

Quantifying the platinum group elements (PGEs) and gold in geological samples using cation exchange pretreatment and ultrasonic nebulization inductively coupled plasma-mass spectrometry (USN-ICP-MS)

James C. Ely^{*}, Clive R. Neal, James A. O'Neill Jr., Jinesh C. Jain

Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, IN 46556-0767, USA

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Abstract

A method for analyzing low abundances of the platinum group elements (PGEs) and gold has been developed using cation exchange chromatography and ultrasonic nebulization inductively coupled plasma mass spectrometry (USN-ICP-MS). Ultrasonic nebulization increases sensitivity over regular pneumatic nebulization so that resolvable signals above background are possible in the fg/g range. Small sample sizes (≤ 250 mg) and low volumes of reagents produce procedural blank levels below the detection limit for Ru, Pd and Ir, in the fg/g range for Rh and in the low pg/g range for Pt and Au. Heterogeneous PGE and Au distributions in geological samples are avoided by a rigorous homogenization/rehomogenization procedure. The reference material UMT-1, which contains rock concentrations of the PGEs and Au at the low ng/g levels, monitored recoverability. Interferences of HfO^+ and TaO^+ on Ir, Pt and Au were not seen in the analyses of UMT-1 because Hf and Ta have low abundances in this reference material. However, these interferences are acute for silicate rocks, even after cation exchange chromatography. Isotope dilution cannot be adapted to this method for Ir and Pt because two interference-free isotopes are not available. An external calibration method has been developed for the accurate and precise determination of the PGEs and Au in rocks with low abundances of Hf and Ta ($< 1 \mu\text{g/g}$ and $< 0.2 \mu\text{g/g}$, respectively); a standard addition method for rocks containing higher concentrations of these elements. The work presented here demonstrates the strengths and weaknesses of cation exchange for PGE and Au analyses in geological materials. It can be a useful tool in solving fundamental geological problems that depend on precise and accurate determination of these elements by taking full advantage of current technology and the sensitivity it provides. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The highly siderophile platinum group elements (PGEs—Ru, Rh, Pd, Os, Ir and Pt) and gold (Au)

are typically present in common terrestrial rocks at the low to sub-ng/g (parts-per-billion) levels. Quantifying PGE and Au abundances in geological samples is critical for exploring areas such as planetary differentiation (e.g., Spettel et al., 1980; Mitchell and Keays, 1981; Morgan et al., 1981; Newsom, 1990;

^{*} Corresponding author

Pattou et al., 1996), core–mantle interaction manifest as plume volcanism (Walker et al., 1995; Jain et al., 1995, 1996; Walker et al., 1997), meteorite impacts and the effects thereof (e.g., Alvarez et al., 1980; Kyte et al., 1980, 1985; O'Neill, 1991; Evans et al., 1993, 1995), and the effects of PGE dissemination into the environment (primarily Pt and Pd) through catalytic converters (e.g., Alt et al., 1993; Wildhagen and Krivan, 1993; Messerschmidt et al., 1994).

Increasingly sophisticated analytical machinery makes possible accurate, precise, and reproducible determination of low PGE and Au abundances in geological samples. Despite significant improvements in machine sensitivity, sample preparation procedures have not improved at the same rate. Sampling strategies have to account for the potentially heterogeneous distribution ('nugget effect') of the PGEs and Au in a given sample which may lead to unreproducible analyses (e.g., Allegré and Luck, 1980; Hall and Pelchat, 1994). The PGEs and Au are often partitioned into discrete trace mineral phases such as sulfides, oxides, and potentially many rare trace phases including metal alloys (see Cabri, 1976 and Cabri, 1981 for review) as well as the pure metallic form (e.g., Schurayatz et al., 1996).

Many analytical techniques for quantifying the PGEs and Au in geological samples require a pre-concentration stage to account for heterogeneity and low abundances. The dominant pre-concentration method is nickel sulfide (NiS) fire assay (e.g., Robert et al., 1971). Fire assay methods have been used for many years (see review by Irving, 1977), but recently these techniques have been modified into excellent geochemical exploration tools (e.g., Shazali et al., 1987; Sun et al., 1993). The NiS fire assay procedure addresses the heterogeneity issue by using between 4–100 g of sample. However, the large amounts of reagents required often elevate blank levels to the pg/g (parts per trillion) or even low ng/g level (e.g., Asif and Parry, 1989; Pattou et al., 1996), which can sometimes approach the PGE and Au abundances in rock samples. Despite these limitations, fire assay continues to be the dominant method of pretreatment. The adaptation of traditional pretreatment methods for use with ICP-MS is acceptable for work involving PGE and Au abundances at the $\mu\text{g/g}$ (ppm) to ng/g range. However, this is not generally acceptable for abundances below the ng/g

