

Determination of Pt, Pd, Ru and Ir in geological samples by ID-ICP-MS using sodium peroxide fusion and Te co-precipitation

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A method is proposed for the determination of Pt, Pd, Ru and Ir in geological samples by isotope dilution-inductively coupled plasma mass spectrometry (ICP-MS). Mono-isotopic elements Rh and Au are determined by external calibration using Lu as the internal standard. Sodium peroxide fusion in corundum crucibles (instead of glassy carbon or zirconium crucibles) is used to decompose the samples. After dissolution of the fused cake in water, the solution is spiked with enriched stable isotopes of Pt, Pd, Ru and Ir, and then acidified with HCl. This solution is then evaporated to dryness promoting the formation of anhydrous silicate from colloidal material. PGEs and Au are then pre-concentrated by Te co-precipitation.

The reagents HCl and SnCl₂ are purified by Te co-precipitation. PGE blank levels are thus only derived from the Na₂O₂ which has PGE concentrations of <0.02 ng/g. Lutetium is added as the internal standard to correct for instrument drift and matrix suppression effects for the determination of the mono-isotopic elements. Method detection limits range from 0.02 to 0.3 ng/g. The results obtained for the CCRMP (CANMET, Ottawa, Canada) certified reference materials WGB-1 (gabbro), TDB-1 (diabase), UMT-1 (ultramafic ore tailings), WPR-1 (altered peridotite), WMG-1 (mineralized gabbro), and WMS-1 (massive sulphide) are in good agreement with certified values.

INTRODUCTION

Accurate determination of the platinum group elements and gold (PGEs and Au) is essential for geochemical and cosmochemical studies. These metals have significant economic values and can also provide important information about the origin, fractionation and transportation of PGEs during geological processes, for example, the Ir anomaly at the Cretaceous-Tertiary boundary (Evans *et al.*, 1993). The determination of PGEs in geological materials is difficult because of their low crustal abundance (with background levels of a few ng/g or less) and heterogeneous distributions and the complexity of sample preparation procedures. However, because of high sensitivity and capability of measure isotope ratios, induc-

tively coupled plasma mass spectrometry (ICP-MS) has been used successfully for the determination of PGEs and Au in geological materials (see reviews in Barefoot, 1998 and Reddi and Rao, 1999; and references therein).

A variety of techniques have been employed for sample decomposition and pre-concentration of PGEs prior to the ICP-MS measurement. Sodium peroxide fusion followed by Te co-precipitation is a common technology (Gowing and Potts, 1991; Enzweiler *et al.*, 1995; Totland *et al.*, 1995). The sodium peroxide fusion has usually been carried out in glassy carbon crucibles (Enzweiler *et al.*, 1995) or in zirconium crucibles (Evans *et al.*, 1993; Enzweiler and Potts, 1995; Yi and Masuda, 1996). However, with the usage of these container, Zr and Hf can be introduced into the solutions and

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interfere with the determination of PGEs during ICP-MS measurement. In these methods, the silicate colloid is produced as a byproduct during the sample preparation and was removed in previous studies using a Millipore filtration apparatus, but takes 4–5 hours to complete when a 2 gram sample is used. Clearly, this feature is not amenable to the analysis of large numbers of samples.

We have developed a method for the determination of PGEs and Au using a sodium peroxide fusion to decompose the sample in a corundum crucible. Isotope dilution (ID)-ICP-MS is used for the determination of Pt, Pd, Ru and Ir, whereas the mono-isotopic elements, Rh and Au, are determined by external calibration using Lu as an internal standard. Os is not measured as its analysis requires different techniques due to its volatile nature (Sun *et al.*, 2001). In this paper, we describe the detailed procedure that reduces PGE blank levels, enabling trace analyses of PGE and Au in geological materials.

