983	1.0891	1.0991	1.0892
CRM 3	1.0873	1.0838	1.0709	1.0873	1.0838
Average	1.0918	1.0929	1.0827	1.0946	1.0897

### 6.5.6 Chemistry/Explanation of $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ instability in solution

The  $[\text{OsCl}_6]^{2-}$  complex is synthesized from the  $\text{OsO}_4$  compound according to **Equation 6.1**.<sup>192,193</sup>



It also well-known that this newly formed chlorido compound is used as starting material in the synthesis of numerous other osmium compounds such as those shown in **Figure 6.14**.



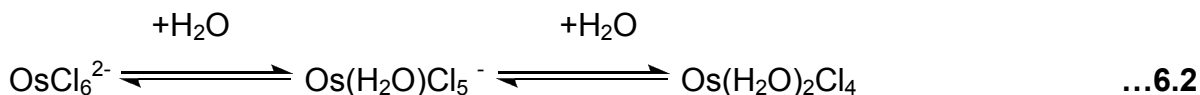
**Figure 6.14:** Reactions of  $[\text{OsCl}_6]^{2-}$  used in the synthesis of numerous osmium compounds<sup>194</sup>

<sup>192</sup> G.K. Schweitzer, *The Aqueous Chemistry of the Elements.*, Oxford University Press, Incl. (2010), pp. 319 - 321.

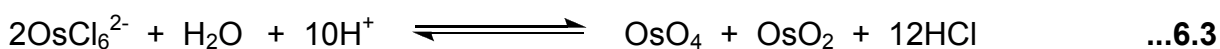
<sup>193</sup> V. P. Khvostova, G. I. Kadyrova, and I. P. Alimarin, *Izv. Akad. Nauk, Ser. Khim.*, (1977), 11, pp. 2418 - 2422.

<sup>194</sup> S. Livingstone, *Ruthenium, Rhodium, Palladium, Osmium, Iridium, and Platinum*; Pergamon, Oxford., (1975).

The use of  $[\text{OsCl}_6]^{2-}$  as reagent in many substitution reactions and therefore the synthesis of new osmium complexes clearly indicate the reactivity and therefore the lability of the chlorido ligands in this complex. This is also confirmed by the step-wise acid hydrolysis of  $[\text{OsCl}_6]^{2-}$  as indicated by **Equation 6.2**.<sup>195</sup>



The resultant products in these substitution reactions have been reported to differ in physical properties that include mobility and volatility which are very essential factors that influence spectrometric (ICP-OES/MS) measurement process.<sup>196</sup> Depending on the pH levels of the analyte solution, these newly formed complexes can also undergo additional reactions (oxidation) to produce volatile  $\text{OsO}_4$  (yellow) and  $\text{OsO}_2$  (yellow-brown) compounds<sup>197</sup> (**Equation 6.3**) as observed by the yellow-black staining of the plastic volumetric tops according to the reverse of **Equation 6.1**



Strong oxidizing acids such as  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , etc. are regarded as dangerous when working with Os solutions because of their oxidizing properties.<sup>198,199</sup>

It is therefore anticipated that the instability of  $[\text{Os}(\text{Cl})_6]^{2-}$  anion in acid solution as suggested by literature and the experimental findings in this study, are responsible for the problems associated with the reproducibility of Os recovery in the CRM. The possible substitution of the chlorido ligands by  $\text{H}_2\text{O}$  can initiate the instability of the osmium complex. This instability compounded by factors such as light and

---

<sup>195</sup> S. Kulprathipanja, D. J. Hnatovich, and S.. Treves, *J. Inorg. Nucl. Chem.*, (1977), 39 (6), pp. 933 - 935.

<sup>196</sup> S. Livingstone, *Ruthenium, Rhodium, Palladium, Osmium, Iridium, and Platinum*; Pergamon, Oxford., (1975).

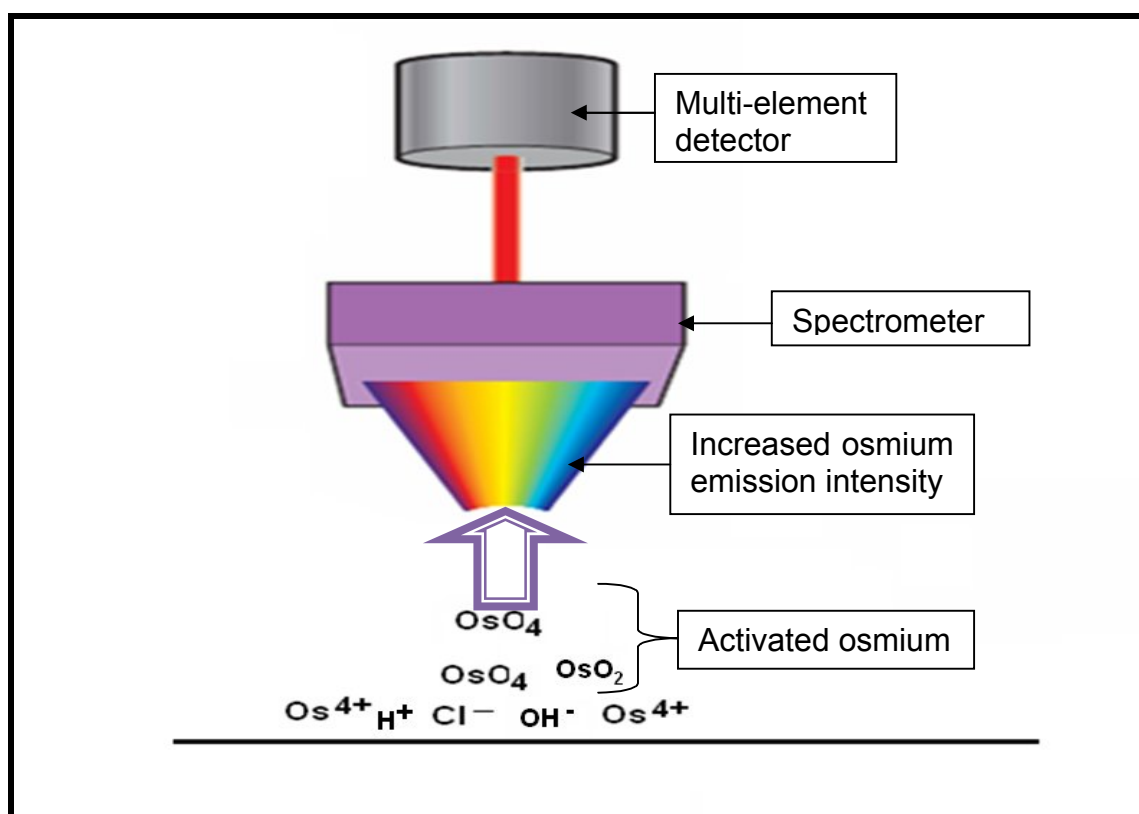
<sup>197</sup> V.P. Khvostova, D.I. Kadyrova and I.P. Alimarin, *Izv.Akad.Nauk, Ser.Khim.*, (1977), 11, pp. 2418 - 2422.

<sup>198</sup> J.P. Byrne, D.C. Gregoire, M.E. Benyounes, C.L. Chakrabarti, *Spectrochim. Acta, Part B.*, (1997), 52, p. 1575.

<sup>199</sup> T.M. Buslaeva and S.A. Simanova., *Koord. Khim.*, (2000), 26, (6), p. 403.

temperature can then lead to its oxidation to  $\text{OsO}_4$  or  $\text{OsO}_2$  as indicated by the instability of the calibration standards and as illustrated by the increased emission intensities of Os with time.

This increased emission intensities are therefore believed to be the result of higher concentrations of the more volatile  $\text{OsO}_4$  or  $\text{OsO}_2$  compounds in solution. The increase in intensity emissions can be the result of larger percentages of Os activation within the flame due the presence of these 'easier' activated Os species as indicated in (**Figure 6.15**). It is therefore postulated that  $[\text{Os}(\text{Cl})_6]^{2-}$  is converted to  $\text{OsO}_4$  and/or  $\text{OsO}_2$  in the presence of high  $\text{HCl}$  concentrations, light and/or heat leading to increase emissions intensities as indicated by the experimental results obtained in this study.



**Figure 6.15:** A postulate of the increase in osmium emission intensities as a result of the  $\text{OsO}_4$  or  $\text{OsO}_2$  production

These results are however counterintuitive to what is expected with a loss of analyte or metal compound from solution. The current results as well as explanation of the chemistry indicate increased emission as a function of time in spite of physical

indications of Os evaporation/loss from solution. These newly formed neutral Os species are volatile and would thereafter evaporate from the solution. This decrease in Os concentration should in fact lead to a decrease in emission intensities (intensities directly proportional to concentration) and hence smaller gradients (decrease in sensitivity) for the calibration curves. This would lead to an increase in Os concentration. It is therefore argued that these newly formed volatile species are more prone to activation (larger portion of Os in activated state plasma flow) which results in an increase in emission.

A repeat of this study showed noticeable traces of this yellow-black stains form after 72 hours. Taddia *et al.*<sup>200</sup> reported extensively on the challenges encountered with solutions containing OsO<sub>4</sub> emphasizing the strong absorption of OsO<sub>4</sub> to plastic surfaces and which causes significant washout problems. These findings corresponded well with the experimental observations found in this study.

The increased calibration line stability, in the absence of temperature and light, also corresponds well with the postulated reactions. It is well known that a decrease in temperature lead to a decrease in reaction rates. It also known that light can enhance oxidation of osmium(IV) complexes.<sup>201</sup> Control of both these factors will ultimately lead to slower 'decomposition', either substitution and/or oxidation of the [OsCl<sub>6</sub>]<sup>2-</sup> complex and hence more stable calibration curves.

The reactions observed in both acidic and basic mediums also correlate well with the lability of the osmium complex in solution. Substitution of the halides by the water molecules (acid hydrolysis) in [OsCl<sub>6</sub>]<sup>2-</sup> has been reported and result in the formation of [Os(H<sub>2</sub>O)<sub>n</sub>X<sub>6-n</sub>]<sup>2-</sup> type of complexes and these substitution reactions are reported to occur at different rates. The addition of HCl (see **Figure 6.1**) resulted in the absence of any spectrum change as expected while the addition of HBr and HF lead to noticeable spectrum changes and hence reactions. The slow spectrum change

---

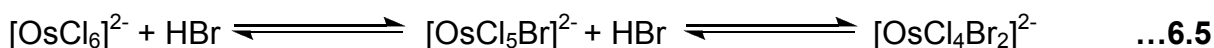
<sup>200</sup> M. Taddia, C. Lucano and A. Juris, *Anal. Chim. Acta*, (**1998**), 375, pp. 285 - 292.

<sup>201</sup> S. Kulprathipanja, D.J. Hnatovich and S. Treves, *J. Inorg. Nucl. Chem.*, (**1977**), 39, pp. 933 - 935.

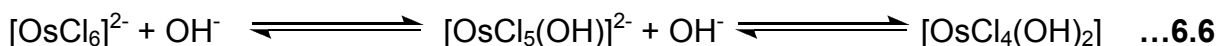
observed with the addition of HF point to the possible stepwise substitution of the Cl<sup>-</sup> anions by F<sup>-</sup> (**Equation 6.4**).<sup>202</sup>



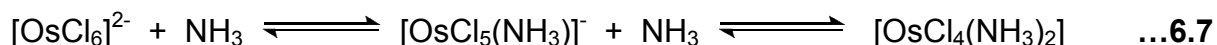
The small but quick spectrum change observed with the addition of HBr on the other hand suggest a rapid reaction with the bromide ions (**Equation 6.5**).<sup>14</sup>



Similar reactions were observed after the addition of base in the form of OH<sup>-</sup>(Na<sup>+</sup>/K<sup>+</sup>), predicting similar type of products. Possible products from this addition may be base hydrolysis with the substitution of chloride ions by the newly added hydroxide anions (**Equation 6.6**).<sup>203</sup>



The completely different reaction observed with the addition of NH<sub>4</sub>OH point to the chloride substitution by NH<sub>3</sub> according to **Equation 6.7**



The presence of an isosbestic point which clearly point to the formation of one product predict the formation of the well characterised product [Os(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)]<sup>3+</sup> obtained by amine substitution.<sup>204</sup>

In conclusion it is quite surprising that a very reactive and labile substance such as [OsCl<sub>6</sub>]<sup>2-</sup> is commercially available as analytical standard for osmium quantification. The type and number of substitution reactions which may be encountered by the

<sup>202</sup> G.K. Schweitzer, *The Aqueous Chemistry of the Elements.*, Oxford University Press, Incl. (2010), pp. 319 - 321.

<sup>203</sup> T. Vrublevska, M. Rydchuk, O. Bonishko and G. Mykhalyna, *Physicochemical mechanics of Material.*, (2010), 3, pp. 108 - 115.

<sup>204</sup> P.A. Lay, R.H. Magnuson, J. Sen and H.Taube, *J. Am.Chem. Soc.*, (1982), 55, p. 239.

osmium complex are compounded if complex mineral matrices, containing numerous and different anions, are investigated. This may lead to either to an increases or a decreased in the slope of calibration curves, depending on the type and the amount of ligands (anions) present in the matrix. This is extremely unsatisfactory for method development in analytical chemistry.

#### **6.5.7 Selection and evaluation of an alternative osmium standard**

The reactivity/lability of the  $[\text{OsCl}_6]^{2-}$  complex in all the chemical environments investigated in this study as well as its instability in normal laboratory conditions necessitated the investigation for an alternative osmium source/complex which can be evaluated and used as osmium standard. In this respect  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  was identified as possible Os standard which can be used as calibration standard.

Research done on the protonation and substitution of different dioxidotetracyanido complexes (Mo, W, Re, Mn and Os) indicated the stepwise protonation of one of the oxygen ligands.<sup>205</sup> In the process these protonation reactions produce the corresponding oxido-hydroxido and oxido-aqua complexes in solution. Crystallography as well as kinetic studies confirmed the displacement of the aqua ligand during substitution reaction. The results from both the crystallography and kinetics indicated that the  $[\text{OsO}_2(\text{CN})_4]^{2-}$  complex is extremely stable ( $\text{pK}_a < 0$ ) in highly acidic environments with no indication of oxygen protonation and therefore no substitution reactions. Structural characterization done by Purcell *et al.*<sup>206</sup> indicated that the  $[\text{OsO}_2(\text{CN})_4]^{2-}$  compound is octahedrally surrounded by two oxygen atoms (*trans* to one another) and four cyanido ligands. The ability of  $[\text{OsO}_2(\text{CN})_4]^{2-}$  to resist protonation was attributed to the relatively strong metal-oxygen bond which implied very weak oxygen-hydrogen bonds.

It is this stability in acid medium with no indication of any detectable reaction which created the interest in this complex as osmium standard.

---

<sup>205</sup> W. Purcell, A. Roodt, S.S. Basson and J.G. Leipoldt, *Transition Met. Chem.*, (1991), 16, pp. 60 - 61.

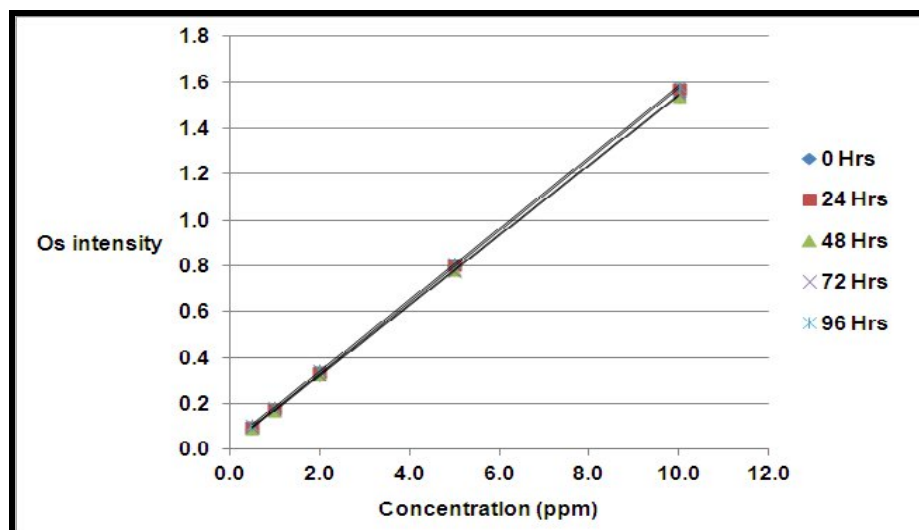
**6.5.7.1 Characterization of  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$** 

IR characterization of the newly synthesized product in this study yielded an Os=O stretching frequency at  $829\text{ cm}^{-1}$  and that of Os-CN at  $2152\text{ cm}^{-1}$  (see **Figure 6.3**). These stretching frequencies correspond well with those reported in literature of  $840\text{ cm}^{-1}$  for Os=O and  $2158\text{ cm}^{-1}$  for the Os-CN bond, confirming the identity of the newly synthesized compound. The ease of preparation also makes this complex ideally suitable as osmium standard.

**6.5.7.2 A comparison of  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  standards kept at ca.  $10\text{ }^\circ\text{C}$  and those kept exposed to light and the quantitative determination of osmium using these standards**

The Os calibration curves prepared using  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  in HCl matrix were found to be stable for a period of 96 hours showing almost identical calibration curves for this period (see **Tables 6.17** and **6.18**). These Os calibration standards were found to be stable up to 3 months whilst kept at ca.  $10\text{ }^\circ\text{C}$  and at least a month whilst kept exposed to light (**Figure 6.16**). Temperature control and the possibility of light determined to be the major factors contributing to the deterioration of the Os standards in the acidic medium. The stability of this newly established  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  standard is believed to be in its ability to resist hydrolysis, protonation or substitution reactions. It is also important to note that osmium is in the +8 state and cannot be oxidized any further.





**Figure 6.16:** Stability test of Os calibration standards in HCl medium prepared from the newly synthesized  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  compound

Quantitative results of Os from the CRM obtained using the  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  standards showed an average percentage recovery of + 100 % using the direct calibration method (see **Table 6.19**). Lower Os percentage recovery was obtained from the onset of the analysis ( $t_{\text{initial}} = 0$  Hrs) using both the direct calibration (88.1 %) and Sc internal standard addition method (99.7 %). This lower recovery was assumed to have been the result of the insufficient time (more than an hour) required to stabilize both the standards and the analyte solutions. Total recoveries (100 %) of Os were obtained using Sc as internal standard for the duration of the experimental analysis (see **Table 6.20**). These experimental results suggested that the newly established  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  standard can be used whilst kept at room temperature and in the presence of ambient light.

The total recovery of osmium for extended periods of time clearly indicate that the  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  complex can successfully be used as osmium standard. Properties such as ease of preparation, calibration curve stability in acidic mediums and total osmium recovery in the presence of Sc as internal standard make it extremely suitable alternative standard for Os determination in different types of samples.

The optimum storage conditions of the  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  calibration standards were determined to be in the absence of light and at *ca.* 10 °C and these storage

conditions were found also to be suitable for the  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  calibration standards.

## **6.6 Conclusion**

Osmium recovery was found to be affected by a gradual shift in Os calibration curves as a function of time. The decrease/increase in the percentage recovery of Os was found to be directly proportional to the upward/downward shift in the calibration curves. The calibration curve shift was mainly attributed to the production of either  $\text{OsO}_2$  or  $\text{OsO}_4$  in the calibration standards  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  solutions in the acidic medium. These volatile species were believed to increase the Os emission intensities during the measurement process which eventually caused an upward shift in the calibration curves. The slopes of calibration curves prepared in HCl matrix increased slower compared to those prepared in HF and HBr. The slopes of osmium standards prepared in basic solutions decreased with time. Research results also indicated improved stability of the osmium calibration standards in HCl using  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  when they are kept in the dark at *ca.* 10 °C. Osmium standards made from the newly synthesized  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  compound in HCl matrix were found to be stable for the period of the investigation (96 Hours) whilst kept at room temperature and at *ca.* 10 °C.

Quantitative results of Os obtained using the direct calibration method showed a low percentage recovery (*ca.* 98 % and below) using both the calibration standards stored under the determined optimum conditions. Experimental results obtained using Sc as an internal method using the same standards under the preferred conditions showed total recovery in all experimental analysis.

Optimal conditions for Os calibration standard storage,  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  and  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ , was determined as 10 °C in the dark. A summary of all the quantitative determination of Os in different conditions using both the direct calibration and the Sc internal standards is given in **Table 6.23**.

**Table 6.23:** Summary of the quantitative results of osmium obtained using the liquid CRM

Sample	Calibration standards	Condition	Method	Average % Os recovery
Liquid CRM	$(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$	Preliminary investigation of the HCl acid matrix (0 - 96 Hrs)	Direct cal.	83(10)
	$(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$	HCl acid matrix at ca. 10 °C (0 - 96 Hrs)	Direct cal.	91(6)
			<b>Sc</b>	<b>100(2)</b>
	$\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$	HCl acid matrix at exposed to the light (0 - 96 Hrs)	Direct cal.	99(6)
			<b>Sc</b>	<b>100.0(6)</b>
	$\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$	HCl acid matrix at ca. 10 °C in the absence of light (0 - 96 Hrs)	Direct cal.	81(8)
			<b>Sc</b>	<b>100.4(5)</b>

Bolded results = total osmium recovery under the given conditions and method

# 7 Determination of precious metal content: Evaluation of scandium as internal standard

---

## 7.1 Introduction

The application of quantitative methods in method development can be influenced by a number of factors, which amongst others include sample preparation and matrices derived from the sample composition. Accurate quantitative determination of precious metals using wet chemical analysis requires a complete conversion of the solid particles into a soluble product which forms the basis of the measurement. Incomplete digestion/dissolution of samples such as inorganic and organometallic compounds or occlusion of the analyte within the grains of the undigested geological ores can result in the non-quantitative recovery of the precious metals. Matrices introduced into the analyte solution after the digestion/dissolution process such as the acid inequality and EIE's can also cause significant errors in the determination of PGM and gold as previously shown in **Chapter 5, Section 5.5.2**. These matrices should be minimized or avoided in order to accurately determine the percentage recoveries of precious metals using the newly developed scandium internal standard as discussed in **Chapter 5**.

In this chapter an assessment on the use of scandium as internal standard in determining the precious metal content in inorganic salts, organometallic compounds and geological mineral ores will be investigated. Quantitative results obtained using this method will be compared against the results obtained using the direct calibration method. All the quantitative results obtained in this part of the study will be validated in **Chapter 8** as part of method validation using ISO 17025 requirements as benchmark.

## **7.2 Reagents and glassware**

Inorganic salts {HAuCl<sub>3</sub>·4H<sub>2</sub>O (99 %), IrCl<sub>3</sub>·3H<sub>2</sub>O (98 %), RhCl<sub>3</sub>·3H<sub>2</sub>O (99 %), RuI<sub>3</sub>·3H<sub>2</sub>O (99 %), OsCl<sub>3</sub>·3H<sub>2</sub>O (99 %), PdCl<sub>2</sub> (99 %) and PtCl<sub>2</sub> (98 %)} including the organic solvents (absolute ethanol, methanol, dichloromethane (DCM) and acetone) were purchased from Inorganic Ventures. Organometallic compounds with known purity such as chlorido(1,5-cyclooctadiene)iridium(I) dimer (97 %), acetylosmium (99 %), acetylruthenium (99 %), [Ru(cod)(Cl)<sub>2</sub>] (97 %) and [Pt(cod)(Cl)<sub>2</sub>] (99 %) were purchased from Sigma Aldrich. All the chemicals and reagents such as ethanol, acetone, acetylacetone (acac), cupferron (cupf) and N,N-dimethylformamide (DMF), 1,2-phenylenediamine, neocuproine, 2,2'-bipyridyl and ethylenediamine were used without further purification in the synthesis of organometallic complexes. Disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>) (99 %) and sodium dihydrogen phosphate monohydrate (NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O), ammonium hydrogen difluoride (NH<sub>4</sub>·HF<sub>2</sub>) (98 %), ammonium hydrogen phosphate (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) (99 %) were purchased from Merck. All the glassware used for the metal analysis in this study was of Schott Duran, grade (A) type.

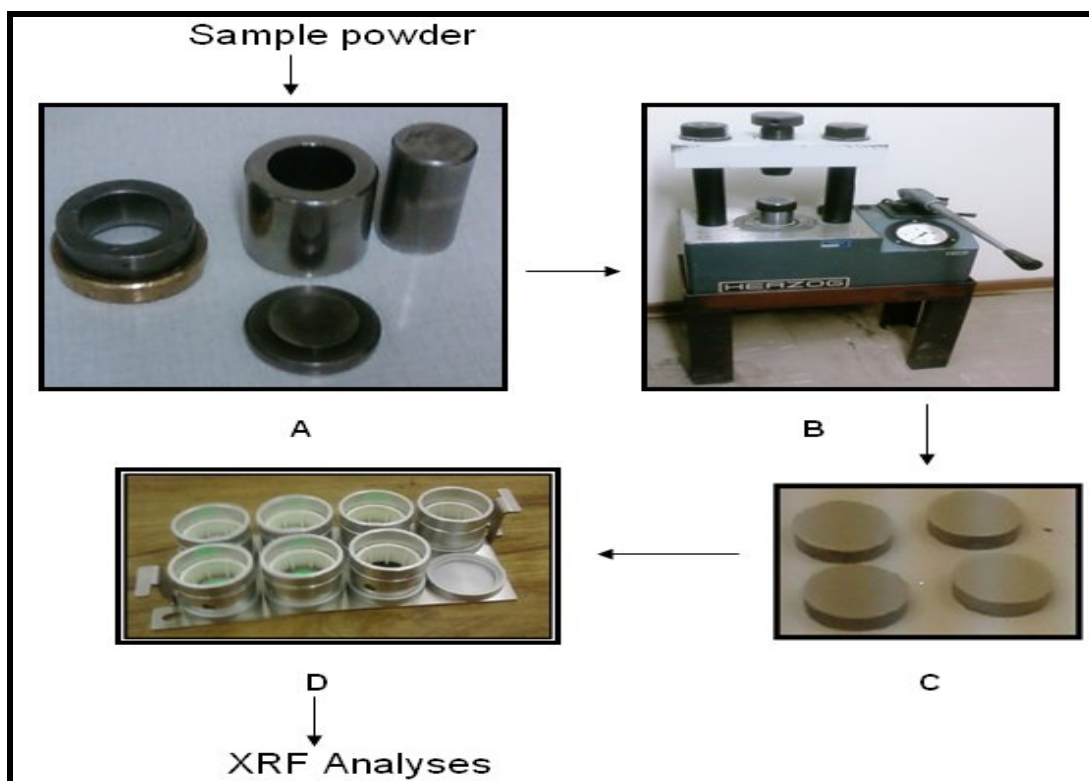
## **7.3 Equipment**

Equipment used in this part of the study include the ICP-OES and ICP-MS, microwave digester, high temperature fusion furnace (*max.* 1 300 °C) and infrared spectrometer which have been described in **Chapter 5, Section 5.3**. The average values for the results are reported based on the standard deviations to indicate the uncertainty in the last digit of the value throughout the chapter. The standard deviations are based on triplicate analyses.

### **7.3.1 X-ray fluorescence spectrometry**

Quantitative measurements of the mineral constituents were obtained from a PANalytical Wavelength Dispersive X-Ray Fluorescence (WDXRF) Spectrometer. The mineral samples were first ground to a fine powder of less than 12 µm by means

of a vibration grinding mill. Sample holders shown in **Figure 7.1** were used to transfer the sample to the XRD instrument for analyses as described in **Section 7.6**.



**Figure 7.1:** Series of steps involved in sample preparation for XRF analysis <sup>207</sup> (A) Sample poured in the dies (B) Pressing instrument (C) Compressed pellets (D) Sample holder

## 7.4 Determination of PGM and gold in inorganic and organometallic compounds

One of the main objectives of this study was to evaluate a working method for the simultaneous determination of the precious metal content in inorganic and organometallic compounds (see **Chapter 1, Section 1.2**). The uses of Sc as internal standard method was first evaluated on various inorganic salts and then on organometallic compounds to assess its ability to accurately determine precious metals in these compounds. The organometallic complexes synthesized during this

<sup>207</sup> M. Nete, *Dissolution and analytical characterization of tantalite ore, niobium metal and other niobium compounds*, MSc thesis, University of the Free State, (2009), p. 52.

study were selected on the basis of ease of preparation, well documented characterization and most importantly purity of the final product. Quantitative results obtained using Sc as internal standard is then compared with the results obtained using the direct calibration method. All the results obtained in this Section will be validated in **Chapter 8** to determine if they are acceptable at 95 % confidence interval.

#### **7.4.1 General experimental procedures**

##### **7.4.1.1 *Preparation of the precious metals calibration standards (direct calibration method)***

The calibration standards for the precious metals were prepared from the original PGM and gold stock solutions (1 000 ppm) to concentrations of 0.0 (blank), 1.0, 2.0, 5.0 and 10.0 ppm in different 100.0 mL volumetric flasks using a 'Transferpette' micro-pipette. Hydrochloric acid (5.0 mL; 32 %) was added to all the flasks and filled up to the mark using double distilled water. The solutions were homogenized and left to stabilize for an hour before it was used.

##### **7.4.1.2 *Preparation of the precious metals calibration standards (internal standard method)***

The calibration standards for the precious metals were prepared from the original PGM and gold stock solutions (1 000 ppm) to concentrations of 0.0 (blank), 1.0, 2.0, 5.0 and 10.0 ppm in different 100.0 mL volumetric flasks using a 'Transferpette' micro-pipette. Equal volumes of the prepared Sc internal standard solutions (0.2 mL; 1 000 ppm) and HCl (5.0 mL; 32 %) were added to the solutions and the volumetric flasks were filled up to the mark using double distilled water. The solutions were homogenized and left to stabilize for an hour before it was used.

#### **7.4.1.3     *Preparation of the osmium calibration standards using the $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ compound***

Two sets of Os calibration standards were prepared from the  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  compound to yield Os concentrations with a working range of 0.5 - 10.0 ppm in different volumetric flasks (100.0 mL). In the first set (Sc as internal standard) equal volumes of Sc standard (0.2 mL; 1 000 ppm) and HCl (5.0 mL; 32 %) were added to the first set. In the second set (direct calibration) HCl (5.0 mL; 32 %) was added and both sets of volumetric flasks and were all filled up to the mark using double distilled water. The solutions were homogenized and allowed to stabilize for an hour before it was used. The calibration standards were stored at room temperature for the duration of the experimental analysis. The Os emission intensities were measured every 24 hours and are reported in **Section 7.4.4.2** together with the graphical presentations of these results.

#### **7.4.2     Qualitative and quantitative determination of iridium in inorganic and organometallic compounds**

##### **7.4.2.1     *Determination of iridium in the inorganic salt $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$***

###### **7.4.2.1.1     *Preparation of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ analyte samples***

A stock solution of  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  (24 mg; 0.07 mmol) was prepared in a volumetric flask (100.0 mL) and filled up to the mark using double distilled water to yield a theoretical iridium concentration of 130.83 ppm. Aliquots (5.35 mL) (in triplicate) of the stock solution were pipetted into volumetric flasks (100.0 mL) to yield analyte concentrations of approximately 7.0 ppm. Scandium internal standard (0.2 mL; 1 000 ppm) and HCl (5.0 mL; 32 %) were added to each of the analyte solutions and the volumetric flasks were filled up to the mark using double distilled water. The solutions were left to stabilize for an hour before it was analyzed for the iridium content using standards prepared in **Section 7.4.1.1** and **7.4.1.2**. Quantitative results obtained from the ICP-OES/MS analysis are reported in **Table 7.1**.



**Table 7.1:** ICP-OES/MS quantitative determination of iridium in  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  obtained using direct calibration and Sc as internal standard

Technique	% Recovery of Ir* (direct calibration)	% Recovery of Ir* (Sc as internal standard)
ICP-OES	81(3)	100.0(3)
ICP-MS	70(1)	100.4(8)

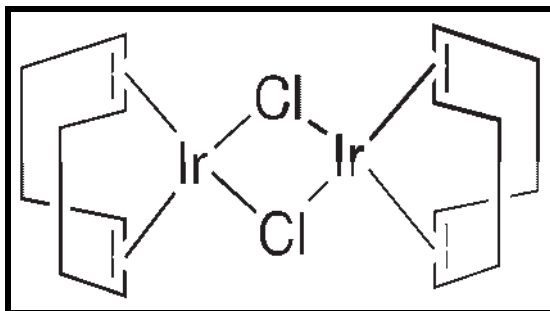
\*Quantitative results given as an average of 3 replicates

Qualitative analysis of  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  revealed trace amounts (below 1 ppm) of Ca, Fe, Mg and Mn which were found to impose no significant interference on the determination of iridium using both techniques. Quantitative results of iridium from both ICP-OES/MS techniques using the direct calibration method revealed low percentage recoveries of 81 % using ICP-OES and 70 % using ICP-MS. The obtained low percentage recovery is probably due to be the result of uncorrected background responses and instrumental drifts which have been previously discussed in **Chapter 4, Section 4.2.2**. Total percentage recoveries (100 %) of the iridium were obtained with Sc as internal standard in both ICP-OES/MS techniques. The effectiveness of the Sc as internal standard in determining iridium using the ICP-OES/MS was confirmed by the similarity in the results obtained using both techniques. These total recoveries obtained using Sc as internal standard is attributed to the ability of the method to effectively compensate for the interferences caused by the background emissions and instrumental drifts.

