

DETERMINATION OF PLATINUM GROUP ELEMENTS IN TERRESTRIAL ROCKS USING NICKEL SULFIDE FIRE ASSAY ISOTOPE DILUTION ICP-MS

(Penentuan Unsur Kumpulan Platinum Dalam Batuan Menggunakan
Pencairan Isotop ICP-MS Assay Api Nikel Sulfida)

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Abstract

Platinum group elements (PGE: Ru, Rh, Pd, Os, Ir, Pt) are highly siderophile elements (HSE) and their abundances in terrestrial rocks are low (~ ppb). This group of elements is important for understanding of geochemical processes, essential in mineral exploration, environmental studies, and identification of impact craters. Determination of PGE is very challenging and a reliable analytical technique is required to obtain high quality data. This study aims to utilize the fire assay isotope dilution inductively coupled plasma mass spectrometry (ICP-MS) for the determination of platinum group elements in terrestrial rock samples (WPR-1, WMG-1, and UMT-1). The nickel sulfide fire assay is applied to preconcentrate PGE from terrestrial rocks. All samples (about 0.2 – 0.5 g) were spiked with enriched isotopes (except Rh) prior to fire assay procedure in order to achieve isotope equilibrium. The NiS beads obtained were dissolved in HCl and the residue containing PGE was then dissolved prior to ICP-MS measurement. Isotopic ratios of PGE were measured and concentrations were calculated using the isotope dilution equation. The recoveries are in the range of 60 – 85% for all PGE except Os, which is prone not to be quantitatively collected due to the formation of OsO₄. However, the loss of analytes does not affect the accuracy of the data obtained once the equilibrium between elements in samples and spikes is established. Actually, an excellent agreement between our data and literature values was confirmed for Os data. The measurement of PGE using ICP-MS requires correction from monoatomic and polyatomic ions having the same mass-to-charge ratio as those of analytes of interest. Instrument memory effect is evident in Os measurements and flushing with HCl and TMSO were adequate to reduce the memory effect. Low sample blanks (< 12 pg/g) and detection limits (< 15 pg/g) were achieved. In conclusion, the present method is able to determine PGE with reasonable accuracy despite of small sample size and is very favorable for application to terrestrial samples.

Keywords: platinum group elements, terrestrial rocks, fire assay, isotope dilution, ICP-MS

Abstrak

Unsur-unsur kumpulan Platinum (PGE: Ru, Rh, Pd, Os, Ir, Pt) adalah unsur-unsur yang cenderung untuk berkumpul dalam logam dan kepekatan unsur-unsur ini dalam batuan adalah rendah (~ ppb). Unsur-unsur ini adalah penting dalam kajian proses geokimia, penerokaan mineral, kajian alam sekitar, dan mengenalpasti kawah impak. Penentuan PGE adalah mencabar dan teknik analisis yang baik diperlukan untuk mendapatkan keputusan yang bermutu. Kajian ini adalah bertujuan untuk menggunakan teknik assay api isotop pencairan dengan plasma gandingan aruhan spectrometer jisim (ICP-MS) dalam penentuan PGE dalam sampel batuan (WPR-1, WMG-1, and UMT-1). Kaedah assay api adalah digunakan untuk pemekatan PGE dari batuan. Semua sampel (kira-kira 0.2 – 0.5 g) ditambah dengan isotop diperkaya (kecuali Rh) sebelum menjalani kaedah assay api supaya keseimbangan isotop boleh dicapai. Manik NiS yang diperolehi itu dicairkan dalam HCl dan mendakan yang mengandungi PGE itu dilarutkan sebelum penentuan dengan ICP-MS. Nisbah isotop PGE diukur dan kepekatan dikira menggunakan persamaan isotop pencairan. Julat pemerolehan semula adalah 60 – 85% untuk PGE kecuali Os disebabkan oleh pembentukan OsO₄ yang susah untuk dikumpul secara kuantitatif. Akan tetapi, kehilangan analit tidak menjejaskan kejutuan keputusan yang diperolehi selepas keseimbangan isotop dalam sampel dicapai. Sebenarnya, keputusan Os yang diperolehi itu adalah bersetuju dengan nilai dalam penerbitan. Pengukuran PGE menggunakan ICP-MS memerlukan pembedaan dari segi ion monoatomik dan poliatomik yang mempunyai nisbah jisim-kepada-cah yang serupa dengan analit. Kesan ingatan alat adalah

ketara dalam pengukuran Os dan pencucian dengan HCl dan TMSC adalah memadai untuk mengurangkan kesan ingatan. Sample kosong (< 12 pg/g) dan had pengesanan (< 15 pg/g) yang rendah telah dicapai. Dalam kesimpulan, kaedah ini dapat mengukur PGE dengan kejituan yang berpatutan untuk size sampel yang kecil dan adalah sesuai untuk digunakan untuk sampel batuan.

