/

Journal of Applied Geochemistry
Vol. 19, No. 2 (2017). pp. 164-170

COMPARISON OF DETECTION LIMITS FOR PLATINUM – GROUP ELEMENTS (PGE'S) BY NICKEL SULFIDE FIRE-ASSAY AND TE CO-PRECIPITATION METHOD WITH ICP-MS USING 99.995% NI POWDER (<150 MESH), 99.995% NI GRANULES AND NICKEL CARBONATE

Ashish Kumar Pandey, B.V.D. Rao, N. Rajamani and P. Vamshi Krishna
Chemical Division, Geological Survey of India, SR, Hyderabad, India
E-mail: ashishprayag@gmail.com

Abstract

Comparison of detection limits for the determination of platinum group elements (PGE's) using inductively coupled plasma mass spectrometry (ICP-MS) was done, after pre-concentration by nickel sulfide fire-assay technique and Te co-precipitation to enhance recovery. The results of the study using 99.995% pure Ni powder (<150mesh), 99.995% purity Ni granules and Nickel carbonate (minimum assay as Ni 40-45%) are presented in the paper. Heterogeneous distribution of PGE's in geological samples is over come by small particle sizes (<200 mesh) and rigorous homogenization/re-homogenization procedure. By optimizing critical parameters such as flux composition, controlled furnace temperature and instrumental drift, etc., best experimental conditions were established to develop a method suitable for routine analysis. Calibrations were performed using synthetic standards and verified by the use of international PGE's reference materials, WMG-1 and CHR PT+. This economically viable improvised procedure offers extremely low detection limits in the range of 0.3 to 5.0 ng/g by using 99.995% Ni powder. The analytical methodology described here can be used for routine analysis of PGE's in geological samples.

Keywords: Platinum Group Elements (PGE's), NiS fire-assay, ICP-MS, Nickel sulfide, Nickel carbonate

1. Introduction

Accurate data of PGE's concentrations below their crustal abundance level are required for exploration and resource evaluation. Fire assay technique after the collection of PGE's into a nickel sulfide button is one of the two established methods, besides Pb as the collector for pre-concentrating prior to analysis. PGE's are often distributed heterogeneously in discrete mineral phases in Earth's crust and have very low crustal abundance level hence it is necessary to take large representative samples weighing as much as 10-100g for analysis. Most acid-digestion methods are not suitable for such large samples in view of low extraction efficiency and consumption of more reagents. Similarly, some minerals e.g., Sperrylite, Laurite, Coopente, Braggite, Iridosmine, Osmiridium and Platiniridium are insoluble in aquaregia (Gowing and Potts, 1991) and not readily attacked using such procedures (Barefoot, 1998) and hence PGE's necessitate adoption of suitable analytical methodologies, which should include a large sample size, elemental pre-concentration and measurement of individual elemental concentration. Hence, Fire Assay technique for estimation of PGE's remains indispensable in spite of it being lengthy, tedious and less suitable for routine analysis.

We have improvised Fire Assay procedure suitable for routine analysis to generate data for the purpose of geochemical mapping. This was done by comparing the detection limits for platinum-group elements (PGE's: Ruthenium, Rhodium, Palladium, Iridium and Platinum (except Osmium) by adopting nickel sulfide fire assaying procedures (Date et al., 1987) using 99.995% pure Ni powder (<150mesh), 99.995% pure Ni granules and nickel carbonate (minimum assay as Ni 40-45%) as an alternative to 99.999% pure Ni powder (<150mesh).The above study was carried out keeping in view the non-availability of 99.999% pure Ni powder (<150mesh) in the market. It was hence felt essential to modify the existing fire assay technique which offers extremely low detection limits and should be economically viable for routine analysis of a large number of samples by using available nickel (in different forms) as mentioned above.

2. Theoretical

Fire assaying is the only "classical method" in vogue for the determination of noble metals. A search of

---

*Orginally Presented in National Symposium - 2015 the available literature shows that the method has been in use since centuries. The technique's indispensability is due to the high degree of familiarity coupled with a high confidence level. The procedure can normally be divided in to two stages-

- Pre-concentration of the analyte from the matrix
- Measurement of the analyte concentration by a highly sensitive analytical technique such as ICP-MS

