

NEUTRON ACTIVATION ANALYSES FOR  
NOBLE METALS IN MATTE LEACH RESIDUES

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A B S T R A C T

The development of the neutron activation analysis technique as a method for rapid and precise determinations of platinum group metals in matte leach residues depends on obtaining a method for effecting complete and homogeneous sample dilution.

A simple method for solid dilution of metal samples is outlined in this study, which provided a basis for the accurate determination of all the noble metals by the Neutron Activation Analysis technique.

## 1. INTRODUCTION

The objective of this study was to investigate the development of the neutron activation analysis (NAA) technique as a method for the determination of platinum group metals (PGM's) in matte leach residues (MLR), with particular reference to rhodium, ruthenium and iridium.

In a previous investigation into this problem by Chaix et al. (unpublished manuscript), three suites of samples were prepared individually from a Lonrho production MLR (WPR Con 134-148) as follows:-

i) solid solutions of the MLR were prepared by dilution with pure silica. The mixture was homogenized in a Siebtechnik chrome-stainless steel barrel.

ii) Liquid solutions were prepared by a pressure leach and fusion technique (Mallet, 1972).

iii) Analyses were also carried out on undiluted MLR of approximately 20 mg in weight.

In each of the above three cases concentrations were obtained by comparison with a National Institute for Metallurgy MLR standard prepared in accordance with the experiment.

The results obtained by Chaix et al. (unpublished manuscript) were compared to the results obtained by the Lonrho Refinery Limited (for the same sample) using the method of atomic absorption. The analyses for the undiluted MLR samples gave the most favourable comparison, which is to be expected, as there are no errors incurred during a dilution process. However, this method suffers from the fact that the short-lived isotopes of palladium and particularly rhodium, which must be counted directly after the sample has been irradiated,

cannot be measured as these samples are too radioactive to handle. Therefore some form of dilution of the MLR's is necessary.

Chaix et al. (unpublished manuscript) noted that the method of liquid dissolution introduced errors related to the reproducibility of uptake as well as interference from bromine and sodium. The bromine and sodium probably originate in the pressure leach and fusion stages of dissolution (Mallet, 1972). Chaix et al. suggest that the solid dissolution method does not effect complete sample homogeneity. This was demonstrated by the fact that "gold smearing" was observed on the walls of the mixing vessel. It is suggested that this phenomena, although not always obvious, provides a potential error for all the metals in question, that are prepared in this manner.

In the present study emphasis is placed on developing a quick and effective method of MLR dilution, which will provide precise and accurate analyses of the MLR's by NAA. Further effort has been devoted to obtaining accurately calibrated artificial standards prepared in a similar manner, and with similar concentrations of PGM's to those of the samples under investigation.

## 2. SAMPLE PREPARATION - HOMOGENISATION PROCEDURE

About 30 mg of finely ground MLR and about 4 g of fine pure silica quartz (giving between 4 and 6% MLR in the mixtures, Table 1)\* were accurately weighed into a glass ampoule and well shaken up in a "red devil" paint mixer for about ten minutes to ensure complete sample homogeneity. The standards (Table 2) were prepared in a similar manner by mixing standard PGM oxides with pure silica quartz. From the

\* NOTE: MLR-1 and MLR-2 are dilutions of WPR Con 134-148 and MLR-B and MLR-C are dilutions of Pom Con 54/AB.

viewpoint of NAA reproducing a matrix in the standard which is comparable to the samples under investigation is often found to be important for accurate analyses. Similar considerations apply to the relative levels of concentrations of the unknown elements in order to obtain comparable activities.

### 3. EXPERIMENTAL PROCEDURE

All the irradiations were carried out using the pneumatic facilities of the Safari I reactor at Pelindaba. An average weight of 30 mg of the prepared sample mixtures were weighed out into polyethylene snap-top ampoules. These were then transferred into the reactor in tufnol containers (rabbits) by means of a pneumatic transfer tube for irradiation.

#### 3.1 Short-lived isotopes (rhodium)

The procedure adopted for irradiating and counting the short-lived isotopes of rhodium is first to load the sample mixture into the pneumatic transfer system. An automatic timer is started on arrival of the sample at the irradiation position inside the reactor. The sample was irradiated for a pre-selected time of 80 seconds and then automatically removed to the sending station. The sample was then removed from the rabbit, using remote handling apparatus, and transferred to the counting station. After a pre-selected decay time of 60 seconds the activated samples were counted on a 45 cm<sup>3</sup> Ge(Li) detector coupled to a 4000 channel analyser.

#### 3.2 Longer-lived isotopes (1 to 20 days)

The procedure for the analysis of the longer-lived isotopes was similar to that described above, except that in this instance the samples were irradiated for two minutes. Each sample was counted for 60 minutes at decay times of 1, 5 and 20 days respectively. The accumulated

spectra were transferred to magnetic tape and the data was processed on an IBM 370/158 computer using a modified version of the Hevesy programme (Yule, 1968).

