

Nickel sulphide fire assay – ICPMS method for the determination of platinum group elements: a detailed study on the recovery and losses at different stages

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Summary. Detailed studies for evaluating the optimum nickel sulphide button size in the estimation of platinum group elements (PGE) by inductively coupled plasma mass spectrometry (ICPMS) were carried out. PGE losses in various stages of the process have been studied. The results indicate that among the three button sizes investigated, i.e., 2.5, 5 and 8 g, the 2.5 g button was found to be adequate for the full recovery of the PGE. Losses of PGE in the fusion slag and in the pulp at the second filtration stage have been found to be negligible. Tellurium coprecipitation was found to minimize the losses during the dissolution of the nickel sulphide button.

Introduction

With the increasing demand for low level determinations of the PGE for the purpose of geochemical exploration, sophisticated instrumental techniques such as ICPOES and GFAAS with the detection capabilities of ng/g have become a necessity. Inductively coupled plasma mass spectrometry (ICPMS) with very low detection limits and rapid multielement analytical capability and freedom from serious matrix interferences would make it an ideally suitable technique for the determination of PGE.

Nickel sulphide fire assay [1] is the accepted procedure for the preconcentration of PGE. Date et al. [2] described the use of NiS fire assay and ICPMS for the analysis of PGE. They used 32 g of nickel carbonates per fusion resulting in button weights of 18–20 g giving high blank values and requiring prolonged button dissolution. Low recoveries have been reported for the samples analysed. Asif et al. [3] reported studies on the recovery of PGE using varying button sizes adopting the INAA instrumental technique. Jackson et al. [4] used a 6.5 g button and reported improved recoveries.

Large sized buttons require prolonged dissolution and subsequently increased filtration time. At the same time reducing button size cannot be at the cost of recovery. Few

studies have been reported using lesser button weights (less than 8 g) for the solution technique using ICPMS.

In the present paper we report results of our study concerning optimization of button size and dissolution technique and the advantages of the tellurium coprecipitation method over the normal direct filtration for the ICPMS determination of platinum, palladium, rhodium, iridium and ruthenium. Losses at different stages have been investigated, i.e. in the fusion slag, dissolved PGE in the filtrate and in the pulp. The South African reference standard SARM 7 and other geological samples have been processed.

Experimental

Instrumental details

Fire assay furnace. Model DFC 4410, manufactured by MSI Industries Inc., 3800 Race Street, Denver (Colorado), USA, oil fired, fitted with silicon carbide muffle.

ICPMS. Sciex Elan Model 250 (1986), Toronto, Canada.

Operating conditions. Plasma, all argon; Forward power, 1.25 KW; Reflected power, < 5 W; Coolant (outer), 12–13 l/min; auxiliary (intermediate), 1.4 l/min; Carrier (inner), 0.4 l/min; Solution uptake, 1 ml/min; Optimization, solution containing Cu, Li, In, Pb.

Sample and standard solutions were introduced into the instrument by conventional pneumatic nebulisation. An eight-roller peristaltic pump was used to feed the solution at a rate of 1.0 ml min⁻¹ and the system was operated in the mass scanning mode covering the complete range from 96 to 207, covering Rh, Pd, Ir, Pt and the internal standards Tl and Tm. 50 ppb of Tl and Tm were added as internal standards to each of the solution to correct for instrumental drift. Under these conditions a complete spectrum gets accumulated in just over 2 min. Each standard or sample solution or blank was aspirated for about 2 min for system equilibration and to avoid any possible memory effects before data acquisition. Calibration curves obtained by counting on 5, 10, 25, 50 and 100 ng ml⁻¹ solutions of PGE with internal standard, were used in estimations of PGE in unknown solutions.

Table 1. Recovery of PGE by varying amounts of nickel collector (tellurium coprecipitation method)

Sample	Weight of NiS button			
		Recovery in %		
		2.5 g	5 g	8 g
SARM 7 ^a	Pt	95	97	94
	Pd	100	99	102
	Rh	95	96	95
	Ir	96	96	98
	Ru	91	88	95
In-house standard MSPT-1	Pt	95	96	93
	Pd	95	92	98
	Rh	92	91	93
	Ir	92	95	90
	Ru	90	92	90
Spiked multielement standard (1 ml of 1 ppm combined PGE solution)	Pt	95	96	93
	Pd	95	92	98
	Rh	92	90	93
	Ir	94	91	92
	Ru	91	95	92

^a Recovery values calculated against the average values given in References 2–5

Isotopes selected: ¹⁰³Rh, ¹⁰⁵Pd, ¹⁹³Ir, ¹⁹⁵Pt, ¹⁶⁹Tm, ²⁰⁵Tl.

Reagents

Laboratory reagent grade chemicals were used for the flux components and analytical reagent grade acids for the dissolution process.

Tellurium solution (1000 µg/ml). Prepared by dissolving 1.24 g of tellurium oxide (BDH Analar grade) in aqua regia, removing traces of nitric acid by two successive evaporations with hydrochloric acid and making up to 1000 ml with DM water.

Standard solutions (100 µg/ml) of Pt, Pd, Rh, Ir and Ru were prepared from the respective spec pure ammonium chlorosalts (Johnson and Mathey, England). Necessary dilutions were made to obtain 1 µg/ml mixed solution in 5% hydrochloric acid.

The fire assay fusion procedure is based on that described by Robert et al. [1] with modifications to suit the purpose.

