Quantitative Spectroscopic Analysis of Co-existing PGMs in Iron-bearing Minerals

Thembakazi Ncedo

9th International PGM Conference
Sun City, Rustenburg, South Africa

27 - 28 October 2025

OUTLINE

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INTRODUCTION[1]

Background

- Platinum Group Metals (PGMs) viz Pt, Pd, Rh, Ir, Ru, Os.
- Exhibit siderophile (iron-loving) and chalcophile (sulfur-loving) tendencies.
- Frequent association with Fe-Ni sulfide deposits in layered intrusions such as the Bushveld Complex.

INTRODUCTION[2]

- Occur in low concentrations, often co-existing with base metals such as iron.
- PGMs are economically and strategically significant due to their catalytic properties and industrial applications.
- High demand, especially for Pt and Rh, stems from their exceptional properties.
- Pt is extremely resistant to corrosion and oxidation at high temperatures.

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INTRODUCTION[3]

❑ Chemistry

- Both iron (Fe) and PGMs are transition metals located in the d-block on the periodic table.
- Oxidation state.
  - *Fe^{2+}(ferrous), Fe^{3+}(ferric)*
  - *PGMs range from 0 to 6^{+} (depending on metal & ligands involved)*
  - *Pt and Pd most commonly form 2^{+} and 4^{+} (e.g., $[PtCl_4]^{2-}$, $Na_2[PdCl_6]$)*
- Strong π-back bonding with ligands such as CO and ethylene,
- Thus, explaining their effectiveness as catalysts in hydrogenation and fuel-cell reactions.

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INTRODUCTION[4]

- Iron-rich oxide (e.g., magnetite) and sulfide (e.g., pyrrhotite) phases commonly coexist with PGM mineralisation.
- Contrasting charge densities and polarities of iron-bearing phases and PGMs control their partitioning during magmatic and post-magmatic processes.
- Iron oxides, with higher ionic character and polar bonds, tend to adsorb or scavenge trace PGMs.

PURPOSE OF STUDY

Aim

- To accurately quantify PGMs in iron-bearing samples.

Objectives

- Validate accuracy, precision, and reproducibility of PGMs.
- Evaluate the performance of spectroscopic techniques in quantifying PGMs in iron-bearing minerals.

MATERIAL

- Two certified reference materials (CRMs) were used in this study as raw material samples.
- The CRMs used are called AMIS530 (PGMs ore) and AMIS165 (PGMs concentrate).
- The raw material samples were bought from African Mineral Standard (AMIS).
- They were prepared five (5) times for validation purposes.