Due to very low crustal abundance, inhomogeneous distribution with high gangue-material and high resistance to chemical attack, PGE-analysis possesses a real challenge. Generalized flux-weights and flux composition that often lead to erroneous results need calculation depending on the sample composition, for eg. the amount of nickel and sulfur contained in the sample is subtracted from the flux mixture. The correct ratio of these elements is important to avoid the formation of NiS_2 which is difficult to dissolve in HCl. It dissolves with the PGE sulfides in the next step on the addition of aqua regia and as nickel would still be in the final solution used for measurement it causes interference during Ru determination by ICP-MS (Juvonen, 1999). Thermodynamic properties and phase relations of the Ni-S system also reveals that, except for native Ni, five mineral phases are now known to exist within the Ni-S systems like heazlewoodite (Ni_3S_2), godlevskite (Ni_9S_8), millerite (NiS), polydymite (Ni_3S_4), and vaesite (NiS_2). High temperature modifications leading to mineral stability are known for Ni_3S_2 (above 533°C), Ni_9S_8 (above 397°C) and NiS (above 282°C) (Henriette Ueckermann, 2002). Of all these phases, only heazlewoodite (Ni_3S_2) is commonly found in slow-cooled metallurgical mattes, which are relatively low in sulphur. The above work is based on the observation by Williamson and Savage (1965) that the composition of nickel sulfide button will be 69.3 % nickel and 27.9 % sulfur, which is close to the eutectic point between the sulfides Ni_3S_2, and Ni_6S_5.

During fusion, major elements are partitioned into the glassy slag while the PGE's are preferentially incorporated into the metallic phase i.e., nickel sulfide. Although it is unique in all aspects, it suffers from some disadvantages. As physical methods of removing nickel sulfide matrix from the button cannot be used, hence in this procedure the nickel sulfide button is usually dissolved in hydrochloric acid to remove nickel and sulphur, leaving a black precipitate of PGE-sulfides. Depending on the sample composition, mixed sulfides of As and base metals might also remain as solids at the bottom of the beaker. Although the nickel sulfide button has been shown to collect all the PGE's quantitatively, losses may occur at the dissolution stage. As much as 20% of the PGE's can be lost, when the button is dissolved in hot hydrochloric acid (Jarvis, 1995). This loss of 20% PGE's could be recovered by Te-coprecipitation (Figueiredo, and Morcelli, 2004) after the evolution of hydrogen sulfide during boiling. It may be mentioned that Te-coprecipitation can be carried out effectively by the addition on $SnCl_2$ at the pH value of about 2 (Schoeller, 1939)

3. Experimental

3.1 Nickel sulfide fire assay

10 g of representative sample with 2 g Ni, 1.5 g calcium fluoride, 1.2 g sulfur, 6 g SiO_2, 40 g Na_2CO_3 and 80 g $Na_2B_4O_7$ were mixed in a disposable plastic bag (Balaram et al., 2006). Reagent grades of chemicals used for the preparation of sample solutions are listed in Table 1. After mixing the flux and the sample, the bag was kept into a fireclay crucible coated with graphite, introduced into a muffle furnace and allowed to fuse at 1050 °C for one hour. At this temperature, the mixture forms a homogeneous melt. The graphite-coated crucible was removed and the melt poured into cast steel moulds carefully and cooled. After cooling, NiS button which settles at the bottom of the iron mould is separated out mechanically from the slag as a clean shiny button. Instead of direct dissolution of NiS button, the button is pulverized in an iron mortar and transferred to a 500ml glass beaker. After wetting, 100ml conc HCl is added slowly and the beaker is transferred to hot plate and heated at 150°C, for 3 to 4 hours till a clear green solution of about 50ml is obtained.

To this solution 2ml of 2000 μg/ml tellurium was added followed by the addition of 5ml of 20% $SnCl_2$ subsequently adding 20ml of distilled water while stirring constantly with a glass rod. Better coagulation was observed using 2000 μg/ml Te-solution instead of 1000

Table 1. Reagents used for preparing sample solution

Reagent	Make
Nickel Powder	Ni Powder. 99.999%, 99.995 % (Sigma -Aldrich)Ni Powder. 99.995 % (Acros Organics)Ni granules. 99.995% (Bam Germany)
Ni Carbonate	Qualigens AR Assay (ex Ni) 40-45%
Sulfur	Rankem (LR) Assay- NLT 99.0%
Calcium fluoride Extra pure	SDFCL Assay (after ignition at 500oc)-97.0%
Silica	Sea sand GR Merck
Borax	Merck LR grade
Sodium Carbonate	Merck LR grade
Tellurium	Rolex, Assay – 99.9 %
Stannous Chloride	Merck, Assay- (SnCl2).2H2O-98.0-103.0 %
Hydrochloric Acid	Fisher Scientific ExcelaR- Assay 35.8-38.0%
Nitric Acid	Merck GR-Assay-69%
Hydrogen peroxide	Merck 30% Assy-H_2O_2 - 29-32 %
Water	Millipore (TDS 0.23mg/l)