ANALYTICAL METHOD

Instrumentation and reagents

A Finnigan MAT ELEMENT magnetic sector ICP-MS has been used in this study. Instrument operating parameters are given in Table 1. Analytical reagent-grade Na_2O_2 is used and is found to contain less than 0.02 ng/g PGEs. Spike solutions of stable enriched isotopes ^{101}Ru , ^{105}Pd , ^{193}Ir , ^{194}Pt (US Services Inc., Oxbow, N.J.) are prepared from metal. Platinum, Pd and Ru are dissolved in aqua regia at room temperature and Ir is prepared by fusion with sodium peroxide. 1000 $\mu\text{g/ml}$ Au and Rh stock solutions (Spex Industries, Edison, N.J., USA) are used and diluted as needed.

Tellurium solution (1 mg/ml) is prepared by dissolving 0.25 g of pure tellurium powder in 10 ml of aqua regia followed by evaporation of the solution to dryness on a water-bath. The residue is dissolved in 1 ml of concentrated HCl and evaporated to dryness (repeated twice), and then dissolved in 1M HCl and diluted to 250 ml with distilled water. Analytical reagent-grade of HCl is purified by Te co-precipitation. SnCl_2 solution

Table 1. Instrumental operating conditions

Parameter	Value
Focus offset	49.78%
Sample time	0.002 ms
Cool gas	13.50 L/min
Aux gas	1.30 L/min
Sample gas	0.720 L/min
Extraction	-2000.0 V
Plasma power	1290 W
Focus	-895.4 V
Resolution	300
Run	4
Pass	5
Points per peak	10

Run: number of passes; Pass: number of scans.

(20%, w/v) is prepared by dissolving 50 g of SnCl_2 in 250 ml of 6M HCl. This solution is heated to boiling and then purified by Te co-precipitation.

As an alternative to quartz-distilled HCl, Te co-precipitation is an effective way to purify large quantities of HCl. The procedure used is the same as that for sample pre-concentration. We also find that the SnCl_2 contains up to 5 ng/g total PGEs. Tellurium co-precipitation is therefore used to purify SnCl_2 by dissolving 50 g of the salt in 250 ml of 6M HCl. After boiling the solution, 6 mg of Te is added while vigorously stirring the solution. This is followed by a second addition of 6 mg of Te solution. After the Te precipitate coagulates, the solution is filtered using a Millipore membrane filter. Table 2 gives the blank of the PGEs in the stock and purified HCl and SnCl_2 .

Sample decomposition and pre-concentration

Two grams of each powdered sample are accurately weighed and placed in a 30 ml corundum crucible. To each sample 8 g of Na_2O_2 is added and thoroughly mixed. The crucible is then transferred into a cold furnace. The temperature of the furnace is slowly increased to 720°C and stabilized at that temperature for 30 minutes. The crucible is removed from the furnace, then placed into a 150 ml beaker after cooling. The fusion cake in the crucible was dissolved in 40 ml of warm de-

Table 2. Comparison of PGEs and Au concentrations (ng/ml) in stock and purified HCl and SnCl₂ solutions

Element	HCl stock	HCl purified	Element	SnCl ₂ stock	SnCl ₂ purified
Pt	0.11	<0.005	Pt	0.58	<0.005
Pd	0.10	<0.005	Pd	0.54	<0.005
Rh	0.02	<0.005	Rh	0.15	<0.005
Ru	0.03	<0.005	Ru	0.52	<0.005
Ir	0.01	<0.005	Ir	0.08	<0.005
Au	0.008	<0.005	Au	0.11	<0.005