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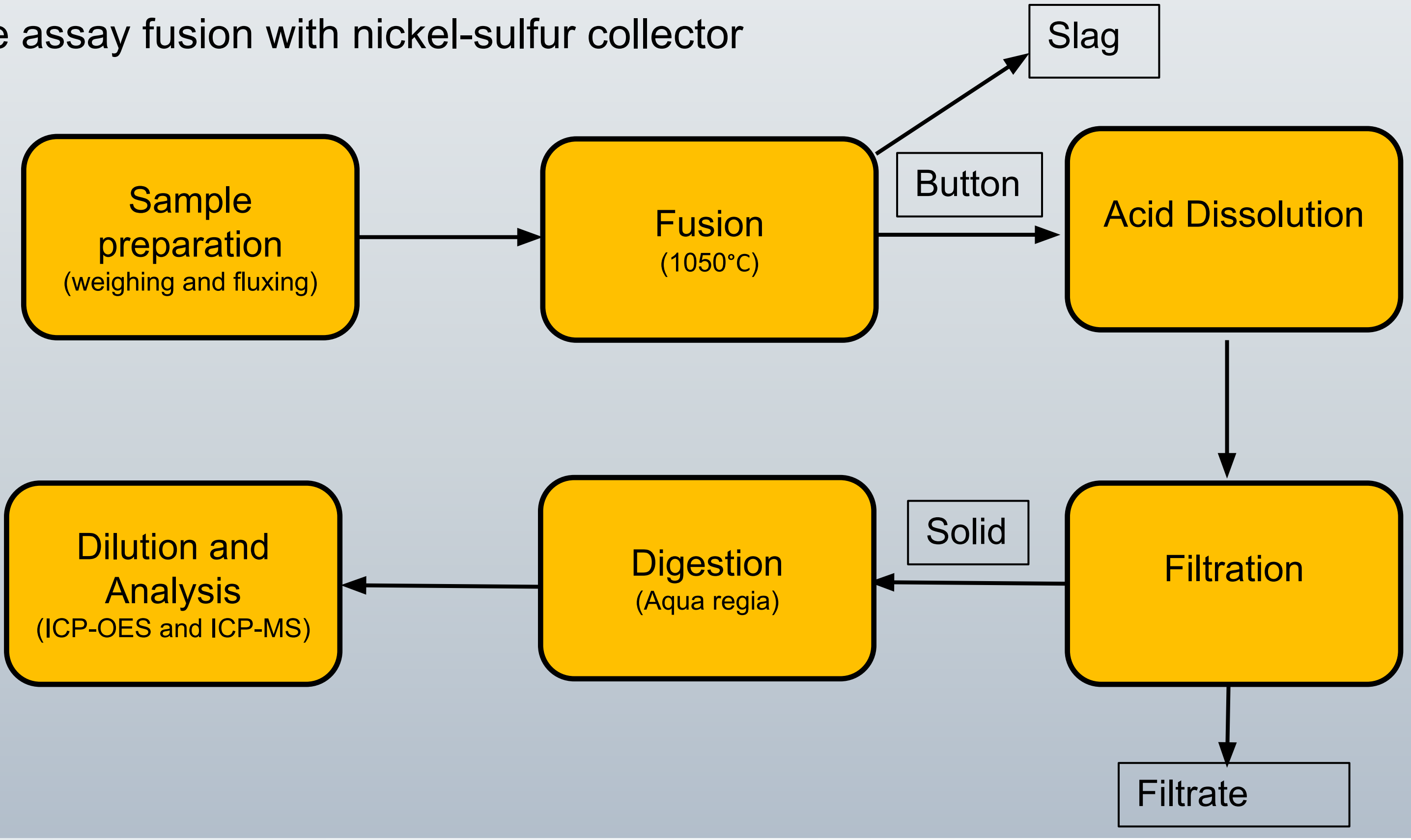
METHODOLOGY

- Fire assay fusion with nickel-sulfur collector



RESULTS and DISCUSSION

- ICP-OES and ICP-MS were employed in this study.

Table 1: Operating parameters for ICP-OES

Parameters	Condition
RF power (kW)	1.2
Viewing mode	Axial
Stabilization time	15s
Replicates	3
Nebulizer flow rate (L/min)	0.7
Plasma gas flow rate (L/min)	12
Auxiliary gas flow rate (L/min)	1

Table 2: Operating parameters for ICP-MS

Parameters	Condition
Plasma power (kW)	1.4
Plasma gas flow rate (L/min)	17
Auxiliary gas flow rate (L/min)	1.4
Nebulizer gas flow rate (L/min)	0.75
Replicates	3
Sample uptake rate (mL/min)	0.8
Sampler cone	Copper (Cu)
Skimmer Cone	Nickel (Ni)

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INSTRUMENTAL PARAMETERS FOR ICP-OES and ICP-MS

Table 3: Wavelengths used in ICP-OES

Analyte	Wavelength (nm)
Au	267.594
Pt	299.796
Pd	340.458
Rh	343.489
Ru	349.894
Ir	224.268

Table 4: Isotopes used in ICP-MS

Analyte	Isotopes m/z
Au	197
Pt	195
Pd	105
Rh	103
Ru	101
Ir	191

CHEMICAL COMPOSITION AND RECOVERIES OF PGMS FOR AMIS 530

- The chemical composition and recoveries of individual PGMs using ICP-OES and ICP-MS for the AMIS 530 sample are presented in Tables 5 and 6, respectively.