#### 4. PEAK IDENTIFICATION AND INTERFERENCE

The noble metal radionuclides were identified by their characteristic half lives and gamma energies (Table 7). Those radionuclides which were free from interference and easily resolved, were selected (Gijbels, 1970) for the PGM determinations.

#### 5. RESULTS

The results of the NAA of the PGM's for the two Lonrho samples WPR Con 134-148 and Pom Con 54/AB are given in Tables 4 and 5. Table 4 also compares the results obtained in this study to those obtained by the Lonrho Refinery Limited using the method of atomic absorption and to the results obtained by NIM (Project 41675), determined gravimetrically, for the sample WPR Con 134-148. A comparison of the results for standard (T) obtained by the NAA method (using standard-N as a reference) to the actual calibrated concentrations (Table 6) provides a measure of the accuracy of the technique. Table 5, which also compares the analyses for different mixtures of the sample (Pom Con 54/AB), provides a measure of the reproducibility of the method. Finally, the standard deviation in ten replica analyses for each of the seven PGM metals (Table 7) gives an indication of the homogeneity of the sample and the standard mixtures.

## 6. DISCUSSION AND CONCLUSIONS

A comparison of the PGM concentrations for WPR Con 134-148 obtained in this study (NAA) to the results reported by the Lonrho Refinery Limited (AA) and those obtained by NIM using gravimetric determinations (Table 4) show that:-

i) the NAA results are all higher (especially Ir and Rh) than the AA results, whereas

ii) the NAA results agree favourably with the results by the gravimetric method for all the PGM's.

The authors are not in a position to decide which of the two alternative methods, namely atomic absorption and gravimetric determinations, provides us with the most accurate basis of comparison. However the good agreement with the results of this study and the results of the latter method as well as the good agreement between the calibrated and the measured values for standard T for all the metals including Ir and Rh, suggests that NAA provided an accurate method of analysis for all the PGM's.

The relatively small variations in the counting statistic on replicate samples for the PGM's suggest that the method of sample dilution described in this study is effective in obtaining a dilute yet homogeneous sample that can be accurately used in the NAA technique and at the same time keeping activity to a minimum.

## 7. REFERENCES

- Chaix, R.P., Erasmus, C.S. and Sargeant, J. (1976)  
The neutron activation analyses of a precious metals  
matte leach residue. Unpublished NIM Project.

Gijbels, R. (1970)

Determination of noble metals by neutron activation analysis.

Talanta, 18, 587-601.

Mallet, R.C. et al. (1972)

The pressure dissolution of platiniferous materials by the sealed tube technique.

National Institute for Metallurgy, Report No. 1401.



APPENDIX I

The ampoules (Fig. 1) which are specially designed for mixing, are made such that the lid fits over the outside of the glass vessel.

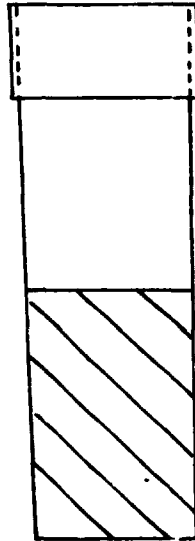


Figure 1. Mixing vessel

When the lid is firmly pressed down a seal is created between the roof of the lid and the glass vessel thus preventing particles being caught up between the lid and the vessel during mixing.

TABLE 1

Preparation of matte leach residue WPR  
Con 134-148 in diluted samples prepared  
for neutron activation analysis

Diluted sample	M.L.R.-1	M.L.R.-2
weight of pure silica (g)	0.60822	0.59257
weight of M.L.R. (g)	0.03942	0.02787
% M.L.R.	6.08	4.409

TABLE 2

Preparation of matte leach residue Pom  
Con 54/AB in diluted samples prepared  
for neutron activation analysis

Diluted sample	M.L.R.-B	M.L.R.-C
weight of pure silica (g)	0.61994	0.62183
weight of M.L.R. (g)	0.02888	0.02726
% M.L.R.	4.45	4.20

TABLE 3

Concentrations of platinum group metals,  
diluted with silica in artificially  
prepared standards

Standard	Std-T	Std-N
quartz	90.671	94.93
platinum	3.207	1.946
palladium	1.484	0.838
rhodium	0.375	0.159
gold	0.557	0.414
iridium	0.478	0.245
ruthenium	0.362	0.171
osmium	1.492	0.466
O <sub>2</sub>	1.423	0.828
TOTAL	100.050	99.99

Concentration given in %.