ionized water. The spike solution containing Pt, Pd, Ru and Ir is added to the alkaline sample solution. The mass of spike added to sample should be about equal to the estimated mass of the analyte in the sample itself. The crucible is then removed from the beaker and rinsed with deionized water and HCl. About 45 ml of concentrated HCl is added to dissolve the hydroxides and to acidify the solution, which is then evaporated to near dryness in a water bath. The beaker is transferred to a hot plate where the sample is gently heated to dryness. The silicate colloid is now dehydrated. 15 ml of 12N HCl and 40 ml H₂O were added and the mixture was heated to about 70°C, periodically stirring the solution with a glass rod. After cooling, the solution is filtered to remove the silica precipitate. Water is added to a volume of about 100 ml and the solution heated to boiling. To this solution is added 2.5 ml solution containing 2.5 mg of Te. After thorough mixing, SnCl₂ solution is added drop-wise until a black precipitate appears. Then an additional 5 ml of SnCl₂ is added. The solution is boiled until the Te precipitate coagulates, followed by a second addition of 2.5 mg of Te with continuous heating until the Te precipitate again coagulates. The solution is then filtered using a Millipore membrane filter (type-HA, 0.45 μm). The precipitate is rinsed with seven 40 ml aliquots of 2M HCl in order to remove residual Sn solution. The membrane is returned to the original beaker using plastic tweezers and is dissolved by adding 20% aqua regia. At this point, 50 ng of Lu in solution is added as an internal standard for the determination of mono-isotopic elements Rh and Au. The solution is evaporated on a hot plate

Table 3. Effect of acidity on the recovery (%) of PGEs and Au by Te co-precipitation

C _{HCl}	1	2	4
Pt	95.5	98.5	93.3
Pd	98.8	98.9	97.9
Rh	96.5	97.4	96.3
Ru	96.5	95.9	102
Ir	85.5	90.4	82.2
Au	96.3	96.9	98.7

C_{HCl}: Concentration of HCl (mol).

to about 1 ml, and then transferred to a 15 ml centrifuge tube and diluted with water to about 5 ml. Blanks are prepared using the same procedure as the sample. The elements, Pt, Pd, Ru and Ir, are determined by isotope dilution, whereas Rh and Au are determined by external calibration using Lu as the internal standard.

DATA REDUCTION AND ANALYTICAL RESULTS

Effect of acidity on the recovery of PGEs

We carried out a study to evaluate the effect of acidity on the recovery of PGEs using Te co-precipitation. 10 ng of Pt, Pd, Rh, Ru, Ir and Au were added to 90 ml of water in a 125 ml beaker. Using this solution and sufficient HCl, three solutions were prepared to provide the acidities of 1, 2, 4 M, respectively. Using the procedure described above to pre-concentrate the PGEs, the recovery of these metals was determined and is shown in Table 3. These data show that using 1M HCl, the recoveries of Rh and Au are 96.5% and 96.3% and

Table 4. Analytical results (ng/g) of reference materials WPR-1 and WMG-1

Sample	WPR-1	WPR-1	WPR-1	WMG-1	WMG-1	WMG-1
Elements	B	A	Certified	B	A	Certified
Pt	271	276	285	720	706	731
Pd	243	224	235	393	407	382
Ru	24.5	23.2	22	34.2	37.8	35
Ir	14.1	14.7	13.5	42.8	43.7	46

B: spiked before fusion; A: spiked after fusion.

that using more acidic solutions does not increase the recovery significantly. This high recovery is especially important because Rh and Au are mono-isotopic elements and must be calculated using external standard. Although the recovery of the other PGEs is also high (except Ir), their recovery efficiency is not important because these elements can be calculated from the isotope dilution calibration. Nevertheless, it is essential to have a high recovery for all elements because this will directly effect the limit of quantification of the overall procedure.

Isotopic equilibration between sample and spike

A spike can be added to the sample either before or after fusion. We have adopted a procedure to add the spikes after fusion because isotope equilibration can still be achieved. The equilibration results from the preparation of the spike using Na₂O₂ fusion and aqua regia dissolution. The spike is diluted in 10% HNO₃, so that it remains its highest oxidation states and can easily equilibrate with the sample. However, equilibration can not be achieved if the spike solution is diluted from the stock solution (50 µg/ml, 10% HNO₃) using HCl.

Comparative results for WPR-1 and WMG-1 are given in Table 4 which shows that there is obviously good agreement between two procedures of sample preparation, i.e., addition of the spike after fusion also provide for the isotope equilibration.