Kata kunci: unsur kumpulan platinum, batuan, assay api, pencairan isotop, ICP-MS

Introduction

Platinum group elements (PGE: Ru, Rh, Pd, Os, Ir, Pt) are noble metals with low abundances in Earth's crust [1]. These elements are useful in geochemical studies such as discussion on planetesimal accretion, late veneer hypothesis, and identification of impactors. Determinations of PGE are rather challenging and do require sensitive analytical methods to obtain reliable data. Preconcentration/decomposition techniques are necessary to separate PGE from their matrices before measurement could be performed. For geological samples, nickel sulfide fire assay is a suitable method for PGE preconcentration in order to provide good sensitivity for measurement. The advantage of this method is that all PGE are collected into nickel sulfide beads.

Isotope dilution (ID) is a method suitable to obtain reliable data for elemental analysis except for monoisotopic elements. Unknown sample is added with enriched isotope of an element and quantitative determination of elemental concentration is based on the measurement of isotopic ratio of element in a sample [2]. The use of isotope dilution technique is able to eliminate the problem of recovery after sample processing and results are precise and accurate [3]. Generally, determinations of isotopic ratios are performed using mass spectrometry. This study aims to utilize the fire assay isotope dilution inductively coupled plasma mass spectrometry (ICP-MS) for the determination of platinum group elements in terrestrial rock samples (WPR-1, WMG-1, and UMT-1).

Experimental

In this experiment three terrestrial rock samples namely UMT-1, WMG-1 and WPR-1 were analyzed and are listed below:

1. UMT-1 is the ultramafic ore tailings containing high concentrations of PGEs.
2. WMG-1 is the mineralized gabbro from Wellgreen Complex, Yukon Territory, Canada.
3. WPR-1 is the altered peridotite.

These samples were obtained from CANMET (Canada) with certified values for Ru, Rh, Pd, Ir and Pt. In addition, proposed values were given to Os while Re is not reported for these standard reference materials.

In this study, quantifications of PGE in rock samples were performed using isotope dilution method except for Rh. Solutions containing enriched isotopes of PGE as indicated in Table 1 were used. All chemicals used in this study were of analytical grade. Fire assay requires mixture of sodium carbonate as basic reagent while silica and sodium tetraborate as acidic reagent. Nickel and sulfur are added to the flux in a 5:3 ratio, which act as collector for PGE. Little amount of flour is added to provide a reducing condition. Figure 1 shows the procedure for nickel sulfide fire assay for PGE determinations. About 0.2 – 0.5 g sample were used and blanks were also included in this procedure. The sample is mixed to the flux in a crucible and subjected to heating in a furnace to about 850°C for about 20 minutes and then 1000°C for about 20 minutes. After that, the crucible was taken out from the furnace and allows it to cool. Once the crucible has cooled, nickel sulfide beads were obtained from the slag by cracking the crucible. The nickel sulfide beads were ground using a nickel mortar. Then, the powder was transferred to a 100 ml beaker and adds 30 ml deionized (DI) water and 30 ml 12M HCl. Heat the solution on a hotplate for a few hours until no effervescent. After the solution had cooled, pass the solution through a vacuum-filter fitted with cellulose filter disc. Collect the PGE containing residue and dilute in 1.5 ml 12M HCl and 1.5 ml H₂O₂ (30%). Heat the solution to about 100°C until no effervescent. Once the residue has dissolved, transfer the solution and internal standards (In, Tl, Bi) were added to make up to 15 ml of measurement solution in 10% HCl.