Procedure

20 g of sample, 40 g of borax, 21 g of sodium carbonate and 3 g of silica sand are weighed into a polythene bag. Nickel powder and sulphur flowers (2.0 g and 1.2 g for the 2.5 g button; 4.0 g and 2.4 g for the 5 g button; 6.7 g and 4 g for the 8 g button respectively) are weighed into the same polythene bag. For the blank and spiked runs a rock sample, previously analysed to have < 50 ppm of the base metals, is used. For spiked fusions the required amount of PGE (1 ml of 1 ppm of combined PGE solution) were added to the blank sample. The samples are fire assayed and the NiS buttons are separated from the melt.

Table 2. Effect of tellurium coprecipitation on the recovery of PGE

Sample		Reported value (µg/g) ^a	PGE obtained (in µg/g) ^b	
			normal method	Te coprecipitation method
SARM 7	Pt	3.395	2.89	3.29
	Pd	1.355	1.22	1.34
	Rh	0.212	0.20	0.22
	Ir	0.071	0.06	0.07
	Ru	0.397	0.31	0.41
In-house Standard MSPT-1 ^c	Pt	0.260	0.22	0.25
	Pd	0.320	0.27	0.30
	Rh	0.090	0.08	0.09
	Ir	0.040	0.03	0.03
	Ru	0.050	0.04	0.05

^a Jackson et al. [4]

^b Each value is an average of five determinations

^c Recommended values

The button is powdered, first in a percussion mortar, and then in a ceramic mortar. The ground material is transferred into 250 ml beakers. 100 ml of hydrochloric acid are added and the beakers are heated on an electric hot plate till the NiS dissolved, adding further quantities of HCl when required. After the dissolution is complete the beakers are removed from the hot plate and allowed to cool.

The contents of the beakers are filtered using Whatman No. 42 filter paper and the residue is rinsed with 20% HCl and water to remove traces of nickel salts.

Tellurium coprecipitation. For the experiments involving tellurium coprecipitation, the NiS button is dissolved in hydrochloric acid. 2 ml of tellurium solution and 3.5 ml of stannous chloride solution (20%) are added. The contents of the beakers are then digested for 1 h and filtered using Whatman No. 42 filter paper.

The filter papers are placed in 100 ml beakers. 10 ml of HCl and 10 ml of hydrogen peroxide (30% Merck) are added and the beakers are kept aside till the reaction subsides. Then 1 ml of nitric acid is added and the beakers heated for 10 min at mild heat¹. The contents are then filtered using What No. 41 paper, washing the pulp with 20% HCl and water. The filtrate obtained is collected in another 100 ml beaker. The beakers are then heated on a hot plate to reduce the volume to beginning dryness². 0.1 ml of internal standard (5 µg/ml thulium and thallium), 0.5 ml of HCl and 9.4 ml of water are added to each of the beakers and the clear solution obtained is collected in polythene vials for ICPMS study.

To determine losses in the pulp, the dried and ignited pulp is acid leached with aqua regia and the solution, after maintaining the required acid strength and internal standard concentration, is read by ICPMS.

¹ Though HCl/H₂O₂ alone is sufficient to bring the PGE salts into solution, on few occasions the solution turned black after peroxide removal. A small volume of nitric acid is effective in eliminating this problem

² The solution should not be taken to complete dryness as otherwise the tellurium and PGE may precipitate as metals and would be difficult to dissolve

Table 3. Study of losses of PGE in the filtrate, slag and pulp for SARM 7

Element	Reported value for SARM-7 ^a	Filtrate		Slag		Pulp	
		Amount recovered ^b (µg/g)	% of total value	Amount recovered ^b (µg/g)	% of total value	Amount recovered ^b (µg/g)	% of total value
Pt	3.395	0.305	9	0.102	3	Trace	<1
Pd	1.355	0.095	7	0.027	2	Trace	<1
Rh	0.212	0.006	3	0.004	2	0.002	1
Ir	0.071	0.006	8	0.003	4	0.001	1
Ru	0.397	0.032	8	0.020	5	0.015	4

^a Jackson et al. [4]

^b Each value is an average of three determinations

Results and discussion

Recovery of PGE by varying button sizes is shown in Table 1. Comparable results are obtained for all the three button sizes studied, i.e., 2.5, 5, and 8 g. The 2.5 g button size, while being adequate for the recovery of PGE, affords much saving in chemicals and reduces sample dissolution time, resulting in increased throughput. Hence the 2.5 g button is utilized for all subsequent studies.

Dissolution losses of platinum group elements, especially platinum and palladium, during the NiS button dissolution stage are known to be considerable. 10 to 15% losses have been reported by various authors. Improved recoveries have been reported by the tellurium coprecipitation technique [4]. To study the effect of Te coprecipitation on the recovery of PGE, standard reference sample SARM 7 and an in-house standard have been analysed several times by the two methods, i.e. with and without tellurium. The results obtained are compiled in Table 2. The results show an increase of 10–15% in the recovery of PGE by the tellurium coprecipitation technique.

In the second study the filtrate obtained after the normal direct filtration process was treated with Te solution and the metal precipitated. This process was utilised to recover the PGE sulphides lost in the solution. The results obtained (Table 3) proved this to be true. Thus it appears to be advantageous to adopt the tellurium coprecipitation while dissolving the NiS button.

It is known that part of the noble metals is lost in the slag during the fusion stage. Losses in the pulp at the second filtration stage have also been reported [5]. Our studies on the determination of these losses (Table 3) have shown that they are not very significant. Bowditch [6] has reported similar results in his study on Australian ores.

With the sample amount and the dilution adopted in this procedure, a detection limit of 0.5 ng g⁻¹ of PGE is obtainable.

Thus the present study indicates that by using a 2.5 g button and the tellurium coprecipitation method, much saving in processing time and chemicals is achieved, while accurate and reproducible values are obtained for the PGE. It was also shown that the extent of losses at different stages of the procedure, i.e. slag and pulp, is not very significant.

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