Internal standard and data calculation

For the determination of the mono-isotope elements Rh and Au, an internal standard is needed

to correct matrix effects (ICP-MS signal suppression) and instrument drift. The internal standard was added after the Te co-precipitation step. This is because there is no element which could be used as an internal standard for PGEs, which would also be co-precipitated along with these elements. Having generally the lowest concentration in the REE series, Lu also cannot be co-precipitated with Te, with an atomic mass (175) between that of Rh and Au. This means that the only Lu present in the PGE-containing solution will be that deliberately added as an internal standard. Lutetium also behaves similarly to Rh and Au with changes in plasma conditions and sample matrix.

For the isotope dilution measurements, the concentrations of Pt, Pd, Ru, and Ir can be calculated by means of the formula:

$$C = \frac{MK(B_i - B_k \cdot R)}{W(A_i \cdot R - A_k)}$$

where C is the analyte concentration (ng/g); M is the mass of the stable isotope spike (ng); B_i is the abundance of the reference isotope in the spike; B_k is the abundance of the spiked isotope; A_i is the natural abundance of the spiked isotope; A_k is the natural abundance of the reference isotope; K is ratio of the natural and spike atomic weights; W is the sample weight (g) and R is the measured reference/spike isotope ratio after spike addition. Table 5 gives the abundance of isotope in the spike for the calculation of isotope dilution.

For the mono-isotopic elements, working standard solutions were prepared as follows:

Table 5. Abundances of isotope in the spike

Isotope	Abundance (%)
¹⁹⁵ Pt	3.78
¹⁹⁴ Pt	95.06
¹⁰⁶ Pd	2.35
¹⁰⁵ Pd	96.58
⁹⁹ Ru	0.24
¹⁰¹ Ru	96.03
¹⁹¹ Ir	0.67
¹⁹³ Ir	99.33

1) Rh, Au 100 ng, Lu 500 ng in 50 ml; 2) Rh, Au 1000 ng, Lu 500 ng in 50 ml; 3) Rh, Au 5000 ng, Lu 500 ng in 50 ml. The concentrations of mono-isotopic elements Rh and Au are calculated by normal external calibration except the concentration unit of Rh, Au and Lu are in ng instead of ng/ml. It is very convenient for both the experimental procedure and subsequent calculation, because the final solution volume will not affect the results. The concentration of Rh and Au can be calculated by means of the formula:

$$C = \frac{I_{Sa}}{W} \frac{C_{St}}{I_{St}} \frac{I_{Stl}}{I_{Sal}} \frac{C_{Sal}}{C_{Stl}}$$

where C is the analyte concentration (ng/g); I_{Sa} is the signal intensity for the sample solution; C_{St} is the concentration of the standard solution (ng); I_{Stl} is the signal intensity for internal standard in the calibration standard solution; C_{Sal} is the concentration of internal standard in the sample solution (ng); I_{St} is the signal intensity for the standard solution; I_{Sal} is the signal intensity for the internal standard in the sample solution; C_{Stl} is the concentration of the internal standard in the standard solution (ng) and W is the sample weight (g).

Polyatomic ion interference corrections

The main interferences for the PGEs determined by ICP-MS arise from the effects of the $^{90}\text{Zr}^{16}\text{O}^+$ ion with $^{106}\text{Pd}^+$, $^{177}\text{Hf}^{16}\text{O}^+$ ion with $^{193}\text{Ir}^+$, $^{178}\text{Hf}^{16}\text{O}^+$ ion with $^{194}\text{Pt}^+$, and the $^{179}\text{Hf}^{16}\text{O}^+$ ion with $^{195}\text{Pt}^+$. In actual fact, the interference of ZrO^+

and HfO^+ from the sample is very low, even though the corundum crucibles used here contain high concentrations of Zr, used in the manufacturing process to protect the crucible against cracking when heated. The interference of Hf from both the sample and crucible are very low. As a test for interferences arising from Zr and Hf, we added 5 mg each of Zr and Hf to 100 ml of 1M HCl. When co-precipitated with Te, the final solution contained 2 μg of Zr and Hf. We believe that the residual Zr and Hf might not be rinsed from the membrane filter or is retained on that part of the filter in contact with the glass components of the filtering apparatus. In any event, it is necessary to correct for interferences from Zr and Hf oxides using the approach described by Parent *et al.* (1997):

$$I = I_M - (I_E R)$$

where I is the corrected ICP-MS count rate, I_M is the Pd or Pt count rate obtained for the sample solution, I_E is the count rate for Zr or Hf measured in the sample solution and R is the ZrO^+/Zr^+ or HfO^+/Hf^+ signal ratio.