#### 7.4.2.2 Preparation of iridium organometallic compounds

##### 7.4.2.2.1 Chlorido(1,5-cyclooctadiene)iridium(I) dimer ( $[\text{Ir}(\text{cod})\text{Cl}]_2$ ) 97 %

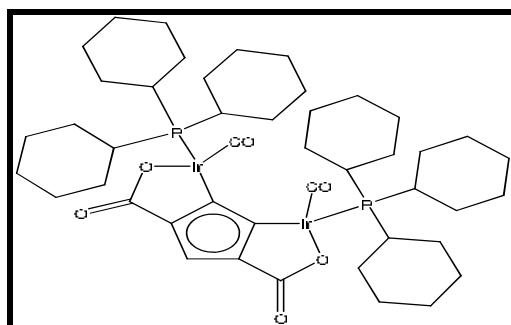
Chlorido(1,5-cyclooctadiene)iridium(I) dimer (97 %) (**Figure 7.2**) was purchased from Sigma Aldrich.



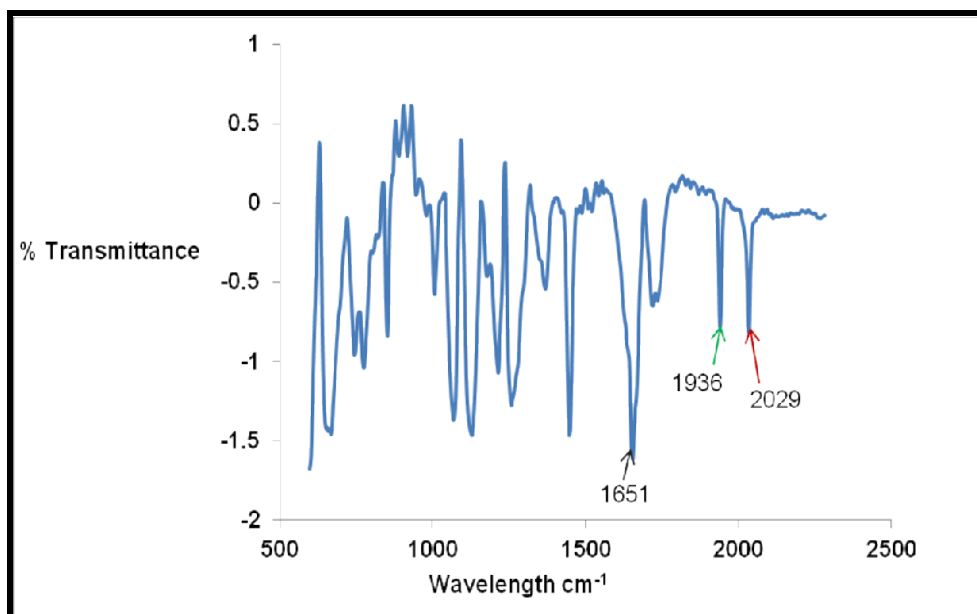
**Figure 7.2:** Molecular structure of  $[\text{Ir}(\text{cod})\text{Cl}]_2$

**7.4.2.2.2**     *Synthesis of tetrabutylammonium- $\mu$ -3,5-dicarboxylatopyrazolatocarbonyl-tricyclohexylphosphineiridate(I),  $(\text{Bu}_4\text{N})[\text{Ir}_2(\mu\text{-Dcbp})(\text{CO})_2(\text{PCy}_3)_2]$*

$(\text{Bu}_4\text{N})[\text{Ir}_2(\mu\text{-Dcbp})(\text{cod})_2]$  (100 mg, 0.14 mmol) was dissolved in 35 mL acetone. Carbon monoxide was bubbled through the solution for 10 min, while stirring and maintaining a nitrogen atmosphere over the solution. The bright yellow solution changed to light yellow during this process. Tricyclohexylphosphine ( $\text{PCy}_3$ ) (220 mg, 0.8 mmol) was added slowly to the first solution while stirring and maintaining a nitrogen atmosphere. A light yellow precipitate formed after 45 min indicating the formation of the product (**Figure 7.3**). The solution was stirred for another 2 hours after which the volume of the solution was reduced to half of its original volume using a flow of nitrogen gas. The precipitate was centrifuged, washed with ether and dried in a desiccator for 8 hours. Yield 63 %, IR data:  $\nu_{(\text{OCO})} = 1651 \text{ cm}^{-1}$ ,  $\nu_{(\text{CO})} = 2029$  and  $1936 \text{ cm}^{-1}$  (**Figure 7.4**). Elemental analysis (calculated values in brackets); C, 55.37 (56.04) %.



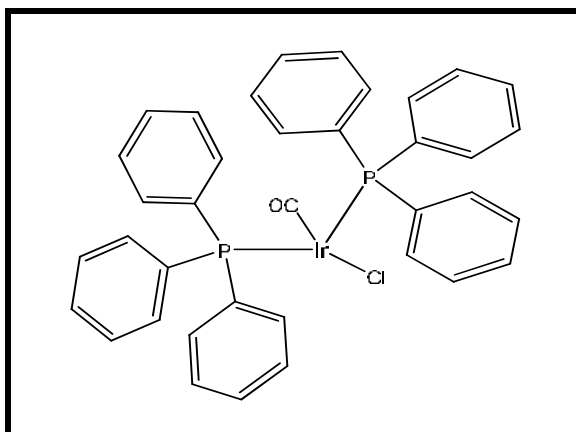
**Figure 7.3:** Structure of  $(\text{Bu}_4\text{N})[\text{Ir}_2(\mu\text{-Dcbp})(\text{CO})_2(\text{PCy}_3)_2]$



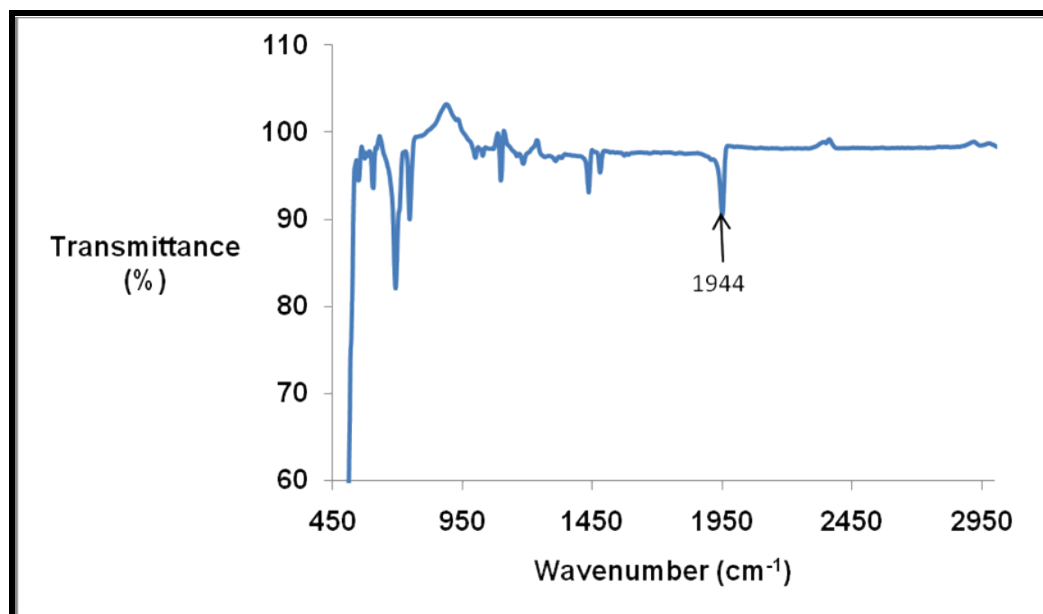
**Figure 7.4:** Infrared spectrum of  $(\text{Bu}_4\text{N})[\text{Ir}_2(\mu\text{-Dcbp})(\text{CO})_2(\text{PCy}_3)_2]$

#### 7.4.2.2.3 Synthesis of carbonylchloridobistriphenylphosphineiridium(I), $[\text{Ir}(\text{CO})(\text{Cl})(\text{PPh}_3)_2]$

Triphenylphosphine ( $\text{PPh}_3$ ) (20 mg; 0.08 mmol) was added to a well stirred solution of  $[\text{Ir}(\text{cod})(\text{Cl})]_2$  (50 mg; 0.07 mmol) in DCM (10 mL) whilst bubbling CO in the reaction mixture for 30 min until a yellow precipitate was formed. The yellow product (**Figure 7.5**) was washed with DCM (3 x 5 mL) and dried in a desiccator before characterized using IR (**Figure 7.6**). Yield: 85 %, IR data:  $\nu_{(\text{CO})} = 1944 \text{ cm}^{-1}$ . Elemental analysis (calculated values in brackets); C, 55.70 (56.95) %.



**Figure 7.5:** Molecular structure of  $[\text{Ir}(\text{CO})(\text{Cl})(\text{PPh}_3)_2]$



**Figure 7.6:** Infrared spectrum of  $[\text{Ir}(\text{CO})(\text{Cl})(\text{PPh}_3)_2]$

#### 7.4.2.2.4 Qualitative and quantitative determination of iridium in organometallic compounds

The obtained carbonyl stretching frequencies of the newly synthesized iridium compounds compared well with those reported in the literature (values in brackets). The experimental  $\nu_{(\text{CO})}$  stretching frequencies for  $(\text{Bu}_4\text{N})[\text{Ir}_2(\mu\text{-Dcbp})(\text{CO})_2(\text{PCy}_3)_2]$ <sup>208</sup> were found to be 1936 (1932) and 2029 (2028)  $\text{cm}^{-1}$  and the  $\nu_{(\text{OCO})}$  stretching frequencies were observed at 1651 (1617)  $\text{cm}^{-1}$ . The carbonyl stretching frequency for  $[\text{Ir}(\text{CO})(\text{Cl})(\text{PPh}_3)_2]$ <sup>209</sup> was found to be 1944 (1960)  $\text{cm}^{-1}$  while the rest of the newly obtained stretching frequencies were in the same range as the reported literature values. Iridium organometallic samples ( $[\text{Ir}(\text{cod})\text{Cl}]_2$ ,  $(\text{Bu}_4\text{N})[\text{Ir}_2(\mu\text{-Dcbp})(\text{CO})_2(\text{PCy}_3)_2]$  and  $[\text{Ir}(\text{CO})(\text{Cl})(\text{PPh}_3)_2]$ ) were accurately weighed (15 - 20 mg) and quantitatively transferred into separate beakers and digested in HCl (5 mL; 32 %) until a complete dissolution was achieved. The resultant clear solutions were quantitatively transferred into 100.0 mL volumetric flasks and filled up to the mark using double distilled water to yield stock solutions

<sup>208</sup> E. Grobbelaar, J. Conradie, J.A. Venter, W. Purcell and T.T. Chiweshe, *Journal of Organometallic Chemistry.*, (2011), 696, pp. 1990 - 2002.

<sup>209</sup> M. Rahim and K.J. Ahmed, *Inorg. Chem.* (1994), 33, pp. 3003 - 3004.

with concentrations between 100 - 150 ppm of iridium. Aliquots of the prepared iridium stock solutions (1 - 5 mL) (triplicate) were pipetted into separate 100.0 mL volumetric flasks and Sc internal standard (0.2 mL; 1 000 ppm) and HCl (5.0 mL; 32 %) were added to yield a theoretical iridium concentration of *ca.* 7.0 ppm. The volumetric flasks were filled up to the mark using double distilled water and the solutions were homogenized before left to stabilize for an hour. The analyte solutions were determined for iridium content using the direct calibration and Sc as internal standard with the calibration standards prepared in **Section 7.4.1.1** and **7.4.1.2** respectively. Results of the quantitative analysis using both methods are reported in **Table 7.2**.

**Table 7.2:** Quantitative results of the iridium in the organometallic compounds using the direct calibration and Sc as internal standard

Element	Organometallic compounds	Method	% Recovery*
Iridium	$[\text{Ir}(\text{cod})\text{Cl}]_2$	Direct cal.	101.7(6)
		Sc int. standard	100.0(5)
	$(\text{Bu}_4\text{N})[\text{Ir}_2(\mu\text{-Dcbp})(\text{CO})_2(\text{PCy}_3)_2]$	Direct cal.	105.0(5)
		Sc int. standard	99.7(8)
	$[\text{Ir}(\text{CO})(\text{Cl})(\text{PPh}_3)_2]$	Direct cal.	89(1)
		Sc int. standard	99(1)

\*Quantitative results given as an average of 3 replicates

Qualitative analysis of the purchased and the newly synthesised organometallic complexes revealed the presence of trace amounts (below 1 ppm) of Ca and Mg as the major trace metals presumably from the reagents and/or mineral acids. Higher percentage recoveries of iridium (+ 102 %) were obtained using the direct calibration method whilst total recoveries (100 %) were obtained using Sc as internal standard. The quantitative results showed that excellent results (100 %) were obtained using scandium as the internal standard in iridium compounds with known purity. This ability to achieve a total recovery of iridium in organometallic compounds demonstrated the effectiveness of using scandium as internal standard in determining iridium in either inorganic or organometallic compounds with known purity or which have been fully characterized.

### 7.4.3 Qualitative and quantitative determination of gold in inorganic and organometallic compounds

#### 7.4.3.1 Determination of gold in the inorganic salt $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$

##### 7.4.3.1.1 Preparation of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ analyte samples

A stock solution of the  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  (26 mg, 0.06 mmol) was prepared in a volumetric flask (100.0 mL) and filled up to the mark using double distilled water to yield a theoretical gold concentration of 124.35 ppm. Aliquots (5.63 mL) (in triplicate) of the stock solution were pipetted into volumetric flasks (100.0 mL) to yield analyte concentrations of approximately 7.0 ppm. Scandium internal standard (0.2 mL; 1 000 ppm) and HCl (5.0 mL; 32 %) were added to each of the analyte solutions and the volumetric flasks were filled up to the mark using double distilled water. The solutions were left to stabilize for an hour before it was analyzed for the gold content using standards prepared in **Section 7.4.1.1** and **7.4.1.2**. Quantitative results obtained from the ICP-OES/MS analysis are reported in **Table 7.3**.

**Table 7.3:** ICP-OES/MS quantitative determination of gold in inorganic salts using the direct calibration and Sc as internal standard

Technique	% Recovery of Au* (direct calibration)	% Recovery of Au* (Sc as internal standard)
ICP-OES	94.2(2)	100(1)
ICP-MS	95.3(5)	99.9(2)

\*Quantitative results given as an average of 3 replicates

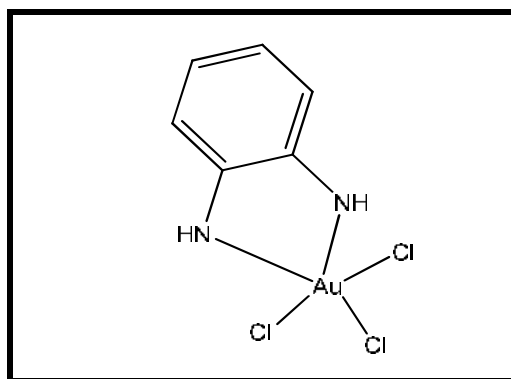
A qualitative analysis of  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  revealed the presence of trace amounts (below 1 ppm) of Ca, Fe and Mg which were found to have no interference on the determination of gold. Quantitative results of gold from both ICP-OES/MS techniques revealed low percentage recoveries of gold (94 % using ICP-OES and 95 % using ICP-MS) using the direct calibration method. The low percentage recovery was assumed to have been the result of uncorrected background responses and instrumental drifts which have been previously discussed in **Chapter 4, Section 4.2.2**. Total percentage recoveries (ca. 100 %) of the gold were obtained using Sc as internal standard with both ICP-OES/MS techniques. The use of Sc as internal

standard was also shown to accurately determine gold in samples with less amount of interfering species.

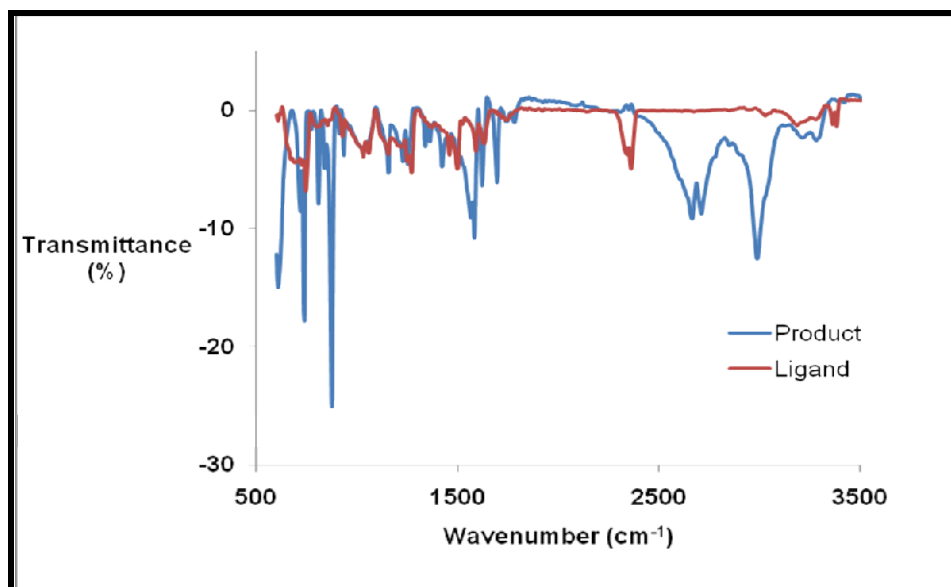
### 7.4.3.2 Preparation of gold organometallic compounds

#### 7.4.3.2.1 Synthesis of $[\text{Au}(\text{opd})(\text{Cl})_3]$

$\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  (64 mg; 0.16 mmol) was dissolved in 5 mL of absolute ethanol at room temperature. A solution of 1,2-phenylenediamine (opd) (17 mg; 0.16 mmol) in ethanol was added drop-wise whilst stirring the reaction mixture gently. An orange-brown product (**Figure 7.7**) was precipitated immediately after the addition of the ligand and the reaction mixture was further stirred for 10 min. The brown product (yield 66 %), was filtered and washed with ethanol (3 x 10 mL) and dried in a dessicator before characterized using IR (**Figure 7.8**). Elemental analysis (calculated values in brackets); C, 16.89 (17.60) and N, 5.27 (6.84) %.



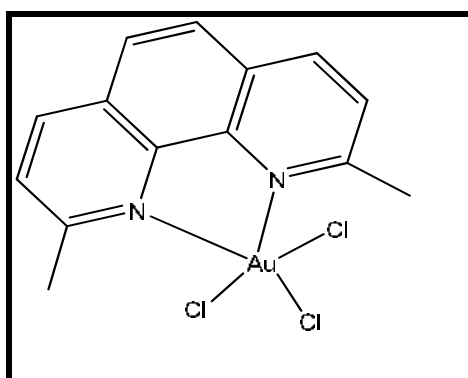
**Figure 7.7:** Molecular structure of  $[\text{Au}(\text{opd})(\text{Cl})_3]$



**Figure 7.8:** Infrared spectrum of  $[\text{Au}(\text{opd})(\text{Cl})_3]$

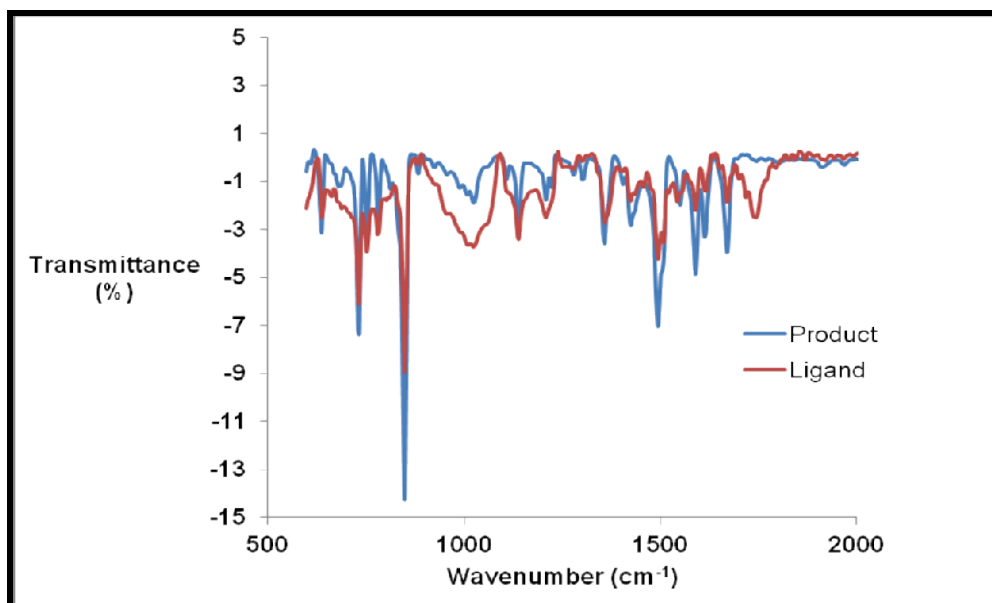
#### 7.4.3.2.2 Synthesis of $[\text{Au}(2,9\text{-Me}_2\text{phen})(\text{Cl})_3]$

$\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  (88 mg; 0.22 mmol) was dissolved in absolute ethanol (5 mL) and 2,9-dimethyl-1,10-phenanthroline (2,9- $\text{Me}_2\text{phen}$ ) (0.04 mL, 0.45 mmol) dissolved in 1 mL absolute ethanol was added drop-wise while stirring. The resultant solution was stirred for further 15 min. This orange-yellow solution was left to crystallize and brightly coloured crystals were formed (yield 53 %) after 48 hours (**Figure 7.9**) and were characterized using IR (**Figure 7.10**). Elemental analysis (calculated values in brackets); C, 31.20 (32.87) and N, 4.76 (5.48) %.



**Figure 7.9:** Molecular structure of  $[\text{Au}(2,9\text{-Me}_2\text{phen})(\text{Cl})_3]$

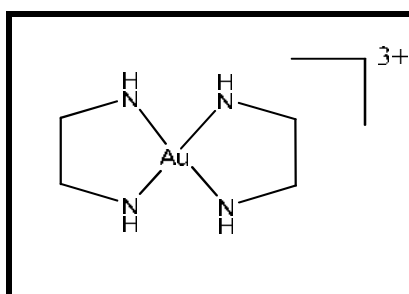




**Figure 7.10:** Infrared spectrum of  $[\text{Au}(2,9\text{-Me}_2\text{phen})(\text{Cl})_3]$

#### 7.4.3.2.3 Synthesis of $[\text{Au}(\text{en})(\text{Cl})_2]\text{Cl}$ <sup>210,211</sup>

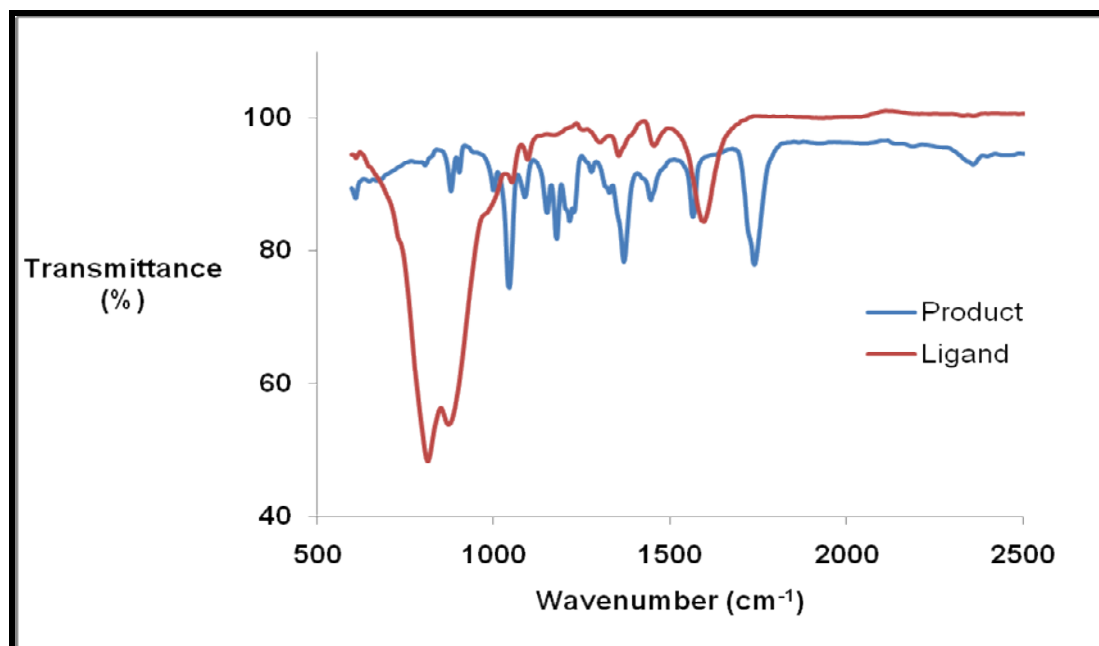
$\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  (48 mg; 0.12 mmol) was dissolved in 10 mL of absolute ethanol at room temperature. To this solution ethylenediamine (0.02 mL; 0.25 mmol) was added whilst gently stirring. A yellow product precipitated immediately after the addition of the ligand and the reaction mixture was further stirred for 10 min. The product (**Figure 7.11**) was filtered and washed with ethanol (3 x 10 mL) and dried in a dessicator (yield 57 %), before characterized using IR (**Figure 7.12**). Elemental analysis (calculated values in brackets); C, 14.48 (15.34) and N, 16.57 (17.89) %.



**Figure 7.11:** Molecular structure of  $[\text{Au}(\text{en})_2]\text{Cl}_3$

<sup>210</sup> S. Zhu, W. Gorski, D.R. Powell and J.A. Walmsley, *Inorg Chem.*, (2006), 45(6), pp. 2688 - 2694.

<sup>211</sup> L. Messori, F. Abbate, G. Marcon, P. Orioli, M. Fontani, E. Mini, T. Mazzei, S. Carotti, T. O'Connell and P. Zanello, *J. Med. Chem.* (2000), 43, pp. 3541 - 3548.



**Figure 7.12:** Infrared spectrum of  $[\text{Au}(\text{en})_2]\text{Cl}_3$

#### 7.4.3.2.4 Qualitative and quantitative determination of gold in organometallic compounds

The Au-Cl ( $\nu_{\text{Cl}}$ ) stretching frequencies of the newly synthesized gold organometallic compounds were compared with those reported in literature. The  $\nu_{\text{Cl}}$  stretching frequencies for  $[\text{Au}(\text{opd})(\text{Cl})_3]$ <sup>212</sup> are found to be  $867\text{ cm}^{-1}$  and that for  $[\text{Au}(2,9\text{-Me}_2\text{phen})(\text{Cl})_3]$ <sup>213</sup> was observed at  $729$  and  $848\text{ cm}^{-1}$  which were reported to be in the region of  $500 - 1000\text{ cm}^{-1}$ . The  $\nu_{\text{Cl}}$  stretching frequency of  $[\text{Au}(\text{en})_2]\text{Cl}_3$  was also observed at  $1045\text{ cm}^{-1}$  which is in agreement with the literature range reported to be in the  $800 - 1200\text{ cm}^{-1}$  region. Gold organometallic samples ( $[\text{Au}(\text{opd})(\text{Cl})_3]$ ,  $[\text{Au}(2,9\text{-Me}_2\text{phen})(\text{Cl})_3]$  and  $[\text{Au}(\text{en})(\text{Cl})_2]\text{Cl}$ ) were weighed accurately ( $5 - 10\text{ mg}$ ) and quantitatively transferred into beakers containing HCl ( $5\text{ mL}$ ;  $32\%$ ). The mixtures were heated to *ca.*  $200 - 300\text{ }^\circ\text{C}$  until complete dissolution was attained. The resultant solutions were quantitatively transferred into  $100.0\text{ mL}$  volumetric flasks and were filled up to the mark to yield stock solutions of approximately  $100 - 150\text{ ppm}$  concentrations. Aliquots of the stock solutions were pipetted into separate  $100.0\text{ mL}$  volumetric flasks and Sc internal standard ( $0.2\text{ mL}$ ;  $1\text{ }000\text{ ppm}$ ) and HCl ( $5.0\text{ mL}$ ;

<sup>212</sup> R. Kockerbauer and P.J. Bednarski, *Journal of Inorganic Biochemistry*, (1996), 62, pp. 281 - 298.

<sup>213</sup> L. Messori, F. Abbate, G. Marcon, P. Orioli, M. Fontani, E. Mini, T. Mazzei, S. Carotti, T. O'Connell and P. Zanello, *J. Med. Chem.* (2000), 43, pp. 3541 - 3548.

32 %) were added to yield theoretical gold concentrations of approximately 7.0 ppm. The volumetric flasks were filled up to the mark using double distilled water and homogenized before left to stabilize for an hour. The analyte solutions were determined for gold content using direct calibration and Sc as internal standard with the calibration standards prepared in **Section 7.4.1.1** and **7.4.1.2** respectively. Results of the quantitative analysis using both methods are reported in **Table 7.4**.

**Table 7.4:** Quantitative results of gold in the organometallic compounds using the direct calibration and Sc as internal standard

Element	Organometallic compounds	Method	% Recovery*
Gold	[Au(opd)(Cl) <sub>3</sub> ]	Direct cal.	94.7(2)
		Sc int. standard	101(1)
	[Au(2,9-Me <sub>2</sub> phen)(Cl) <sub>3</sub> ]	Direct cal.	108.0(2)
		Sc int. standard	99.1(7)
	[Au(en)(Cl) <sub>2</sub> ]Cl	Direct cal.	104(1)
		Sc int. standard	99.7(9)

\*Quantitative results given as an average of 3 replicates

The use of scandium as internal standard was evaluated during the determination of gold in various organometallic compounds. Excellent percentage recoveries (+ 99 %) were obtained using scandium as internal standard in all analyses. These results, compared to the quantitative results obtained using the direct calibration method, indicates the effectiveness of scandium as internal standard as the best method for gold analysis. However, low percentage recoveries of gold (ca. 95 %) were obtained for [Au(opd)(Cl)<sub>3</sub>] whilst higher percentage recoveries (ca. + 104 %) were obtained for [Au(2,9-Me<sub>2</sub>phen)(Cl)<sub>3</sub>] and [Au(en)(Cl)<sub>2</sub>]Cl using direct calibration method. The fluctuation of the using the direct calibration method was most probably attributed to the uncorrected background responses and instrumental drifts which have been previously discussed in **Chapter 4, Section 4.2.2**. The ability to achieve a total recovery of gold in organometallic compounds demonstrated the success of using scandium as internal standard in the determination of gold in either inorganic or organometallic compounds with known purity or which have been fully characterized.

#### 7.4.4 Qualitative and quantitative determination of osmium in inorganic and organometallic compounds

##### 7.4.4.1 Determination of osmium in the inorganic compound $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$

###### 7.4.4.1.1 Preparation of the $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ analyte samples

A stock solution of  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  (27 mg, 0.08 mmol) was prepared in a volumetric flask (100.0 mL) and filled up to the mark using double distilled water to yield a theoretical concentration of 146.48 ppm. Aliquots (4.78 mL) (in triplicate) of the stock solution were pipetted into volumetric flasks (100.0 mL) to yield an analytical solution of approximately 7.0 ppm. Scandium internal standard (0.2 mL; 1 000 ppm) and HCl (5.0 mL; 32 %) were added to each of the analyte solutions and the volumetric flasks were filled up to the mark using double distilled water. The solutions were left to stabilize for an hour before it was analyzed for their Os content using  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  standards prepared in **Section 7.4.1.1** and **7.4.1.2**. Quantitative results obtained from the ICP-OES/MS analysis are reported in **Table 7.5**.

**Table 7.5:** ICP-OES/MS quantitative determination of osmium in  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  using the direct calibration and Sc as internal standard

Technique	% Recovery of Os* (direct calibration)	% Recovery of Os* (Sc as internal standard)
ICP-OES	89.0(6)	99(1)
ICP-MS	88.9(5)	100.1(5)

\*Quantitative results given as an average of 3 replicates

Quantitative determination of Os in  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  as inorganic salt using ICP-OES/MS was characterised by low percentage recoveries (ca. 89 %) using the direct calibration method. Both techniques indicated a similar discrepancy in the obtained results indicating that the direct calibration method is most probably affected by the same kind of error or interference. Total recoveries (100 %) of Os were obtained using scandium as internal standard within 24 hours. The success of this analysis was entirely dependent on the stability of both the analyte ( $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ ) and the calibration standards ( $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ ). Since the analyte composition had the potential to undergo hydrolysis similar to the standard  $(\text{OsCl}_6)^{2-}$ , a further investigation into the stability of  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  was conducted for a period of 5 days.

#### 7.4.4.2 Continued investigation of the osmium percentage recovery from $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$

Solutions of  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  (4.78 mL; 146.48 ppm) (in triplicate) were prepared by pipetting aliquots of the analyte solution into 100.0 mL volumetric flasks. The solutions were acidified with HCl (5.0 mL; 32 %), Sc internal standard (0.2 mL; 1 000 ppm) was added and the volumetric flasks were filled up to the mark using double distilled water. The analyte solutions were homogenized and left to stabilize for few minutes to prevent substantial changes for longer periods before determined for their Os content using the freshly prepared standards as described in **Section 7.4.1.3** which were kept at room temperature. Both the calibration standards and the analyte solutions,  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ , were kept at room temperature for the duration of the experimental analysis. Experimental results of the Os emission intensities and percentage recovery are reported in **Table 7.6** and **7.7** respectively using the direct calibration and **Table 7.8** and **7.9** respectively using Sc as internal standard. Graphical representation of the Os recovery obtained using  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  is shown in **Figure 7.1.3** and the ANOVA test results are reported in **Chapter 8**.