Ni-S Fire Assay (PGE)

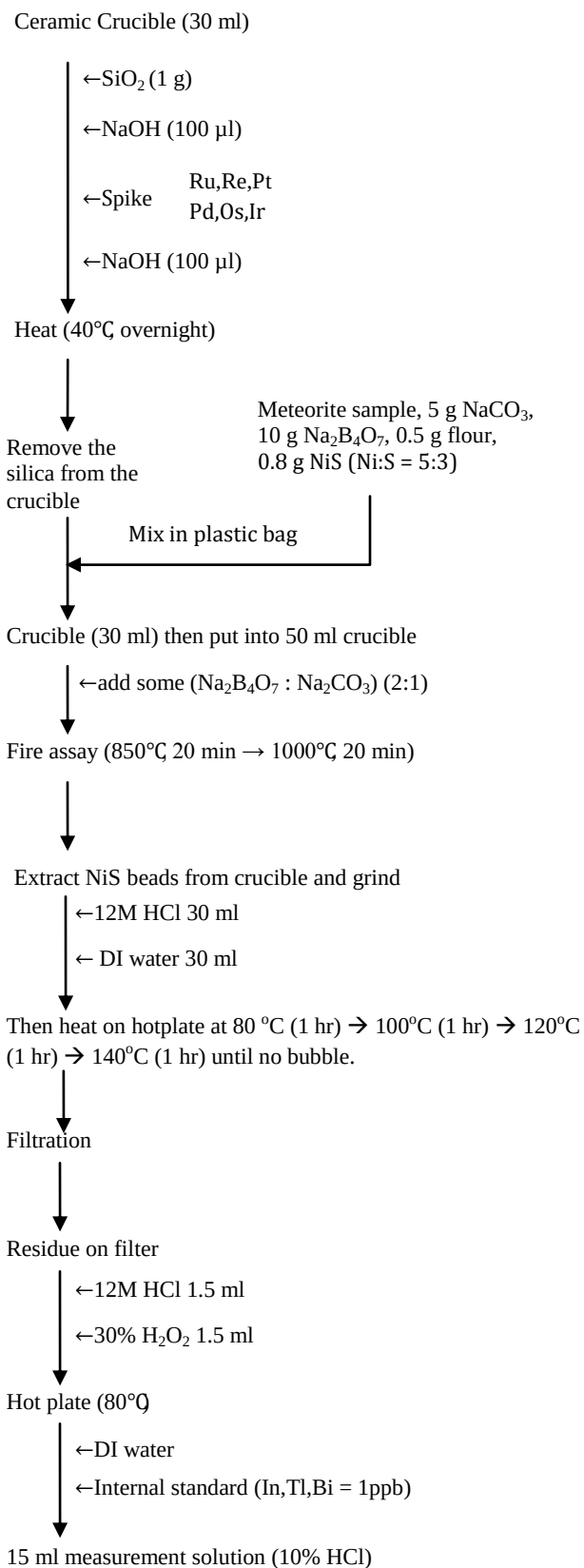


Figure 1: Fire assay procedure for PGE preconcentration.

Table 1: Enriched isotopes for PGE determinations rock samples.

Enriched Isotopes	Natural abundances (%)	Spike abundances (%)
⁹⁹ Ru	12.76	97.69
¹⁰⁵ Pd	22.33	97.00
¹⁸⁹ Os	16.15	95.26
¹⁹¹ Ir	37.30	98.23
¹⁹⁶ Pt	25.24	94.57

The VG PlasmaQuad 3 (Fision Instruments, UK) was used to determine the PGE isotopes in the solution samples. The instrument was optimized by using a monitoring solution containing ¹¹⁵In (10 ppb) to obtain count rates of about 7 to 10 × 10⁵ cps. All sample solutions were added with 1 ppb of ¹¹⁵In, ²⁰⁵Tl and ²⁰⁹Bi as internal standards. Detail operating condition for PGE determination using ICP-MS is presented in Table 2. Scanning for each isotope was done using peak jump mode and repeated five times for each sample. Count rates obtained for these ¹¹⁵In, ²⁰⁵Tl and ²⁰⁹Bi are about 3 – 4 × 10⁴ cps. About 5 to 6 samples were measured in each run to avoid instrument instability due to prolong measuring time.

Table 2: ICP-MS operating condition during PGE measurement.

Plasma incident power	1360 W	Detection mode	Peak jumping
Cooling gas	14 l/min	Sweeps	250
Auxiliary gas	1.25 l/min	Repeat integration	5
Nebulizer gas	0.90 l/min	Dwell time per isotope	1000 μs
Points per peak	5	Acquisition time	50 s

Results and Discussion

ICP-MS measurement of PGE

For isotope dilution method, the following isotopic ratios were determined: ⁹⁹Ru/¹⁰⁰Ru, ⁹⁹Ru/¹⁰¹Ru, ⁹⁹Ru/¹⁰²Ru, ¹⁰⁵Pd/¹⁰⁶Pd, ¹⁰⁵Pd/¹⁰⁸Pd, ¹⁸⁹Os/¹⁸⁸Os, ¹⁸⁹Os/¹⁹⁰Os, ¹⁹¹Ir/¹⁹³Ir, ¹⁹⁴Pt/¹⁹⁶Pt, and ¹⁹⁵Pt/¹⁹⁶Pt. For ¹⁰³Rh, external calibration with internal standards (In and Tl) were used for quantification. Low mass PGE isotopes are normalized to ¹¹⁵In while high mass PGE are normalized to ²⁰⁵Tl. Standard solutions in the range of 0.1 – 15 ppb were used for external calibration for all PGE and to monitor the recovery of each element by calculating the difference between isotope dilution data.