Table 5: Chemical composition and recoveries of PGMs from the ICP-OES

AMIS 530	Au(ppm)	Pd (ppm)	Pt (ppm)	Rh(ppm)	Ru (ppm)	Ir (ppm)
AMIS 530/1	0.035	0.974	1.561	0.297	0.471	0.080
/2	0.030	1.034	1.627	0.314	0.524	0.100
/3	0.031	0.968	1.567	0.299	0.483	0.100
/4	0.037	0.974	1.550	0.299	0.488	0.093
/5	0.034	0.981	1.576	0.303	0.471	0.096
Acc. Value	0.030	1.00	1.70	0.32	0.52	0.11
Mean	0.033	0.986	1.576	0.302	0.487	0.094
STD Dev	0.003	0.027	0.030	0.007	0.022	0.008
%RSD	8.626	2.749	1.899	2.262	4.468	8.705
Recovery (%)	**111.333**	**98.620**	**92.718**	**94.500**	**93.731**	**85.091**

Table 6: Chemical composition and recoveries of PGMs from the ICP-MS

AMIS 530	Au (ppm)	Pd (ppm)	Pt (ppm)	Rh (ppm)	Ru (ppm)	Ir (ppm)
AMIS 530/1	0.031	0.992	1.692	0.311	0.513	0.111
/2	0.033	0.999	1.699	0.301	0.532	0.109
/3	0.03	0.988	1.697	0.333	0.517	0.108
/4	0.032	0.994	1.658	0.316	0.521	0.114
/5	0.035	0.996	1.685	0.299	0.516	0.112
Acc. Value	0.03	1.00	1.70	0.32	0.52	0.11
Mean	0.032	0.994	1.686	0.312	0.520	0.111
STD Dev	0.002	0.004	0.017	0.014	0.007	0.002
%RSD	5.974	0.417	0.988	4.383	1.423	2.155
Recovery (%)	**107.333**	**99.380**	**99.188**	**97.500**	**99.962**	**100.727**

CHEMICAL COMPOSITION AND RECOVERIES OF PGMS FOR AMIS 165

- The chemical composition and recoveries of individual PGMs using ICP-OES and ICP-MS for the AMIS 165 sample are presented in Tables 7 and 8.

Table 7: Chemical composition and recoveries of PGMs from the ICP-OES

AMIS 165	Au(ppm)	Pd(ppm)	Pt(ppm)	Rh(ppm)	Ru(ppm)	Ir(ppm)
AMIS 165/1	1.546	17.415	16.278	1.577	1.869	0.494
/2	1.573	18.218	16.11	1.581	1.931	0.501
/3	1.538	17.116	15.405	1.517	1.762	0.458
/4	1.552	18.719	16.874	1.658	1.991	0.453
/5	1.584	18.235	16.119	1.598	1.947	0.492
Acc. Value	1.66	19.1	16.9	1.72	2.02	0.52
Mean	1.559	17.941	16.157	1.586	1.900	0.480
STD Dev	0.019	0.657	0.524	0.050	0.089	0.022
%RSD	1.234	3.661	3.243	3.183	4.667	4.654
Recovery (%)	**93.892**	**93.930**	**95.605**	**92.221**	**94.059**	**92.231**

Table 8: Chemical composition and recoveries of PGMs from the ICP-MS

AMIS 165	Au(ppm)	Pd(ppm)	Pt(ppm)	Rh(ppm)	Ru(ppm)	Ir(ppm)
AMIS 165/1	1.612	19.164	16.988	1.738	2.046	0.487
/2	1.589	19.351	16.794	1.695	1.995	0.513
/3	1.599	18.987	16.431	1.689	2.038	0.4973
/4	1.621	18.996	16.527	1.721	1.989	0.488
/5	1.654	18.897	16.668	1.695	2.017	0.522
Acc. Value	1.66	19.1	16.9	1.72	2.02	0.52
Mean	1.615	19.079	16.682	1.708	2.017	0.501
STD Dev	0.025	0.180	0.220	0.021	0.025	0.016
%RSD	1.547	0.944	1.318	1.231	1.252	3.094
Recovery (%)	**97.289**	**99.890**	**98.708**	**99.279**	**99.851**	**96.435**

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EVALUATION OF THE ACCURACY OF RESULTS

A Student's t-test was used to evaluate the accuracy of the sample results

$$t = \frac{\bar{x} - \mu_0}{s/\sqrt{n}}$$

t_{calc} - calculated value of replicate measurements
t_{crit} - critical value of |t| for a particular significance level given by
DF - degrees of freedom (n-2)
0.05 - alpha value for a 95% confidence level
μ = true concentration value
$\bar{x}$ = the mean of replicates measurements
s = standard deviation