level because low blank levels and low quantities of sample and/or reagents cannot be achieved simultaneously. Ravizza and Pyle (1997) used NiS fire assay pre-concentration for determination of PGE abundances by isotope dilution through a combination of N-TIMS and ICP-MS. Procedural blanks were at the low pg/g level but this method still required 5 g of sample to be processed. Jarvis et al. (1997) used ICP-MS to analyze for the PGEs and Au without fire assay pre-concentration. Instead, a combination of acid digestion and $\text{Na}_2\text{O}_2/\text{NaCO}_3$ fusion was employed to dissolve the 1-g sample and this produced blank levels in the low ng/g range.

This paper presents a method for analyzing PGEs and Au in geological samples which improves upon previous analytical techniques because it: (a) significantly reduces sample size (50–200 mg vs. 4–100 g in other methods), yet still addresses sample heterogeneity; (b) yields extremely low blank levels through sample preparation in clean lab, use of double distilled acids for digestion and cleaning of materials, and low volumes of reagents; (c) reduces sample handling to minimize potential contamination; (d) yields reproducible results at the ng/g to pg/g levels. The method uses ultrasonic nebulization inductively coupled plasma mass spectrometry (USN-ICP-MS) in combination with cation exchange chromatography to determine PGE and Au abundances in geological samples precisely and accurately. Osmium is not quantified because of OsO_4 volatility during the preparation procedure.

Cation exchange chromatography was used for several reasons: (a) the PGEs and Au form chlorocomplexes in HCl media which are not retained on this type of resin (Strelow, 1960), requiring much lower acid concentrations, thus, rendering the procedure safer and less expensive; (b) the negatively charged PGE and Au chlorocomplexes will bind to anion exchange resins, which may be more difficult to remove quantitatively at low abundances (Al-Bazi and Chow, 1984; Rehkämper and Halliday, 1997); and (c) the complete separation of the individual PGEs is possible using anion exchange resins but unnecessary and overly complex for the purposes of this study. This method was developed over a number of years and the problems involved with analysis of PGEs and Au using cation exchange chromatography were explored in detail (Jain et al., 1995, 1996;

O'Neill, 1996; O'Neill et al., 1996; Ely and Neal, 1997a,b; Neal et al., 1997).

2. Method development for analysis of geological samples

2.1. Sample preparation

As geological samples generally contain ng/g to sub-ng/g levels of PGEs and Au and a mg-sized sample was desirable, every possible care was taken to ensure that there was no PGE or Au contamination during preparation. Potential contaminants include weathered surfaces, coolant oil from the rock saw, and any metallic object that comes into contact with the sample (the rock saw, hammer, splitter, jaw crushers, personal jewelry, etc.).

The sample preparation procedure required that all jewelry be removed from hands/wrists and that hands must be washed before handling the rock sample. A water-cooled rock saw was used to trim off weathered surfaces and cut the sample into 1.5–2 cm thick slabs. Each surface was then ground in two directions on a diamond wheel to ensure that sawn or weathered surfaces were completely removed. The ground sample was washed, allowed to air dry, and then placed in two plastic bags to be broken up into peanut-sized chips (or smaller) using a hammer. In order to eliminate contact with metal, the metal hammer was simply covered with cloth duct tape (which was replaced for each new sample). The resulting chips were placed in a beaker and covered with ultra-pure (18-M Ω) water and put in an ultrasonic bath for 30 min. The water was decanted off and the sample was rinsed with ultra-pure water before being air-dried. The sample was examined under a binocular microscope and any chip with a weathered surface was removed.

The chips were then crushed further in a SPEX alumina jaw crusher (model 4200), and finally ground to a fine powder in a SPEX alumina ball mixer/mill (model 8000). Both jaw crushers and the mixer/mill were cleaned between samples using ultra-pure water and a non-metallic scouring pad. A small amount of the next sample was passed through both and discarded to avoid any chance of cross-contamination. By preparing rock samples in this way, sources of

contamination for the PGEs and Au can be eliminated.