**Table 7.6:** Osmium emission intensities of the calibration standard solutions of  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  kept at room temperature (direct calibration)

Os standards concentrations (ppm)	Measured emission intensities				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
0.5	0.0864	0.0946	0.0993	0.1047	0.1009
1.0	0.1675	0.1758	0.1822	0.1892	0.1947
2.0	0.3205	0.3370	0.3348	0.3491	0.3604
5.0	0.7855	0.8027	0.7905	0.8127	0.8087
10.0	1.5586	1.5615	1.5481	1.5791	1.5908

**Table 7.7:** Osmium percentage recovery from  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  with calibration standard solutions of  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  kept at room temperature (direct calibration)

$\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$	Osmium recovery (%)				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
<b>Sample 1</b>	88.51	88.97	92.75	102.98	108.58
<b>Sample 2</b>	89.64	88.37	92.70	103.07	108.29
<b>Sample 3</b>	88.91	88.95	93.59	102.93	108.58
<b>Average</b>	<b>89.0(6)</b>	<b>88.8(3)</b>	<b>93.0(5)</b>	<b>103.0(1)</b>	<b>108.5(2)</b>

**Table 7.8:** Osmium emission intensities of the calibration standard solutions of  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  kept at room temperature (Sc as internal standard)

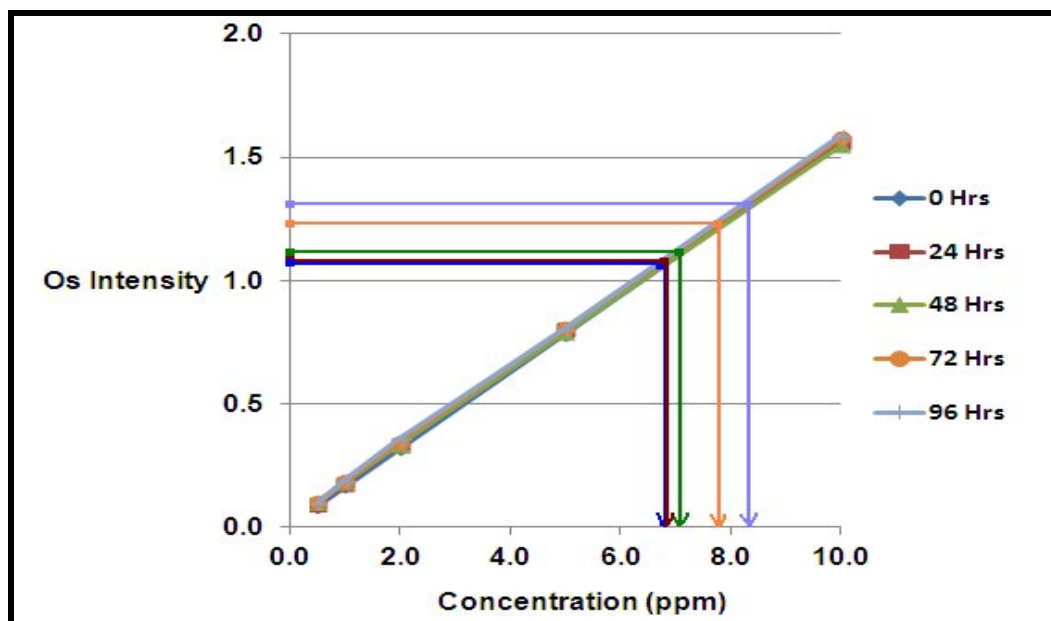
Os standards concentrations (ppm)	Measured emission intensities				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
<b>0.5</b>	0.0784	0.0858	0.0901	0.0950	0.0915
<b>1.0</b>	0.1499	0.1573	0.1631	0.1693	0.1743
<b>2.0</b>	0.2795	0.2938	0.2920	0.3043	0.3142
<b>5.0</b>	0.6985	0.7138	0.7029	0.7227	0.7192
<b>10.0</b>	1.3764	1.3790	1.3671	1.3946	1.4049

**Table 7.9:** Osmium percentage recovery from  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  with calibration standard solutions of  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  kept at room temperature (Sc as internal standard)

$\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$	Osmium recovery (%)				
	0 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
<b>Sample 1</b>	99.61	100.27	104.48	115.90	122.08
<b>Sample 2</b>	100.55	99.29	104.09	115.63	121.37
<b>Sample 3</b>	97.82	97.98	103.01	113.21	119.29
<b>Average</b>	<b>99(1)</b>	<b>99(1)</b>	<b>103.9(8)</b>	<b>115(2)</b>	<b>121(1)</b>

Results obtained in this part of the investigation to determine the stability of  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  showed an increase of Os percentage recovery after 24 hours. No shift in the Os calibration curves (increase in emission intensities) was observed and these results were in agreement with the previous results on the stability of  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  (see **Chapter 6, Section 6.4.6**). This increase in emission intensities of  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  is believed to be the result of the production of  $\text{OsO}_4$  or  $\text{OsO}_2$  in the analyte solution or the hydrolysis of  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  (see **Chapter 6**,

**Section 6.5.6).** The increase in the Os analyte emission intensities was shown to be directly proportional to the increase in the percentage recovery as shown in **Figure 7.13**.



**Figure 7.13:** Increase in Os emission intensity for the  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  analyte sample

Quantitative results obtained using both the direct calibration and Sc as internal standard in this part of the investigation showed an increase in Os percentage recoveries after 24 hours. Contrary to the instability of the calibration standards that were shown to be increasing in slope and ultimately causing an increase in Os recoveries, in this case the slope was stable but the  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  was unstable after 24 hours at room temperature as reflected by the slow increase in emission values which ultimately led to an increase in recovery. According to literature,<sup>214</sup>  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  is one of the intermediate species produced during the hydrolysis of  $(\text{OsCl}_6)^{2-}$  and has the potential to undergo further hydrolysis. These hydrolysis reactions have been shown to result in the formation of  $\text{OsO}_4$  or  $\text{OsO}_2$  as final products (see **Chapter 6, Section 6.5.2**) which was also shown to increase the Os emission intensities. It was however determined from the previous experience that the optimum conditions for Os analysis was either to keep the analyte sample below 10 °C or it should be analyzed within 24 hours. Total recoveries (100 %) of Os were

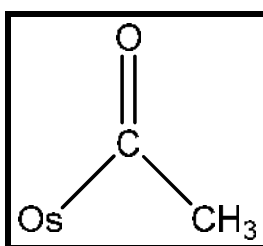
<sup>214</sup> S. Kulprathipanja, D.J. Hnatovich and S. Treves, *J. Inorg. Nucl. Chem.*, (1977), 39 (6), pp. 933 - 935.

obtained within 24 hours of having prepared the analyte solutions using Sc as internal standard. These results confirmed that  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  can accurately be quantified within 24 hours using ICP-OES/MS.

#### 7.4.4.3 Preparation of osmium organometallic compounds

##### 7.4.4.3.1 Acetylosmium ( $\text{OsC}_2\text{OH}_3$ )

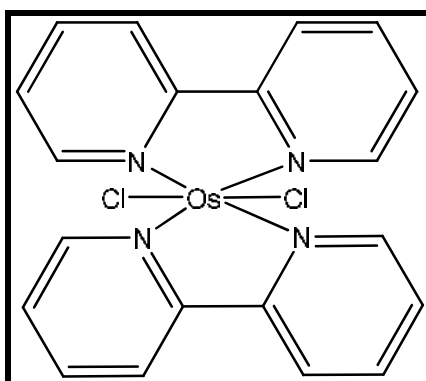
Acetylosmium (99 %) (**Figure 7.14**) was purchased from Sigma Aldrich



**Figure 7.14:** Molecular structure of acetylosmium

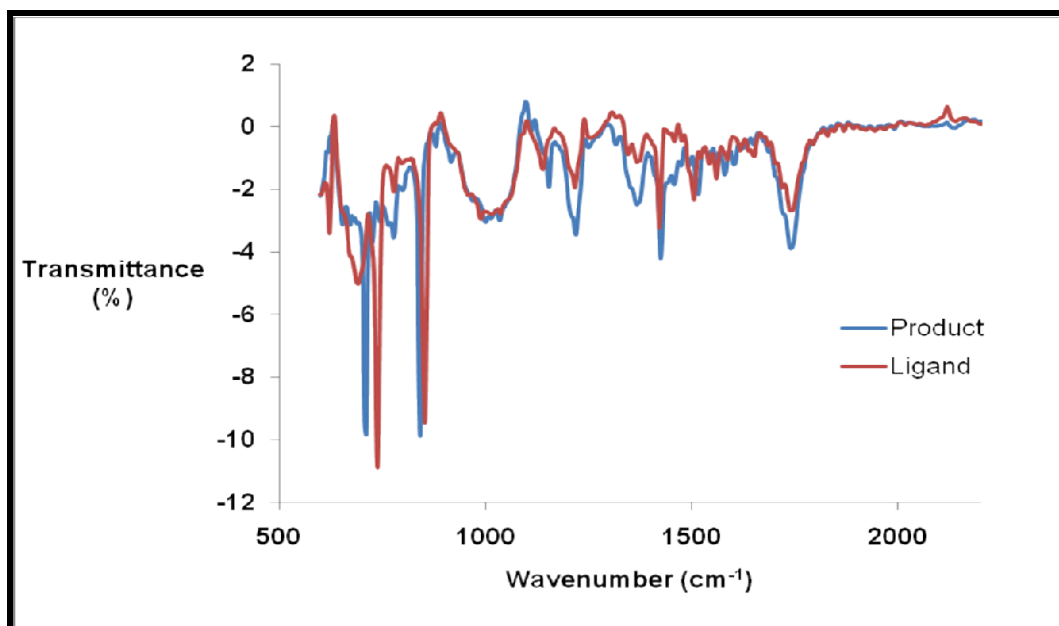
##### 7.4.4.3.2 Synthesis of osmium bis(2,2'-bipyridine)dichloride [ $\text{Os}(\text{bpy})_2\text{Cl}_2$ ]

A solution of 2,2'-bipyridyl (bpy) (44 mg; 0.28 mmol) in ethanol was added to a well stirred solution containing  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  (49 mg; 0.14 mmol) in absolute ethanol (5 mL). The reaction mixture was stirred for a further 15 min and a brown product was obtained. The product (**Figure 7.15**) was isolated through filtration and was washed with ethanol (3 x 5 mL) and dried in a dessicator (yield 74 %) before characterized using IR (**Figure 7.16**). Elemental analysis (calculated values in brackets); C, 40.29 (41.88) and N, 9.52 (9.77) %.



**Figure 7.15:** Molecular structure of [ $\text{Os}(\text{bpy})_2(\text{Cl})_2$ ]

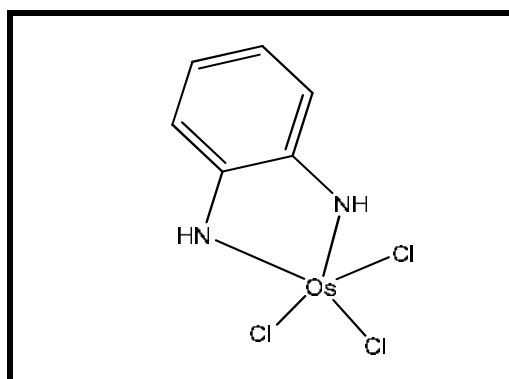




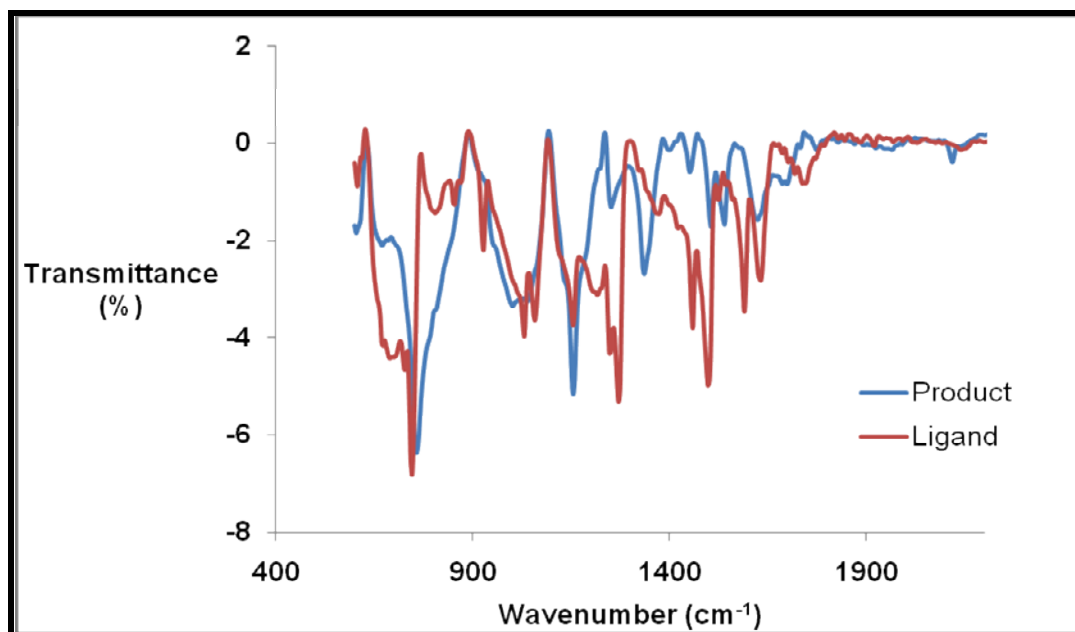
**Figure 7.16:** Infrared spectrum of  $[\text{Os}(\text{bpy})_2(\text{Cl})_2]$

#### 7.4.4.3.3 Synthesis of osmium (1,2-diphenylenediamine)trichloride $[\text{Os}(\text{opd})(\text{Cl})_3]$

A solution of 1,2 phenylenediamine (opd) (14 mg; 0.13 mmol) in ethanol was added to a well stirred solution of  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  (45 mg; 0.13 mmol) in absolute ethanol (5 mL). The reaction mixture was stirred for further 15 min and a green-brown product was obtained. The product (**Figure 7.17**) was isolated through filtration and was washed with ethanol (3 x 5 mL) and dried in a dessicator (yield 57 %), before characterized using IR (**Figure 7.18**). Elementary analysis (calculated values in brackets); C, 15.50 (17.89) and N, 7.02 (6.96) %.



**Figure 7.17:** Molecular structure of  $[\text{Os}(\text{opd})(\text{Cl})_3]$



**Figure 7.18:** Infrared spectrum of  $[\text{Os}(\text{opd})(\text{Cl})_3]$

#### 7.4.4.3.4 Preparation of the organometallic compounds for osmium analyte determination

Characterization of the newly prepared complexes was done by comparing the IR spectra of these complexes with those cited in the literature. The Os-Cl ( $\nu_{\text{Cl}}$ ) stretching frequencies for  $[\text{Os}(\text{bpy})(\text{Cl})_2]$ <sup>215</sup> (703 and 709  $\text{cm}^{-1}$ ) and  $[\text{Os}(\text{opd})(\text{Cl})_2]$ <sup>216</sup> (756  $\text{cm}^{-1}$ ) were found to be within the same region of 500 - 1000  $\text{cm}^{-1}$  as reported in literature. Osmium organometallic samples ( $[\text{Os}(\text{COCH}_3)]$ ,  $[\text{Os}(\text{bpy})(\text{Cl})_2]$  and  $[\text{Os}(\text{opd})(\text{Cl})_2]$ ) were weighed accurately (5 - 10 mg) and quantitatively transferred into a beaker containing HCl (5 mL; 32 %). The mixture was heated to ca. 200 - 300 °C until complete dissolution was attained. The resultant translucent solutions were quantitatively transferred into 100.0 mL volumetric flasks and were filled up to the mark to yield stock solutions with concentrations of approximately 100 - 150 ppm. Aliquots of the stock solutions were pipetted into separate 100.0 mL volumetric flasks and Sc internal standard (0.2 mL; 1 000 ppm) and HCl (5.0 mL; 32 %) were added to yield a theoretical osmium concentration of approximately 7.0 ppm. The volumetric flasks were filled up to the mark using double distilled water and homogenized before left to stabilize for an hour. The analyte solutions were determined for osmium

<sup>215</sup> A. Mamo, A. Aureliano and A. Recca, *Molecules*, (2010), 15, pp. 1324 -1339.

<sup>216</sup> M. Rahim and K.J. Ahmed, *Inorg. Chem.* (1994), 33, pp. 3003 - 3004.

content using the direct calibration and Sc as internal standard methods with the calibration standards prepared in **Section 7.4.1.1** and **7.4.1.2** respectively. Results of the quantitative analysis using both methods are reported in **Table 7.10**.

**Table 7.10:** Quantitative results of the determination of osmium in the organometallic compounds using direct calibration and Sc as internal standard

Organometallic compounds	Elements	Method	% Recovery*
Osmium	[Os(COCH <sub>3</sub> ) <sub>3</sub> ]	Direct cal.	91.3(8)
		Sc int. standard	99.5(9)
	[Os(bpy)(Cl) <sub>2</sub> ]	Direct cal.	101.0(4)
		Sc int. standard	98(1)
	[Os(opd)(Cl) <sub>2</sub> ]	Direct cal.	97(1)
		Sc int. standard	100(1)

\*Quantitative results given as an average of 3 replicates

The use of scandium as internal standard was evaluated during the determination of osmium in various organometallic compounds. Quantitative results obtained using the direct calibration method showed lower percentage recoveries of osmium (below 98 %) in most of the organometallic compounds. All organometallic compounds were stored in a cool dark place and determined for their osmium content within a period of 24 hours to avoid any unexpected changes in Os species as previously seen in **Chapter 6**. The quantitative results showed that excellent recoveries (+ 99 %) except for [Os(bpy)(Cl)<sub>2</sub>] (98 %) were obtained using scandium as the internal standard. This ability to achieve a total recovery of osmium in organometallic compounds demonstrated the efficiency of using scandium as internal in the determination of osmium in either inorganic or organometallic compounds with known purity or which have been fully characterized.

#### 7.4.5 Qualitative and quantitative determination of palladium in inorganic and organometallic compounds

##### 7.4.5.1 Determination of palladium in the inorganic salt PdCl<sub>2</sub>

7.4.5.1.1 Preparation of the PdCl<sub>2</sub> analyte samples

A stock solution of PdCl<sub>2</sub> (23 mg, 0.13 mmol) was prepared by digesting the PdCl<sub>2</sub> in *aqua regia* (5 mL) and the resultant clear solution was quantitatively transferred to a volumetric flask (100.0 mL) and filled up to the mark using double distilled water to yield a theoretical palladium concentration of 138.03 ppm. Aliquots (5.07 mL) (in triplicate) of the stock solution were pipetted into volumetric flasks (100.0 mL) to yield analyte concentrations of approximately 7.0 ppm. Scandium internal standard (0.2 mL; 1 000 ppm) and HCl (5.0 mL; 32 %) were added to each of the analyte solutions and the volumetric flasks were filled up to the mark using double distilled water. The solutions were left to stabilize for an hour before it was analyzed for their palladium content using standards prepared in **Section 7.4.1.1** and **7.4.1.2**. Quantitative results obtained from the ICP-OES/MS analysis are reported in **Table 7.11**.

**Table 7.11:** ICP-OES/MS quantitative determination of palladium in inorganic salts using the direct calibration and Sc as internal standard

Technique	% Recovery of Pd* (direct calibration)	% Recovery of Pd* (Sc internal standard)
ICP-OES	102(4)	101.7(9)
ICP-MS	103.7(7)	100.5(9)

\*Quantitative results given as an average of 3 replicates

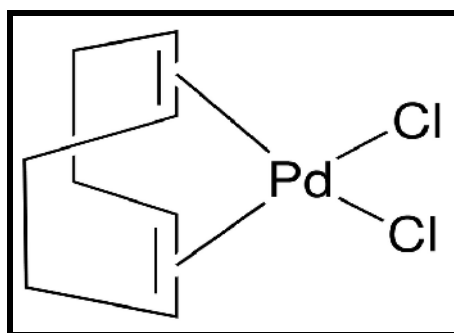
A complete dissolution of the anhydrous PdCl<sub>2</sub> was achieved through open beaker digestion in *aqua regia*. Qualitative analysis of PdCl<sub>2</sub> revealed the presence of trace amounts (below 1 ppm) of Ca, Fe and Mg which were found to have no interference on the determination of palladium. Quantitative results of palladium from both ICP-OES/MS techniques revealed higher than expected percentage recoveries of palladium (102 % using ICP-OES and 104 % using ICP-MS) using the direct calibration method. This higher than expected percentage recovery is assumed to be the result of uncorrected background responses and instrumental drifts which have been previously discussed in **Chapter 4, Section 4.2.2** to limit the use of direct calibration method in precious metals determination. Total percentage recoveries (ca. 100 %) of the palladium were obtained using Sc as internal standard with both

ICP-OES/MS techniques. The use of Sc as internal standard was also shown to accurately determine palladium in samples with less amount of interfering species.

#### 7.4.5.2 Preparation of palladium organometallic compounds

##### 7.4.5.2.1 Dichlorido(1,5-cyclooctadiene)palladium(II), $[Pd(cod)(Cl)_2]$ (99 %)

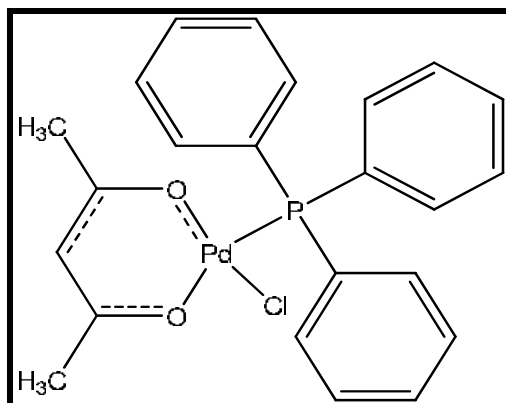
Dichlorido(1,5-cyclooctadiene)palladium(II) (99 %) (**Figure 7.19**) was purchased from Sigma Aldrich.



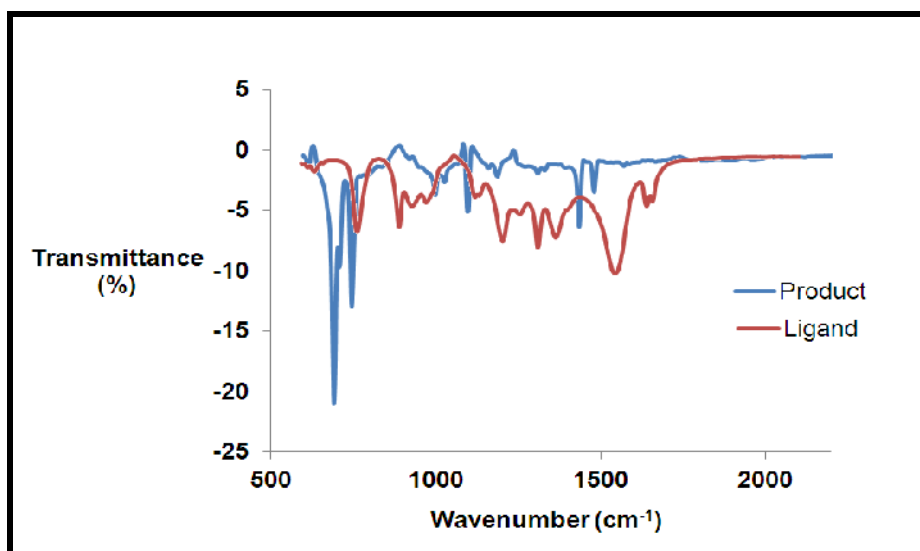
**Figure 7.19:** Molecular structure of  $[Pd(cod)(Cl)_2]$

##### 7.4.5.2.2 Synthesis of chloridotriphenylphosphine(acetylacetonate)palladium(I), $[Pd(acac)(PPh_3)(Cl)]$

$Pd(Cl)_2$  (58 mg; 0.33 mmol) was dissolved in DCM (10 mL) and the mixture was slightly heated (30 °C) whilst constantly stirring. Acetylacetone (acac) (0.04 mL; 0.39 mmol) was added drop-wise and the solution was gently stirred for 10 min before triphenylphosphine (87 mg; 0.33 mmol) was added. A yellow-orange precipitate was formed and was washed in DCM (3 x 10 mL). The product (**Figure 7.20**) was dried in a dessicator (yield 86 %) and characterized using IR (**Figure 7.21**). Elemental analysis (calculated values in brackets); C, 53.60 (54.88) %.



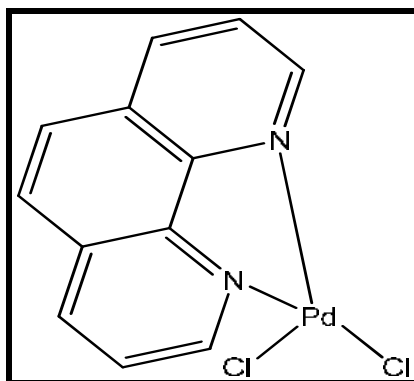
**Figure 7.20:** Molecular structure of [Pd(acac)(PPh<sub>3</sub>)(Cl)]



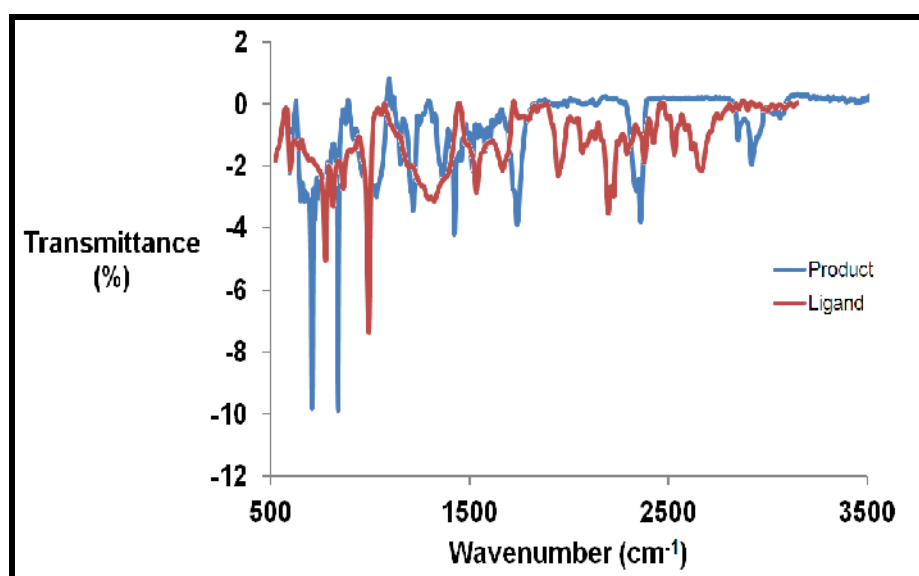
**Figure 7.21:** Infrared spectrum of [Pd(acac)(PPh<sub>3</sub>)(Cl)]

#### 7.4.5.2.3 Synthesis of dichlorido(1,10-phenanthroline)palladium(II), [Pd(phen)(Cl)<sub>2</sub>]

1,10-Phenanthroline (phen) (63 mg; 0.35 mmol) was added to a well stirred solution of Pd(Cl)<sub>2</sub> (61 mg; 0.34 mmol) in DCM (5 mL) at approximately 30 °C. The reaction mixture was stirred for further 10 min and a deep yellow precipitate was formed which was isolated through filtration. The product (**Figure 7.22**) was washed with DCM (3 x 5 mL) was dried in a dessicator (yield 66 %) before characterized using IR (**Figure 7.23**). Elemental analysis (calculated values in brackets); C, 39.45 (40.31) and N, 6.67 (7.84) %.



**Figure 7.22:** Molecular structure of [Pd(phen)(Cl)<sub>2</sub>]



**Figure 7.23:** Infrared spectrum of [Pd(phen)(Cl)<sub>2</sub>]

#### 7.4.5.2.4 Preparation of the organometallic compounds for palladium analyte determination

The literature values of the Pd-Cl ( $\nu_{\text{Cl}}$ ) stretching frequencies are reported to be in the region of 500 - 1000 cm<sup>-1</sup>. The stretching frequencies of the newly synthesized palladium were determined and were found to be 686 cm<sup>-1</sup> for [Pd(acac)(PPh<sub>3</sub>)(Cl)]<sup>217</sup> and 710 and 837 cm<sup>-1</sup> for [Pd(phen)(Cl)<sub>2</sub>]<sup>218</sup>. These values fall in the region as those reported in literature. Palladium organometallic samples ([Pd(cod)(Cl)<sub>2</sub>], [Pd(acac)(PPh<sub>3</sub>)(Cl)] and [Pd(phen)(Cl)<sub>2</sub>]) were weighed accurately (5 - 10 mg) and

<sup>217</sup> D.R. Coulson, L.C. Satek and S.O. Grim, *Inorg. Synth*, (1972), 13, p. 121.

<sup>218</sup> F. Shi, Y. He, D. Li, Y. Ma, Q. Zhang and Y. Deng, *Journal of Molecular Catalysis.*, (2006), 244, pp. 64 - 67.

quantitatively transferred into a beaker containing HCl (5 mL; 32 %). The mixtures were heated to *ca.* 200 - 300 °C until translucent solutions were obtained. The resultant solutions were quantitatively transferred into 100.0 mL volumetric flasks and were filled up to the mark to yield stock solutions with concentrations of approximately 100 - 150 ppm. Aliquots of the stock solution were pipetted into separate 100.0 mL volumetric flasks and Sc internal standard (0.2 mL; 1 000 ppm) and HCl (5.0 mL; 32 %) were added to yield theoretical palladium concentrations of approximately 7.0 ppm. The volumetric flasks were filled up to the mark using double distilled water and homogenized before left to stabilize for an hour. The analyte solutions were determined for palladium content using direct calibration and Sc as internal standard with the calibration standards prepared in **Section 7.4.1.1** and **7.4.1.2** respectively. Results of the quantitative analysis using both methods are reported in **Table 7.12**.

**Table 7.12:** Quantitative results of the palladium in the organometallic compounds using the direct calibration and Sc as internal standard

Organometallic compounds	Elements	Method	% Recovery*
Palladium	[Pd(cod)(Cl) <sub>2</sub> ]	Direct cal.	100.2(2)
		Sc int. standard	99.0(2)
	[Pd(acac)(PPh <sub>3</sub> )(Cl)]	Direct cal.	106.0(9)
		Sc int. standard	101.1(6)
	[Pd(phen)(Cl) <sub>2</sub> ]	Direct cal.	102.6(8)
		Sc int. standard	101.2(9)

\*Quantitative results given as an average of 3 replicates

The use of scandium as internal standard was evaluated during the determination of palladium in various organometallic compounds. Quantitative results obtained using the direct calibration method showed higher percentage recoveries of palladium (+ 100 %) compared to the theoretical values. These results were also showed to be in agreement with the results obtained from the inorganic salt where higher palladium percentage recoveries were obtained using the direct calibration method. These higher percentage recoveries, except for [Pd(cod)(Cl)<sub>2</sub>] which were obtained using the direct calibration method, were attributed to the choice of the method and the



uncertainty brought about the purity of these newly synthesized compounds. Excellent percentage recoveries (+ 99 %) were obtained using scandium as internal standard. The ability to recover approximately a total recovery in palladium compounds confirmed the successfulness of the use of scandium as internal standard in accurately quantifying palladium in both inorganic and organometallic compounds.

#### 7.4.6 Qualitative and quantitative determination of platinum in inorganic and organometallic compounds

##### 7.4.6.1 Determination of platinum in the inorganic salt $\text{PtCl}_2$

###### 7.4.6.1.1 Preparation of $\text{PtCl}_2$ analyte samples

A stock solution of  $\text{PtCl}_2$  (20 mg, 0.08 mmol) was prepared in a volumetric flask (100.0 mL) and filled up to the mark using double distilled water to yield a platinum concentration of 146.68 ppm. Aliquots (4.77 mL) (in triplicate) of the stock solution were pipetted into volumetric flasks (100.0 mL) to yield analyte concentrations of approximately 7.0 ppm. Scandium internal standard (0.2 mL; 1 000 ppm) and HCl (5.0 mL; 32 %) were added to each of the analyte solutions and the volumetric flasks were filled up to the mark using double distilled water. The solutions were left to stabilize for an hour before it was analyzed for their platinum content using standards prepared in **Section 7.4.1.1** and **7.4.1.2**. Quantitative results obtained from the ICP-OES/MS analysis are reported in **Table 7.13**.

**Table 7.13:** ICP-OES/MS quantitative determination of platinum in inorganic salts using the direct calibration and Sc as internal standard methods

Technique	% Recovery of Pt* (direct calibration)	% Recovery of Pt* (Sc as internal standard)
ICP-OES	104(1)	99.4(3)
ICP-MS	102(1)	101(1)

\*Quantitative results given as an average of 3 replicates

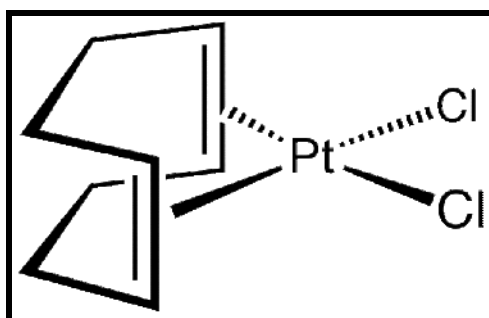
The complete dissolution of the anhydrous  $\text{PtCl}_2$  was achieved through open beaker digestion in *aqua regia*. A qualitative analysis of  $\text{PtCl}_2$  revealed the presence of trace amounts (below 1 ppm) of Ca, Fe and Mg which were found to have no or little

interference on the determination of platinum. Quantitative results of platinum from both ICP-OES/MS techniques revealed high percentage recoveries of platinum (104 % using ICP-OES and 102 % using ICP-MS) with the direct calibration method. These high percentage recoveries were believed to have been the result of uncorrected background responses and instrumental drifts which have been previously discussed in **Chapter 4, Section 4.2.2**. Total percentage recoveries (ca. 100 %) of the platinum were obtained using Sc as internal standard with using both ICP-OES/MS techniques.