Detection limits and precision

Detection limits for the PGEs can be calculated as the analyte concentration equivalent to three times the standard deviation of the ion counts obtained for the reagent blank. The precision of PGE determinations is calculated as the percent RSD obtained from five separate determinations of PGE concentration in UMT-1 reference materials. Table 6 shows that the PGEs can be determined at levels from 0.02 to 0.2 ng/g with a precision of from 1.5 to 6.5% RSD. Gold can be determined at concentration of 0.23 ng/g with a precision of 2.5% RSD.

Analysis of reference materials

Analytical results are presented in Table 6 for six CCRMP reference materials using the method outlined above. These reference materials are WGB-1 (gabbro), TDB-1 (diabase), UMT-1 (ultramafic ore tailings), WPR-1 (altered

Table 6. Analytical results (ng/g) of CCRMP certified reference materials

Samples		WGB-1	TDB-1	UMT-1	WPR-1	WMG-1	WMS-1	DL
Pt	Found \pm S.D.	6.5 \pm 0.5	6.3 \pm 0.4	121 \pm 7	294 \pm 11	751 \pm 15	1805 \pm 85	0.23
	Certified	6.1	5.8	128	285	731	1741	
Pd	Found \pm S.D.	14.5 \pm 0.9	23.5 \pm 1.5	112 \pm 8	242 \pm 8	395 \pm 10	1216 \pm 68	0.11
	Certified	13.9	22.4	106	235	382	1185	
Rh	Found \pm S.D.	0.34 \pm 0.04	0.43 \pm 0.04	9.1 \pm 0.6	12.8 \pm 0.9	25.1 \pm 1.5	232 \pm 11	0.024
	Certified	0.32	/	9.5	13.4	26	225	
Ru	Found \pm S.D.	0.28 \pm 0.04	0.44 \pm 0.05	10.2 \pm 0.9	20.6 \pm 2.1	36.5 \pm 2.8	105 \pm 5	0.045
	Certified	0.3	/	10.9	22	35	99	
Ir	Found \pm S.D.	0.35 \pm 0.04	0.49 \pm 0.05	9.1 \pm 0.5	12.7 \pm 0.6	49.2 \pm 3.1	247 \pm 13	0.020
	Certified	0.33	/	8.8	13.5	46	235	
Au	Found \pm S.D.	3.4 \pm 0.6	6.7 \pm 0.7	54 \pm 7	45 \pm 5	116 \pm 7	285 \pm 12	0.32
	Certified	2.9	6.3	48	42	110	279	

DL: Detection limits; S.D.: Standard Deviation.

peridotite), WMG-1 (mineralized gabbro), and WMS-1 (massive sulphide). For WMG-1, 1 gram of sample was used, for WMS-1, 0.5 grams was used, and for all other reference materials a sample mass of 2 grams was taken. The results shown are the average of three separate preparations (five separate preparations for UMT-1). Good agreement is obtained when compared with the certified ranges of the reference materials.

DISCUSSION

The determination of PGEs in geological materials requires sensitive, reliable and rapid instrumental techniques. The ICP-MS technique is ideal for the analyses of these metals because of its sensitivity and isotope ratio measurement capability (Gregoire, 1988; Jackson *et al.*, 1990; Colodner *et al.*, 1993; Enzweiler *et al.*, 1995; Sen Gupta and Gregoire, 1989; Yi and Masuda, 1996; Pearson and Woodland, 2000). Two main approaches have been used for decomposing samples and pre-concentrating the PGEs. One is nickel sulfide fire assay (Date *et al.*, 1987; Sun *et al.*, 1993; Hall and Pelchat, 1994; Frimpong *et al.*, 1995; Juvonen *et al.*, 1994; McDonald *et al.*, 1994; Li and Tong,

1995; Li *et al.*, 1996; Plessen, 1998; Oguri *et al.*, 1999; Sun *et al.*, 2001; Zhou *et al.*, 2001), and the other is aqua regia leach followed by sodium peroxide fusion and Te co-precipitation (Sen Gupta and Gregoire, 1989; Gowing and Potts, 1991; Enzweiler *et al.*, 1995; Totland *et al.*, 1995).