2.2. Sample digestion

Complete dissolution of samples, especially the PGE- and Au-bearing phases, is crucial for quantitative and representative PGE and Au analysis using this method. Use of Savillex screw top Teflon bombs on a hot plate with hydrofluoric (HF) and nitric (HNO₃) acids was insufficient to completely dissolve some of the samples.

High pressure (8.27 MPa/1200 psi) 'Parr' bombs were used to completely digest non-silicate phases. These are made up of a Teflon liner inside a steel case. Great care was taken to avoid introducing contamination during the opening of the bombs following the digestion treatment. In this study, the PGE and Au standard reference material UMT-1 (CANMET, Ontario, Canada) was used. The mineralogy is predominantly silicate (pyroxene, amphibole, and chlorite), with minor, yet significant proportions of magnetite, ilmenite, goethite, spinel, pentlandite, and chalcopyrite. The final protocol used for the digestion of UMT-1 and other ore samples included standard HF/HNO₃ dissolution (3:4), followed by an aqua regia stage (HCl:HNO₃ = 3:1) in Parr bombs for 24 h at 150°C. The resulting solution is evaporated, treated with 12 M HCl, evaporated again and fully dissolved in 2–4 ml of 0.6 M HCl for loading onto the columns.

2.3. Instrumentation

A VG Elemental PQII STE inductively coupled plasma-mass spectrometer (ICP-MS) was used to quantify PGE and Au abundances. The average operating parameters of the ICP-MS for the duration of this study are given in Table 1. Peak jumping was used as the mode of analysis with 10 ml of sample solution and an uptake rate of 1 ml per minute used throughout. Forty elements were quantified (10 ms/peak) during a 60-s acquisition period. Relative standard deviations were typically 2–3% for the raw cps. To achieve the desired machine detection limits (< 1 pg/g) which allows for the quantitative determination of PGE and Au concentrations in small (mg-sized) rock samples, a CETAC U-5000AT UI-

Table 1
ICP-MS operating parameters

Parameter	Average setting
<i>Power (W)</i>	
Forward	1348
Reflected	0.5
<i>Vacuum (Torr)</i>	
Expansion	1.9×10^0
Intermediate	6.3×10^{-5}
Analyzer	1.8×10^{-6}
<i>Gas flows (l / min)</i>	
Cool	14.0
Auxiliary	1.65
Nebulizer	0.957
<i>Lens settings (unitless)</i>	
Extractor	1.70
Collector	7.83
L1	7.91
L2	5.20
L3	5.83
L4	3.50
<i>Flow rate (ml / min)</i>	1.0

trasonic Nebulizer was used as an enhanced sample introduction system for the ICP-MS.

The combination of the USN with the ICP-MS leads to a significant improvement in overall sensitivity relative to standard Meinhardt pneumatic nebulization (Fig. 1) and only a slight increase in oxide levels (2–4% vs. 1–2%, respectively). The lowest response is obtained from a pneumatic Meinhardt nebulizer with a 9 mm spacing between the sample and skimmer cones. The intermediate response in Fig. 1 is obtained when the standard pneumatic nebulizer is replaced with the USN yielding an average increase in sensitivity of approximately 17 times for the masses ranging between 59 and 238 AMU. By decreasing the spacing between the sample and skimmer cones from 9 mm to 7 mm through the addition of a 2 mm spacer mounted behind the skimmer cone, the USN-ICP-MS sensitivity can be doubled again, leading to the highest response curve shown in Fig. 1. The latter hardware configuration was used throughout this study.

2.4. Memory effects

The benefits of the USN are obvious in that there is a tremendous increase in overall ICP-MS sensitiv-

ity. The USN operates by desolvating the sample and allowing more sample into the plasma, thus, increasing the signal to noise ratio. By removing the solvent, potential chloride interferences are greatly reduced. In the desolvating process, the sample is exposed to the large glass surface area of the USN. Elements being quantified by USN-ICP-MS are often retained on these extensive glass surfaces and then released slowly throughout an analytical run, increasing the background signal for a particular element, which in turn lowers the sensitivity (e.g., Jarvis et al., 1992). Artificially high concentrations could be obtained or actual rock values could be below detection limits due to elevated background counts. Retention of elements by the USN can also lead to the cross-contamination of samples, blanks, calibration standards, and standard reference materials. Therefore, the increase in background levels for a particular isotope could lead to inaccurate results if memory effects are not eliminated.