#### 7.4.6.2 Preparation of platinum organometallic compounds

##### 7.4.6.2.1 Dichlorido(cycloocta-1,5-diene)platinum(II), $[Pt(cod)(Cl)_2]$ (99 %)

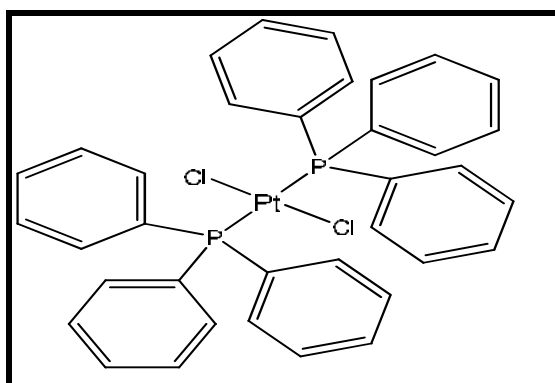
Dichlorido(cycloocta-1,5-diene)platinum(II) (**Figure 7.24**) was purchased from Sigma Aldrich.



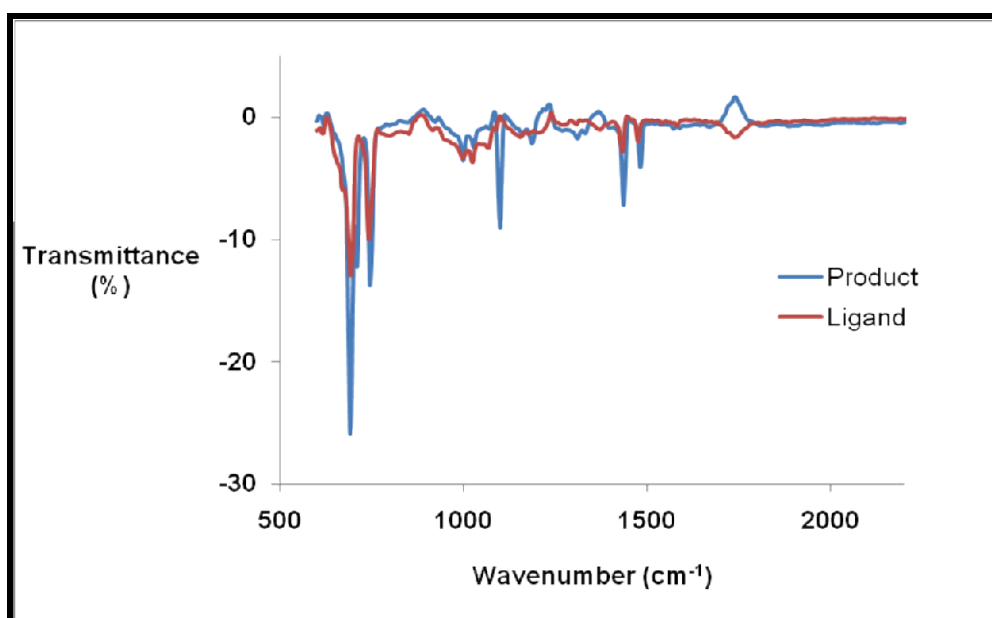
**Figure 7.24:** Molecular structure of  $[Pt(cod)(Cl)_2]$

##### 7.4.6.2.2 Synthesis of *cis*-dichloridobis(triphenylphosphine)platinum(II), $[Pt(Cl)_2(PPh_3)_2]$

Platinum chloride (27 mg; 0.1 mmol) was dissolved in DCM and the mixture was slightly heated (< 35 °C) whilst constantly stirring. A solution of triphenylphosphine ( $PPh_3$ ) (30 mg; 0.1 mmol) in DCM (2 mL) was added slowly whilst stirring at room temperature. A yellow product precipitated from the solution. The product (**Figure 7.25**) was filtered and washed with DCM (2 x 10 mL) and dried in a dessicator (yield 82 %) before characterized using infrared spectroscopy (**Figure 7.26**). Elemental analysis (calculated values in brackets); C, 53.70 (54.69) %.



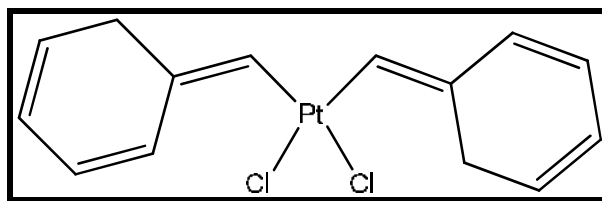
**Figure 7.25:** Molecular structure of [Pt(Cl)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]



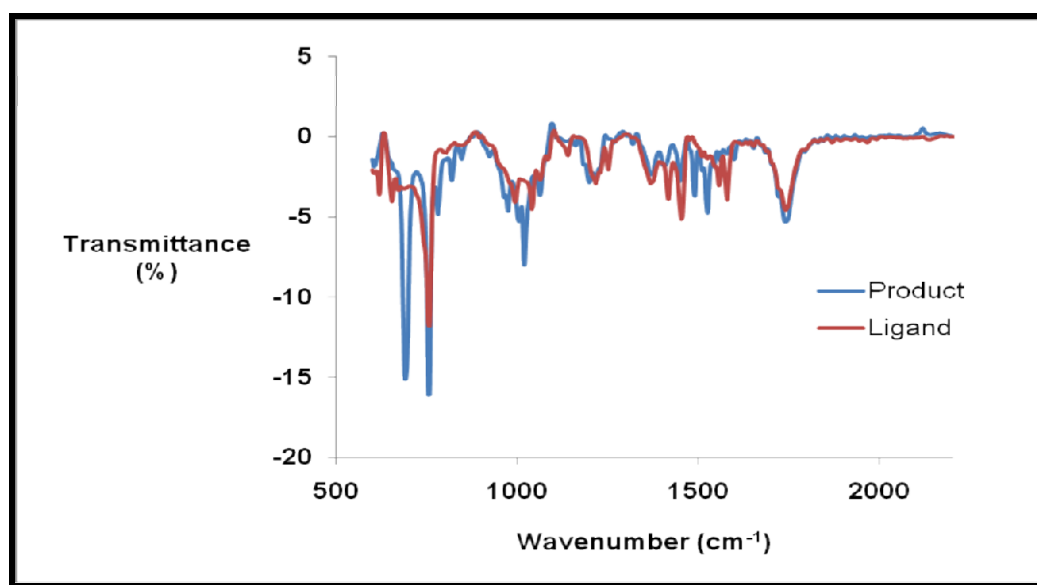
**Figure 7.26:** Infrared spectrum of [Pt(Cl)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]

#### 7.4.6.2.3 Synthesis of *cis*-dichloridobis( $\eta$ -(2)styrene)platinum(II), [*cis*-PtCl<sub>2</sub>(PhCH=CH<sub>2</sub>)<sub>2</sub>]

A suspension of PtCl<sub>2</sub>, (251 mg, 945 mmol) in 6 mL of freshly distilled styrene was stirred for 48 hours. The yellow suspension that resulted was filtered and the residue washed with 10 mL of benzene and 25 mL of pentane. The product (**Figure 7.27**) was dried in a dessicator (yield 84 %) and characterised using IR (**Figure 7.28**). Elemental analysis (calculated values in brackets); C, 36.87 (37.68) %.



**Figure 7.27:** Structure of [cis-PtCl<sub>2</sub>(PhCH=CH<sub>2</sub>)<sub>2</sub>]



**Figure 7.28:** Infrared spectrum of [cis-PtCl<sub>2</sub>(PhCH=CH<sub>2</sub>)<sub>2</sub>]

#### 7.4.6.2.4 Preparation of the organometallic compounds for platinum analyte determination

The Pt-Cl stretching frequencies ( $\nu_{\text{Cl}}$ ) of the newly synthesized platinum compounds were compared with the literature values to confirm the chemical identity of the complexes. The Pt-Cl stretching frequencies for [Pt(PPh<sub>3</sub>)<sub>2</sub>(Cl)<sub>2</sub>]<sup>219</sup> were observed at 687 and 744 cm<sup>-1</sup> and for [cis-PtCl<sub>2</sub>(PhCH=CH<sub>2</sub>)<sub>2</sub>]<sup>220</sup> at 683 and 748 cm<sup>-1</sup>. These stretching frequencies of the newly synthesized platinum compounds were found to be within the 500 - 1000 cm<sup>-1</sup> region which was reported in literature. Platinum organometallic samples ([Pt(cod)(Cl)<sub>2</sub>], [Pt(PPh<sub>3</sub>)<sub>2</sub>(Cl)<sub>2</sub>] and [cis-PtCl<sub>2</sub>(PhCH=CH<sub>2</sub>)<sub>2</sub>]) were weighed accurately (5 - 10 mg) and quantitatively transferred into beakers containing HCl (5 mL; 32 %). The mixtures were heated to *ca.* 200 - 300 °C until complete dissolution was attained. The resultant solutions were quantitatively

<sup>219</sup> M. Rahim and K.J. Ahmed, *Inorg. Chem.* (1994), 33, pp. 3003 - 3004.

<sup>220</sup> W.R. Caseri and P.S. Pregosin, *Organometallics*, (1987), 6, (4), pp. 789 - 793.

transferred into 100.0 mL volumetric flasks and were filled up to the mark to yield stock solutions with concentrations of approximately 100 - 150 ppm. Aliquots of the stock solutions were pipetted into separate 100.0 mL volumetric flasks and Sc internal standard (0.2 mL; 1 000 ppm) and HCl (5.0 mL; 32 %) were added to yield theoretical platinum concentrations of approximately 7.0 ppm. The volumetric flasks were filled up to the mark using double distilled water and homogenized before left to stabilize for an hour. The analyte solutions were determined for platinum content using direct calibration and Sc as internal standard with the calibration standards prepared in **Section 7.4.1.1** and **7.4.1.2** respectively. Results of the quantitative analysis using both methods are reported in **Table 7.14**.

**Table 7.14:** ICP-OES/MS quantitative results of the platinum in the organometallic compounds using the direct calibration and Sc as internal standard

Organometallic compounds	Elements	Method	% Recovery*
Platinum	[Pt(cod)(Cl) <sub>2</sub> ]	Direct cal.	106.7(2)
		Sc int. standard	100.8(3)
	[Pt(PPh <sub>3</sub> ) <sub>2</sub> (Cl) <sub>2</sub> ]	Direct cal.	111.2(1)
		Sc int. standard	99.4(2)
	[Cis-PtCl <sub>2</sub> (PhCH=CH <sub>2</sub> ) <sub>2</sub> ]	Direct cal.	102.2(9)
		Sc int. standard	101(1)

\*Quantitative results given as an average of 3 replicates

The use of scandium as internal standard was further evaluated during the determination of platinum in organometallic compounds. Quantitative determination of platinum from these compounds using the direct calibration method revealed a higher percentage recovery (+ 102 %) of platinum than the expected theoretical values. These higher percentage recoveries were found to be consistent with the results obtained from the previous determination of platinum in the inorganic salt. Results obtained from platinum and palladium determination (see **Section 7.4.5**) showed higher percentage recoveries using the direct calibration method. These similarities in the percentage recoveries were attributed to the chemical similarities in the flame of these metals since they are found in the same group of the periodic table. Furthermore, background emissions and instrumental drifts which were

previously reported to affect the direct calibration method were also assumed to have contributed to the higher yields. Total percentage recoveries (100 %) of platinum were obtained from all the newly synthesized compounds using scandium as internal standard. The ability to recover approximately a total recovery in platinum compounds confirmed that the use of scandium as internal can be used to accurately quantify platinum in both inorganic and organometallic compounds.

#### 7.4.7 Qualitative and quantitative determination of rhodium in inorganic and organometallic compounds

##### 7.4.7.1 Determination of rhodium in the inorganic salt $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$

###### 7.4.7.1.1 Preparation of the $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ analyte samples

A stock solution of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (26 mg, 0.10 mmol) was prepared in a volumetric flask (100.0 mL) and filled up to the mark using double distilled water to yield a theoretical rhodium concentration of 101.62 ppm. Aliquots (6.89 mL) (in triplicate) of the stock solution were pipetted into volumetric flasks (100.0 mL) to yield analytical solutions of approximately 7.0 ppm. Scandium internal standard (0.2 mL; 1 000 ppm) and HCl (5.0 mL; 32 %) were added to each of the analyte solutions and the volumetric flasks were filled up to the mark using double distilled water. The solutions were left to stabilize for an hour before it was analyzed for their rhodium content using standards prepared in **Section 7.4.1.1** and **7.4.1.2**. Quantitative results obtained from the ICP-OES/MS analysis are reported in **Table 7.15**.

**Table 7.15:** ICP-OES/MS quantitative determination of rhodium in  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  using the direct calibration and Sc as internal standard

Technique	% Recovery of Rh* (direct calibration)	% Recovery of Rh* (Sc as internal standard)
ICP-OES	95(9)	101.5(6)
ICP-MS	83(1)	102.6(5)

\*Quantitative results given as an average of 3 replicates

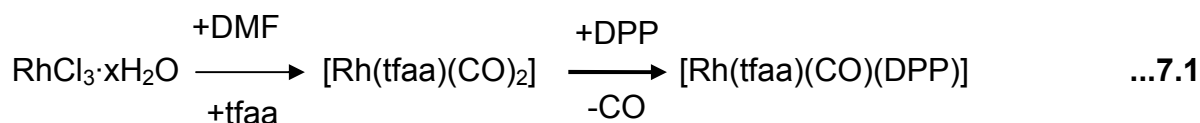
Qualitative analysis of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  showed the presence of Ca, Mg, Fe and S (below 1 ppm) which were found to have no effect on the quantitative determination of rhodium using both techniques. Low percentage recoveries of rhodium (95 % using

the ICP-OES and 82 % using ICP-MS) were obtained using the direct calibration method. Total recoveries of rhodium (+ 100 %) were obtained using Sc as internal standard which suggested the ability of this method to accurately determine rhodium in inorganic salts. The slightly higher percentage recovery of rhodium was assumed to have been the result of the fluctuating number of crystal waters in the  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  compound. This uncertainty in the number of crystal waters was found to cause systematic errors in quantitative determination of hygroscopic compounds from our previous study on the determination of the crystal waters in  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ .<sup>221</sup>

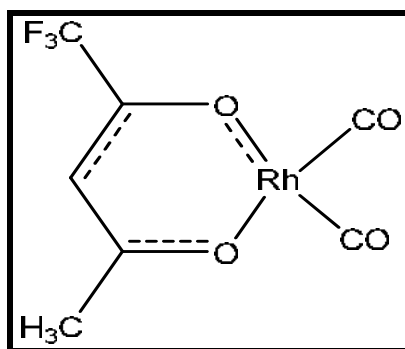
#### 7.4.7.2 Preparation of rhodium organometallic compounds

##### 7.4.7.2.1 Synthesis of $[\text{Rh}(\text{hfaa})(\text{CO})_2]$

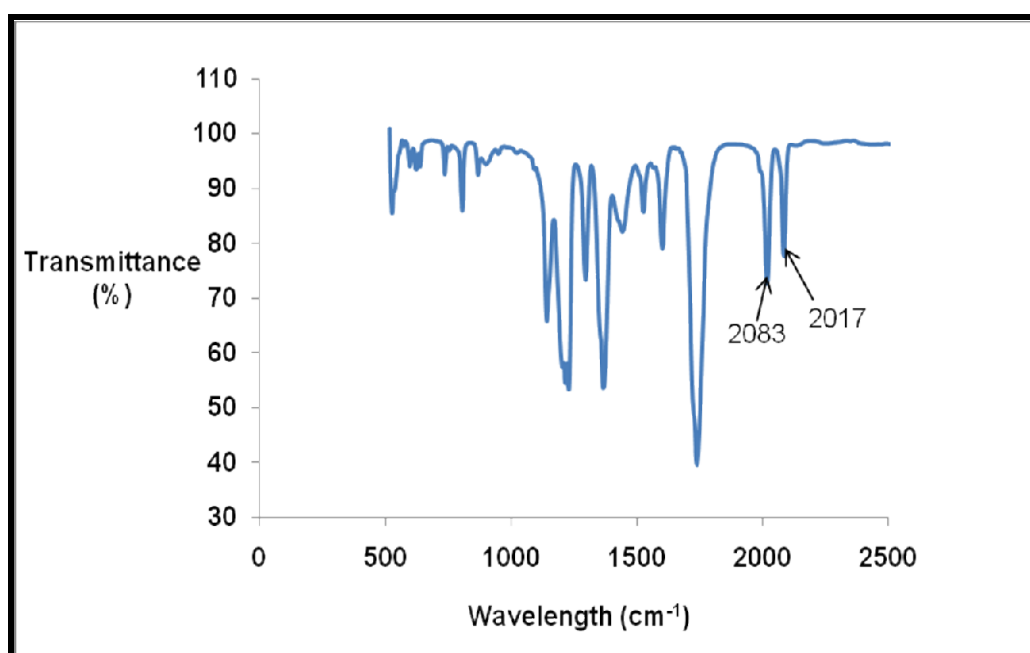
A solution of the  $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$  dimer was prepared by refluxing  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (202 mg; 0.97 mmol) in 10 mL of N,N-dimethylformamide (DMF) for ca. 30 min to a light orange colour. An equivalent amount of 1, 1, 1 - trifluoro - 2, 4 - pentanedione (tfaa) (0.12 mL; 0.98 mmol) was added and stirred for 30 min. Addition of 50 mL cold water to the reaction mixture precipitated an orange  $[\text{Rh}(\text{tfaa})(\text{CO})_2]$  which was removed by centrifugation and purified by recrystallization from acetone. The orange product was dried at room temperature and characterized by IR spectroscopy (**Figure 7.29**). Yield 37.07 %, IR data:  $\nu_{(\text{CO})} = 2083$  and  $2017 \text{ cm}^{-1}$  in **Figure 7.30**. Elemental analysis (calculated values in brackets); C, 30.43 (32.58) %.



<sup>221</sup> T.T. Chiweshe, *Quantification of rhodium in series of inorganic and organometallic compounds*, MSc thesis, University of the Free State, Bloemfontein, South Africa, (2010), pp. 65 - 70.



**Figure 7.29:** Molecular structure of [Rh(tfaa)(CO)<sub>2</sub>]



**Figure 7.30:** Infrared spectrum of [Rh(tfaa)(CO)<sub>2</sub>]

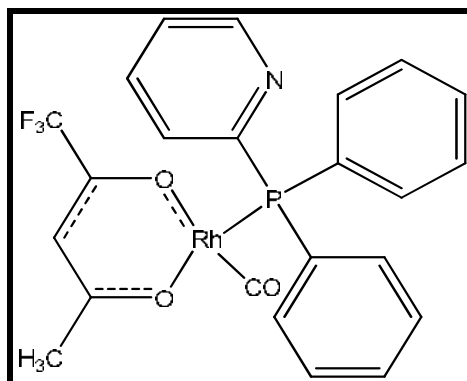
#### 7.4.7.2.2 Synthesis of [Rh(tfaa)(dpp)(CO)]

[Rh(tfaa)(CO)<sub>2</sub>] was synthesized as reported by Goswami and Singh.<sup>222</sup> [Rh(tfaa)(CO)<sub>2</sub>] (200 mg, 0.64 mmol) was dissolved in 10 mL methanol and the solution was slightly heated to 30 °C for 5 min to ensure homogeneity. Diphenyl-2-pyridylphosphine (dpp) (200 mg, 0.76 mmol) was added gently whilst stirring and the solution changed colour from yellow to red. An orange-red product precipitated immediately from the solution. The precipitate was removed by filtration, washed with methanol and dried in a fume cupboard. A red-brown powdered product (**Figure 7.31**) was obtained and characterised by IR (**Figure 7.32**). Yield: 60 %, IR

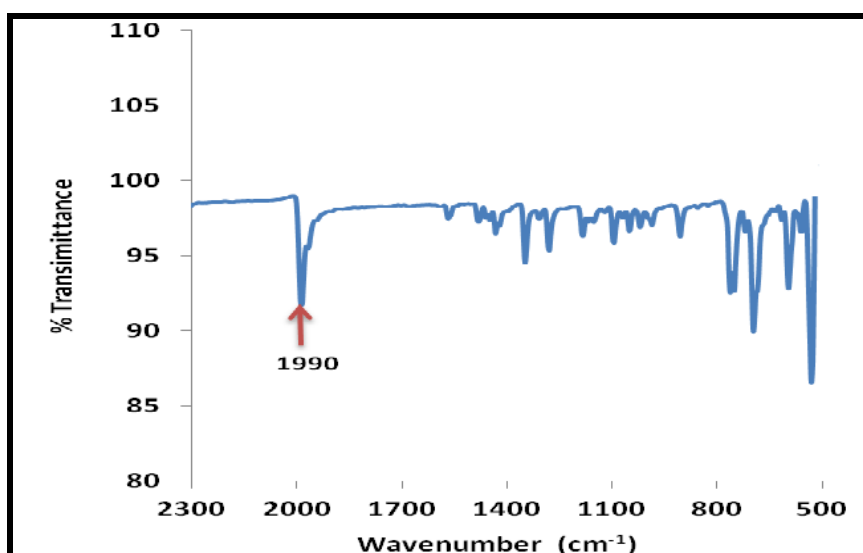
<sup>222</sup> K. Goswami, M.M. Singh, *Transition Met. Chem.*, (1980), 5, pp. 83 - 85.



data:  $\nu_{(\text{CO})} = 1990 \text{ cm}^{-1}$ . Elemental analysis (calculated values in brackets); C, 52.90 (53.56) and N, 2.80 (2.84) %.



**Figure 7.31:** Molecular structure of  $[\text{Rh}(\text{tfaa})(\text{dpp})(\text{CO})]$



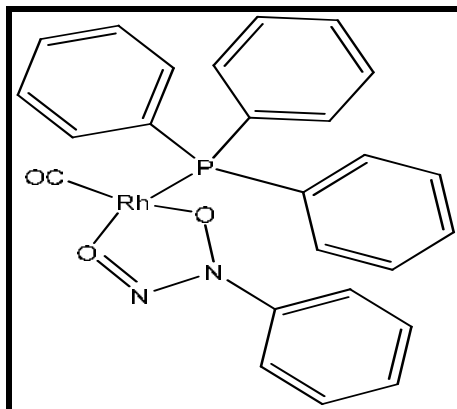
**Figure 7.32:** Infrared spectrum of  $[\text{Rh}(\text{tfaa})(\text{dpp})(\text{CO})]$

#### 7.4.7.2.3 Synthesis of $[\text{Rh}(\text{cupf})(\text{PPh}_3)(\text{CO})]$

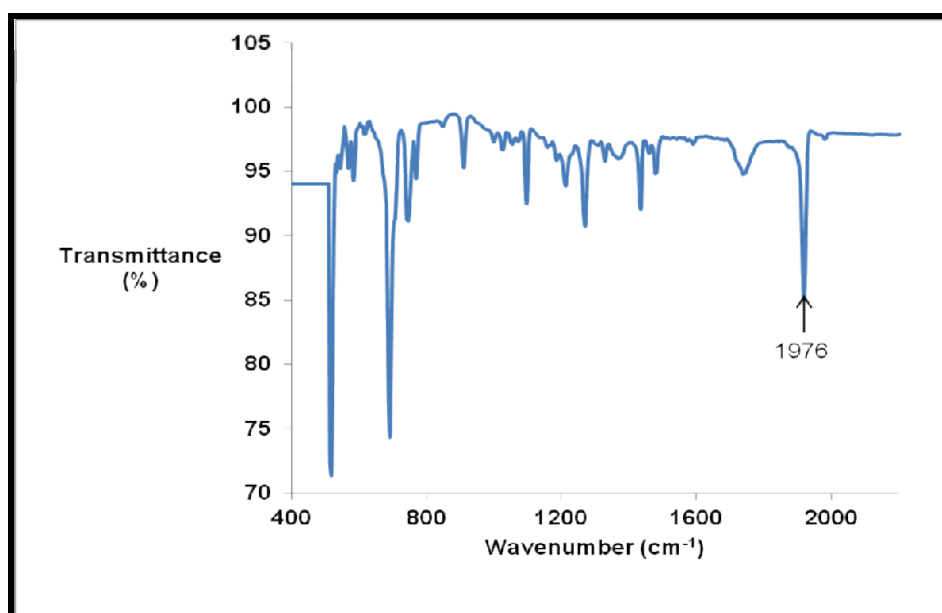
$[\text{Rh}(\text{cupf})(\text{CO})_2]$  was prepared according to Basson *et al.*<sup>223</sup> To a well stirred solution of  $[\text{Rh}(\text{cupf})(\text{CO})_2]$  (0.2087 g; 0.67 mmol) in 10 mL of absolute ethanol, an equivalent amount of triphenylphosphine ( $\text{PPh}_3$ ) (0.1745 g; 0.67 mmol) was added. The resultant yellow solution was gently stirred for 10 min at room temperature. A yellow precipitate was formed which was filtered and washed with absolute ethanol (3 x 5 mL) and left to dry overnight. The product (**Figure 7.33**) was characterised by

<sup>223</sup> S.S. Basson, J.G. Leipoldt, A. Roodt and J.A. Venter, *Inorg. Chim. Acta*, (1986), 118, pp. 45 - 47.

IR spectroscopy and the carbonyl stretching frequency appeared at  $1976\text{ cm}^{-1}$  (yield 59 %). The carbonyl peak was in the same frequency region of  $1982\text{ cm}^{-1}$  (**Figure 7.34**) as that reported by Basson *et al.*<sup>223</sup> Elemental analysis (calculated values in brackets); C, 54.70 (56.61) and N, 5.09 (5.28) %.



**Figure 7.33:** Molecular structure of  $[\text{Rh}(\text{cupf})(\text{PPh}_3)(\text{CO})]$



**Figure 7.34:** Infrared spectrum of  $[\text{Rh}(\text{cupf})(\text{CO})(\text{PPh}_3)]$

#### 7.4.7.2.4 Preparation of the organometallic compounds for rhodium analyte determination

The carbonyl stretching frequencies of the newly synthesized rhodium compounds were compared against the reported literature values (in the brackets). The carbonyl

stretching frequencies ( $\nu_{\text{CO}}$ ) for  $[\text{Rh}(\text{tfaa})(\text{CO})_2]$ <sup>224</sup> were found to be 2083 (2080) and 2017 (2015)  $\text{cm}^{-1}$ ;  $[\text{Rh}(\text{tfaa})(\text{dpp})(\text{CO})]$ <sup>222</sup> were observed at 1990 (1986)  $\text{cm}^{-1}$  and that of  $[\text{Rh}(\text{cupf})(\text{CO})(\text{PPh}_3)]$ <sup>223</sup> were found to be 1976 (1975)  $\text{cm}^{-1}$ . Rhodium organometallic samples  $[\text{Rh}(\text{tfaa})(\text{CO})_2]$ ,  $[\text{Rh}(\text{tfaa})(\text{dpp})(\text{CO})]$  and  $[\text{Rh}(\text{cupf})(\text{CO})(\text{PPh}_3)]$  were weighed accurately (5 -10 mg) and quantitatively transferred into beakers containing HCl (5 mL; 32 %). The mixtures were heated to ca. 200 - 300 °C until complete dissolution was attained. The resultant solutions were quantitatively transferred into 100.0 mL volumetric flasks and filled up to the mark to yield stock solutions with concentrations of approximately 100 - 150 ppm. Aliquots of the stock solutions were pipetted into separate 100.0 mL volumetric flasks and Sc internal standard (0.2 mL; 1 000 ppm) and HCl (5.0 mL; 32 %) were added to yield theoretical rhodium concentrations of approximately 7.0 ppm. The volumetric flasks were filled up to the mark using double distilled water and homogenized before left to stabilize for an hour. The analyte solutions were determined for rhodium content using direct calibration and Sc as internal standard with the calibration standards prepared in **Section 7.4.1.1** and **7.4.1.2** respectively. Results of the quantitative analysis using both methods are reported in **Table 7.16**.

**Table 7.16:** ICP-OES/MS quantitative results of the rhodium in the organometallic compounds using direct calibration and Sc as internal standard

Organometallic compounds	Elements	Method	% Recovery*
Rhodium	$[\text{Rh}(\text{tfaa})(\text{CO})_2]$	Direct cal.	99.8(1)
		<b>Sc int. standard</b>	<b>100.5(8)</b>
	$[\text{Rh}(\text{tfaa})(\text{CO})(\text{dpp})]$	Direct cal.	98.0(1)
		<b>Sc int. standard</b>	<b>99.3(9)</b>
	$[\text{Rh}(\text{cupf})(\text{CO})(\text{PPh}_3)]$	Direct cal.	101.5(2)
		<b>Sc int. standard</b>	<b>99.8(2)</b>

\*Quantitative results given as an average of 3 replicates

The use of scandium as internal standard was further evaluated during the determination of rhodium in various organometallic compounds. Overall good percentage recoveries (+ 98 %) were obtained using both methods. Quantitative

<sup>224</sup> F. Bonati and G. Wilkinson, *J. Chem. Soc.*, (1964), p. 3156.

results with both high precision and accuracy were obtained using scandium as internal standard showing average percentage recoveries in excess of + 99 % and an uncertainty value of approximately 0.09 %. The ability to achieve total percentage recoveries of rhodium in organometallic compounds demonstrated the effectiveness using scandium as internal standard to accurately quantify rhodium in both inorganic and organometallic compounds. These results also confirmed that scandium can be used for the accurate determination of rhodium in organometallic compounds with known purity and which have been fully characterized.

#### 7.4.8 Qualitative and quantitative determination of ruthenium in inorganic and organometallic compounds

##### 7.4.8.1 Determination of ruthenium in the inorganic compound ( $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ )

###### 7.4.8.1.1 Preparation of the $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ analyte samples

A stock solution of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (29 mg, 0.39 mmol) was prepared in a volumetric flask (100.0 mL) and filled up to the mark using double distilled water to yield a theoretical ruthenium concentration of 112.09 ppm. Aliquots (6.24 mL) (in triplicate) of the stock solution were pipetted into volumetric flasks (100.0 mL) to yield analytical solutions of approximately 7.0 ppm. Scandium internal standard (0.2 mL; 1 000 ppm) and HCl (5.0 mL; 32 %) were added to each of the analyte solutions and the volumetric flasks were filled up to the mark using double distilled water. The solutions were left to stabilize for an hour before it was analyzed for the ruthenium content using standards prepared in **Section 7.4.1.1** and **7.4.1.2**. Quantitative results obtained from the ICP-OES/MS analysis are reported in **Table 7.17**.

**Table 7.17:** Quantitative determination of ruthenium in inorganic salts using direct calibration and Sc as internal standard

Technique	% Recovery of Ru* (direct calibration)	% Recovery of Ru* (Sc as internal standard)
ICP-OES	90(3)	100.9(8)
ICP-MS	94.6(4)	102.0(7)

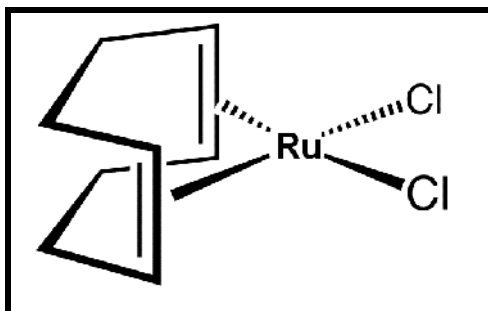
\*Quantitative results given as an average of 3 replicates

Qualitative analysis of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  showed the presence of Ca, Mg, Fe and S (below 1 ppm) which were found to have no effect on the quantitative determination of ruthenium using both techniques. Low percentage recoveries of ruthenium (91 % using the ICP-OES and 95 % using ICP-MS) were obtained using the direct calibration method with both techniques. Total recoveries of ruthenium (+ 100 %) were obtained using Sc internal standard which suggested the ability of this method to accurately determine ruthenium in inorganic salts.

#### 7.4.8.2 Preparation of ruthenium organometallic compounds

##### 7.4.8.2.1 Dichlorido(cycloocta-1,5-diene)ruthenium(II), $[\text{Ru}(\text{cod})(\text{Cl})_2]$ (97 %)

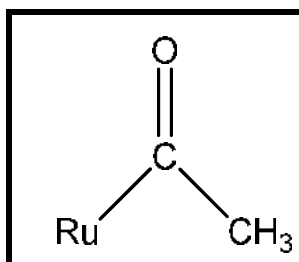
Dichlorido(cycloocta-1,5-diene)ruthenium(II) (97 %) (**Figure 7.19**) was purchased from Sigma Aldrich.



**Figure 7.35:** Molecular structure of  $[\text{Ru}(\text{cod})(\text{Cl})_2]$

##### 7.4.8.2.2 Acetyl ruthenium (99 %)

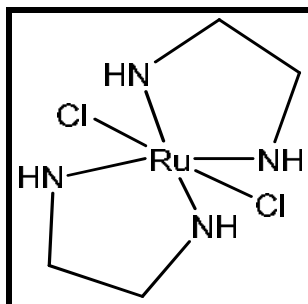
Acetyl ruthenium (99 %) (**Figure 7.36**) was purchased from Sigma Aldrich.



