

QUALITY OF PGE FIRE ASSAYS USING SPARK ANALYSIS ON LEAD BUTTONS

Dr P. K. Hofmeyr

Innovative Met Products, P.O. Box 1110, Boksburg 1460, South Africa

ABSTRACT. Traditional fire assay dates back over 3000 years and has changed very little over that time. The only improvement is to replace the gravimetric finish with dissolution of the Precious Metal bead followed by AA or ICP analysis of the solution. The newly developed FIFA (Fast In-line Fire Assay) method allows full automation of the fire assay process from sample preparation to spark analysis of the Pb button. This results in fully quantitative analyses for Pt, Pd, Rh, Ru, Ir, Au and Ag in typically less than an hour after a sample is entered into the system. Detection limits are theoretically Pt 0.08 ppm, Pd 0.002 ppm, Rh 0.002 ppm, Au 0.08 ppm and Ag 0.002 ppm but in practice the lower measurable limits are about double these figures. Few opportunities have been available to present data obtained using the FIFA system as all FIFA laboratories have been in the domain of a Pt mining company which prefers to keep all Pt analytical matters confidential. However, IMP has recently participated in the round robin exercise to establish recommended values for a new series of Merensky Reef and UG-2 Layer reference materials produced by African Mineral Standards. The precision of the results was excellent being on average Pt 2.05%, Pd 1.25%, Rh 4.08% and Ru 4.94% being expressed as Relative Standard Deviation. The excellent precision is a reflection of the efficient collection of PGEs in the Pb buttons and the homogeneity of the Pb buttons. However, the accuracy was not as good. The poorer accuracy is interpreted as the calibration of the spectrometer not being as good as desired due to the difficulty in acquiring a suitable range of standards with reliable recommended values for the PGEs. The most recent spectrometer was calibrated with the greatest care and produced slightly better results for Pt, Pd and Rh and slightly worse for Ru.

1 INTRODUCTION

Traditional fire assay for Au has remained virtually unchanged for 3000 years. It has survived for so long because it is accurate, has relatively low detection limits and is relatively inexpensive. However, it is labour intensive, has a long turn-around time (typically at least 7 hours for Au), is environmentally unfriendly and exposes assay operators to potentially unsafe conditions. Conventional fire assay using Pb collection gives poor results for the PGEs as some PGEs are lost during the cupellation procedure. The only accurate method for the PGEs is the nickel sulphide collection route but this is very expensive and very slow. A rapid, accurate, cost-effective method for the determination of the Precious Metals has become a necessity in assay practice and this gap has now been filled by the new FIFA system which uses automation and OES spark analysis of Pb buttons to meet the required objectives. Spark analysis of Pb buttons has been carried out in the past but never became an established technique. This was the SAFT (Spectral Analysis for Traces) technique which never established itself as an accepted method. The FIFA system uses a Thermo spectrometer specially developed for

the analysis of precious metals in a Pb matrix. As this technique is being revisited it is necessary to carry out a critical evaluation of PGE data obtained by the FIFA system to validate the method as a whole. This paper attempts to do that.

2 CONVENTIONAL FIRE ASSAY

Samples of Precious Metal (PGE, Au or Ag) bearing ore are mixed with a litharge-containing flux, placed in a fire-clay crucible and heated in a furnace at 1000-1200°C for about an hour. Typically Ag is added as a silver nitrate solution to make the Precious Metal (PM) bead easier to handle after cupellation. This is particularly necessary if small sample charges are used. During the fluxing process litharge is reduced to molten Pb which percolates down through the molten charge collecting the PM contained in the sample. The crucible is removed from the furnace, the charge is poured into a cast-iron mould, allowed to cool and the molten Pb freezes at the base of the mould. After cooling the Pb button is removed from the mould and any adhering slag is removed by hammering. The Pb button is then placed on a cupel and heated in a cupelling furnace for typically an hour to remove the Pb by oxidation leaving behind a bead of PM. If it is an unsilvered Au ore sample the mass of the bead is a measure of the bullion content (Au +Ag) of the ore. This bead can then be parted ie. acid-treated, to remove the Ag and the remaining mass is the Au content. In modern times the finish for a silvered Au ore sample is to dissolve the bead in acid and then analyse the solution by AA. For a Platinum Group Element (PGE) determination an additional high temperature (HT) cupellation (typically at 1300° C) is carried out to volatilise the Ag. The mass of the bead is used to calculate what is typically known as the 4PGE+Au or 4E value as this is a measure of the Pt+Pd+Rh+Ir+Au content of the ore. However, it is not accurate as about half of the Ir and virtually all the Ru and Os have been lost during the HT cupellation. Even up to 10% of the Pt, Pd, Rh and Au can be lost during HT cupellation. Fusion and dissolution of the PGE bead followed by AA or ICP analysis gives the individual PGE content of the bead. However, PGE losses sustained during cupellation have to be taken into account to estimate the original concentrations in the sample making it an inaccurate measurement.