TABLE 4

Comparison between results obtained by NAA in  
this study and those obtained by the atomic  
absorption and the chromatographic separation  
and gravimetric determination method for  
WPR Con 134-148

Metal	This study (%)	Atomic absorption <sup>1</sup> (%)	Chromatographic separation <sup>2</sup> / Gravimetric determination (%)
platinum	25.28	25.65	25.35
palladium	11.99	11.26	11.30
rhodium	1.40	1.20	1.44
gold	2.64	2.37	2.42
iridium	0.33	0.27	0.36
ruthenium	2.58	2.42	-
osmium	0.40	-	-

1 Lonrho Refinery Limited

2 National Institute for Metallurgy

TABLE 5

Concentrations of the PGM in the sample  
Con 54/AB by the neutron activation  
analysis method

Metal	M.L.R.-B (%)	M.L.R.-C (%)	Average (%)	% difference
platinum	12.05	11.90	11.97	1.24
palladium	4.00	3.85	3.92	3.75
rhodium	13.42	14.06	13.74	4.77
gold	3.92	3.91	3.91	0.26
irridium	4.13	4.18	4.15	1.21
ruthenium	29.71	31.20	30.46	5.02
osmium	1.98	2.17	2.08	9.60

TABLE 6

Concentrations of the PGM metals in standard T  
by the neutron activation analysis method

Metal	Calibrated concentration (%)	N.A.A. (%)	% difference
platinum	3.21	3.07	4.36
palladium	1.48	1.46	1.35
rhodium	0.37	0.37	0.00
gold	0.56	0.57	1.75
irridium	0.47	0.48	2.08
ruthenium	0.36	0.36	0.00
osmium	1.49	1.47	1.34

TABLE 7

Replicate analyses of platinum group metals  
by the neutron activation analysis technique

Sample	N.L.R.-C	M.L.R.-1	M.L.R.-1	M.L.R.-1	M.L.R.-1	Std-T	Std-T
Concentration %	0.60	0.73	0.16	1.51	0.02	0.36	1.49
Isotope	Rh-104	Pd-103	Au-198	Pt-199	Ir-192	Ru-103	Os-191
Peak energy (KeV)	555.8	88.1	411.8	158.3	316.5	496.6	129.5
Decay time	60 seconds	~ 8 - 12 hrs	4.5 - 4.9 days	4.5 - 4.9 days	14.2-14.5 days	14.2-14.5 days	14.2-14.5 days
Corrected peak area counts for ten replica samples	6800 7200 6814 6843 6935 7159 7038 7030 6951 7042	1323 x 10 <sup>3</sup> 1233 x 10 <sup>3</sup> 1229 x 10 <sup>3</sup> 1242 x 10 <sup>3</sup> 1237 x 10 <sup>3</sup> 1252 x 10 <sup>3</sup> 1337 x 10 <sup>3</sup> 1221 x 10 <sup>3</sup> 1338 x 10 <sup>3</sup> 1248 x 10 <sup>3</sup>	3635 x 10 <sup>4</sup> 3386 x 10 <sup>4</sup> 3417 x 10 <sup>4</sup> 3414 x 10 <sup>4</sup> 3451 x 10 <sup>4</sup> 3536 x 10 <sup>4</sup> 3541 x 10 <sup>4</sup> 3459 x 10 <sup>4</sup> 3499 x 10 <sup>4</sup> 3547 x 10 <sup>4</sup>	9237 x 10 <sup>2</sup> 8526 x 10 <sup>2</sup> 8304 x 10 <sup>2</sup> 8602 x 10 <sup>2</sup> 8820 x 10 <sup>2</sup> 8212 x 10 <sup>2</sup> 9438 x 10 <sup>2</sup> 8643 x 10 <sup>2</sup> 8773 x 10 <sup>2</sup> 9331 x 10 <sup>2</sup>	6925 x 10 <sup>2</sup> 6749 x 10 <sup>2</sup> 6708 x 10 <sup>2</sup> 6707 x 10 <sup>2</sup> 7016 x 10 <sup>2</sup> 6732 x 10 <sup>2</sup> 6878 x 10 <sup>2</sup> 6834 x 10 <sup>2</sup> 6823 x 10 <sup>2</sup> 6746 x 10 <sup>2</sup>	34699 36045 29030 36781 37513 35881 34486 29866 37561 32667	1951 x 10 <sup>3</sup> 1865 x 10 <sup>3</sup> 2023 x 10 <sup>3</sup> 1982 x 10 <sup>3</sup> 1930 x 10 <sup>3</sup> 1925 x 10 <sup>3</sup> 1935 x 10 <sup>3</sup> 1657 x 10 <sup>3</sup> 1880 x 10 <sup>3</sup> 1943 x 10 <sup>3</sup>
Average	6982	1266 x 10 <sup>3</sup>	3489 x 10 <sup>4</sup>	8789 x 10 <sup>2</sup>	6812 x 10 <sup>2</sup>	35704	1937 x 10 <sup>3</sup>
Std. dev.	138	57 x 10 <sup>3</sup>	77 x 10 <sup>4</sup>	422 x 10 <sup>2</sup>	103 x 10 <sup>2</sup>	1680	47 x 10 <sup>3</sup>
% error	2.0	3.7	2.2	4.8	1.5	4.7	2.5