The nickel sulfide fire assay method offers the advantage of accommodating a large sample mass, and all of the PGEs can be concentrated by this procedure. However, the disadvantages of nickel sulfide fire assay are the relatively large amounts of reagents used, often resulting in analytical blank with higher concentration of PGEs, introduction of Cu and Ni to the solutions which cause interference problems with the PGEs (Zhou *et al.*, 2001) and the requirement that the composition of the flux be changed according to the composition of the sample matrix. Anion exchange has also been used to separate dissolved PGEs from matrix elements (Enzweiler *et al.*, 1995; Jarvis *et al.*, 1997; Rehkamper and Halliday, 1997; Ely *et al.*, 1999; Pearson and Woodland, 2000; Li and Chai, 1997).

The other sample preparation techniques are based on simple acid attack, fusion or a combination of these methods. Digestion with aqua regia

is rapid and the blank levels are very low, except for samples containing refractory minerals (e.g., chromite), giving low PGE recoveries (Gowing and Potts, 1991). Aqua regia with HF digestion combined with sodium peroxide fusion is an effective method for most geological samples. However, this procedure is relatively complex requiring many procedural steps. Compared with these techniques, fusion and Te co-precipitation is a relatively simple method. Enzweiler *et al.* (1995) described a relatively simple sample digestion method in which following sodium peroxide fusion in a glassy carbon crucible, the PGEs were pre-concentrated by Te co-precipitation.

The fusion and Te co-precipitation procedure described in this study is similar to that reported by Enzweiler *et al.* (1995). The main differences in our method are the use of cheaper corundum crucibles, the removal of silicate colloid and the use of Lu as an internal standard. The resulting method is less costly and less time consuming, allowing for the analysis of more samples in any given time.

Glassy carbon crucibles (Enzweiler *et al.*, 1995) or zirconium crucibles (Evans *et al.*, 1993; Enzweiler and Potts, 1995; Yi and Masuda, 1996) are usually used for Na₂O₂ fusions. Both types of crucibles are relatively expensive compared to crucibles made of other materials. It has also been reported that the use of zirconium crucibles results in an interference in ICP-MS, i.e., zirconium dissolved during the fusion step lead to the production of ⁹⁰Zr¹⁶O⁺ and ¹⁷⁹Hf¹⁶O ions which are isobaric with ¹⁰⁶Pd⁺ and ¹⁹⁵Pt⁺ ions, respectively (Sen Gupta and Gregoire, 1989). The lifetime of glassy carbon crucibles is very dependent on the relative amounts of sample and flux added and the nature of the flux used, but can be about six to fifteen fusions when used properly. The brittle nature of glassy carbon makes breakage and cracking another cause of premature crucible failure. To date, there are no other reports on use of corundum crucibles for the determination of the PGEs using Na₂O₂ fusion. Corundum crucibles are cheap and have the advantage of giving very low blanks in terms of PGEs. In our experience, these

crucibles can be reused about 10 times for Na₂O₂ fusions before replacement is required.

We note that the proposed method may not be suitable for analysis of chromite or large amounts of chromite-bearing samples. This is mainly because, in the presence of large quantities of dissolved chromium, it is not possible to reduce the Te using SnCl₂.

CONCLUSIONS

The proposed method for the determination of the PGEs (except Os) and Au in geological samples is suitable for an analytical laboratory tasked with the analysis of a large number of samples on a daily basis. The procedure is simple, fast, reliable and relatively easy to complete.

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