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EVALUATION OF THE ACCURACY OF AMIS 165

Null hypothesis (H_0): $t_{calc}<t_{crit}$; i.e. $\mu=\bar{x}$; Accurate results
Alternative hypothesis (H_1): $t_{calc}>t_{crit}$; i.e. $\mu\neq\bar{x}$; Inaccurate results

Table 9: AMIS 530

Analyte	**µ**		**s**	**n**	**Technique**	**t-calc**	**t-crit**	**Valid hypothesis**
Au	0.03	0.03	0.003	5	ICP-OES	2.64	3.182	H0
Au	0.03	0.03	0.002	5	ICP-MS	2.56	3.182	H0
Pd	1.00	0.99	0.027	5	ICP-OES	1.14	3.182	H0
Pd	1.00	0.99	0.004	5	ICP-MS	3.34	3.182	H1
Pt	1.70	1.58	0.030	5	ICP-OES	9.25	3.182	H1
Pt	1.70	1.69	0.017	5	ICP-MS	1.85	3.182	H0
Rh	0.32	0.30	0.007	5	ICP-OES	5.75	3.182	H1
Rh	0.32	0.31	0.014	5	ICP-MS	1.31	3.182	H0
Ru	0.52	0.49	0.022	5	ICP-OES	3.35	3.182	H1
Ru	0.52	0.52	0.007	5	ICP-MS	0.06	3.182	H0
Ir	0.11	0.09	0.008	5	ICP-OES	4.50	3.182	H1
Ir	0.11	0.11	0.002	5	ICP-MS	0.75	3.182	H0

EVALUATION OF THE ACCURACY OF AMIS 165

Null hypothesis (H_0): t_{calc}<t_{crit}; i.e. $\mu=\bar{x}$; Accurate results

Alternative hypothesis (H_1): t_{calc}>t_{crit}; i.e. $\mu\neq\bar{x}$; Inaccurate results

Table 10: AMIS 165

Analyte	μ		s	n	Technique	t-calc	t-crit	Valid hypothesis
Au	1.66	1.56	0.019	5	ICP-OES	11.8	3.182	H1
Au	1.66	1.62	0.025	5	ICP-MS	4.03	3.182	H1
Pd	19.1	17.9	0.657	5	ICP-OES	3.95	3.182	H1
Pd	19.1	19.1	0.180	5	ICP-MS	0.26	3.182	H0
Pt	16.9	16.2	0.524	5	ICP-OES	3.17	3.182	H0
Pt	16.9	16.7	0.220	5	ICP-MS	2.22	3.182	H0
Rh	1.72	1.59	0.050	5	ICP-OES	5.93	3.182	H1
Rh	1.72	1.71	0.021	5	ICP-MS	1.32	3.182	H0
Ru	2.02	1.90	0.089	5	ICP-OES	3.03	3.182	H0
Ru	2.02	2.02	0.025	5	ICP-MS	0.27	3.182	H0
Ir	0.52	0.48	0.022	5	ICP-OES	4.05	3.182	H1
Ir	0.52	0.50	0.016	5	ICP-MS	2.67	3.182	H0

CONCLUSION

- The comparative analysis between ICP-OES and ICP-MS demonstrates that both techniques are effective for quantifying platinum group metals (PGMs) in iron-bearing matrices, yet they differ in analytical performance.
- ICP-MS exhibited superior sensitivity, accuracy, and recovery for Pt, Pd, Rh, Ru, and Ir, confirming its reliability for trace and ultra-trace PGM determination.
- In contrast, ICP-OES displayed a consistent negative bias, likely influenced by matrix interferences and signal suppression effects inherent to complex Fe-rich samples.
- These findings highlight the importance of instrument optimisation or correction models to enhance ICP-OES performance.
- Overall, the study validates ICP-MS as a preferred technique.

ACKNOWLEDGEMENTS

- Mintek

- Southern African Institute of Mining And Metallurgy (SAIMM)

200 Malibongwe Drive
Randburg
South Africa

Tel: +27 11 709 4111

www.mintek.co.za

Private Bag X3015
Randburg
2125
South Africa

Mintek MintekSA Mintek_RSA Mintek_RSA