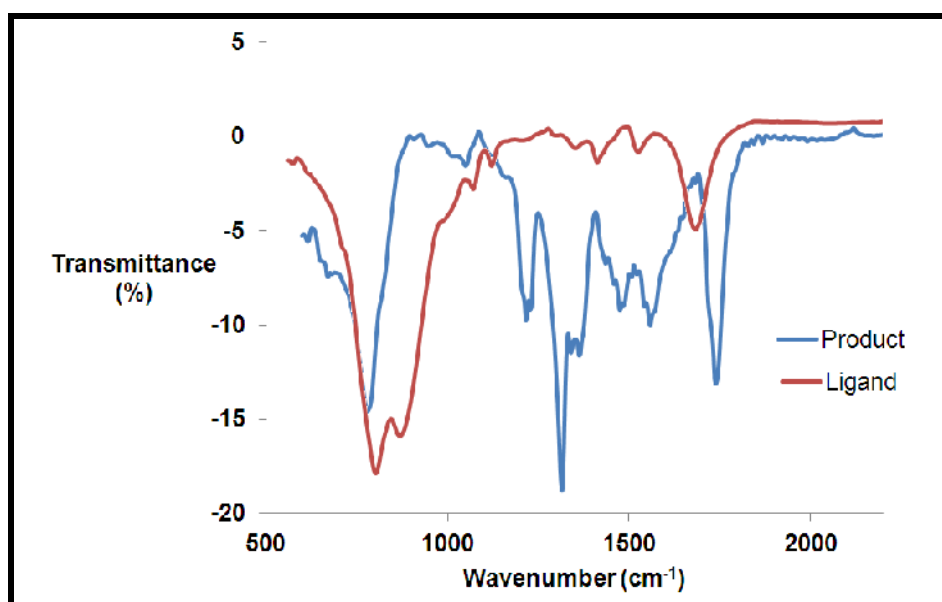
**Figure 7.36:** Molecular structure of acetyl ruthenium

7.4.8.2.3      *Synthesis of cis-dichloridobis(ethylenediamine)ruthenium(II),*  
 $[Ru(en)_2(Cl)_2]$

$RuCl_3 \cdot 3H_2O$  (22 mg; 0.05 mmol) was dissolved in 10 mL of absolute ethanol at room temperature. To this solution, ethylenediamine (0.004 mL; 0.06 mmol) was added gently whilst stirring the reaction mixture. An orange-brown product precipitated immediately after the addition of the ligand and the reaction mixture was stirred for a further 10 min. This yellow product (**Figure 7.37**) was filtered and washed with ethanol (3 x 10 mL) and dried in a dessicator (yield 57 %), before characterized using IR (**Figure 7.38**). Elemental analysis (calculated values in brackets); C, 15.91 (16.67) and N, 20.84 (19.45) %.



**Figure 7.37:** Molecular structure of  $[Ru(en)_2(Cl)_2]$



**Figure 7.38:** Infrared spectrum of  $[Ru(en)_2(Cl)_2]$

#### 7.4.8.2.4 Preparation of the organometallic compounds for ruthenium analyte determination

The Ru-Cl ( $\nu_{\text{Cl}}$ ) stretching frequency of the newly synthesized organometallic compound was compared against the reported literature value. The obtained stretching frequency of  $[\text{Ru}(\text{en})_2(\text{Cl})_2]\text{Cl}$ <sup>225</sup> was observed at  $1310\text{ cm}^{-1}$  which was in the same range as the reported literature value of  $1300\text{ cm}^{-1}$ . Ruthenium organometallic samples ( $[\text{Ru}(\text{cod})(\text{Cl})_2]$ ,  $[\text{Ru}(\text{COCH}_3)]$  and  $[\text{Ru}(\text{en})_2(\text{Cl})_2]\text{Cl}$ ) were accurately weighed (5 - 10 mg) and quantitatively transferred into beakers containing HCl (5 mL; 32 %). The mixtures were heated to ca. 200 - 300 °C until complete dissolution was attained. The resultant solutions were quantitatively transferred into 100.0 mL volumetric flasks and filled up to the mark to yield stock solutions with concentrations of approximately 100 - 150 ppm. Aliquots of the stock solutions were pipetted into separate 100.0 mL volumetric flasks and Sc internal standard (0.2 mL; 1 000 ppm) and HCl (5.0 mL; 32 %) were added to yield theoretical ruthenium concentrations of approximately 7.0 ppm. The volumetric flasks were filled up to the mark using double distilled water and homogenized before left to stabilize for an hour. The analyte solutions were determined for ruthenium content using the direct calibration and Sc as internal standard with the calibration standards prepared in **Section 7.4.1.1** and **7.4.1.2** respectively. Results of the quantitative analysis using both methods are reported in **Table 7.18**.

**Table 7.18:** Quantitative results of the ruthenium in the organometallic compounds using direct calibration and Sc as internal standard

Organometallic compounds	Elements	Method	% Recovery*
Ruthenium	$[\text{Ru}(\text{cod})(\text{Cl})_2]$	Direct cal.	98.7(5)
		Sc int. standard	101.0(2)
	$[\text{Ru}(\text{COCH}_3)]$	Direct cal.	99.6(9)
		Sc int. standard	99.7(8)
	$[\text{Ru}(\text{en})_2(\text{Cl})_2]\text{Cl}$	Direct cal.	95(1)
		Sc int. standard	101.1(6)

\*Quantitative results given as an average of 3 replicates

<sup>225</sup> D.M. Lemal, J.V.Staros and V. Austel, *Journal of the American Chemical Society.*, (1969), p. 3374.

The use of scandium as internal standard was further evaluated during the determination of ruthenium in various organometallic compounds. Excellent percentage recoveries (+ 99 %) of ruthenium were obtained using scandium as internal standard. Quantitative results obtained from [Ru(COCH<sub>3</sub>)] revealed a total recovery of ruthenium from both methods which suggested the dependence of the success of the method on the sample composition. Quantitative results obtained using direct calibration method were also shown to yield excellent results (ca. 99 %) for [Ru(cod)(Cl)<sub>2</sub>] and [Ru(COCH<sub>3</sub>)] except for [Ru(en)<sub>2</sub>(Cl)<sub>2</sub>]Cl. The ability to accomplish a total recovery of ruthenium in organometallic compounds demonstrated the effectiveness of scandium as internal in accurately quantifying ruthenium in both inorganic and organometallic compounds. These results also confirmed that scandium can be used for the accurate determination of ruthenium in organometallic compounds with known purity or which have been fully characterized.

#### **7.4.9 Overall assessment of the use of scandium as internal standard in quantifying precious metals in inorganic and organometallic compounds**

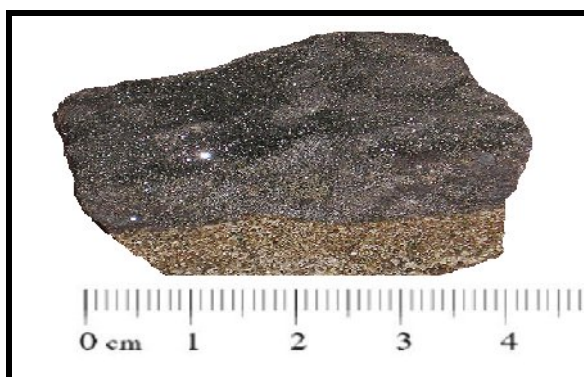
Quantitative determination of precious metals from the inorganic, purchased and the newly synthesised organometallic compounds showed an excellent percentage recoveries (+ 99 %) using scandium as internal standard. The success of this method to accurately quantify precious metals in these compounds was found to be dependent on the purity and well characterized compounds. Fluctuating percentage recoveries (below 98 % and above 102 %) of precious metals in these compounds were obtained using direct calibration method. These fluctuations were believed to have been the result of the uncorrected emission intensities, instrumental drifts and background emissions. These effects were shown to limit the use of the direct calibration method in the accurate determination of precious metals (see **Chapter 4, Section 4.2.2**). The ability to yield approximately total recoveries of precious metals using scandium as internal standard confirmed the success of this method in quantifying precious metals in various inorganic and organometallic compounds. The success of this method coupled to its ability to effectively correct for the instrumental drifts and background emissions suggests that this method can be successfully applied to quantify precious metals in compounds with unknown purity and composition.



## **7.5 Determination of precious metals from the mineral ores**

Geological samples such as mineral ores, sediments, soils, *etc.* contain high TDS which may cause spectral interferences, high background emissions and instrumental drifts. These solid particles may even be deposited on the cone orifices of ICP-MS which limit the use of this equipment in the quantitative determination of precious metals (see **Chapter 4, Section 4.2.4.2.2**). Quantitative analysis of precious metals in geological materials were however successfully determined using ICP-OES due to its capabilities to handle samples with high TDS and analyze many elements (up to 70) sequentially.

A chromitite mineral ore was obtained from a location near Rustenburg, which is situated in the Bushveld igneous complex (BIC). The composition of the UG2 reef which is found in the BIC (see **Chapter 2, Section 2.2.4**) is rich in chromite and has twice as much PGM reserves as those of the Merensky Reef. The most common mineral ores found in the UG2 reef are the chromitite layers which occur commonly in large mafic layered intrusions. The composition of these chromitites mineral ores (**Figure 7.39**) has been determined to consist mainly of mafic and felsic materials. According to literature the PGM content in the chromitite mineral ore varies depending on the site in which the ore was mined and is estimated to be in the range of 0.5 - 0.8 g/t with varying percentage composition of each element in the ore.<sup>226</sup>



**Figure 7.39:** Chromitite mineral ore mined from the Rustenburg platinum mine

---

<sup>226</sup> [www.pincock.com](http://www.pincock.com) (accessed on the 20/09/2013)

### 7.5.1 Microwave digestion of the chromitite mineral ore

#### 7.5.1.1 Experimental procedure

Two sets of the grounded chromitite mineral ore samples (0.5 g) which were dried at 105 °C for 8 hours were accurately weighed and quantitatively transferred to microwave PTFE vessels. Equal volumes (10 mL) of *aqua regia* (1<sup>st</sup> set) and HCl (32 %) (2<sup>nd</sup> set) were added to the separate vessels and the mixtures were digested under the microwave conditions specified in **Chapter 5, Section 5.2.3**. The resultant mixtures were filtered to separate the soluble product from the insoluble residue. The collected filtrates were then heated to reduce the acid volume to approximately 2 mL. The resultant solutions were quantitatively transferred to 100.0 mL volumetric flasks and Sc internal standard (0.2 mL; 1 000 ppm) together with HCl (5.0 mL, 32 %) were added to the solutions. The analyte solutions were filled up to the mark using double distilled water and homogenized before it was left to stabilize for an hour. The analyte solutions were determined for their precious metals content using direct calibration and Sc as internal standard with the calibration standards prepared in **Section 7.4.1.1** and **7.4.1.2** respectively. Results of the quantitative analysis using both methods are reported in **Table 7.19**.

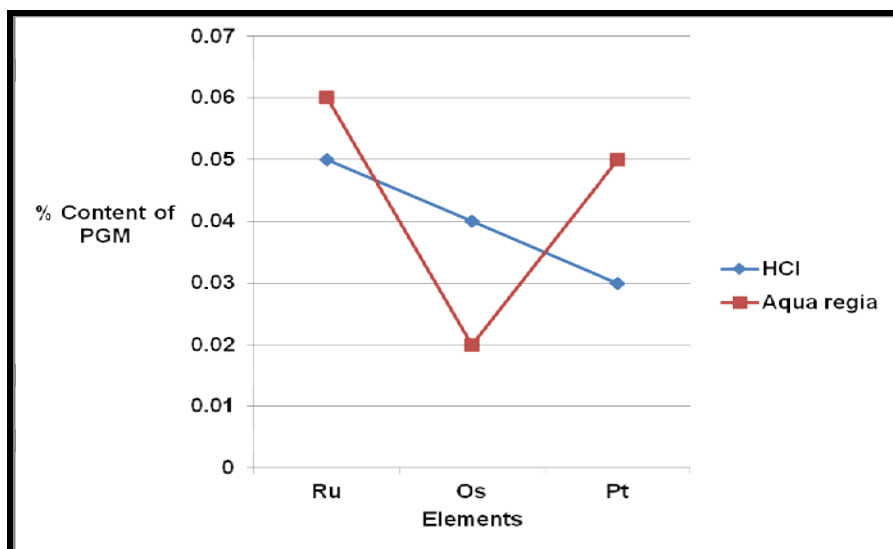
**Table 7.19:** Quantitative results of the chromitite mineral ore after microwave digestion in *aqua regia* and hydrochloric acid

Acid matrix	Elements	Method	% Recovery in 0.5 g ore
HCl	Ru	Direct cal.	0.05(6)
		Sc Internal std	<b>0.06(5)</b>
	Os	Direct cal.	0.04(6)
		Sc Internal std	<b>0.06(4)</b>
	Pt	Direct cal.	0.03(3)
		Sc Internal std	<b>0.04(2)</b>
<i>Aqua regia</i>	Ru	Direct cal.	0.06(8)
		Sc Internal std	<b>0.07(5)</b>
	Os	Direct cal.	0.02(7)
		Sc Internal std	<b>0.03(2)</b>
	Pt	Direct cal.	0.05(5)
		Sc Internal std	<b>0.06(6)</b>

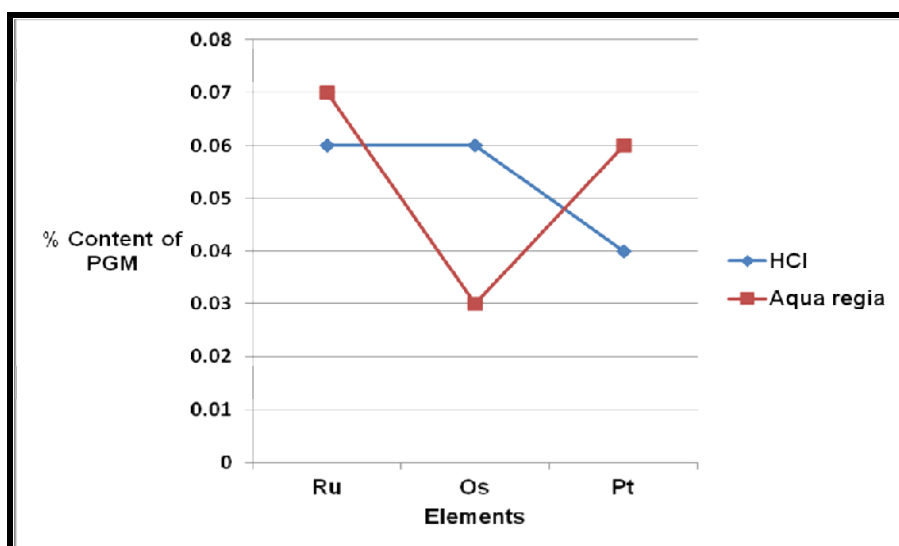
#### **7.5.1.1.1      Discussion of results**

Digestion of the chromitite mineral ore using microwave digestion in *aqua regia* and HCl solutions which were previously found (see **Chapter 5, Section 5.8.1**) to be the preferred mineral acids for precious metals digestion in the dissolution of the geological CRM. However, incomplete dissolution of the chromitite samples was obtained for all the samples that were digested in this study using *aqua regia* and HCl. The solid residue that remained after the dissolution process was presumed to have been the result of the presence of the silica and other highly acid resistant geological phases in the mineral ore. Qualitative results obtained from both filtrates after HCl and *aqua regia* dissolution revealed the presence of 18 elements which included Cr, Rb and Cs (above 100 ppm); Fe (above 10 ppm); Mg, Ti, Al, Pb (above 1 ppm); Be, Ni, Mn, Zn, Sn, Sb; Th (above 0.1 ppm) as well as the PGM, Ru, Os and Pt (above 1 ppm).

Quantitative determinations of the PGM (Ru, Os and Pt) in the chromitite mineral ore were conducted using the previously selected lines shown in **Chapter 5, Section 5.4.1** and **Table 5.3**. These lines were continuously monitored to ensure no interference from the presence of other metals identified during the qualitative analysis. Quantitative results of the PGM (Ru, Os and Pt) revealed a higher percentage recovery (0.06, 0.06 and 0.04 % in HCl and 0.07, 0.03 and 0.06 % in *aqua regia*, respectively) using Sc as internal standard compared to the direct calibration (0.05, 0.04, 0.03 % in HCl and 0.06, 0.02 and 0.05 % in *aqua regia*, respectively). Higher percentage recovery of Os (0.06 %) was obtained using HCl whilst higher percentage recovery of Pt (0.06 %) and Ru (0.07 %) were obtained using *aqua regia* as shown in **Figure 7.40** and **7.41** respectively.



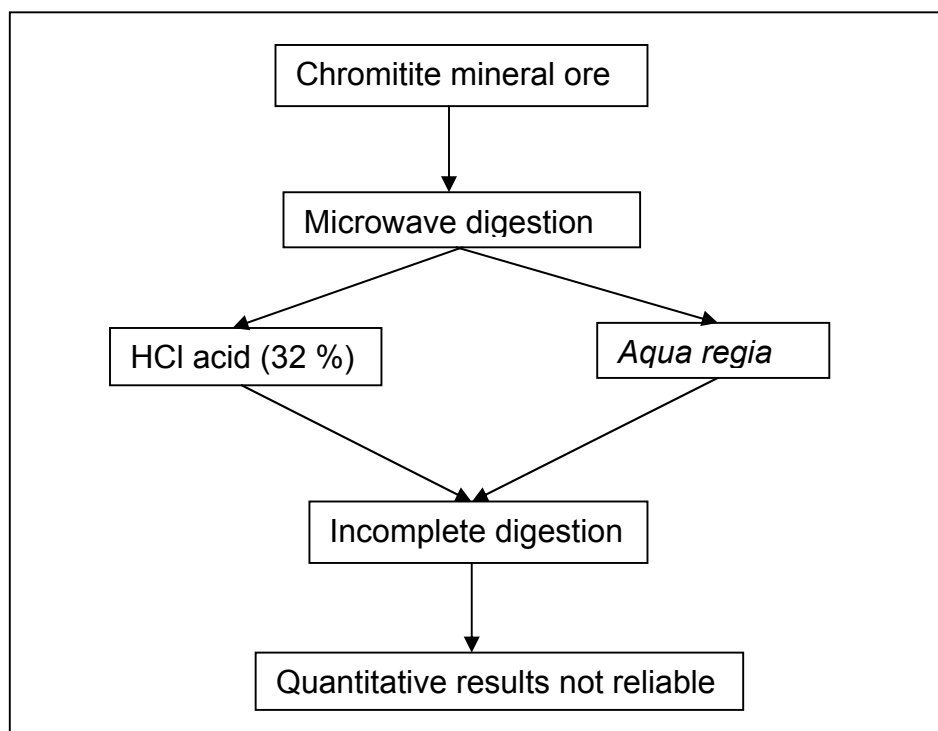
**Figure 7.40:** Determination of PGM in the chromitite mineral ore using the direct calibration method



**Figure 7.41:** Determination of PGM in the chromitite mineral ore using scandium as internal standard

These differences in the percentage recoveries suggested the uniqueness in chemical properties (acid strength) of these mineral acids to digest this chromitite mineral ore. *Aqua regia* was found to be effective for the dissolution of Pt and Ru whilst on the other hand HCl was found to be effective for the dissolution of Os. The difference in percentage recovery between the Os results obtained after the dissolution of the ore in *aqua regia* (0.03 %) and HCl (0.06 %) was believed to have been the result of the oxidation of Os to  $\text{OsO}_4$  by the  $\text{HNO}_3$  in the *aqua regia*. The  $\text{HNO}_3$  in the *aqua regia* is a strong oxidizing agent and has the potential to oxidise Os

to  $\text{OsO}_4$ . The obtained results in this part of the analysis were not conclusive and needed to be compared with other results from more reliable analysis due to the incomplete digestion procedure (**Scheme 7.1**). It was assumed that other PGM particles in the chromitite ore might have been still trapped in the residue and hence the quantitative results obtained in this part may not have been a true reflection of the PGM content in the chromitite mineral ore.



**Scheme 7.1:** Quantitative determination of the precious metals after the microwave digestion of the chromitite ore in *conc.* HCl and *aqua regia*

### 7.5.2 Fusion of the chromitite mineral ore

Fusion methods are commonly preferred for digestion of geological materials<sup>227</sup> such as mineral ores, sediments and soils. One of the major advantages of this method is its ability to effectively decompose the acid resistant phases in the mineral ores and to break the strong silica (Si-O) bonds as discussed in **Chapter 4, Section 4.3.3**. The chromitite mineral ore digestion was first attempted using  $\text{NH}_4\text{F}\cdot\text{HF}$  which was found to be suitable for the complete digestion of the geological CRM.

<sup>227</sup> L. Kotz, G. Kaiser, P. Tschopel and G. Tolg, *Z. Anal. Chem.*, (1972), 260, pp. 207 - 209.

**7.5.2.1 Quantitative determination of the precious metals in chromitite mineral ore after fusion digestion with ammonium hydrogen difluoride ( $\text{NH}_4\text{F}\cdot\text{HF}$ )**

**7.5.2.2 Experimental procedure**

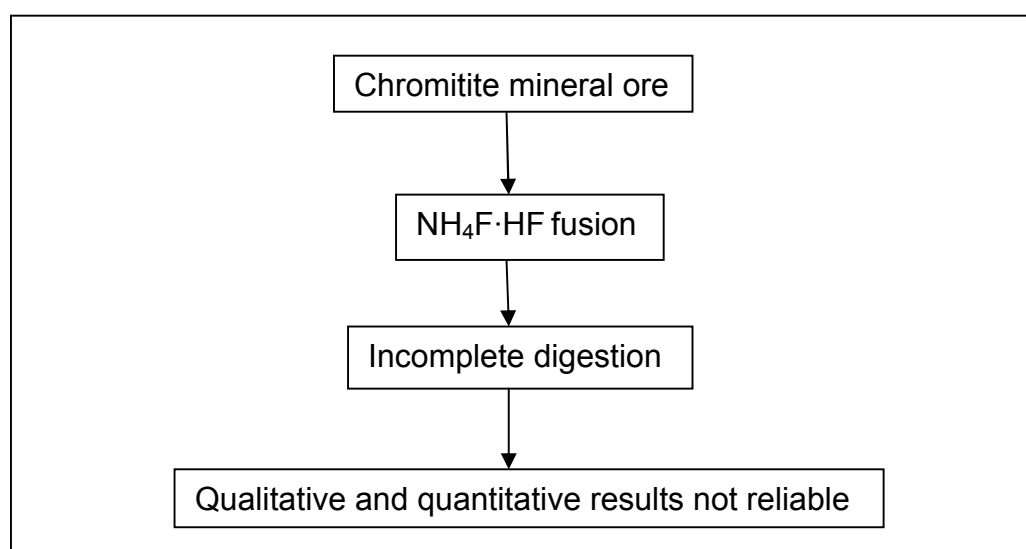
Finely grounded chromitite mineral ore samples (0.5 g) were dried at 105 °C for 8 hours and mixed with  $\text{NH}_4\text{F}\cdot\text{HF}$  flux in the ratio of 1: 20 respectively. The triplicate mixtures were quantitatively transferred to separate platinum crucibles and mixed thoroughly to obtain homogeneous mixtures before placed in a pre-heated oven at 250 °C (m.p  $\text{NH}_4\text{F}\cdot\text{HF}$ ; 239.5 °C) for 1 hour. The resultant undigested black solid was further heated in *aqua regia* (20 mL) whilst stirring. The obtained mixtures were filtered to separate the soluble product from the insoluble residue and the volumes of the filtrates were reduced to approximately 2 mL. The resultant solutions were quantitatively transferred to 100.0 mL volumetric flasks and Sc internal standard (0.2 mL; 1 000 ppm) together with HCl (5.0 mL, 32 %) were added to the solutions. The flasks were filled up to the mark using double distilled water and homogenized before left to stabilize for an hour. The analyte solutions were determined for the precious metals content using direct calibration and Sc as internal standard with the calibration standards prepared in **Section 7.4.1.1** and **7.4.1.2** respectively. Results of the quantitative analysis using both methods are reported in **Table 7.20**.

**Table 7.20:** Quantitative results of chromitite digested using  $\text{NH}_4\text{F}\cdot\text{HF}$  flux

Sample	Elements	Method	% Recovery in 0.5 g ore
Chromitite	Ru	Direct cal.	0.083(4)
		Sc Internal std	0.085(1)
	Os	Direct cal.	0.093(7)
		Sc Internal std	0.095(4)
	Pt	Direct cal.	0.072(5)
		Sc Internal std	0.073(3)

#### 7.5.2.2.1 Discussion of results

Prior to the fusion digestion of the chromitite sample, the ore was first grounded to fine powdered particles similar to the  $\text{NH}_4\text{F}\cdot\text{HF}$  salt (flux) to prevent segregation before mixed. The mixture was mixed thoroughly to ensure intimate contact between these particles. This contact was necessary to ensure the complete reaction between the chromitite sample and the flux to produce a homogeneous melt. In an effort to accomplish the complete digestion of the chromitite sample, the temperature of the oven was constantly adjusted and maintained at 250 °C until a heterogeneous molten mixture was formed. Contrary to a glassy melt which was obtained during the digestion of the geological CRM (see **Chapter 5, Section 5.8.1.1**), a brown residue, almost the same as the original colour of the chromitite ore, collected at the bottom of the platinum crucible which indicated incomplete digestion of the ore using this method. Qualitative analysis of the filtrate obtained after the dissolution in *aqua regia* showed the presence of Ru, Os and Pt and all the other metals (below 10 ppm) as identified in the **Section 7.5.1.1.1**. Due to the incomplete digestion of the chromitite mineral ore using the  $\text{NH}_4\text{F}\cdot\text{HF}$  flux, the obtained quantitative results of the PGM (Ru, Os and Pt) were again regarded not a true reflection of the percentage composition of the PGM in the chromitite mineral sample (**Scheme 7.2**) therefore an alternative digestion method was investigated.



**Scheme 7.2:** Quantitative determination of the precious metals after  $\text{NH}_4\text{F}\cdot\text{HF}$  fusion with the chromitite mineral ore

**7.5.2.3 Quantitative determination of precious metals in chromitite mineral ore after fusion with a mixture of disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) and sodium dihydrogen phosphate monohydrate ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ )**

**7.5.2.3.1 Experimental procedure**

Finely grounded chromitite mineral ore samples (0.5 g) were dried at 105 °C for 8 hours and mixed with a mixture of  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  fluxes in the ratio of 1: 25 respectively. The triplicate mixtures were quantitatively transferred to platinum crucibles and mixed thoroughly before placed in a pre-heated oven at 1 000 °C for 30 min. The resultant molten melts were cooled at room temperature until glassy green melts formed. The melts were dissolved in distilled water (20 mL) and stirred until homogeneous solutions were formed. The resultant solutions were quantitatively transferred to 100.0 mL volumetric flasks and Sc internal standard (0.2 mL; 1 000 ppm) together with HCl (5.0 mL, 32 %) were added to the solutions. The flasks were filled up to the mark using double distilled water and homogenized before left to stabilize for an hour. The analyte solutions were determined for the precious metals content using direct calibration and Sc as internal standard with the calibration standards prepared in **Section 7.4.1.1** and **7.4.1.2** respectively. Results of the quantitative analysis using both methods are reported in **Table 7.21**.

**Table 7.21:** Quantitative results of chromitite digested using a mixture of  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  flux

Sample	Elements	Method	% Recovery in 0.5 g ore
Chromitite	Ru	Direct cal.	0.37(3)
		<b>Sc Internal std</b>	<b>0.34(8)</b>
	Os	Direct cal.	0.25(1)
		<b>Sc Internal std</b>	<b>0.22(2)</b>
	Pt	Direct cal.	0.32(4)
		<b>Sc Internal std</b>	<b>0.31(9)</b>

**7.5.2.3.2 Discussion of results**

Qualitative analysis of the chromitite solution revealed the present of twenty five elements (excluding Ru, Os and Pt) which included the EIE's, Na (>1 000 ppm), Li,



Mg, Ca, Rb, Ba, Be and Cs; transition metals, Al, Ti, V, Ga, Mn, Sr, Tl and Pb other metals, Sn, Sb, Si and Th and base metals, Cr, Fe, Ni, Cu and Zn (>10 ppm). A constant monitor of the Ru, Os and Pt lines (see **Chapter 5, Table 5.3**) on the ICP-OES profile function showed no direct spectral interference but did indicate a suppression of the emission intensities on these selected wavelengths, possibly due to the presence of EIE's which were in relatively high concentrations (above 1 000 ppm). Quantitative analysis of the 3 PGM (Ru, Os and Pt) present in the chromitite revealed increased percentage recoveries using both the direct calibration (0.37, 0.25 and 0.32 % respectively) and Sc as internal standard (0.34, 0.22 and 0.31 % respectively) compared to the previously obtained results after the microwave and  $\text{NH}_4\text{F}\cdot\text{HF}$  fusion digestion methods.

#### **7.5.2.4     *Quantitative determination of precious metals in the chromitite mineral ore after removal of EIE's***

##### **7.5.2.4.1     *Experimental procedure***

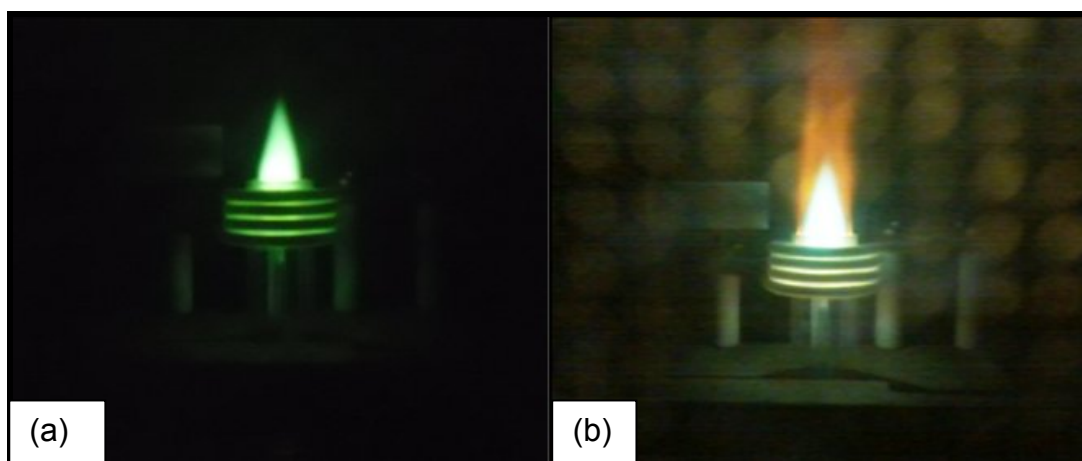
The experimental procedure of the chromitite mineral ore from the previous **Section 5.6.2.2** was repeated. The dissolved melts (ca. 30 mL) were transferred into separate evaporating basins. Equal volumes of HCl (20 mL; 32 %) were added to each basin and the solutions were left to stand overnight. Colourless crystals (5.10 - 5.60 g) formed and were subsequently removed from the solution through filtration. The filtrate were reduced to ca. 2 mL by heating and were quantitatively transferred to 100.0 mL volumetric flasks and Sc internal standard (0.2 mL; 1 000 ppm) together with HCl (5.0 mL, 32 %) were added to the solutions. The volumetric flasks were filled up to the mark using double distilled water and homogenized before left to stabilize for an hour. The analyte solutions were determined for their precious metals content using direct calibration and Sc as internal standard with the calibration standards prepared in **Section 7.4.1.1** and **7.4.1.2** respectively. Results of the quantitative analysis using both methods are reported in **Table 7.22**.

**Table 7.22:** Quantitative results of the PGM (Ru, Os and Pt) obtained after the fusion of chromitite ore with a flux mixture of  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  and the subsequent removal white precipitate

Sample	Elements	Method	% Recovery in 0.5 g ore
Chromitite	Ru	Direct cal.	0.18(2)
		Sc Internal std	<b>0.18(1)</b>
	Os	Direct cal.	0.09(4)
		Sc Internal std	<b>0.09(2)</b>
	Pt	Direct cal.	0.19(2)
		Sc Internal std	<b>0.25(9)</b>

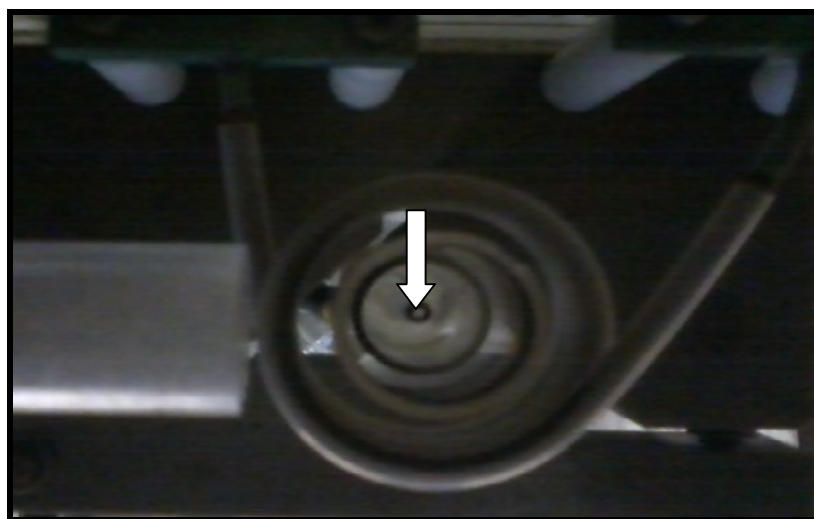
#### 7.5.2.4.2 Discussion of results

The increase in Ru, Os and Pt percentage recoveries are believed to have been the result of the complete digestion of the ore using a mixture of  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ . Another possibility of this increase may be due to the influence of the sodium (EIE's) on the PGM percentage recoveries. The effects of EIE's have been shown in **Chapter 5, Section 5.5.2** to alter both the Sc and the analyte emission signals to cause both false-high (positive error) and false-low (negative error) percentage recoveries depending on the element in question. This increase in EIE's content in the chromitite solution was found to have a profound effect on the ICP-OES flame properties by not only increasing the flame height but also altering the flame colour as shown in **Figure 7.42**.