Instrument mass fractionation during measurement was monitor using isotopic ratios of standard solutions of low and high concentrations as presented in Table 3. The deviations of isotopic ratios between standard solutions and literature values were ranged from 0.3% (¹⁹¹Ir/¹⁹³Ir) to 6.3% (⁹⁹Ru/¹⁰²Ru). The measured mean ratios were independent of concentrations with relative standard deviations between 0.6% and 2.4%, which correspond to the linearity of ICP-MS at large concentration range. At low concentrations (0.10 ppb and 0.15 ppb), data show slightly more variable due to random error at low count rates.

Table 3: Measured isotope ratios in standard solutions containing PGE. Literature values were from [4].

Concentration	$^{99}\text{Ru}/^{100}\text{Ru}$	$^{99}\text{Ru}/^{101}\text{Ru}$	$^{99}\text{Ru}/^{102}\text{Ru}$	$^{105}\text{Pd}/^{106}\text{Pd}$	$^{105}\text{Pd}/^{108}\text{Pd}$
0.10 ppb	1.003 ± 0.090	0.713 ± 0.041	0.378 ± 0.023	0.828 ± 0.034	0.805 ± 0.024
0.15 ppb	1.002 ± 0.046	0.716 ± 0.028	0.384 ± 0.012	0.804 ± 0.020	0.792 ± 0.022
10 ppb	0.992 ± 0.007	0.705 ± 0.002	0.375 ± 0.002	0.807 ± 0.004	0.801 ± 0.002
15 ppb	0.990 ± 0.006	0.701 ± 0.004	0.372 ± 0.003	0.806 ± 0.002	0.799 ± 0.002
Average	0.997 ± 0.006	0.709 ± 0.006	0.377 ± 0.004	0.811 ± 0.010	0.799 ± 0.005
Literature	1.013	0.748	0.404	0.817	0.844
Average/Literature	0.984	0.948	0.933	0.993	0.947

Concentration	$^{189}\text{Os}/^{188}\text{Os}$	$^{189}\text{Os}/^{190}\text{Os}$	$^{191}\text{Ir}/^{193}\text{Ir}$	$^{194}\text{Pt}/^{196}\text{Pt}$	$^{195}\text{Pt}/^{196}\text{Pt}$
0.10 ppb	1.199 ± 0.074	0.606 ± 0.019	0.608 ± 0.017	1.314 ± 0.074	1.380 ± 0.044
0.15 ppb	1.247 ± 0.028	0.617 ± 0.015	0.595 ± 0.012	1.315 ± 0.052	1.317 ± 0.058
10 ppb	1.237 ± 0.007	0.607 ± 0.003	0.594 ± 0.003	1.251 ± 0.005	1.318 ± 0.007
15 ppb	1.234 ± 0.002	0.610 ± 0.001	0.590 ± 0.002	1.256 ± 0.002	1.310 ± 0.005
Average	1.229 ± 0.018	0.610 ± 0.004	0.597 ± 0.007	1.284 ± 0.031	1.331 ± 0.028
Literature	1.220	0.615	0.595	1.306	1.340
Average/Literature	1.007	0.992	1.003	0.983	0.993

Interference in PGE measurements

Interferences from monoatomic and polyatomic ions were monitored using single standard solution of Cd, Cu, Hg, Hf, Mo, Ni, Ta, W, Zn and Zr during sample analysis. Corrections of interferences were performed for all samples and blanks using common spreadsheet program. The measurement of ^{100}Ru requires correction for ^{100}Mo in the range of 20 – 60%, ^{101}Ru requires correction of 1 – 33%, and ^{102}Ru requires correction of 1 – 48%. For ^{106}Pd , ^{108}Pd , ^{190}Os and ^{198}Pt , their interference corrections are less than 10%.