A wash protocol was developed for the USN-ICP-MS using a Gilson Model 222 Autosampler to reduce memory effects to background levels and involved 120 s of 1 M HCl and 1 M HNO₃ (3:1) (to strip the tubing and USN spray chamber of adhering elements), 90 s of 1.2 M HCl (intended to continue to clean the equipment while at the same time it is equilibrating the system with the HCl matrix), and two separate 90 s washes of 0.6 M HCl. The final

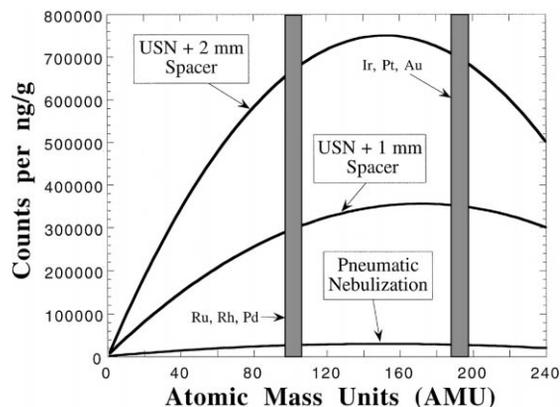


Fig. 1. Diagram demonstrating the increased sensitivity of the ICP-MS (in counts per ppb) over the mass range using the ultrasonic nebulizer in conjunction with the spacer behind the skimmer cone. The two hatched areas represent the atomic masses of gold and the two PGE groups (Ru, Rh, Pd and Ir, Pt, Au).

two washes allow the system to equilibrate with the 0.6 M HCl sample solution matrix while allowing for the continued cleaning of the system. This wash protocol followed each sample, standard, standard reference material, and blank in a given analytical run. Acid blanks were initially placed between every sample/calibration standard/standard reference material during an analysis to monitor memory, but their number was reduced once memory effects were proven to be non-existent. The acid blanks did not exhibit any significant increase in registered counts for the PGEs and Au in analytical runs lasting 20 h or more. Therefore, by using this wash protocol, memory effects associated with the USN were effectively eliminated.

2.5. Cation exchange pretreatment

The cation exchange resin used was Dowex AG 50 W-X8 strong cation exchanger, H⁺ form, 200–400 mesh. The 200–400 mesh size was selected in order to reduce the flow rate through the column allowing a better separation of the base metals from the PGEs and Au. Eight percent cross-linked resins were selected because they are the most widely used commercial resins, which provided a larger body of previous work to reference (e.g., Sen Gupta, 1989; Strelow and Victor, 1991; Sen Gupta, 1993). The resin was housed in quartz columns (23 cm long, 0.5 cm ID with a 22 ml reservoir) isolated in compartmentalized plexi-glass stands.

The PGEs and Au form anionic chlorocomplexes species in HCl media and pass through the resin relatively quickly and are collected in the eluate while all positive and neutral species are retained on the resin. Other base metals and some major element species also form chlorocomplexes and pass through with the PGEs, although at a slower rate (Strelow et al., 1971).

Most PGEs can form aquocomplexes in dilute HCl media that carry either a lower negative charge than the chlorocomplexes or even a slight positive charge, depending on equilibration time and kinetics of the reactions involved (Goldberg and Hepler, 1968; Baes and Mesmer, 1976). As this procedure uses 0.6 M HCl, potentially low yields are avoided by diluting the PGE solutions only immediately prior to placing the solution on the resin (as noted by

Al-Bazi and Chow, 1984; Strelow and Victor, 1991, 1992). The solutions must be analyzed during the next 3 days after the completion of the column chemistry in order to limit aquocomplex formation or transformations that may cause PGE and Au precipitation (Strelow and Victor, 1991, 1992).

The columns were packed with 4-ml (3.2 g) of resin and cleaned by passing 100 ml (25 bed volumes) of 6 M HCl through the columns before being repacked and equilibrated with 50 ml of the 0.6 M HCl matrix used in the calibration experiments. A 10 ng/g solution of PGEs and Au was used to calibrate the columns, being flushed with a gradient elution of successive 5 ml washes with the following concentrations: 0.6, 0.75, 1, 2, 3, 4, and 6 M HCl. The PGE and Au solution was prepared from a SPEX 10 µg/g multielement standard solution. The PGEs and Au passed directly through the cation exchange resins and were collected in the first two to three 5-ml washes (Fig. 2). Recoverability was optimal for a 0.6 M HCl acid matrix for the loading and washing volumes (Fig. 3). An artificial matrix was created to investigate any potential recovery problems caused by elevated levels of other elements. The PGEs and Au were set at 10 ng/g, while Si, Ca, Mg, Fe, Ti, Al, Cr, and Mn were set at 10 µg/g in solutions of varying HCl concentration. Two milliliters of this solution was passed through the cation exchange columns. The loading solution was followed by nine