µg/ml solution. A black turbid precipitate of Te metal was obtained, which was covered with watch glass and digested for two hours till coagulation. The resulting solution was filtered and washed well with a cold 10% HCl solution followed by demineralized (D.M.) water, treated with 5 ml of freshly prepared aqua regia and the content along with filter paper was heated on a hot plate at 150°C for 10 minutes. 2ml hydrogen peroxide was added, filtered, and the pulp washed with 10% warm hydrochloric acid solution. The content of the beaker was evaporated to dryness followed by dilution to 25 ml to reduce the TDS in the solution to prevent the nebulizer of ICPMS from getting blocked. Figure. 1 shows the schematic representation of various steps involving separation, pre-concentration and ICPMS determination of PGE in the NiS fire assay technique.

4. Instrumental Determination

ICP-MS for the determination of the PGE's after NiS fire assay pre-concentration is being routinely used. The ICP-MS instrument used was an Agilent 7700X Series ICP-MS. The operating conditions and measurement parameters for ICP-MS are given in Table 2. Measurement of sample solutions: For the ICP-MS determinations, a 20 ng/g calibration solution was prepared from a 1000 mg/l multi-element standard solution (Merck) in 0.5 mol/l HNO3 and 0.5 mol/1 HCl. Acids used in calibration and dilution of sample solutions were Merck Suprapur grade 69% v/v nitric acid and 36% v/v hydrochloric acid. All dilutions were made D.M water obtained with a Millipore purification system. Fire assay furnace of rating 18KW, 400V with heating element material 11SWG Kanthal A1 has been used.

5. Result and Discussion

5.1 Method Modification

The time-tested method described earlier has been subjected to a slight variation in order to suit our needs of fast and more accurate routine analysis of a large number of samples. Table-3 presents the three steps that were modified along with the reasons for modification.

The new procedure has reduced the processing time and cost of the analysis considerably thus making it suitable for a routine analysis of large number of samples which is verified by percentage recovery in the two international PGE reference materials WMG-1 which is a mineralized gabbro and CHR-Pt+ which is a chromitite reference sample. The results of analysis of the reference materials are presented in Table-4. As the recovery for each element varied between 76-87% which is considerable, the modified method was adopted for routine analysis.

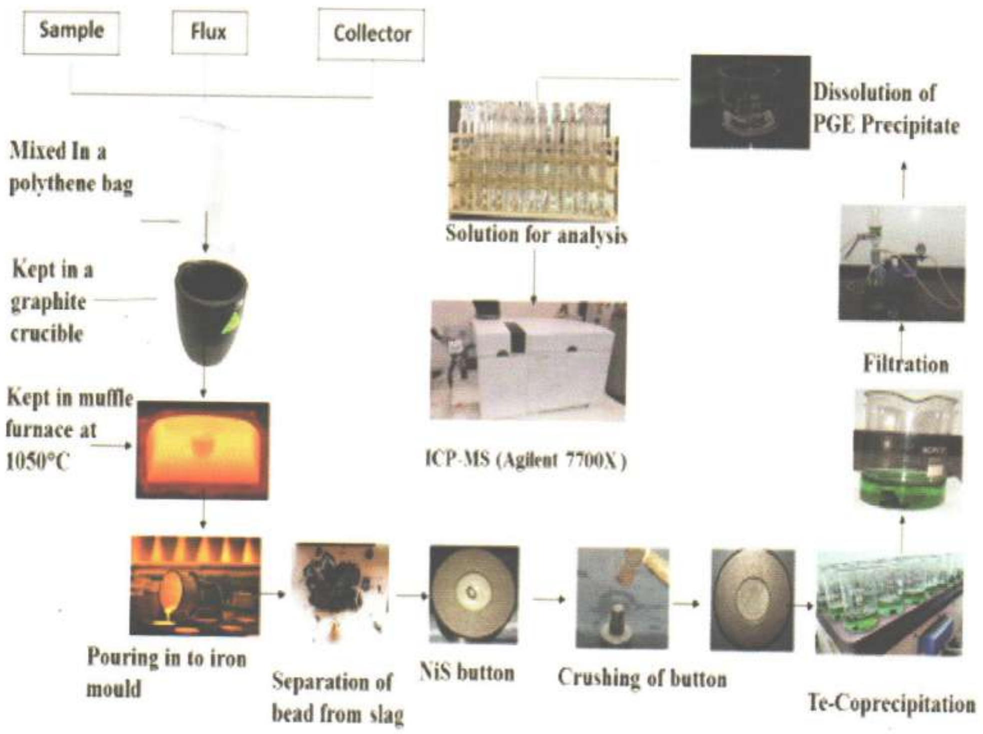

Fig. 1. Schematic and visual representation of various steps involved in the experiment.