Instrument memory effect

During the course of measurements, background counts were monitored by measuring blank solution 10% HCl before each sample. Generally, background counts for lower mass PGE (^{99}Ru to ^{108}Pd) were below 50 cps while at higher mass PGE (^{188}Os to ^{196}Pt) were below 80 cps. Instrument memory effect is evident for Os especially after measurement of standard solutions of high concentrations (10 – 15 ppb). For sample solutions, Os count rates were generally below 5000 cps in most cases and memory effects were reduced to background level of 30 – 50 cps after about 15 – 20 minutes washing using dilute TMS followed by 5% HCl. For other PGE no memory effects were observed.

Procedure blank and detection limits

A procedure blank was included for each batch of analysis for blank correction. For procedure blank, PGE concentrations are given as pg/g assuming 1:1 dilution factor. Data from the procedure blank showed that contributions of PGE from chemical reagents were in pg/g order (Table 4). Platinum and Pd show higher

concentrations than other PGE elements in procedure blanks measured in this study. Similar observations were reported by Ravizza and Pyle [5] that such variability may be caused by contamination. In most cases, contribution from blank is below 1%.

Detection limits were estimated based on three times standard deviation from previous four runs. Platinum and Pd show higher detection limits than other member of the PGE. Similar observation was reported by Ravizza and Pyle [5] that Pt data are more variable possibly due to contamination. From the low procedure blank and detection limits, the current procedure is able to cater for the analysis of rock samples in this study.

Table 4: NiS fire assay procedure blank (concentrations in pg/g).
Detection limit (DL) is 3σ of blank.

Run	Os	Ir	Ru	Pt	Rh	Pd
Mean	2.1	1.7	4.3	9.6	2.6	11.8
$\pm$	1.2	0.7	1.2	4.6	2.6	4.7
DL	3.7	2.2	3.7	13.7	7.9	14.0

Determinations of PGE in UMT-1, WMG-1 and WPR-1

Results from the measurement of the rock samples are presented in Tables 5a to 5c. Most of the results were found to be within error of the certified values [6] of these rock samples. For Os, our data were in good agreement with non-certified values. In the case of Pt, uncertainty for UMT-1 was about 29%, which is higher than those of WMG-1 and WPR-1. Variation of Pt value in UMT-1 maybe due to heterogeneity or ‘nugget effect’ commonly found in PGE analysis. For other PGEs, uncertainties are less than 5% in WMG-1 and WPR-1 whereas uncertainties in UMT-1 are about 12% or less. The use of isotope dilution gives good reproducibility for PGE analysis even though the sample size is less than 1 g in this study.

The recovery (calculated using data of external calibration and isotope dilution) of PGE using fire assay method shows that more than 50 – 80% of the PGE are collected into NiS bead except for Os. The volatile OsO_4 escapes during the dilution of NiS bead causing the recovery of Os to be lower than 10%. The recovery of Pt in WPR-1 is rather low (14%) which may be due to loss of NiS beads during crushing or filtration. However, the use of isotope dilution is able to give good results disregard of the recovery of PGE in NiS beads. Isotope ratios are not affected by loss of analytes during NiS beads digestion. For the determination of Rh, correction of recovery was done by taking average between Ru and Pd due to their similar masses.

Table 5a: PGE concentrations in UMT-1 (n = 6)

Elements	Measured	$\pm$	Certified	$\pm$	Recovery (%)
Os	8.89	1.07	8		6.9
Ir	10.1	1.2	8.8	0.6	61
Ru	10.9	0.5	10.9	1.5	73
Rh	10.4	0.8	9.5	1.1	69
Pt	129	38	129	5	60
Pd	111	5	106	3	65

Table 5b: PGE concentrations in WMG-1 (n = 3)

Elements	Measured	±	Certified	±	Recovery (%)
Os	26.8	0.6	24		5.0
Ir	53.4	0.9	46	4	65
Ru	30.7	0.7	35	5	70
Rh	26.1	0.7	26	2	67
Pt	726	98	731	36	63
Pd	392	9	382	11	64

Table 5c: PGE concentrations in WPR-1 (n = 3)

Elements	Measured	±	Certified	±	Recovery (%)
Os	16.6	0.6	13		7.2
Ir	16.7	0.4	13.5	1.8	83
Ru	23.6	0.7	22	4	56
Rh	11.8	2.2	13.4	0.9	53
Pt	322	49	285	11	14
Pd	251	13	235	9	51

Conclusion

This study showed that the use of NiS fire assay with isotope dilution ICP-MS is very suitable for analysis of PGE in geological sample. Good accuracy and precision could be achieved using this method even for small sample size (0.2 – 0.5 g). Besides, the low procedure blanks of this method are favorable for various geological samples with low PGE contents.

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