The most accurate method available for the determination of the individual PGEs is the nickel sulphide collection method. This method is analogous to the Pb collection method but nickel sulphide is used instead of Pb. As there is no HT cupellation step there is no loss of PGEs due to that process. The NiS button obtained is pulverised and dissolved in a hydrochloric acid/ammonium chloride mix. The PGE sulphides and Au remain undissolved and are collected by filtration. The PM residue is dissolved typically using chlorine at high temperature and pressure and the solution is then analysed by ICP/OES or MS.

3 DEVELOPMENT OF THE NEW AUTOMATED FIRE ASSAY SYSTEM

It was realised that to develop a new improved fire assay system automation would have to be incorporated. Although most of the principles of conventional fire assay would still be used new equipment would have to be developed to suit automation.

As the conventional fusion furnace was unsuitable for use with a robot, a new furnace was developed which was loaded from below on pneumatically driven platforms. This

furnace retains heat while being loaded and unloaded far better than the conventional fusion furnace thus reducing fusion times.

The crucibles used are essentially the same as for conventional manual fire assay, but are made to close tolerances which is necessary for robot handling.

Although conventional fusion fluxes can be used in the automated fire assay system, a new caustic soda-containing flux was developed which was faster acting and thus enabled shorter fusion times to be achieved. By pre-heating crucibles, fusion times using the new flux for quartzitic Au ore samples are typically 8 minutes and the most refractory chromititic Pt ore samples take no longer than 15 minutes for 50g samples. Conventional sodium carbonate containing fluxes can be used but have longer fusion times.

To avoid the problems inherent in the HT cupellation route, it was decided to carry out a direct spark analysis on the Pb button. A Pb button separator was developed whereby after fusion the fusion charge is poured by robot through the separator. The Pb flows through narrow apertures into a chilled mould and is instantly frozen while the molten slag drains elsewhere. This system has the advantages of producing a homogeneous Pb button (essential for spark analysis) because it is instantly chilled and of being environmentally and operator friendly because there is no cupellation stage to produce toxic litharge fumes and dust.

Essential to this new method has been the development of a new spectrometer, the ARL Fire Assay Analyzer by Thermo of Switzerland, for the determination of the PM in a Pb matrix. This is a state of the art instrument using TRS (Time Resolved Spectroscopy) and detection limits in the Pb button are calculated by Thermo to be Pt 0.08 ppm, Pd 0.002 ppm, Rh 0.002 ppm, Au 0.08 ppm and Ag 0.002 ppm. The lower detection limits for Pd, Rh and Ag are due to the more sensitive analysis lines for these elements.

The new automated fire assay system has been named FIFA for *Fast In-line Fire Assay*.

4 FIFA LABORATORY DESIGN

A fully automated laboratory would include sample input, drying, weighing, primary crushing and splitting, secondary crushing and splitting, milling, fluxing, fusion, Pb button separation and spark analysis of the Pb button. Additional analyses such as XRF, XRD, wet chemical analysis, particle size distribution measurement, relative density by pycnometer and loss on ignition can be included as part of the automated laboratory.

The numbers of crushers, mills, fluxers, fusion furnaces, separators, OES spark spectrometers etc. depends on the required sample masses, maximum particle sizes in sample, hardness of rock types to be analysed and, very important, mineralogy of ore minerals. The largest automated FIFA laboratory constructed to date has been designed to handle 2000 samples per day fused in duplicate.

5 SAMPLE PREPARATION

Sampling, sub-sampling and comminution stages need to be properly planned to obtain reproducible results and these aspects are often neglected. Representative samples

should be obtained but this is usually outside the scope of the laboratory. However, planning the sub-sampling and comminution stages is the responsibility of the laboratory.

In this exercise all the sample preparation stages were carried out by African Mineral Standards who rigidly adhered to the best sampling and sub-sampling protocols so it can be presumed that any errors in the data should not be due to sampling or sampling preparation but only due to the analytical method itself.

6 REFERENCE MATERIALS BEING ANALYSED

The reference materials analysed were:-

1. AMIS0005 UG2 Ore Grade
2. AMIS0006 UG2 Low Feed Grade
3. AMIS0007 Merensky Reef Feed Grade
4. AMIS0008 Merensky Reef Ore Grade

About 20 laboratories world-wide participated in the round robin. Each laboratory was sent 8 splits of each reference material with the request to analyse each reference material for all the elements

7 METHODOLOGY

The 8 aliquots of each reference material were fused in triplicate on a manual FIFA system at IMP in South Africa generating 24 Pb buttons for each reference material. These buttons were then sent to Thermo in Switzerland where they were analysed on the demo ARL FAA spark spectrometer. Each Pb button was sparked 4 times generating 96 spark analyses for each reference material. These measurements were carried out in 2005.

SARM 65 was also analysed twice during the duration of these tests.

In 2006 a new improved spectrometer was constructed by Thermo for a commercial laboratory in Australia primarily for Au assay but also to be calibrated for the PGEs. During the factory acceptance tests of this new spectrometer every effort was made to optimise the calibration for the PGEs and Au and Ag. As part of the tests new buttons were prepared for AMIS0005 and AMIS0008 from new aliquots of these reference materials. The results could then be compared with those obtained on the previous demo instrument. Four new buttons were prepared for each reference material.