Table 2. ICP-MS (Agilent 7700X Series) operating conditions and measurement parameters

RF power (W)		1550
Argon flow rate (l min-1)	Plasma	15.0
	Nebuliser	1.0
	Auxiliary	1.0
Nebulizer	Concentric	
Sampler and skimmer Cone	Ni	
Data acquisition parameters	Peak hopping mode	
	Points per spectral peak Dwell time	1
	(ms)	30
	Sweeps per reading	100
	Replicates	3
Lens settings	Off-axis lens	< 1.5%
Oxide level	CeO+/Ce+	25
Delay time (s)		35
Wash time (s)		

The recovery obtained can further be improved by incorporating step 1 in Table-3 but the time of analysis will increase, thus compromising the objective of this study i.e. time. It may be observed that special care was

Table 3. Modifications Made

S.No	Modifications Made	Advantage
1.	Avoid secondary fusion, i.e. Reprocessing of slag from the first fusion.	Step avoided in view of cost effectiveness.
2.	Used 2000 μg/ml Te-solution in place of 1000 μg/ml followed by the addition of 5ml of 20% $SnCl_2$	Better co-agulation, leading to the formation of bigger particle size.
3.	Used Whatman Grade 41 quantitative filter paper in place of 0.45μm cellulose nitrate membrane filter paper.	Bigger particle size requires use of quantitative filter paper.

Table 4. Recovery verification by WMG-1 and CHRPt+

CRM Used	Elements	Observed value (ng/g)	Certified Values (ng/g)	Recovery (%)
WMG-1	Pt	595	731	81%
	Pd	321	382	84%
	Ir	35	46	76%
	Ru	28	35	80%
	Rh	19	24	80%
CHRPt+	Pt	50793	58000	87%
	Pd	67135	80800	83%
	Ir	4953	6200	79%
	Ru	6728	9200	73%
	Rh	3965	4700	84%

taken to collect PGE's by adding a calculated sulphur content during the initial fusion step thus maximizing PGE's recovery in to the nickel sulfide button. Care was also taken in subsequent steps to avoid losses. For example, in the 2nd step solution of higher concentration of Te was added to increase the coagulant size of the co-precipitated PGE's tellurides so that the slow process of filtration through 0.45 μm can be replaced by a fast Whatman Grade 41 quantitative filter paper.

5.2 Comparative Study

Availability of 99.999% pure Ni-Powder became scare in the market thus compelling us to carry out a study on the process blank values obtained from alternate brands with different assays and textures available in the market. The results are presented in the Table. 5. Figs. 2 and 3. show the mean blank, %RSD and LOQ obtained by using alternate of Ni-Powder. It is conspicuous that the value of %RSD and LOQ obtained from 99.995% purity Ni powder (<150mesh) is comparable with 99.999% pure Ni powder (<150mesh) and hence Ni-Powder of 99.999% purity (<150mesh) can be replaced by 99.995% purity Ni powder (<150mesh). Results obtained from 99.995% purity of Ni granules and nickel carbonate (minimum assay as Ni 40-45%) show that they are not suitable.

6. Conclusion

The proposed economically viable and improvised method for the determination of the PGE's (Except for Os) in geological samples has shown good recovery of the PGE's, thus making it suitable for analytical laboratories tasked with the analysis of a large number of samples on a daily basis with accuracy and precision. The Ni-powder of 99.995% purity has proved to be at par with the Ni-powder of 99.999% purity. Because of high %RSD and high LOQ for Pd with Ni granules and Nickel carbonate (minimum assay as Ni 40-45%) respectively, they have been considered unfit for our purpose. It hence emerges that Ni-powder of 99.995% purity using the modifications described is best suitable for the analysis of large number of samples without compromising on accuracy and precision.