**Figure 7.42:** (a) Original ICP-OES flame (b) Effects of sodium phosphate flux on the ICP-OES flame

This comparison of the ICP-OES flames between the original and the EIE's contaminated flame clearly showed the yellowing of the flame as a result of the presence of the EIE's ( $\text{Na}^+$  ions) in the chromite solution from the original flux. This yellowing of the flame is also reported in literature to be caused by the strong emission of sodium ions in the yellow region (580 nm) of the visible spectrum.<sup>228</sup> This flame alteration is believed to either suppress or enhance the PGM emission intensities during this sample measurement (see **Chapter 3, Section 3.2.4**) to yield a false-high percentage recovery of PGM (Ru, Os and Pt) in the current chromitite ore. This yellowing of the flame was accompanied by the deposition of a black substance (presumably soot) at the tip of the torch nozzle as shown in **Figure 7.43**. This deposition action is believed to have an effect on the stability of the flame which results in the disruption of the ionization-atomization equilibrium in the plasma. This disturbance in equilibrium is often reported in literature<sup>229</sup> to result in either emission enhancement or suppression which will eventually lead to random errors in the quantitative analysis.



**Figure 7.43:** A section through an ICP-OES torch nozzle showing a clog

The quantitative determination of PGM in the chromitite ore was found to be influenced by the effects of the EIE's on the ICP-OES flame. Alternative digestion or separation methods which can minimize the EIE's content in solution but also afford

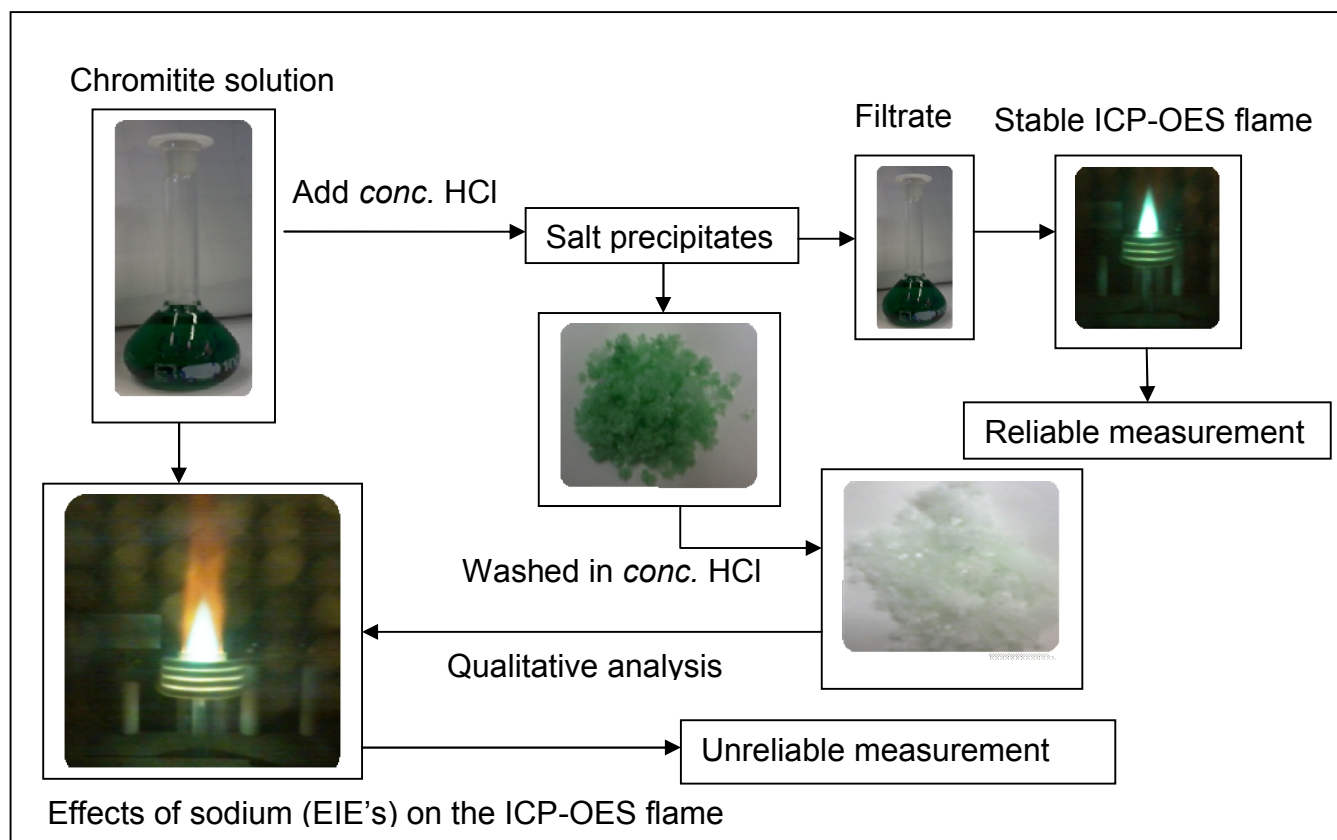
---

<sup>228</sup> P. Gaines and B. Brodin, *ICP operations, spectral interferences, types, avoidance and correction*, (2004).

<sup>229</sup> M.M. Cheatham, W.F. Sangrey, W.M. White, *Spectrochim. Acta Part B*, (1993), 48, pp. 487 - 506.

total dissolution of the mineral sample was required to avoid the uncertainty in the percentage recoveries of the PGM (Ru, Os and Pt) in the chromitite ore. The next experimental investigation was aimed at establishing or developing a procedure that could remove/isolate the  $\text{Na}^+$  ions from the digested chromitite analyte solution. The removal of the sodium ions (EIE's) from the chromitite solution was considered critical for the accurate determination of PGM (Ru, Os and Pt) from the chromitite solution.

In this part of the investigation concentrated hydrochloric acid was added to the reaction mixture which precipitated the  $\text{Na}^+$  ions as colourless  $\text{NaCl}$  crystals. Qualitative analysis of the colourless crystals showed only the presence of  $\text{Na}^+$  ions whilst filtrate solution was found to contain the PGM (Ru, Os and Pt) and other metals which were previously determined in **Section 7.5.2.3.1**. Results of the qualitative analysis of the filtrate further showed no spectral interference on the selected lines for the precious metals (Ru, Os and Pt) and no yellowing of the ICP-OES flame (**Scheme 7.3**).



**Scheme 7.3:** The removal of  $\text{NaCl}$  from the chromitite analyte solution after digestion with a mixture of  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  flux

Quantitative results of the PGM (Ru, Os and Pt) obtained after the removal of Na<sup>+</sup> ions using Sc as internal standard method showed that Pt had the highest percentage (0.25 %) recovery in the chromitite ore followed by Ru (0.18 %) and Os (0.09 %). The same order of percentage proportion was shown using the direct calibration with Pt having the highest recovery of 0.19 % followed by Ru (0.18 %) and Os (0.09 %).

**7.5.2.5      *Quantitative determination of precious metals in the chromitite mineral ore after fusion with ammonium dihydrogen phosphate ((NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub>) flux***

**7.5.2.5.1      *Experimental procedure***

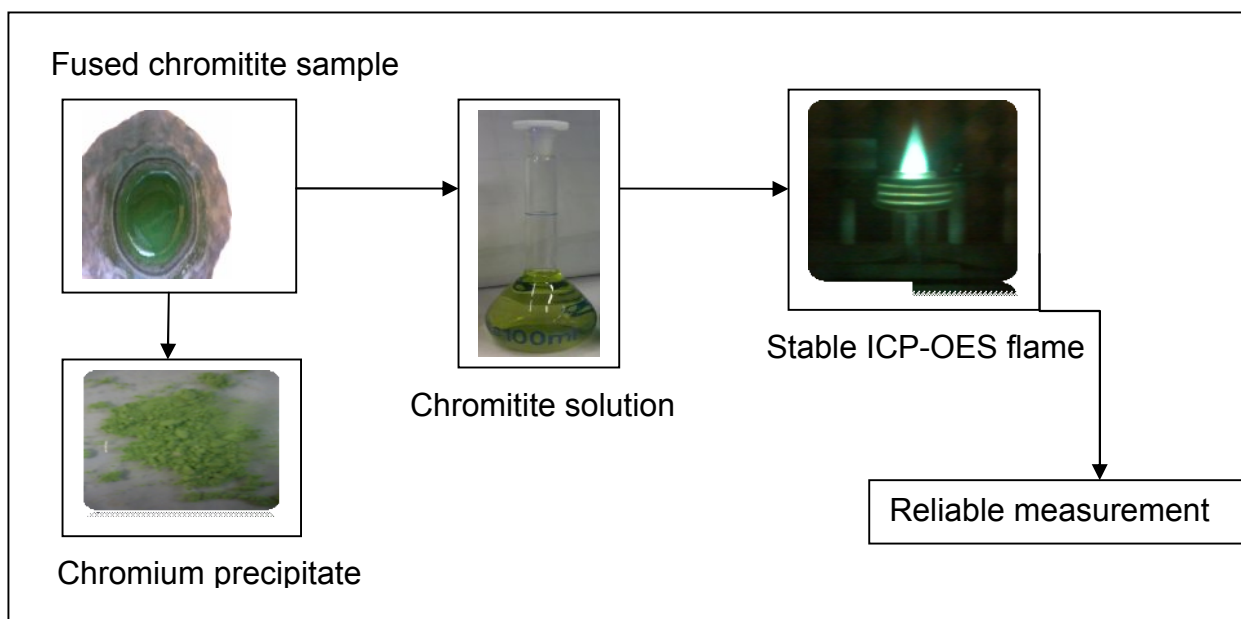
Finely grounded chromitite mineral ore samples (0.5 g) were dried at 105 °C for 8 hours and mixed with (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> flux in the ratio of 1: 25 respectively. These triplicate mixtures were quantitatively transferred to platinum crucibles and mixed thoroughly before they were placed in a pre-heated oven at 800 °C (m.p.(NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub>; 190 °C) for 30 min. The resultant melts were cooled to room temperature until glassy solids were obtained. These glassy solids were dissolved in distilled water (20 mL) and heated whilst stirring, *aqua regia* was added and green-yellow precipitates formed during this step. The resultant mixtures were filtered and the filtrates were quantitatively transferred into separate 100.0 mL volumetric flasks, Sc internal standard (0.2 mL; 1 000 ppm) together with HCl acid (5.0 mL, 32 %) were added to these solutions. The volumetric flasks were filled to the mark using double distilled water and homogenized before left to stabilize for an hour. The analyte solutions were determined for precious metals content using direct calibration and Sc as internal standard with the calibration standards prepared in **Section 7.4.1.1** and **7.4.1.2** respectively. Results of the quantitative analysis using both methods are reported in **Table 7.23**.

**Table 7.23:** Quantitative results of chromitite digested using  $(\text{NH}_4)_2\text{HPO}_4$  flux

Sample	Elements	Method	% Recovery in 0.5 g ore
Chromitite	Ru	Direct cal.	0.176(2)
		Sc Internal std	<b>0.19(3)</b>
	Os	Direct cal.	0.07(1)
		Sc Internal std	<b>0.09(4)</b>
	Pt	Direct cal.	0.24(1)
		Sc Internal std	<b>0.26(3)</b>

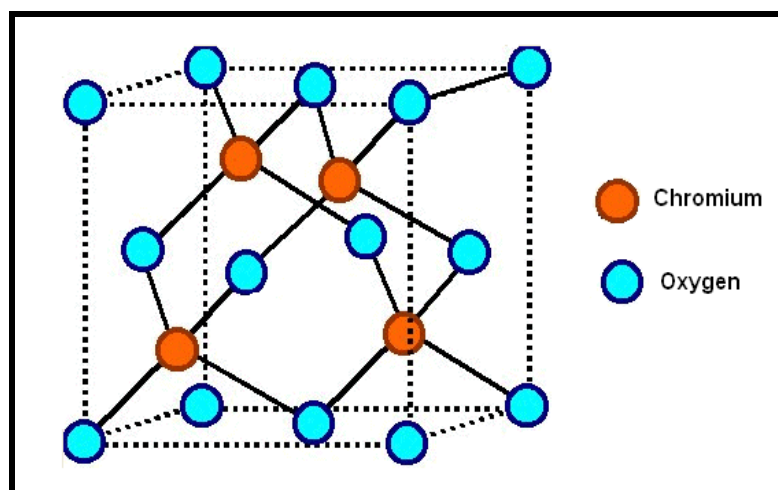
#### 7.5.2.5.2 Discussion of results

The use of an alternative fusion method of the chromitite ore dissolution using  $(\text{NH}_4)_2\text{HPO}_4$  flux was undertaken in an attempt to avoid the introduction of sodium ions (EIE's) during the fusion step. Complete digestion of the chromitite ore was achieved using  $(\text{NH}_4)_2\text{HPO}_4$  flux in the ratio 1: 25 respectively. The  $(\text{NH}_4)_2\text{HPO}_4$  flux had an advantage of not only achieving a complete digestion but also of not introducing EIE's into the chromitite analyte solution. During the dissolution of the melt in distilled water a clear yellow-green solution was obtained and upon reducing the analyte volume in an HCl environment whilst heating, a yellow-green precipitate was formed which was separated from the solution by filtration (**Scheme 7.4**). Qualitative analysis of this precipitate revealed the presence of a large quantity of chromium and trace amounts of Ca and Mg (below 1 ppm) whilst the filtrate showed the presence of Ru, Os and Pt together with other metal impurities listed in the previous **Section 7.5.2.3.1**.



**Scheme 7.4:** Sample preparation of the chromitite ore using  $(\text{NH}_4)\text{H}_2\text{PO}_4$  flux and the isolation of chromium

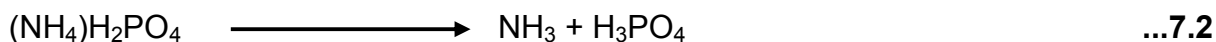
The isolation of the insoluble  $\text{Cr}_2\text{O}_3$  product from this reaction mixture was highly unexpected, but it produced excellent beneficiation opportunities since it facilitated the easy isolation and subsequent separation of this major element from the rest of the reaction mixture. According to literature the chromium present in the chromitite mineral is normally associated with metals such as iron and magnesium as  $(\text{Mg,Fe})\text{Cr}_2\text{O}_4$ . This compound is believed to have an  $\text{AB}_2\text{O}_4$  spinel structure as shown **Figure 7.44**.



**Figure 7.44:** The spinel structure of  $\text{Cr}_2\text{O}_3$ <sup>230</sup>

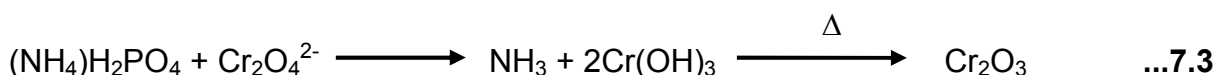
<sup>230</sup> [http://www.tf.uni-kiel.de/matwis/amat/def\\_en/kap\\_2/basics/b2\\_1\\_6.html](http://www.tf.uni-kiel.de/matwis/amat/def_en/kap_2/basics/b2_1_6.html) (accessed on 21/11/2013)

The precipitation of Cr<sub>2</sub>O<sub>3</sub> (chromia) is believed to have been the result of the use of (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> as flux in the digestion of the chromitite mineral ore. During the fusion process, NH<sub>3</sub> gas is liberated from the (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> flux which is evident from the odour of this pungent gas during the digestion process. The liberation of ammonia from the reaction mixture at this high temperature can be due to the decomposition of the flux (melting point 190 °C) which produces H<sub>3</sub>PO<sub>4</sub> in situ. (**Equation 7.2**)



The formation of the chromia according to this hypothesis should therefore be the result of the reaction between the chromitite and phosphoric acid (low pH), but no evidence was found in literature or in this study that supports this idea.

Contrary, literature indicate that Cr<sub>2</sub>O<sub>3</sub> is produced via the reaction/decomposition of species such as Cr(OH)<sub>3</sub> at higher pH values and at elevated temperatures. The production and release of NH<sub>3</sub> from the reaction mixture can be the direct acid-base reaction between the NH<sub>4</sub><sup>+</sup> cation and the chromitite in the mineral which result in the in situ production of Cr(OH)<sub>3</sub> which then decomposes at elevated temperatures to produce chromia according to the following reaction:



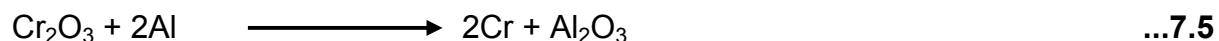
It is also possible that the Cr<sub>2</sub>O<sub>3</sub> ( O=Cr-O-Cr=O) is formed by the direct reaction of the NH<sub>4</sub><sup>+</sup> proton on the chromitite compound (no formation of hydroxo species) as illustrated in **Equation 7.4** (the structure already contains O-Cr-O-Cr bonds). Systematic protonation of oxygen is followed by metal oxygen bond breakage at higher pH values and at high temperatures to produce the chromite compound.



It is important to note that the use of the sodium salts (Na<sub>2</sub>HPO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub>) did not produce chromia during the digestion step. The main difference between these



phosphate salts appear to be the pH which is 4.6<sup>231,232</sup> for (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> and that for Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> are 9.4 and 4.5<sup>233,234</sup> respectively. This difference in the pH of the melts may be the main reason for the production of Cr<sub>2</sub>O<sub>3</sub> from this reaction. It is important to note that current commercial dissolution, separation and isolation procedure of chromium from chromite type minerals consists of three procedures namely (i) roasting of chromite ore, (ii) water leaching and (iii) multi-stage evaporation and crystallization.<sup>235</sup> The chromite is mixed with sodium carbonate and a large amount of limestone and dolomite to give sodium chromate, Na<sub>2</sub>CrO<sub>4</sub>, which is leached out with water, precipitated and then reduced to the Cr(III) oxide by carbon. Chromium metal is then obtained by the reduction of Cr<sub>2</sub>O<sub>3</sub> with aluminium (aluminothermic process) or silicon as shown in **Equation 7.5** and **7.6**.



The precipitated Cr<sub>2</sub>O<sub>3</sub> was found to be insoluble in *aqua regia*, HCl and HNO<sub>3</sub> and even at an elevated temperature (300 °C) and pressure (60 bar) using the microwave digester. Successful digestion of the obtained Cr<sub>2</sub>O<sub>3</sub> was achieved using a mixture of Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O flux.

Quantitative results obtained of the PGM (Ru, Os and Pt) using both the direct and Sc as internal standard methods showed slightly higher percentage recoveries of Pt, Ru and Os in the same percentage composition as previously determined in **Section 7.5.2.4** in the chromitite ore. Results obtained using Sc as internal standard showed a higher percentage recovery of Pt (0.26 %), Ru (0.19 %) and Os (0.09 %) compared to the results obtained using the direct calibration Pt (0.24 %), Ru (0.18 %) and Os

---

<sup>231</sup> R.C. Weast, *Handbook of chemistry and Physics*, 56th. Edition, CRC Press Inc., Cleveland, Ohio, USA. (1974).

<sup>232</sup> J.R. van Wazer. *Phosphorus and its compounds - Chemistry*. New York, Interscience Publishers, Inc., (1958), 1, p. 503

<sup>233</sup> <http://www.fao.org/ag/agn/jecfa-additives/specs/Monograph1/Additive-166.pdf> (accessed on 25/11/2013)

<sup>234</sup> B. Mysen, F.J. Ryerson and D. Virgo, *Amer. Mineral.*, (1981), 66, pp. 106 - 17.

<sup>235</sup> M.P. Antony, V.D. Tathavadkar, C.C. Calvert and A. Jha, *Metallurgical and Materials transactions B*, (2001), 32, pp. 987 - 995.

(0.07 %). Quantitative results obtained using Sc as internal standard were similar to the percentage recoveries obtained after the removal of Na<sup>+</sup> ions using Sc as internal standard (**Table 7.24**). This similarity in the percentage recovery of PGM indicates the effectiveness of (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> as well as the mixture of Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O flux towards the complete digestion of the chromitite mineral. The (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> was chosen as the best fusion flux based on its ability not only to achieve a complete digestion of the ore but also to avoid introducing EIE's in the analyte solution. Although (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> flux has proved to be one of the preferred fluxes for the digestion of the chromitite ore, the digestion process needed to be executed in a well ventilated place to avoid exposure to NH<sub>3</sub> gas which is generated during the digestion process. The use of flux mixture Na<sub>2</sub>HPO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O was considered as an alternative method for the digestion of the chromitite ore on condition that the Na<sup>+</sup> ions were completely removed from the analyte solution.

**Table 7.24:** Comparison of the PGM (Ru, Os and Pt) results obtained after (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O fusion of the chromitite mineral ore using Sc as internal standard

Sample	Elements	Fusion method	% Recovery in 0.5 g ore
Chromitite	Ru	(NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub>	0.19(3)
		Na <sub>2</sub> HPO <sub>4</sub> /NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	0.18(1)
	Os	(NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub>	0.09(4)
		Na <sub>2</sub> HPO <sub>4</sub> /NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	0.09(2)
	Pt	(NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub>	0.26(3)
		Na <sub>2</sub> HPO <sub>4</sub> /NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	0.25(9)

### 7.5.3 Quantitative determination of precious metals in the Merensky reef mineral ore after fusion with flux mixture of Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O

#### 7.5.3.1 Experimental procedure

The Merensky reef mineral ore was supplied by the Impala Platinum mine and was grounded to a fine powder of less than 75 µm using the Crushers and ball mill. Three finely grounded chromitite mineral ore samples (0.5 g x 4) were dried at 105 °C for 8 hours and mixed with the flux mixture Na<sub>2</sub>HPO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O in the ratio of 1: 25

respectively. The mixtures were quantitatively transferred into separate platinum crucibles and mixed thoroughly before placed in a pre-heated oven at 1 000 °C for 30 min. The resultant molten melts were cooled to room temperature until glassy solids formed. The glassy solids were subsequently dissolved in distilled water (20 mL) and transferred into separate evaporating basins. Equal volumes of concentrated HCl (20 mL; 32 %) were added to each basin and the solutions were left to stand overnight. Colourless crystals (NaCl) formed during this period and were removed from the solution via filtration. The resultant solutions were quantitatively transferred to 100.0 mL volumetric flasks and Sc as internal standard (0.2 mL; 1 000 ppm) together with HCl (5.0 mL; 32 %) were added to the solutions. The volumetric flasks were then filled to the mark using double distilled water, homogenized and left to stabilize for an hour. The analyte solutions were analyzed for precious metals content using direct calibration and Sc as internal standard with the calibration standards prepared in **Section 7.4.1.1** and **7.4.1.2** respectively. Results of the quantitative analysis using both methods are reported in **Table 7.25**.

**Table 7.25:** Quantitative results of the Merensky reef ore digested using a mixture of Na<sub>2</sub>HPO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O flux

Sample	Elements	Method	% Recovery in 2.0 g ore
Merensky reef	Ru	Direct cal.	0.02(1)
		<b>Sc Internal std</b>	<b>0.02(1)</b>
	Os	Direct cal.	0.01(1)
		<b>Sc Internal std</b>	<b>0.02(2)</b>
	Ir	Direct cal.	0.01(2)
		<b>Sc Internal std</b>	<b>0.01(2)</b>
	Pt	Direct cal.	0.04(3)
		<b>Sc Internal std</b>	<b>0.04(2)</b>

#### **7.5.3.1.1 Discussion of results**

The determination of the PGM in the geological ores was extended to include the Merensky reef mineral ore sample. Complete digestion of this mineral ore was achieved using a mixture of Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O/NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> flux as indicated by the absence of any visual solid particles. Qualitative analysis of the ore showed

the presence of 25 elements including the precious metals (Ru, Os, Ir and Pt). The mixture present in the glassy melt includes the EIE's, ( $\text{Na}^+$  ions above 1 000 ppm from a mixture of  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  flux) Ba, Ca, Sr and Mg (above 10 ppm); transition elements Cu, Cr, Co, Ni, Zn, Fe, Mn, Sn and V (above 10 ppm) and the elements Al, P, S, Sn, Sb, Si and Se (above 1 ppm). Further analysis using the ICP-OES profile function showed that the selected lines for the precious metals (Ru, Os, Ir and Pt) are not interfered by the presence of these impurities (see **Chapter 5, Table 5.3**). The low concentration of the precious metals in the sample imposed a larger challenge on the accurate determination of these metals using the ICP-OES since the concentration of these metals in a 0.5 g sample was found to be below the detection limits. The low PGM content in this mineral sample required an increase in the amount ( $4 \times 0.5$  g) of mineral sample for digestion to ensure that the metal concentration falls within the calibration range (working range). The drawback of this procedure was the accumulation of the  $\text{Na}^+$  ions in the analyte solution from the flux.

The quantitative determination of the PGM (Ru, Os, Ir and Pt) in the Merensky reef mineral sample showed very low concentrations of the precious metals compared to the chromitite ore sample. Similar results were obtained for Ru (0.02 %), Ir (0.01 %) and Pt (0.04 %) using both the direct calibration and Sc internal standard except for Os (see **Table 7.24**) after  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  digestion. This close similarity in the quantitative results also suggested the existence of low matrix levels of  $\text{Na}^+$  ions (EIE's) derived from the flux in the analyte solution. These results further proved the effectiveness of the isolation and separation process of  $\text{Na}^+$  ions as NaCl salt, which not only enabled the stabilization of the flame but also allowed for the reliable measurement process.

### **7.5.3.2      *Quantitative determination of precious metals in the Merensky reef mineral ore after flux fusion with $(\text{NH}_4)\text{H}_2\text{PO}_4$***

#### **7.5.3.2.1      *Experimental procedure***

Three finely grounded chromitite mineral ore samples ( $0.5 \text{ g} \times 4$ ) were dried at  $105^\circ\text{C}$  for 8 hours and then mixed with  $(\text{NH}_4)\text{H}_2\text{PO}_4$  flux in the ratio of 1:25

respectively. The triplicate mixtures were quantitatively transferred to separate platinum crucibles and mixed thoroughly before placed in a pre-heated oven at 800 °C for 30 min. The resultant molten melts were cooled to room temperature until glassy solids were formed. The glassy solids were dissolved in distilled water (20 mL) and heated whilst stirring. *Aqua regia* was then added and green-yellow precipitates formed during this step. The resultant mixtures were filtered and the filtrates were quantitatively transferred into separate volumetric flasks. The filtrate solutions were quantitatively transferred into separate 100.0 mL volumetric flasks and Sc internal standard (0.2 mL; 1 000 ppm) together with HCl (5.0 mL, 32 %) were added to the solutions. The volumetric flasks were filled up to the mark using double distilled water and homogenized before left to stabilize for an hour. The analyte solutions were determined for the precious metals content using direct calibration and Sc as internal standard using the calibration standards prepared in **Section 7.4.1.1** and **7.4.1.2** respectively. Results of the quantitative analysis using both methods are reported in **Table 7.26**.

**Table 7.26:** Quantitative results of Merensky reef mineral ore digested using  $(\text{NH}_4)\text{H}_2\text{PO}_4$  flux

Sample	Elements	Method	% Recovery in 2.0 g ore
Merensky reef ore	Ru	Direct cal.	0.01(2)
		<b>Sc Internal std</b>	<b>0.02(2)</b>
	Os	Direct cal.	0.01(5)
		<b>Sc Internal std</b>	<b>0.02(6)</b>
	Ir	Direct cal.	0.01(5)
		<b>Sc Internal std</b>	<b>0.01(6)</b>
	Pt	Direct cal.	0.03(1)
		<b>Sc Internal std</b>	<b>0.04(2)</b>

#### 7.5.3.2.2 Discussion of results

Slightly lower percentage recoveries for Ru (0.01 %), Os (0.01 %), Ir (0.01 %) and Pt (0.03 %) were obtained using the direct calibration compared to those obtained using Sc as internal standard namely 0.02 % for Ru, 0.02 % for Os, 0.01 % for Ir and 0.04 % for Pt. The results obtained using Sc as internal standard were shown to be

in agreement with the previous results (see **Section 7.5.3.1, Table 7.25**) obtained after the fusion of the ore with  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ . The lower than expected recoveries obtained using the direct calibration in the current experiment is the result of the uncorrected matrix and emission in the analyte solution. The similarity between the recovered concentrations of the PGM (Ru, Os, Ir and Pt) obtained after the fusion of the ore with  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  and  $(\text{NH}_4)\text{H}_2\text{PO}_4$  (**Table 7.27**) was believed to be the final concentration of these metals in the ore. The final concentration of Ru, Os, Ir and Pt was estimated to be 0.02, 0.02, 0.01 and 0.04 % in the Merensky reef mineral ore.

**Table 7.27:** Comparison of the PGM (Ru, Os, Ir and Pt) results obtained after  $(\text{NH}_4)\text{H}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  fusion of the chromitite mineral ore using Sc as internal standard

Sample	Elements	Fusion method	% Recovery in 2.0 g ore
Merensky reef ore	Ru	$\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	0.02(1)
		$(\text{NH}_4)\text{H}_2\text{PO}_4$	0.02(2)
	Os	$\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	0.02(2)
		$(\text{NH}_4)\text{H}_2\text{PO}_4$	0.02(6)
	Ir	$\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	0.01(5)
		$(\text{NH}_4)\text{H}_2\text{PO}_4$	0.01(6)
	Pt	$\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	0.04(2)
		$(\text{NH}_4)\text{H}_2\text{PO}_4$	0.04(2)

## 7.6 Determination of precious metals in mineral ores using X-ray fluorescence (XRF)

### 7.6.1 Determination of precious metals in the chromitite mineral ore

#### 7.6.1.1 Experimental procedure

XRF was used as alternative analytical technique mainly to compare the results with those obtained using the ICP-OES. The precious metals calibration standards were prepared by mixing the PGM and gold bearing Pyroxenite Reference Material-Concentrate CRM (IA-MIM C2) (see the certificate in the **Appendix**) with  $\text{SiO}_2$  as

shown in **Table 7.28**. Approximately 8.0 g of the powdered chromitite ore sample was mixed thoroughly with 3.0 g of the Hoechst wax (binder material) to obtain a homogeneous mixture. The mixtures were quantitatively transferred into the pellet discs and manually compressed (30 tons pressure) to obtain a flat disc measuring 30 mm in diameter and 9 mm thickness. The pellets were placed in the sample holder and then transferred to the XRF for quantitative analysis (**Table 7.29**).

**Table 7.28:** XRF calibration standards for precious metals determination

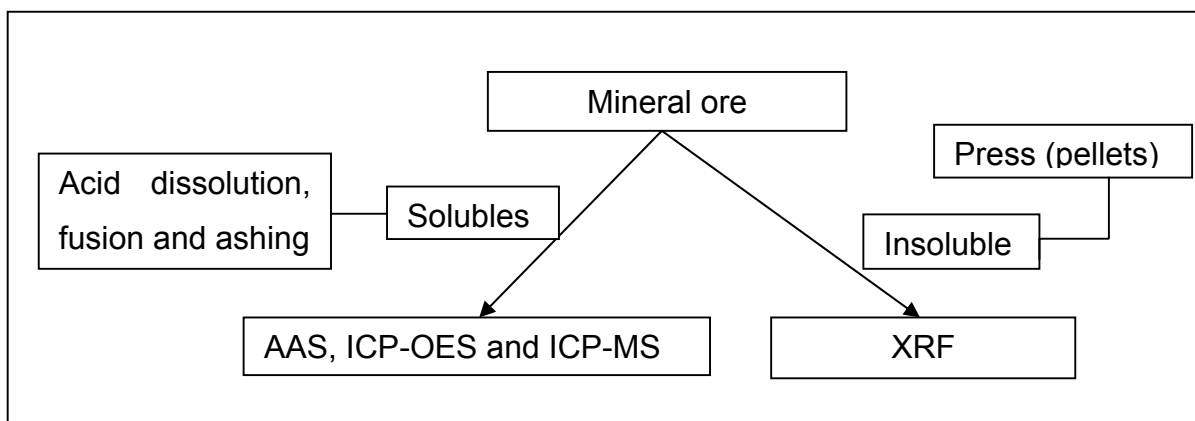
CRM (%)	PGM and Au (ppm)	SiO <sub>2</sub> (%)
0	0.0	100
25	0.5	75
50	1.0	50
75	2.0	25
100	5.0	0

**Table 7.29:** XRF quantitative results of the metals in the chromitite ore

Sample	Elements	% Recovery in 1 g ore
Chromitite	Cr <sub>2</sub> O <sub>3</sub>	66.58
	Fe <sub>2</sub> O <sub>3</sub>	29.30
	TiO <sub>2</sub>	2.52
	CaO <sub>2</sub>	0.87
	V <sub>2</sub> O <sub>3</sub>	0.54
	NiO	0.08
	ZnO	0.06
	CoO	0.04
	BaO	0.01
	PGM and Au	below detection limits

#### 7.6.1.2 Discussion of results

The XRF technique has been proven as expected to be a fast, effective and accurate method in solid sample analysis compared to wet digestion analysis. This technique has been highly recommended<sup>236</sup> as an alternative method for the PGM analysis due to the less interference and labour involved in the sample preparation (**Scheme 7.5**).