8 RESULTS

The results obtained for AMIS0005, AMIS 0006, AMIS 0007, AMIS 0008 are shown in Tables 1 to 4. The abbreviations mean the following :-

FIFA = PGE values determined by FIFA
Rec v = Recommended value
SD = standard deviation

RSD = Relative standard deviation

Table 1 The Results for Standard AMIS0005

	Pt	Pd	Rh	Ru
	ppm	ppm	ppm	ppm
FIFA	3.57	2.62	0.671	1.27
Rec v	3.38	2.23	0.66	1.24
SD	0.09	0.04	0.013	0.02
RSD%	2.61	1.63	1.98	1.80

Table 2 The Results for Standard AMIS0006

	Pt	Pd	Rh	Ru
	ppm	ppm	ppm	ppm
FIFA	1.352	1.018	0.288	0.469
Rec v	1.38	0.91	0.29	0.42
SD	0.04	0.008	0.025	0.038
RSD%	2.85	0.83	8.58	8.18

Table 3 the Results for Standard AMIS0007

	Pt	Pd	Rh	Ru
	ppm	ppm	ppm	ppm
FIFA	2.58	1.74	0.262	0.499
Rec v	2.48	1.50	0.25	0.45
SD	0.05	0.04	0.014	0.037
RSD%	1.95	2.01	5.17	7.34

Table 4 The Results for Standard AMIS0008

	Pt	Pd	Rh	Ru
	ppm	ppm	ppm	ppm
FIFA	9.04	5.12	0.707	1.449
Rec v	8.66	4.36	0.68	1.26
SD	0.07	0.03	0.004	0.035
RSD%	0.79	0.53	0.57	2.42

Table 5 The Results for Standard SARM 65

	Pt	Pd	Rh	Ru
	ppm	ppm	ppm	ppm
FIFA 1	2.84	1.465	0.552	0.933
FIFA 2	2.74	1.439	0.542	0.943
Rec v	2.64	1.28	0.522	0.853

Table 6 The Comparison of Results for AMIS0005 using the old (demo) Spectrometer and the new Spectrometer

	Pt	Pd	Rh	Ru
	ppm	ppm	ppm	ppm
Demo	3.57	2.62	0.671	1.27
New	3.40	2.38	0.699	1.42
Rec v	3.38	2.23	0.66	1.24

Demo - data obtained previously on Thermo demo spectrometer

New - data obtained on new spectrometer

Rec v - Recommended value

Table 7 The Comparison of Results for AMIS0008 using the old (demo) Spectrometer and the new Spectrometer

	Pt	Pd	Rh	Ru
	ppm	ppm	ppm	ppm
Demo	9.04	5.12	0.707	1.449
New	8.52	4.46	0.686	1.303
Rec v	8.66	4.36	0.68	1.26

9 COMMENT ON RESULTS

For the data obtained initially on the demo spectrometer it is obvious that the precision of the FIFA method is excellent. The RSD for Pt varies from 2.85% at the 1.38ppm level to 0.79% at the 9ppm level. For Pd the RSD varies from 2.01% at the 1.5ppm level to 0.53% at the 4.4ppm level. For Rh the RSD varies from 8.58% at the 0.25ppm level to 0.57% at the 0.7ppm level. For Ru the RSD varies from 8.18% at the 0.42ppm level to 1.8% at the 1.24ppm level. It is even more remarkable considering the concentration levels.

The excellent precision obtained for the PGEs is especially important because it proves the complete collection of the PGEs in the Pb button using the new flux of the FIFA system. It also proves the homogeneity of the Pb button which is essential for spark analysis of the Pb button but was not necessary when using the old cupellation system.

The accuracy of the PGE data using the original demo spectrometer at Thermo proves that the new assay method of spark analysis of homogeneous Pb buttons produces good quality PGE data. The even better data produced by the new spectrometer with a new calibration proves that the FIFA fire assay system can produce excellent quality PGE data if the spectrometer is reliably calibrated with matrix-matched standards.

The theoretical detection limits as determined by Thermo are considered at this stage to be only applicable under ideal conditions and using matrix-matched standards and samples. Until more data are available the usable detection limits will be considered to be twice the theoretical limits. These are listed in the Conclusions.

10 CONCLUSIONS

It is concluded that :-

1. The FIFA fire assay system can produce excellent quality PGE data if homogeneous Pb buttons can be obtained and the ARL FAA spectrometer is reliably calibrated with matrix-matched standards.
2. The usable limits of detection for the PGEs and Au using the FIFA system are Pt 0.15 ppm, Pd 0.04 ppm, Rh 0.04 ppm, Ru 0.04 ppm and Au 0.15 ppm.

11 ACKNOWLEDGEMENTS

I would like to acknowledge the help and enthusiasm of Dr Jean-Marc Bohlen of Thermo Electron, Switzerland, in carrying out all the spark analyses at their factory in Switzerland. I would also like to thank Charles Lötter of IMP for carrying out the FIFA fusions and separation of the Pb buttons at IMP, Boksburg.