Table 5. Comparison of % RSD and LOQ

Analytical data by using		Ru	Rh	Pd	Ir	Pt
99.999% Ni Powder	MEAN	0.2	0.2	1.0	0.1	0.6
	%RSD	16.4	17.1	19.2	22.4	19.6
	LOQ	0.6	0.4	3.0	0.2	1.8
99.995% Ni Powder	MEAN	0.1	0.2	1.9	0.2	0.5
	%RSD	19.3	8.2	17.7	20.4	16.6
	LOQ	0.3	0.4	5.2	0.5	1.4
99.995% Ni granules	MEAN	5.1	0.7	1.7	2.5	1.1
	%RSD	79.4	58.5	39.6	75.2	67.1
	LOQ	45.8	4.7	8.6	21.3	8.7
Ni carbonate	MEAN	0.9	0.6	51.2	0.4	2.8
	%RSD	35.9	18.0	24.1	18.1	26.7
	LOQ	4.0	1.7	174.6	1.1	10.2

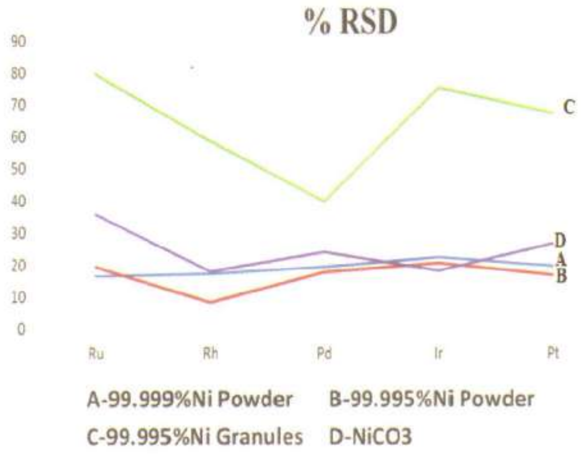

Fig. 2. Graphical representation of %RSD.

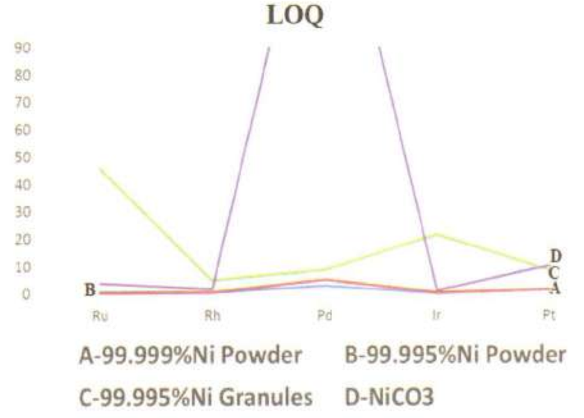

Fig. 3. Graphical representation of LOQ.

References

Ana Maria G. Figueiredo, Claudia P.R. Morcelli (2004), Determination of Platinum-Group Elements in Geological Reference Materials by High Resolution-ICP-MS after Nickel Sulfide Fire-Assay Collection and Te Co-Precipitation, Geostandards and Geoanalytical Research v.28, Issue 2, July, pp.305-310.

Balaram V, Mathur R., Banakar V.K, Hein J.R., Rao C.R.M., Rao T.G, Dasaram B, (2006) Determination of the platinum - group elements (PGE) and gold (Au) in the manganese nodule reference samples by nickel sulfide fire-assay and Te coprecipitation with ICP-MS, Indian Journal of Marine Sciences, v.35(1), pp. 7-16p.

Date A.R., Davis A.E. and Cheung Y.Y. (1987). The potential of fire assay and inductively coupled plasma source-mass spectrometry for the determination of platinum-group elements in geological materials, The Analyst, 112, pp. 1217-1222.

Gowing, C. J. B. and Potts, P. J. (1991) Evaluation of a rapid technique for the determination of precious metals in geological samples based on a selective aqua regia leach. Analyst 116, pp. 773–779.

Henriette Ueckermann (2002). Partitioning of platinum-group elements between metal and sulphide melt in the Cu-S and Ni-S Systems Submitted in partial fulfillment of the requirements for the degree of Master of Science in Applied Mineralogy at the Faculty of Natural Sciences and Engineering University of pretoria. February.

Juvonen, Riitta (1999). Analysis of Gold and the Platinum Group Elements in Geological Samples, Geological Survey of Finland Academic Dissertation.

K.E. Jarvis, J.G. Williams, S.J. Parry, E. Bertalan (1995). Quantitative determination of the platinum-group elements and gold using NiS fire assay with laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), Chemical Geology 124 pp. 37-46.

R. R. Barefoot, (1998). Determination of the precious metals in geological materials by inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. 13, pp. 1077-1084.

W. R. Schoeller (1939) Stannous chloride as a quantitative reagent for selenium and tellurium Analyst, 64, pp. 318-323.

Williamson JE, SavageJA (1965) The determination of osmiridium in Witwatersrand ores. Jour. of the S. Africa Institute of Mining and Metallurgy, pp. 343—356.

Received on 14-09-16; Revised Ms accepted on 04-03-17