**Scheme 7.5:** A schematic presentation showing the selection process between a wet-chemical method and a dry analytical technique

The quantitative results obtained using XRF as analytical technique showed the presence of the major amounts of Cr and Fe with minor amounts of Ti and trace amounts of Ca, V, Ni, Zn, Co and Ba. These results indicate that the sample contains a higher percentage of chromium 67 % as  $\text{Cr}_2\text{O}_3$  followed by iron 29 % as  $\text{Fe}_2\text{O}_3$ . This high chromium content in the chromitite mineral ore is in excellent agreement with the high amount of  $\text{Cr}_2\text{O}_3$  (66.5 %) that was precipitated after the fusion of the ore with  $(\text{NH}_4)\text{H}_2\text{PO}_4$ .

The PGM content in the chromitite ore was too low to be quantified using this technique. The analytical drawback using XRF is the dilution of the samples and the establishment of standards with the binder during the sample preparation which further decreased the final PGM concentration content. This inability to quantify PGM at trace levels was in agreement with the limitations cited in literature (see **Chapter 3, Section 3.2.4**) which reports<sup>237</sup> the minimum permissible range detected by this technique is in ppb to sub-ppb range. The results in **Table 7.29** also expose the limitations of XRF as analytical method for the quantification of precious metals in geological samples. The total percentage composition of the PGM (Ru, Os and Pt) in the chromitite ore was calculated to be 0.52 % (ca. 27 ppm) which confirmed the need for the development of more sensitive analytical methods for precious metals

<sup>236</sup> P.S. Parreira, C.R. Appoloni, R.M.L. Vieira, R.B. Scorzelli, L. LeCorre and M.F. Guerra, *ArcheoSciences*, (2009), 33, pp. 313 - 318.



determination compared to XRF. The determination of the PGM in the mineral ores could not be extended to the Merensky reef mineral ore because of its even lower PGM content (ca. 14 ppm; 0.09 %).

## 7.7 Conclusion

The application of scandium as internal standard in the quantitative determination of precious metals in inorganic, organometallic compounds and geological ores was shown to yield excellent recoveries compared to the direct calibration method. Fluctuating percentage recoveries of the precious metals as shown by the larger standard deviation ( $\pm 8$  %) were obtained using the direct calibration method from both the inorganic and organometallic type compounds. Quantitative results obtained using scandium as internal standard from inorganic and organometallic compounds were found to be more accurate and precise as shown by the lower standard deviations ( $\pm 2$  %). In this process the use of scandium as internal standard was further shown to be effective in correcting background emissions and instrumental drifts which may have been the reason for the errors obtained in quantitative analysis. Total recoveries (100 %) of all the PGM as well as gold were obtained using Sc as internal standard if the purity and the chemical composition of these compounds were accurately known. A summary of all the precious metals results obtained from the inorganic and organometallic compounds are given in **Table 7.30** and **7.31** respectively.

**Table 7.30:** A summary of the results of the determination of PGMs and gold in inorganic compounds using direct calibration and Sc as internal standard

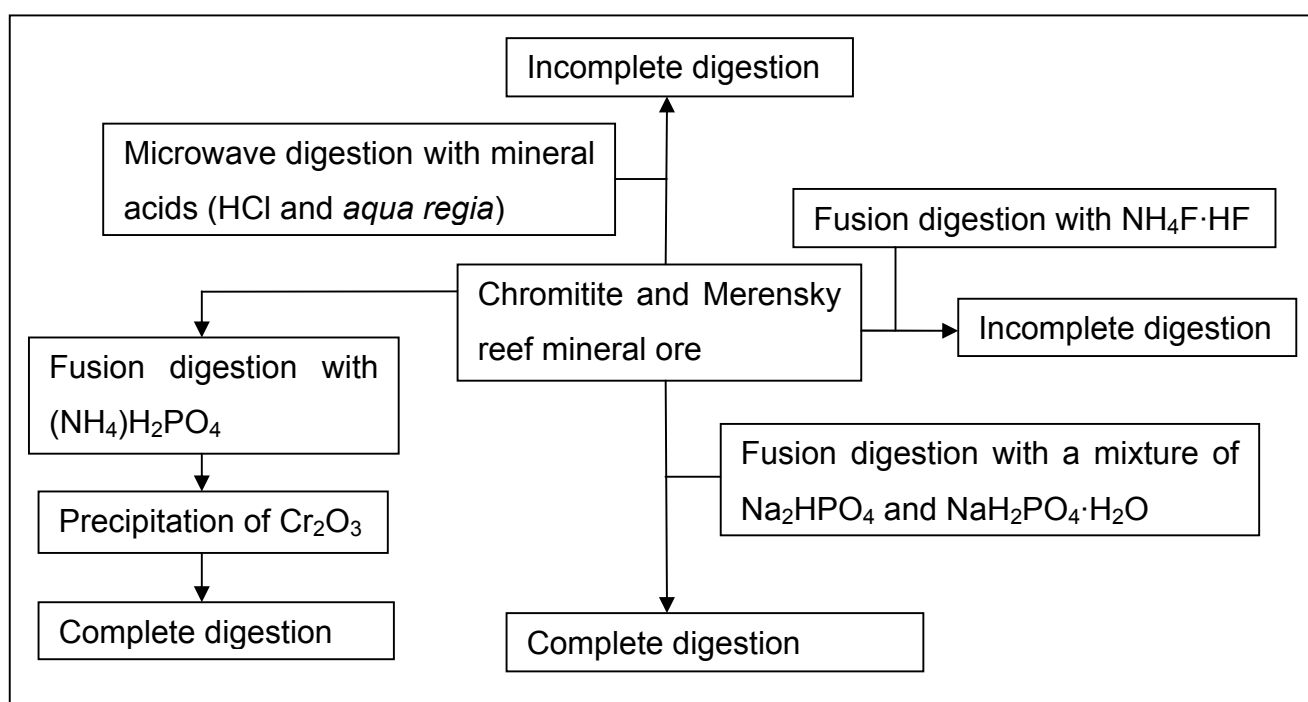
Technique	Ru	Rh	Pd	Os	Ir	Pt	Au
Direct calibration	94.6(4)	95(9)	103.7(7)	88.9(6)	81(3)	102(1)	95.3(5)
Sc internal standard	100.9(8)	101.5(6)	100.5(9)	100.1(5)	100.0(3)	99.4(3)	99.9(2)

<sup>237</sup> E. Margui, I. Queral, M.L. Carvalho and M. Hidalgo, *Analytica Chimica Acta.*, (2005), 549, pp. 197-204.

**Table 7.31:** A summary of the results of the determination of the PGM and gold in the organometallic compounds using direct calibration and Sc as internal standard

Organometallic compounds	Elements	Method	% Recovery
Iridium	[Ir(cod)Cl] <sub>2</sub>	Direct cal.	101.7(6)
		<b>Sc int. standard</b>	<b>100.0(5)</b>
	(Bu <sub>4</sub> N)[Ir <sub>2</sub> (μ-Dcbp)(CO) <sub>2</sub> (PCy <sub>3</sub> ) <sub>2</sub> ]	Direct cal.	105.0(5)
		<b>Sc int. standard</b>	<b>99.7(8)</b>
	[Pd(acac)(PPh <sub>3</sub> )]	Direct cal.	89(1)
		<b>Sc int. standard</b>	<b>99(1)</b>
Gold	[Au(opd)(Cl)]	Direct cal.	94.7(2)
		<b>Sc int. standard</b>	<b>101(1)</b>
	[Au(2,9-Me <sub>2</sub> phen)(Cl) <sub>3</sub> ]	Direct cal.	108.0(2)
		<b>Sc int. standard</b>	<b>99.1(7)</b>
	[Au(en)(Cl) <sub>2</sub> ]Cl	Direct cal.	104(1)
		<b>Sc int. standard</b>	<b>99.7(9)</b>
Osmium	[Os(COCH <sub>3</sub> )]	Direct cal.	91.3(8)
		<b>Sc int. standard</b>	<b>99.5(9)</b>
	[Os(bpy)(Cl) <sub>2</sub> ]	Direct cal.	101.0(4)
		<b>Sc int. standard</b>	<b>98(1)</b>
	[Os(opd)(Cl) <sub>2</sub> ]	Direct cal.	97(1)
		<b>Sc int. standard</b>	<b>100(1)</b>
Palladium	Pd(cod)(Cl) <sub>2</sub>	Direct cal.	100.2(2)
		<b>Sc int. standard</b>	<b>99.0(2)</b>
	[Pd(acac)(PPh <sub>3</sub> )(Cl)]	Direct cal.	106.0(9)
		<b>Sc int. standard</b>	<b>101.1(9)</b>
	[Pd(phen)(Cl) <sub>2</sub> ]	Direct cal.	102.6(8)
		<b>Sc int. standard</b>	<b>101.2(9)</b>
Platinum	[Pt(cod)(Cl) <sub>2</sub> ]	Direct cal.	106.7(2)
		<b>Sc int. standard</b>	<b>100.8(3)</b>
	[Pt(PPh <sub>3</sub> ) <sub>2</sub> (Cl) <sub>2</sub> ]	Direct cal.	111.2(1)
		<b>Sc int. standard</b>	<b>99.4(2)</b>
	[Cis-PtCl <sub>2</sub> (PhCH=CH <sub>2</sub> ) <sub>2</sub> ]	Direct cal.	102.2(9)
		<b>Sc int. standard</b>	<b>101(1)</b>
Rhodium	[Rh(tfaa)(CO) <sub>2</sub> ]	Direct cal.	99.8(1)
		<b>Sc int. standard</b>	<b>100.5(8)</b>
	[Rh(tfaa)(CO)(dpp)]	Direct cal.	98.0(1)
		<b>Sc int. standard</b>	<b>99.3(9)</b>
	Rh(cupf)(CO)(PPh <sub>3</sub> )	Direct cal.	101.5(2)
		<b>Sc int. standard</b>	<b>99.8(2)</b>
Ruthenium	[Ru(cod)(Cl) <sub>2</sub> ]	Direct cal.	98.7(5)
		<b>Sc int. standard</b>	<b>101.0(2)</b>
	[Ru(COCH <sub>3</sub> )]	Direct cal.	99.6(9)
		<b>Sc int. standard</b>	<b>99.7(8)</b>
	[Ru(en)(Cl) <sub>2</sub> ]Cl	Direct cal.	95(1)
		<b>Sc int. standard</b>	<b>101.1(6)</b>

The accurate determination of the mineral ore content required the complete conversion of the solid particles of the mineral sample into a soluble form for both the chromitite and the Merensky reef mineral ore. The complete digestion of the mineral ores was achieved using two flux digestion techniques namely  $(\text{NH}_4)_2\text{HPO}_4$  and a mixture of  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  (**Scheme 7.6**). However, the biggest drawback of using the  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  flux mixture was the introduction of the sodium ions (EIE's) into the analyte solution which resulted in inaccurate quantification.



**Scheme 7.6:** A summary of the dissolution/digestion procedures for the chromitite mineral ore

Percentage recoveries of PGM from both the chromitite and the Merensky reef ore were found to be affected by the increase in  $\text{Na}^+$  ion concentration which was introduced by the flux. The scandium internal standard method was found to be ineffective to compensate for all these matrix effects caused by this substantial increase in the sodium ions concentrations in the analyte solutions. The use of  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  flux was found to be a better alternative for the chromitite and Merensky reef ore digestion and had an advantage of precipitating chromium as  $\text{Cr}_2\text{O}_3$  from both samples. This precipitation of the chromium using the  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  flux prompted another research into the separation of chromium from the mineral ores

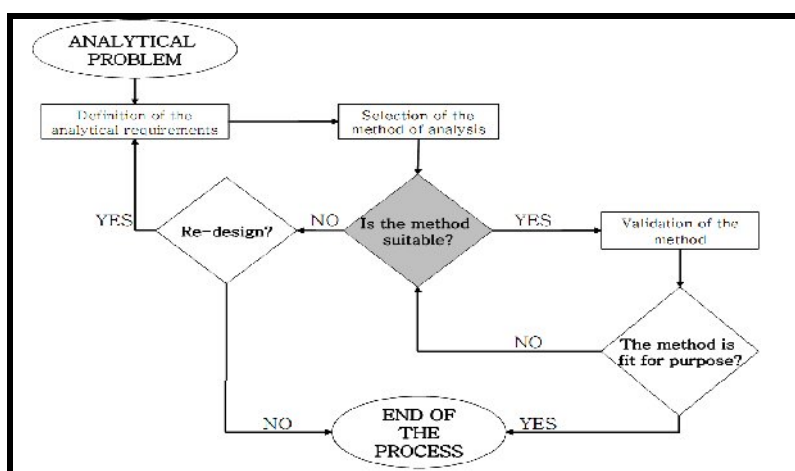
(see **Chapter 9**). The quantitative determination of the precious metals from the mineral ore using the ICP-OES revealed a total percentage content of 0.52 % for all the PGM (Ru, Os and Pt) in the chromitite mineral ore and 0.09 % for all the PGM (Ru, Os, Ir and Pt) in the Merensky reef mineral ore using Sc as internal standard.

# 8 Statistical validation of results

## 8.1 Introduction

Quality assurance forms an important part of analytical chemistry. Good laboratory practice and method validation are two aspects that allow for quality assurance and production of acceptable, accurate results. Good laboratory practices and method validation procedures have been established and controlled by international bodies such as the Organization for Economic Cooperation and Development (OECD) and the International Organization for Standardization (ISO) of which the ISO 17025 standard is one of the most well known and globally recognized standards for testing and calibration of laboratories.<sup>238</sup> The guidelines for appropriate method validation, especially for regulatory institutions, include selectivity, linearity, precision, specificity, LOD, LOQ, ruggedness and robustness (see **Chapter 3, Section 3.3.2**).

The basis of method validation in this study is to confirm whether the newly established analytical procedures are suitable for the accurate determination of the different precious metals (fitness for purpose) as outline in **Figure 8.1**.



**Figure 8.1:** Method validation procedure<sup>239</sup>

<sup>238</sup> R.P. Gerg, D. Christian, *Analytical Chemistry 6<sup>th</sup> Edition*, John. Wiley and Sons Inc.,(2004), p. 126.

<sup>239</sup> Eurachem, *The Fitness for Purpose of Analytical Methods. A Laboratory Guide to Method Validation and Related Topics*, (1998).

The main objective of this chapter is to statistically evaluate all the experimental results obtained from the CRM, inorganic, organometallic compounds and geological samples using the newly developed scandium internal standard method. Statistical tests such as the student  $t$ -test (hypothesis testing) and ANOVA will be used to determine whether the experimental results obtained are accepted or rejected at 95 % confidence interval.

## **8.2 Validation of the CRM results and the experimental parameters**

Validation of the ICP-OES was carried out to ensure that the chosen analytical conditions specified in **Chapter 4, Section 4.4** were acceptable for precious metals determination. Results obtained from measuring the intensities of the blank solution (see **Appendix**) were not only used to evaluate selectivity and specificity but it is very important to ensure consistency of the measurement. A relative standard deviation (RSD) of at least 0.22 % of the blank measurement was considered to be adequate since it indicated little fluctuations in the measurement process. Accuracy and precision of the method needs to be verified to ensure the proper performance of the method. Certified reference materials (CRMs) (liquid and geological CRMs) were used to determine the performance of the method during the initial steps in the development process. These CRMs were also used to ensure compatibility of the measurements and to improve the credibility and reliability of the results. All the calculations for the percentage recoveries of precious metals were performed in accordance with the description of the CRM.

The  $t$ -statistic test was used to determine the acceptance and rejection region for the results obtained in a triplicate analysis of each sample. If more than 20 replicate samples were analyzed the  $z$ -statistic would be the most appropriate test to use since the estimated mean ( $\bar{x}$ ) and standard deviation ( $s$ ) will be a good estimator of the actual mean ( $\mu_0$ ) and the standard deviation ( $\sigma$ ). The acceptance and rejection regions were defined as described in **Chapter 4, Section 4.4** for all the  $t$ -values in the  $t \geq t_{crit}$  or  $t \leq t_{crit}$  region. Experimental results with large positive or negative values exceeding the range  $t_{crit}$  of  $\pm 4.30$  for 2 degrees of freedom will be rejected.

### 8.2.1 Validation of the experimental parameters and results in the determination of precious metal and from the liquid CRM

Validations of the experimental results of precious metals (**Table 8.1**) obtained from the liquid CRM using scandium as internal standard were performed using the  $t$ -statistic at 95 % confidence interval. The null hypothesis states that there is no statistical difference between the theoretical ( $\mu_0$ ) value and that of the experimentally determined average value ( $\bar{x}$ ),  $H_0: \mu_0 = \bar{x}$ . The rejection region for the alternative hypothesis,  $H_a: \mu_0 \neq \bar{x}$  was defined for 3 replicates for all the  $t$  values in the region of  $\pm 4.30$  at 2 degrees of freedom. Experimental results with large positive or negative values exceeding the range  $t_{crit}$  will be rejected.

**Table 8.1:** Validation of the experimental parameters and results in the determination of precious metals from the liquid CRM using Sc as internal standard

Validation criteria	Parameter	Precious metals						
		Ru	Rh	Pd	Os	Ir	Pt	Au
Recovery	Mean % (STD)	100.8(8)	99.4(9)	99.8(6)	82(9)	102(1)	99.2(3)	101.7(5)
Precision	RSD	0.84	0.89	0.56	10.46	1.36	0.34	0.48
Robustness		Results reproducible			Results not reproducible	Results reproducible		
Working range	Calibration curve	0.5 - 10.00						
	LOD	0.00015	0.00025	0.00018	0.00015	0.00024	0.00012	0.00031
	LOQ	0.0015	0.0025	0.0018	0.0015	0.0024	0.0012	0.0031
Linearity	R <sup>2</sup>	0.9995	0.9994	0.9994	0.9999	0.9993	0.9996	0.9985
Sensitivity	Slope	0.7440	1.1487	1.9616	4.2157	0.5570	0.1349	0.5028
Selectivity	S <sub>m</sub>	0.0170	0.0496	0.0141	0.0499	0.0519	0.0185	0.0307
Error of the slope	Intercept	0.0049	-0.0295	-0.0399	0.0901	0.0790	0.0015	0.0071
Specificity	S <sub>c</sub>	0.0065	0.0233	0.0053	0.0218	0.0232	0.0070	0.0125
t-value (t <sub>crit</sub> = 4.30)		1.7	0.0	0.0	3.46	-1.7	-1.7	-1.7
Decision		Accept	Accept	Accept	Reject	Accept	Accept	Accept

$S_m$  = standard deviation of the slope

$S_c$  = standard deviation for results obtained from the calibration curve

The calculated  $t$ -statistic values for all the experimentally determined results for the precious metals in the liquid CRM were found to be within the acceptance region of  $\pm 4.30$  except for the osmium results which was above the  $t_{crit}$ . Further validation of osmium results and experimental parameters was performed under different conditions using  $(NH_4)_2[Os(Cl)_6]$  and  $Cs_2[OsO_2(CN)_4]$  calibration standards. All the

experimentally determined results for precious metals obtained from the liquid CRM were accepted at 95 % confidence interval.

### 8.2.2 Validation of the osmium results in the liquid CRM

Validation of osmium results and experimental parameters (**Table 8.2 - 8.5**) using  $((\text{NH}_4)_2[\text{Os}(\text{Cl})_6])$  and  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  calibration standards kept at room temperature and at 10 °C from the liquid CRM and using scandium as internal standard. The  $t$ -statistic was performed for all the experimental results at 95 % confidence interval. The null hypothesis states that there is no statistical difference between the theoretical ( $\mu_0$ ) value and that of the experimentally determined average value ( $\bar{x}$ ),  $H_0: \mu_0 = \bar{x}$ . The rejection region for the alternative hypothesis  $H_a: \mu_0 \neq \bar{x}$  was defined for 3 replicate measurements for all the  $t$  values in the region of  $\pm 4.30$  at 2 degrees of freedom. Experimental results with large positive or negative values exceeding the range  $t_{crit}$  will be rejected.

**Table 8.2:** Validation of the experimental parameters and results in the determination of osmium from the liquid CRM using Sc as internal standard and  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  calibration solutions kept at ca. 10 °C and in the absence of light

Validation criteria	Parameter	Osmium recovery (Hrs)				
		0	24	48	72	96
Recovery	Mean %	100.7(3)	100.9(7)	100(1)	99.0(6)	97.4(6)
Precision	RSD	0.27	0.73	0.96	0.60	0.59
Robustness		Results reproducible				
Working range	Calibration curve	0.5 - 10.0				
	LOD	0.00015				
	LOQ	0.0015				
Linearity	$R^2$	0.9998	1.0000	1.0000	1.0000	0.9999
Sensitivity	Slope	0.1522	0.1546	0.1524	0.1527	0.1548
Selectivity	$S_m$	0.0012	0.0005	0.0006	0.0004	0.0008
Error of the slope	Intercept	0.0204	0.0237	0.0168	0.0183	0.0343
Specificity	$S_c$	0.0042	0.0019	0.0021	0.0013	0.0026
LSD-value		0.9742				
Differences in mean		3.26	3.47	2.31	2.31	0.00
$t$ -value ( $t_{crit} = 4.30$ )		4.04	3.40	0.00	2.89	7.51
Decision		Accept	Accept	Accept	Accept	Reject

$S_m$  = standard deviation of the slope;

$S_c$  = standard deviation for results obtained from the calibration curve and

LSD = least significance difference



**Table 8.3:** Validation of the experimental parameters and in the determination of osmium from the liquid CRM using Sc as internal standard and  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  calibration solutions kept at room temperature and exposed to light

Validation criteria	Parameter	Osmium recovery (Hrs)				
		0	24	48	72	96
Recovery	Mean %	99.7(5)	99(2)	100(1)	100(1)	100.8(7)
Precision	RSD	0.48	2.09	2.28	3.20	1.96
Robustness		Result reproducible				
Working range	Calibration curve	0.5 - 10.0				
	LOD	0.00015				
	LOQ	0.0015				
Linearity	$R^2$	0.9998	1.0000	1.0000	1.0000	0.9999
Sensitivity	Slope	0.1522	0.1546	0.1524	0.1527	0.1548
Selectivity	$S_m$	0.0005	0.0009	0.0006	0.0007	0.0009
Error of the slope	Intercept	0.0204	0.0237	0.0168	0.0183	0.0343
Specificity	$S_c$	0.0018	0.0033	0.0020	0.0026	0.0033
LSD-value		0.9242				
Differences in mean		0.70	0.00	1.00	1.00	1.80
Decision		Accept	Accept	Accept	Accept	Accept

$S_m$  = standard deviation of the slope

$S_c$  = standard deviation for results obtained from the calibration curve

LSD = least significance difference

**Table 8.4:** Validation of the experimental parameters and results in the determination of osmium from the liquid CRM using Sc as internal standard and  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  calibration solutions kept at ca. 10 °C and in the absence of sunlight

Validation criteria	Parameter	Osmium recovery (Hrs)				
		0	24	48	72	96
<b>Recovery</b>	<b>Mean %</b>	100(1)	101(1)	101.0(4)	100.4(9)	100 (1)
<b>Precision</b>	<b>RSD</b>	1.28	1.35	0.40	0.92	1.35
<b>Robustness</b>		Results reproducible				
<b>Working range</b>	<b>Calibration curve</b>	0.5 - 10.00				
	<b>LOD</b>	0.00015				
	<b>LOQ</b>	0.0015				
<b>Linearity</b>	<b>R<sup>2</sup></b>	0.9998	1.0000	1.0000	1.0000	0.9999
<b>Sensitivity</b>	<b>Slope</b>	0.0126	0.0139	0.0136	0.0132	0.0138
<b>Selectivity</b>	<b>S<sub>m</sub></b>	0.0004	0.0010	0.0064	0.0003	0.0009
<b>Error of the slope</b>	<b>Intercept</b>	0.0204	0.0237	0.0168	0.0183	0.0343
<b>Specificity</b>	<b>S<sub>c</sub></b>	0.0013	0.0035	0.0015	0.0010	0.0033
<b>LSD-value</b>		1.4386				
<b>Differences in mean</b>		0.00	1.00	1.00	0.40	0.00
<b>Decision</b>		<b>Accept</b>	<b>Accept</b>	<b>Accept</b>	<b>Accept</b>	<b>Accept</b>

S<sub>m</sub> = standard deviation of the slope

S<sub>c</sub> = standard deviation for results obtained from the calibration curve

LSD = least significance difference

**Table 8.5:** Validation of the osmium results from the liquid CRM using the ANOVA test (Sc internal standard)

	Sum of squares (SS)	Degrees of freedom	Mean square (MS)	F-value (tables)	Experimental F-value	Decision
Standards	(NH <sub>4</sub> ) <sub>2</sub> [Os(Cl) <sub>6</sub> ] standards at room temperature					
Between groups (SSF)	1184.62	4	296.16	3.48	342.39	Reject
Within groups (SSE)	8.65	10	0.86			
Total	1193.27	14	297.02			
Standards	(NH <sub>4</sub> ) <sub>2</sub> [Os(Cl) <sub>6</sub> ] standards at 10 °C in the absence of sunlight					
Between groups (SSF)	23.90	4	205.99	3.48	13.49	Reject
Within groups (SSE)	4.43	10	0.41			
Total	28.33	14	206.4			
Standards	Cs <sub>2</sub> [OsO <sub>2</sub> (CN) <sub>4</sub> ] standards at room temperature and in the presence of light					
Between groups (SSF)	4.73	4	1.18	3.48	0.94	Accept
Within groups (SSE)	12.56	10	1.26			
Total	17.29	14	2.44			
Standards	Cs <sub>2</sub> [OsO <sub>2</sub> (CN) <sub>4</sub> ] standards at 10 °C in the absence of sunlight					
Between groups (SSF)	4.27	4	1.07	3.48	0.84	Accept
Within groups (SSE)	12.68	10	1.27			
Total	16.95	14	2.34			

The calculated *t*-statistic values for all the osmium results except for the result obtained from using (NH<sub>4</sub>)<sub>2</sub>[Os(Cl)<sub>6</sub>] calibration standards after a period of 96 days, were found to be within the acceptance region of  $\pm 4.30$ . Percentage recoveries obtained from the liquid CRM using both the (NH<sub>4</sub>)<sub>2</sub>[Os(Cl)<sub>6</sub>] and Cs<sub>2</sub>[OsO<sub>2</sub>(CN)<sub>4</sub>] calibration standards kept below 10 °C and Cs<sub>2</sub>[OsO<sub>2</sub>(CN)<sub>4</sub>] kept at room temperature were found to be acceptable at 95 % confidence interval. It is important to note from this set of calculations that the RSD at 10 °C and in the absence of sunlight are in general lower than those obtained at room temperature (see **Table 8.3**). The calculated *F*-values for all the osmium results obtained from the liquid CRM using both the (NH<sub>4</sub>)<sub>2</sub>[Os(Cl)<sub>6</sub>] and Cs<sub>2</sub>[OsO<sub>2</sub>(CN)<sub>4</sub>] calibration standards kept below 10 °C and Cs<sub>2</sub>[OsO<sub>2</sub>(CN)<sub>4</sub>] kept at room temperature were found to be in the acceptance level of 3.48 at 95 % confidence interval. However, the *t*-statistic values of osmium results obtained using (NH<sub>4</sub>)<sub>2</sub>[Os(Cl)<sub>6</sub>] calibration standards were found to

be above the acceptance level (above F-value of 3.48) and were all rejected at 95 % confidence interval.

### 8.2.3 Validation of the experimental parameters and results obtained in the determination of precious metals from geological CRM

Validations of the experimental parameters and results (**Table 8.6**) obtained from the determination of precious metals in the geological CRM using scandium as internal standard were performed using the *t*-statistic at 95 % confidence interval. The null hypothesis states that there is no statistical difference between the theoretical ( $\mu_0$ ) value and that of the experimentally determined average value ( $\bar{x}$ ),  $H_0: \mu_0 = \bar{x}$ . The rejection region for the alternative hypothesis  $H_a: \mu_0 \neq \bar{x}$  was defined for all the *t* values in the region of  $\pm 4.30$  at 2 degrees of freedom. Experimental results with large positive or negative values exceeding the range  $t_{crit}$  will be rejected.

**Table 8.6:** Validation of the experimental parameters and results in the determination of precious metals from the geological CRM using Sc as internal standard

Validation criteria	Parameter	Precious metals					
		Ru	Rh	Pd	Ir	Pt	Au
Recovery	Mean % (STD)	101(7)	100.4 (6)	99 (7)	100 (5)	102 (4)	100.9 (8)
Precision	RSD	7.04	0.65	7.88	5.21	3.53	0.76
Robustness		Results reproducible					
Working range	Calibration curve	0.05 - 1.00					
	LOD	0.000154	0.000253	0.000177	0.000240	0.000124	0.000314
	LOQ	0.00154	0.00253	0.00177	0.00240	0.00124	0.00314
Linearity	$R^2$	0.9999	0.9999	1.0000	0.9999	0.9999	1.0000
Sensitivity	Slope	0.7695	1.1851	2.0561	0.6041	0.1340	0.5136
Selectivity	$S_m$	0.0005	0.0006	0.0006	0.0003	0.0001	0.0002
Error of the slope	Intercept	0.0018	0.072	0.004	-0.00009	0.0001	0.00031
Specificity	$S_c$	0.0017	0.0023	0.0020	0.0012	0.0003	0.0006
<i>t</i> -value ( $t_{crit} = 4.30$ )		0.00	-0.17	-1.39	0.00	0.97	-0.87
Decision		Accept	Accept	Accept	Accept	Accept	Accept

$S_m$  = standard deviation of the slope

$S_c$  = standard deviation for results obtained from the calibration curve

The calculated *t*-statistic values for all the precious metals in the geological CRM were found to be within the acceptance region of  $\pm 4.30$ . All the experimentally

determined results for precious metals obtained from the geological CRM were accepted at 95 % confidence interval.

### 8.3 Validation of the inorganic salts results

Validations of the experimental results and conditions for the determination of precious metals in inorganic salts ( $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{PtCl}_2$ ,  $\text{PdCl}_2$ ,  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ ) using scandium as internal standard were performed using the  $t$ -statistic at 95 % confidence (**Table 8.7**). The null hypothesis states that there is no statistical difference between the theoretical ( $\mu_0$ ) value and that of the experimentally determined average value ( $\bar{x}$ ),  $H_0: \mu_0 = \bar{x}$ . The rejection region for the alternative hypothesis  $H_a: \mu_0 \neq \bar{x}$  was defined for 3 replicate measurements for all the  $t$  values in the region of  $\pm 4.30$  at 2 degrees of freedom. Experimental results with large positive or negative values exceeding the range  $t_{\text{crit}}$  will be rejected.

**Table 8.7:** Validation of the experimental results and parameters in the determination of precious metals from the inorganic compounds using Sc as internal standard

Validation criteria	Parameter	Precious metals						
		Ru	Rh	Pd	Os	Ir	Pt	Au
Recovery	Mean % (STD)	100.9(8)	101.5(7)	100.5(9)	114.6(1)	100.0(3)	99.4(5)	99.9(2)
Precision	RSD	0.83	0.62	0.90	0.01	0.27	0.44	0.28
Robustness		Results reproducible			Results not reproducible	Results reproducible		
Working range	Calibration curve	0.5 - 10.00						
	LOD	0.00015	0.00025	0.00018	0.00015	0.00024	0.00012	0.00031
	LOQ	0.0015	0.0025	0.0018	0.0015	0.0024	0.0012	0.0031
Linearity	R <sup>2</sup>	1.0000	0.9999	1.0000	0.9986	0.9982	1.0000	1.0000
Sensitivity	Slope	0.1971	0.5801	0.1606	2.2414	0.4804	0.1464	0.2879
Selectivity	S <sub>m</sub>	0.0001	0.0001	0.0001	0.3801	0.0002	0.0000	0.0000
Error of the slope	Intercept	-0.0046	-0.0162	-0.0030	0.4241	-0.0868	0.0022	-0.0018
Specificity	S <sub>c</sub>	0.0003	0.0005	0.0004	1.3732	0.0008	0.0001	0.0001
t-value (t <sub>crit</sub> = 4.30)		1.95	3.71	0.96	79.67	0.00	2.08	0.87
Decision		Accept	Accept	Accept	Reject	Accept	Accept	Accept

$S_m$  = standard deviation of the slope

$S_c$  = standard deviation for results obtained from the calibration curve

The calculated  $t$ -statistic values for all the experimental results in the determination of precious metals from the inorganic salts were found to be within the acceptance region of  $\pm 4.30$  except for osmium. Further validation of osmium results from  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  analysis and experimental parameters was performed using  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  calibration standards. All the experimentally determined results for precious metals in the inorganic salts were accepted at 95 % confidence interval except for osmium.

### **8.3.1 Validation of osmium results and experimental conditions in the determination of osmium from $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ using $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$ calibration standards kept at room temperature in the presence of light**

Validations of the experimental conditions and results (**Table 8.8** and **8.9**) in the determination of osmium from  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  using scandium as internal standard were performed using the  $t$ -statistic at 95 % confidence interval. The null hypothesis states that there is no statistical difference between the theoretical ( $\mu_0$ ) value and that of the experimentally determined average value ( $\bar{x}$ ),  $H_0: \mu_0 = \bar{x}$ . The rejection region for the alternative hypothesis  $H_a: \mu_0 \neq x$  was defined for all the  $t$  values in the region of  $\pm 4.30$  at 2 degrees of freedom. Experimental results with large positive or negative values exceeding the range  $t_{crit}$  will be rejected.

**Table 8.8:** Validation of experimental parameters and results in the determination of osmium from the  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  using  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  standards kept at room temperature and in the presence of light (Sc internal standard)

Validation criteria	Parameter	Osmium recovery (Hrs)				
		0	24	48	72	96
Recovery	Mean %	99(1)	99(1)	103.9(8)	115(2)	121(1)
Precision	RSD	0.014	0.012	0.007	0.013	0.012
Robustness		Results reproducible				
Working range	Calibration curve	0.5 - 10.00				
	LOD	0.00015				
	LOQ	0.0015				
Linearity	$R^2$	0.9998	1.0000	1.0000	1.0000	0.9999
Sensitivity	Slope	0.1522	0.1546	0.1524	0.1527	0.1548
Selectivity	$S_m$	0.0005	0.0006	0.0003	0.0004	0.0006
Error of the slope	Intercept	0.0204	0.0237	0.0168	0.0183	0.0343
Specificity	$S_c$	0.0016	0.0021	0.0011	0.0014	0.0022
$t$ -value ( $t_{\text{crit}} = 4.30$ )		1.73	1.73	8.44	12.99	36.37
LSD-value		1.8136				
Differences in mean		0.00	0.00	4.90	6.00	22.00
Decision		Accept	Accept	Reject	Reject	Reject

$S_m$  = standard deviation of the slope

$S_c$  = standard deviation for results obtained from the calibration curve

LSD = least significance difference

**Table 8.9:** Validation of osmium results (ANOVA test) of  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  using  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  standards and Sc as internal standard kept at room temperature and in the presence of light

Source of variation	Sum of squares (SS)	Degrees of freedom	Mean square (MS)	F-value (tables)	Experimental F-value	Decision
Between groups (SSF)	0.03	2	0.01	3.48	0.01	Accept
Within groups (SSE)	6.48	4	0.65			
Total	6.51	6	0.66			

The calculated  $t$ -statistic and F-values of osmium percentage recoveries in  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  within a period of 24 hours were found to be in the acceptance region of  $\pm 4.30$  and 3.48 respectively. Osmium results obtained after 24 hours were found to be outside the accepted region and level and were all reject at 95 % confidence interval.

## 8.4 Validation of the organometallic compounds results

Validations of the experimental parameters and results (Table 8.10 and 8.11 respectively) obtained from organometallic compounds using scandium as internal standard were performed using the  $t$ -statistic at 95 % confidence interval. The null hypothesis states that there is no statistical difference between the theoretical ( $\mu_0$ ) value and that of the experimentally determined average value ( $\bar{x}$ ),  $H_0: \mu_0 = \bar{x}$ . The rejection region for the alternative hypothesis  $H_a: \mu_0 \neq \bar{x}$  was defined for 3 replicate measurements for all the  $t$  values in the region of  $\pm 4.30$  at 2 degrees of freedom. Experimental results with large positive or negative values exceeding the range  $t_{crit}$  will be rejected.

**Table 8.10:** Validation of the experimental parameters in the determination of precious metals from the organometallic compounds using Sc as internal standard

Validation criteria	Parameter	Precious metals						
		Ru	Rh	Pd	Os	Ir	Pt	Au
Robustness		Results reproducible						
Working range	Calibration curve	0.5 - 10.0						
	LOD	0.00015	0.00025	0.00018	0.00015	0.00024	0.00012	0.00031
	LOQ	0.0015	0.0025	0.0018	0.0015	0.0024	0.0012	0.0031
Linearity	$R^2$	0.9986	0.9999	1.0000	0.9934	0.9999	1.0000	0.9999
Sensitivity	Slope	0.0037	0.0131	0.0208	0.0086	0.0038	0.0006	0.004
Selectivity	$S_m$	0.0001	0.0001	0.0001	0.0004	0.0000	0.0000	0.0001
Error of the slope	Intercept	0.0004	0.0005	0.0007	-0.0009	-0.00006	0.00002	0.0004
Specificity	$S_c$	0.0003	0.0003	0.0002	0.0014	0.0001	0.0000	0.0002

$S_m$  = standard deviation of the slope

$S_c$  = standard deviation for results obtained from the calibration curve



**Table 8.11:** Validation of the experimental results in the determination of precious metals in various organometallic compounds using Sc as internal standard

Compound	Element	Theoretical mean ( $\mu_0$ )	Experimental mean ( $\bar{x}$ )	% Recovery	$t$ -value ( $t_{crit} = 4.30$ )	Decision
[Ir(cod)Cl] <sub>2</sub>	Ir	7.00	7.0(9)	100.0(5)	0.00	Accept
(Bu <sub>4</sub> N)[Ir <sub>2</sub> ( $\mu$ -Dcbp)(CO) <sub>2</sub> (PCy <sub>3</sub> ) <sub>2</sub> ]		7.00	6.9(3)	99.7(8)	-1.15	Accept
[Ir(CO)(Cl)(PPh <sub>3</sub> ) <sub>2</sub> ]		7.00	6.9(9)	99(1)	-0.77	Accept
[Au(opd)(Cl)]	Au	7.00	6.9(7)	101(1)	-0.49	Accept
[Au(2,9-Me <sub>2</sub> phen)(Cl) <sub>3</sub> ]		7.00	6.9(1)	99.1(7)	-10.39	Reject
[Au(en)(Cl) <sub>2</sub> ]Cl		7.00	7.1(8)	99.7(9)	1.52	Accept
[Os(COCH <sub>3</sub> )]	Os	7.00	7.0(6)	99.5(9)	0.00	Accept
[Os(bpy)(Cl) <sub>2</sub> ]		7.00	6.8(1)	98(1)	-3.46	Accept
[Os(opd)(Cl) <sub>2</sub> ]		7.00	7.0(9)	100(1)	0.58	Accept
Pd(cod)(Cl) <sub>2</sub>	Pd	7.00	6.93	99.0(2)	-3.03	Accept
[Pd(acac)(PPh <sub>3</sub> )(Cl)]		7.00	7.2	101.1(6)	3.46	Accept
[Pd(phen)(Cl) <sub>2</sub> ]		7.00	7.1(6)	101.2(9)	2.31	Accept
[Pt(cod)(Cl) <sub>2</sub> ]	Pt	7.00	7.1(8)	100.8(3)	1.30	Accept
[Pt(PPh <sub>3</sub> ) <sub>2</sub> (Cl) <sub>2</sub> ]		7.00	7.0(1)	99.4(2)	0.00	Accept
[Cis-PtCl <sub>2</sub> (PhCH=CH <sub>2</sub> ) <sub>2</sub> ]		7.00	7.1(8)	101(1)	1.73	Accept
[Rh(tfaa)(CO) <sub>2</sub> ]	Rh	7.00	7.0(7)	100.5(8)	0.99	Accept
[Rh(tfaa)(CO)(dpp)]		7.00	6.9(7)	99.3(9)	-0.99	Accept
Rh(cupf)(CO)(PPh <sub>3</sub> )		7.00	7.0(2)	99.8(2)	0.00	Accept
[Ru(cod)(Cl) <sub>2</sub> ]	Ru	7.00	7.1(1)	101.0(2)	1.73	Accept
[Ru(COCH <sub>3</sub> )]		7.00	7.0(1)	99.7(8)	0.00	Accept
[Ru(en)(Cl) <sub>2</sub> ]Cl		7.00	7.1(4)	101.1(6)	3.46	Accept

The calculated  $t$ -statistic values for all the precious metals percentage recoveries in organometallic compounds except for gold percentage recovery in [Au(2,9-Me<sub>2</sub>phen)(Cl)<sub>3</sub>] ( $t$ -value = -10.39) were found to be within the acceptance region of  $\pm 4.30$ . All the experimentally determined percentage recoveries for precious metals except for gold percentage recovery in [Au(2,9-Me<sub>2</sub>phen)(Cl)<sub>3</sub>] were accepted at 95 % confidence interval.

## 8.5 Validation of geological samples results

### 8.5.1 Validation of the experimental parameters and results in the determination of precious metals from the chromitite mineral ore

Validations of the experimental parameters and results in the determination of precious metals from the chromitite mineral ore using  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}/\text{Na}_2\text{HPO}_4$  and  $(\text{NH}_4)\text{H}_2\text{PO}_4$  fusion methods (**Table 8.12** and **8.13** respectively). The  $t$ -statistic for the comparison of the experimental percentage mean of the recoveries was performed at 95 % confidence interval (**Table 8.14**). The null hypothesis states that there is no statistical difference between the theoretical ( $\mu_0$ ) value and that of the experimentally determined average value ( $\bar{x}$ ),  $H_0: \mu_0 = \bar{x}$ . The rejection region for the alternative hypothesis  $H_a: \mu_0 \neq \bar{x}$  was defined for 3 replicate measurements for all the  $t$  values in the region of  $\pm 4.30$  at 2 degrees of freedom. Experimental results with large positive or negative values exceeding the range  $t_{crit}$  will be rejected.

**Table 8.12:** Validation of the experimental parameters and results in the determination of Ru, Os and Pt in the chromitite mineral ore using Sc as internal standard ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4$  digestion)

Validation criteria	Parameter	Precious metals		
		Ru	Os	Pt
Working range	Calibration curve	0.05 - 1.00		
	LOD	0.000154	0.000150	0.000124
	LOQ	0.00154	0.00150	0.00124
Linearity	$R^2$	1.0000	0.9970	0.9991
Sensitivity	Slope	0.0164	0.0111	0.0026
Selectivity	$S_m$	0.0000	0.0004	0.0001
Error of the slope	Intercept	0.0012	0.0076	-0.00004
Specificity	$S_c$	0.0001	0.0013	0.0002

$S_m$  = standard deviation of the slope

$S_c$  = standard deviation for results obtained from the calibration curve

**Table 8.13:** Validation of the experimental parameters and results in the determination of Ru, Os and Pt in the chromitite reef mineral ore using Sc as internal standard ((NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> digestion)

Validation criteria	Parameter	Precious metals		
		Ru	Os	Pt
Working range	Calibration curve	0.05 - 1.00		
	LOD	0.00015	0.00015	0.00012
	LOQ	0.0015	0.0015	0.0012
Linearity	R <sup>2</sup>	0.9999	0.9970	0.9996
Sensitivity	Slope	0.0078	0.0077	0.0012
Selectivity	S <sub>m</sub>	0.0000	0.0003	0.0000
Error of the slope	Intercept	0.001	0.00073	0.00002
Specificity	S <sub>c</sub>	0.0002	0.0009	0.0000

S<sub>m</sub> = standard deviation of the slope

S<sub>c</sub> = standard deviation for results obtained from the calibration curve

**Table 8.14:** Validation of the experimental results (Ru, Os and Pt) obtained after the fusion of the chromitite reef mineral ore with NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O/Na<sub>2</sub>HPO<sub>4</sub> and (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> using Sc as internal standard

Validation criteria	Parameter	Precious metals		
NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O and Na <sub>2</sub> HPO <sub>4</sub> results				
	Chromitite	Ru	Os	Pt
Recoveries	Replicate 1	0.1973	0.0876	0.2457
	Replicate 2	0.1816	0.0900	0.2382
	Replicate 3	0.1703	0.0906	0.2571
	Mean %	0.18(1)	0.09(2)	0.25(9)
Precision	RSD	7.43	1.79	3.84
Robustness	Results reproducible			
(NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub> results				
Recoveries	Replicate 1	0.1975	0.0878	0.2573
	Replicate 2	0.1993	0.0886	0.2589
	Replicate 3	0.1931	0.0811	0.2539
	Mean %	0.19(3)	0.09(4)	0.26(3)
Precision	RSD	1.61	4.80	0.99
Robustness	Results reproducible			
Spooled		0.0113	0.0029	0.0155
t-value (tables)	2.78			
t-values (results)		0.0182	-0.0040	0.0948
Comment		No significant difference	No significant difference	No significant difference
Decision		Accept	Accept	Accept

The calculated  $t$ -statistic values for the mean percentage recoveries of Ru, Os and Pt in the chromitite mineral ore were found to have no significant differences (below  $t_{crit}$  value of 2.78) and the results were acceptable at 95 % confidence interval.

### 8.5.2 Validation of the experimental results and conditions in the determination of precious metals in the Merensky reef mineral ore

Validations of the experimental parameters and percentage recoveries in the determination of precious metals from the Merensky reef mineral ore using  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4$  and  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  fusion methods (**Table 8.15 and 8.16** respectively). The  $t$ -statistic for the comparison of the experimental percentage mean of the recoveries was performed at 95 % confidence interval (**Table 8.17**). The null hypothesis states that there is no statistical difference between the theoretical ( $\mu_0$ ) value and that of the experimentally determined average value ( $\bar{x}$ ),  $H_0: \mu_0 = \bar{x}$ . The rejection region for the alternative hypothesis  $H_a: \mu_0 \neq \bar{x}$  was defined for 3 replicate measurements for all the  $t$  values in the region of  $\pm 4.30$  at 2 degrees of freedom. Experimental results with large positive or negative values exceeding the range  $t_{crit}$  will be rejected.

**Table 8.15:** Validation of the experimental parameters in the determination of Ru, Os, Ir and Pt from the Merensky reef mineral ore using Sc as internal standard ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4$  digestion)

Validation criteria	Parameter	Precious metals			
		Ru	Os	Ir	Pt
Working range	Calibration curve	0.05 - 1.00			
	LOD	0.000154	0.000150	0.000240	0.000124
	LOQ	0.00154	0.00150	0.00240	0.00124
Linearity	$R^2$	1.0000	0.9970	0.9999	0.9999
Sensitivity	Slope	0.0073	0.0165	0.0059	0.0013
Selectivity	$S_m$	0.0000	0.0008	0.0000	0.0000
Error of the slope	Intercept	0.0007	0.0001	0.0003	0.0068
Specificity	$S_c$	0.0001	0.0029	0.0001	0.0000

$S_m$  = standard deviation of the slope

$S_c$  = standard deviation for results obtained from the calibration curve

**Table 8.16:** Validation of the experimental parameters in the determination of Ru, Os, Ir and Pt from the Merensky reef mineral ore using Sc as internal standard ((NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> digestion)

Validation criteria	Parameter	Precious metals			
		Ru	Os	Ir	Pt
Working range	Calibration curve	0.05 - 1.00			
	LOD	0.000154	0.000150	0.000240	0.000124
	LOQ	0.00154	0.00150	0.00240	0.00124
Linearity	R <sup>2</sup>	0.9999	0.9997	0.9992	1.0000
Sensitivity	Slope	0.0089	0.0158	0.0068	0.0016
Selectivity	S <sub>m</sub>	0.0001	0.0001	0.0001	0.0000
Error of the slope	Intercept	0.0007	0.0041	0.0002	0.0001
Specificity	S <sub>c</sub>	0.0002	0.0005	0.0004	0.0000

S<sub>m</sub> = standard deviation of the slope

S<sub>c</sub> = standard deviation of results obtained from the calibration curve

**Table 8.17:** Validation of the experimental results (Ru, Os, Ir and Pt) obtained after the fusion of the chromitite reef mineral ore with NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O/Na<sub>2</sub>HPO<sub>4</sub> and (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> using Sc as internal standard

Validation criteria	Parameter	Precious metals			
NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O and Na <sub>2</sub> HPO <sub>4</sub> results					
		Ru	Os	Ir	Pt
Recoveries	Replicate 1	0.021	0.017	0.009	0.042
	Replicate 2	0.019	0.017	0.009	0.038
	Replicate 3	0.018	0.014	0.005	0.040
	Mean %	0.02(1)	0.02(2)	0.01(2)	0.04(2)
Precision	RSD	6.95	10.58	28.66	5.74
Robustness		Results reproducible			
(NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub> results					
Recoveries	Replicate 1	0.0174	0.0169	0.0089	0.0414
	Replicate 2	0.0173	0.0168	0.0081	0.0386
	Replicate 3	0.0207	0.0179	0.0076	0.0418
	Mean %	0.02(2)	0.02(6)	0.01(6)	0.04(2)
Precision	RSD	10.40	3.53	7.82	4.32
Robustness		Results reproducible			
Spooled		0.001653	0.08689	0.001656	0.002039
t-value (tables)		2.78			
t-values (results)		-0.00096	-0.00403	0.000429	0.00082
Comment		No significant difference	No significant difference	No significant difference	No significant difference
Decision		Accept	Accept	Accept	Accept

The calculated  $t$ -statistic values for the percentage recoveries of Ru, Os, Ir and Pt in the Merensky reef mineral ore were found to have no significant differences (below  $t_{crit}$  value of 2.78) and the results were acceptable at 95 % confidence interval.

## **8.6 Conclusion**

Validation results of the instrumental parameters and conditions used in this study showed to be the optimum conditions for precious metal analysis. Excellent calibration curves with linear regression line ( $r^2$ ) values of above 0.997, low detection limits (at least 0.0001 ppm) and wide working range of between (0.5 - 10 ppm) were used. Most of the quantitative results for the precious metals in CRMs, inorganic salts, various organometallic compounds and geological mineral ores using Sc as internal standard were found to acceptable as indicated by the  $t$ -values which are smaller than the  $t_{crit}$  ( $\pm 4.30$ ) at a 95 % confidence interval (**Table 8.18**). The calculated  $t$ -statistic values for the mean percentage recoveries of PGM (Ru, Os, Ir and Pt) in the chromitite and Merensky reef mineral ore were found to have no significant differences (below  $t_{crit}$  value of 2.78) and the results were acceptable at 95 % confidence interval.

**Table 8.18:** A summary of the results accepted or rejected using scandium as internal standard

Material	Accept	Reject
<b>Certified reference materials (CRMs)</b>		
<b>Liquid CRM</b>	√	
<b>Geological CRM</b>	√	
<b>Inorganic compounds</b>		
$\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$	√	
$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	√	
$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$	√	
$\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$	Conditional	
$\text{PtCl}_2$	√	
$\text{PdCl}_2$	√	
$\text{HAuCl}_3 \cdot 4\text{H}_2\text{O}$	√	
<b>Organometallic complexes</b>		
Iridium compounds	√	
Gold compounds	√	
Osmium compounds	√	
Palladium compounds	√	
Platinum compounds	√	
Rhodium compounds	√	
Ruthenium compounds	√	
<b>Geological mineral ores</b>		
Chromitite	√	
Merensky reef	√	

Validation of osmium percentage recoveries results were performed using the ANOVA and the *t*-statistic analysis. The osmium results obtained from the use of  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  calibration standards kept at 10 °C and in the absence of light for more than 96 days were found to be not acceptable at 95 % confidence interval. However, osmium recoveries obtained from using  $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$  and  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  calibration standards kept below 10 °C were found to be acceptable including those determined using  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  calibration standards left at room temperature. The use of scandium internal standard was found to yield acceptable results in the region of  $\pm 4.30$  at 2 degrees of freedom for most of the organometallic samples analyzed in this study depending on the purity of the samples.

# 9 Evaluation of this study and future work

---

## 9.1 Degree of success with regard to the set objectives

This chapter evaluates the achievements of this study in terms of the objectives set out at the beginning of this study. The main objective as it was outlined in **Chapter 1, Section 1.2** was to:

- Develop a simple indoor digestion/dissolution procedure for PGM and gold compounds;
- Establish an effective and reliable internal reference element that is compatible with all the PGM and gold;
- Apply the spectrometric analytical method(s) for the determination of PGM and gold in inorganic, organometallic compounds and geological materials;
- Establish measurement traceability in analysing PGM and gold from a certified reference material (CRM);
- Validate the suitability of the newly developed/optimized method in determining PGM and gold from the inorganic, organometallic compounds and geological materials.

This study has been successful in achieving these objectives as revealed in the previous chapters. The results obtained during this study clearly showed that the use of scandium as internal standard method is very capable of accurately quantifying precious metals in all the samples investigated in this study. The efficiency of this method is demonstrated by its ability to recover precious metals to a level of 100 % as was shown from the results obtained using both CRMs. Its applicability to accurately quantify precious metals was verified on different inorganic salts, organometallic compound and geological mineral ores. Total recoveries (100 %) of



the precious metals were obtained using this method in inorganic and organometallic compounds which had well documented characterization and purity.

Quantitative determination of osmium using scandium as internal standard was shown to be affected by the instability of the commercially obtained calibration standards. Accurate determination of osmium required that the calibration standards  $(\text{NH}_4)_2[\text{OsCl}_6]$  be kept below 10 °C and in the absence of light. It was however established that the use of the stable  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  complex as calibration standard is a better alternative to avoid errors related to the calibration shift. The use of scandium as internal standard was further shown to yield experimental results which were reproducible except in the cases where the sample matrix was unmatched or undefined. Acid matrix and the effects of the EIE's were shown to affect the use of scandium as internal standard. Quantitative results obtained under these conditions were shown to yield false-high or false-low percentage recoveries compared to the expected theoretical values. Validation of the spectrometric technique (ICP-OES) and method showed a remarkable performance of ICP-OES parameters such as accuracy, precision, specificity, limit of detection, limit of quantitation and linearity towards the quantification of precious metals.

## **9.2 Future work**

The use of scandium as internal standard method in quantifying precious metals can also be extended to include the quantification of silver since it is member of the precious metals. Improvements on both selectivity and specificity of this method can be investigated through the separation of the total dissolved solutes (TDS) introduced in the analyte solutions during the sample preparation. Results obtained in this study indicated that the presence of various metal contaminants in samples such as geological mineral ores (see **Chapter 7, Section 7.5.2.3**) reduce the accuracy and the precision of the use of scandium as internal standard by either suppressing or enhancing the emission intensities of the precious metals. Various separation techniques such as the use of solvent extraction, gravimetric and chromatographic techniques can be employed to minimize or eliminate the effects of TDS or EIE's content prior to the quantification of precious metals. Different metals such as the rare earth metals (REE) can be investigated as the alternative internal standards for

the quantification of precious metals since these metals are scarcely found with PGM and gold in mineral ores and other environmental samples.

Fluctuating percentage recoveries of precious metals from the liquid CRM were found to be affected by the presence of EIE's introduced during the sample preparation step (see **Chapter 5, Section 5.7.3.2**). Although  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$  flux mixture was shown to have an advantage of achieving a complete digestion of the mineral it was however found to have a drawback of introducing  $\text{Na}^+$  ions in the analyte solution. Therefore, alternative fusion fluxes which do not contribute to the addition of  $\text{Na}^+$  ions or EIE's in the analyte solutions needs to be researched to improve the accuracy and precision in the quantitative determination of precious metals. Other methods of choice which might be studied to minimize the effects of EIE's in the determination of precious metals includes the use of ionization buffers such as cesium and the standard addition method. The standard addition method is reported to be an ideal method for analyzing samples whose matrices are undefined and cannot be matched and can be possibly examined as an alternative method.

The precipitation of chromium oxide was assumed to be dependent on few conditions which include pH, temperature and time. Optimum conditions necessary for the precipitation of chromium oxide during fusion of the chromitite mineral ore with  $\text{NH}_4\text{H}_2\text{PO}_4$  can be investigated in detail with a possibility of generating a new method for recovering chromium from mineral ores. The use of  $(\text{NH}_4)\text{H}_2\text{PO}_4$  as well as the  $(\text{NH}_4)_2\text{HPO}_4$  and  $(\text{NH}_4)_3\text{PO}_4$  fluxes in the digestion of geological mineral ores can be further investigated to determine the similarities and/or differences in chemical properties of these fluxes. The differences in the reaction pathway between  $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}/\text{Na}_2\text{HPO}_4$  (where chromium is solubilized) and  $(\text{NH}_4)\text{H}_2\text{PO}_4$  (when  $\text{Cr}_2\text{O}_3$  is precipitated) needs to be further investigated together with the aqua-chromium chemistry that exists from using these fluxes.

Quantitative determination of osmium using both the direct calibration and scandium as internal standard were shown to be affected by temperature, pH and light (see **Chapter 6, Section 6.5**). An in-depth investigation of each of these conditions can be investigated separately in order to determine precisely the effects of each parameter. The use of osmium stabilizers such as 2-methyl-2-propanol

(tert-butanol) or other alternative storage conditions can also be applied to minimize the oxidation of osmium to  $\text{OsO}_4$  and also to increase the shelf life of osmium solutions. Investigation of possible loss of osmium during the digestion of the chromitite and Merensky reef mineral ore using both the  $(\text{NH}_4)\text{H}_2\text{PO}_4$  as well as the mixture of  $(\text{NH}_4)_2\text{HPO}_4$  and  $(\text{NH}_4)_3\text{HPO}_4$  fluxes can be conducted to determine whether these fluxes are suitable for digesting compounds containing osmium. Alternative stable osmium calibration standard to the currently used standard  $(\text{NH}_4)_2[\text{OsCl}_6]$  can be researched with the objective of minimizing or preventing sensitivity errors in the determination of osmium.

Probably the most interesting future study could be the application of the use of scandium as internal standard in the quantification of precious metals from clinical samples, inorganic and organometallic compound with unknown purity and waste products. Most of the precious metals used as catalysts in various sectors needs to be reactivated periodically and/or recovered from the by-products for re-use. The application of this method can be of benefit in determining the precious metal content in these samples.

# Summary

---

The present thesis presents the use of scandium as internal standard in the quantification of precious metals from the CRM, inorganic salts, organometallic compounds and geological mineral ores. This method was developed using both the liquid and the geological CRMs and applied to various inorganic salts, organometallic compounds and geological mineral ores. Quantitative determination of precious metals from both CRMs using scandium as internal standard yielded total recoveries (100 %) for all the precious metals present in the samples except for osmium (83 %). Osmium recovery in the liquid CRM was found to be affected by the instability of the osmium calibration standards  $(\text{NH}_4)_2[\text{OsCl}_6]$ . This instability in the calibration standards were mainly due to the production of  $\text{OsO}_2$  or  $\text{OsO}_4$  which was found to result in a steady increase in the slope of the calibration curves. Experimental results showed improved stability and osmium percentage recoveries (+ 99 %) using  $(\text{NH}_4)_2[\text{OsCl}_6]$  calibration standards kept in the dark and at ca. 10 °C. Total percentage recoveries of osmium was obtained using the Sc as internal standard in the liquid CRM using the newly established calibration standards  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  which was found to be stable at room temperature and at 10 °C for a period of up to 5 days.

The application of scandium as internal standard in the quantitative determination of precious metals in inorganic, organometallic compounds and geological ores was shown to yield excellent recoveries (+ 99 %) compared to the direct calibration methods. Fluctuating percentage recoveries were obtained using the direct calibration method as shown by the larger standard deviation ( $\pm 8$  %) compared to those obtained using scandium as internal standard ( $\pm 2$  %). Accurate determination of precious metals from inorganic and organometallic compounds was found to be dependent on the purity and the chemical composition of these compounds. The use of scandium as internal standard was also found to be affected by unmatched HCl and the presence of  $\text{Na}^+$  ion concentrations (EIE's) of more than 10 % and 10 ppm respectively.

Complete digestion of the chromitite and the Merensky reef mineral ore was achieved using the  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  mixture and  $(\text{NH}_4)\text{H}_2\text{PO}_4$  flux. However, the biggest drawback of using the  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  flux mixture was the introduction of the  $\text{Na}^+$  ion (EIE's) into the analyte solution which resulted in inaccurate quantification. The use of Sc as internal standard was found to be ineffective to compensate for all these matrix effects caused by this substantial increase in the  $\text{Na}^+$  ion concentrations in the analyte solutions. The use of  $(\text{NH}_4)\text{H}_2\text{PO}_4$  flux was found to be a better alternative since it had an advantage of not introducing EIE's but precipitating chromium as  $\text{Cr}_2\text{O}_3$  from both mineral ores. The quantitative determination of precious metals from the mineral ore using the ICP-OES revealed a total percentage content of 0.52 % for all the PGM (Ru, Os and Pt) in the chromitite mineral ore and 0.09 % for all the PGM (Ru, Os, Ir and Pt) in the Merensky reef mineral ore using Sc as internal standard.

Validation results of the instrumental parameters and conditions used in this study were shown to be the optimum conditions for precious metal analysis. Excellent calibration curves with linear regression line ( $r^2$ ) values of above 0.997, low detection limits (of at least 0.0001 ppm) and a wide working range of between (0.5 - 10 ppm) were used. The obtained results of precious metals in CRMs, inorganic salts, organometallic compounds and the geological mineral ores were validated using the  $t$ -statistic and were found to be acceptable at 95 % confidence interval. All osmium results were validated using the ANOVA test. Osmium recoveries (+ 99 %) obtained using  $(\text{NH}_4)_2[\text{OsCl}_6]$  and  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  calibration standards kept at ca. 10 °C using scandium as internal standard were accepted at 95 % confidence interval.

# Opsomming

---

Die huidige tesis beskryf die gebruik van skandium as interne standaard in die kwantifisering van edelmetale van die GVM, anorganiese soute, organometaalverbindinge en geologiese minerale erts. Hierdie metode is ontwikkel met behulp van beide die vloeistof en die geologiese GVM'e en is toegepas op verskeie anorganiese soute, organometaalverbindinge en geologiese minerale erts. Kwantitatiewe bepaling van edelmetale van beide GVM'e met die gebruik van skandium as interne standaard het totale herwinning (100 %) opgelewer vir al die edelmetale teenwoordig in die monsters, behalwe vir osmium (83 %). Osmium herwinning in die vloeibare GVM word beïnvloed deur die onstabiliteit van die osmium kalibrasiestandaarde  $(\text{NH}_4)_2[\text{OsCl}_6]$ . Hierdie onstabiliteit in die kalibrasie standaard is hoofsaaklik te wyte aan die produksie van  $\text{OsO}_2$  of  $\text{OsO}_4$  wat gevind is om te lei tot 'n geleidelike toename in die helling van die kalibrasiekurwes. Eksperimentele resultate het verbeterde stabiliteit en osmium persentasie herwinning (99 %) getoon deur gebruik te maak van  $(\text{NH}_4)_2[\text{OsCl}_6]$  kalibrasiestandaarde wat in die donker en ca 10 °C gehou is. Totale persentasie herwinning van osmium is verkry met behulp van die Sc interne standaard in die vloeistof GVM deur gebruik te maak van die nuut ontwikkelde kalibrasiestandaarde  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  wat gevind is om stabiel te wees by kamertemperatuur en by 10 °C vir 'n tydperk van tot 5 dae.

Die toepassing van skandium as interne standaard in die kwantitatiewe bepaling van edelmetale in anorganiese, organometaalverbindinge en geologiese erts het uitstekende herwinning (99 %) gelever in vergelyking met die direkte kalibrasiemetodes. Wisselende persentasie herwinning is verkry met behulp van die direkte kalibrasiemetode, soos getoon deur die groter standaardafwyking ( $\pm 8$  %) in vergelyking met dié verkry met behulp van skandium as interne standaard ( $\pm 2$  %). Akkurate bepaling van edelmetale uit anorganiese en organometaalverbindinge is afhanklik van die suiwerheid en die chemiese samestelling van hierdie verbindinge. Die gebruik van skandium as interne standaard word ook beïnvloed deur die ongelyke HCl-konsentrasie van die standaardoplossings en die analietoplossing asook die teenwoordigheid van  $\text{Na}^+$ -ioon konsentrasies (EIE se) van meer as 10 % en 10 dpm onderskeidelik.

Volledige vertering van die chromiet en die Merensky-rif minerale erts is verkry deur gebruik te maak van 'n  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  mengsel en  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  flux. Die grootste nadeel van die gebruik van  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  flux mengsel was die toevoeging van die  $\text{Na}^+$ -ioon (EIE) tot die analietoplossing wat gelei het tot onakkurate kwantifisering. Die gebruik van Sc as interne standaard is gevind om oneffektief te vergoed vir al hierdie matriks effekte wat veroorsaak word deur die aansienlike toename in die  $\text{Na}^+$ -ioon konsentrasie in die analiet oplossings. Die gebruik van  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  flux blyk 'n beter alternatief te wees, aangesien dit nie net EIE toevoeg nie maar chroom presipiteer as  $\text{Cr}_2\text{O}_3$  uit beide minerale erts. Die kwantitatiewe bepaling van edelmetale uit die minerale erts met behulp van die ICP-OES onthul 'n totale persentasie inhoud van 0,52 % vir al die PGM (Ru, Os en Pt) in die chromitiet minerale erts en 0,09 % vir al die PGM (Ru, Os , Ir en Pt) in die Merensky rif minerale erts deur gebruik te maak van Sc as interne standaard.

Geldige resultate vanaf die instrumentele parameters en toestande wat tydens hierdie studie gebruik is, blyk om die optimum toestande vir die analise van die kosbare metale te wees. Uitstekende kalibrasiekurwes met lineêre regressielyn ( $r^2$ ) waardes van hoër as 0,997, lae deteksielimiete (van minstens 0,0001 dpm) en wye reeks tussen (0,5 - 10 dpm) is gebruik. Die resultate verkry van edelmetale in GVM'e, anorganiese soute, organometaalverbindinge en die geologiese minerale erts is geldig verklaar deur gebruik te maak van die  $t$ -statistiek en is gevind om aanvaarbaar te wees by 'n 95 % vertrouwe interval. Alle osmium resultate is bevestig met behulp van die ANOVA toets. Osmium herwinning (99 %) verkry tydens die gebruik van  $(\text{NH}_4)_2[\text{OsCl}_6]$  en  $\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$  as kalibrasiestandaarde by ca. 10 °C met behulp van skandium as interne standaard was aanvaar by 'n 95 % vertrouwe interval.