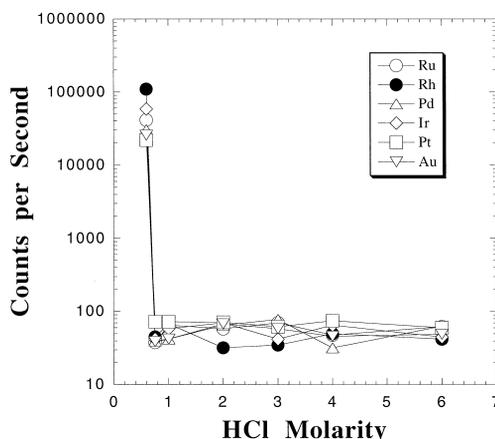


Fig. 2. Elution of the PGEs and Au from the cation exchange resin with increasing strength of hydrochloric acid, demonstrating that the PGEs and Au elute immediately.

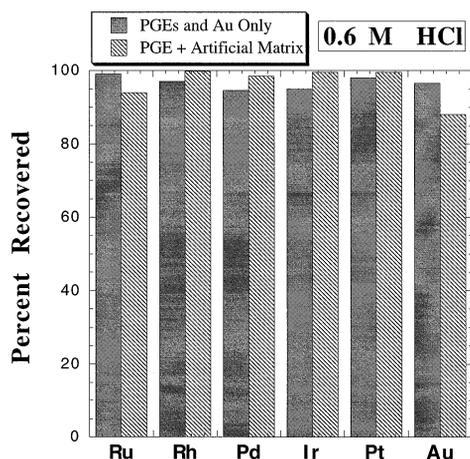


Fig. 3. Recoverability from the cation exchange columns using 0.6 M in conjunction with a 10 ng/g solution of only PGEs and Au as well as an artificial rock solution (PGEs and Au = 10 ng/g; Si, Ca, Mg, Fe, Ti, Al, Cr, and Mn = 10 $\mu\text{g/g}$).

2-ml washes of HCl of the same concentration as the HCl matrix of the solution. Again the 0.6 M HCl provided the best recoverability for all the PGEs and Au (Fig. 3). This is consistent with published distribution coefficients in HCl media (Strelow, 1960) and close to the 0.5 M HCl matrix used by Jarvis et al. (1997). However, when applied to rock samples, each sample is required to pass through 8 ml of resin (i.e., through our columns twice) in order to ensure adequate separation of the PGEs and Au from the matrix (see below).

The amount of HCl wash necessary to remove the PGEs and Au quantitatively from the columns was also determined. The same procedure and solutions used to examine the recoverability of an artificial matrix was applied in the experiments. The PGE concentrations of the loading solution and the nine washes were plotted against the cumulative volume of wash placed through the column. The concentrations of Ru, Rh, Pd, Ir and Pt reach background levels after approximately 6 ml of 0.6 M HCl solution has passed through the column while Au concentrations reach background levels after approximately 8 ml of wash have passed through the column (Fig. 4). To demonstrate 20 bed volumes of 6 M HCl removed all elements from the resin, standard reference material UMT-1 (see above) was run through the column and the solution used to clean this col-

umn was analyzed. This cleaning solution only showed background cps for all elements after the 20 bed volumes had passed through the resin. While 100 ml of 6 M HCl is required to clean the columns, this is at a lower concentration (making it safer) and generally at a lower quantity (making it cheaper) than for anion exchange.

2.6. Limits of detection

Detection and determination limits were calculated using the method outlined in Skoog and Leary (1991). The calculated detection and determination limits for a given mass or isotope are based on the slope of a line generated by two points, a blank and a standard of known concentration. Each solution was measured six times for 60 s and the average and standard deviation of the counts obtained for the solutions were calculated. The minimum distinguishable signal, S_m , is calculated using the following relationship:

$$S_m = \bar{S}_{bl} + k\sigma_{bl} \quad (1)$$

where \bar{S}_{bl} = mean blank signal, k = constant, σ_{bl} = standard deviation of average blank signal.

Following the determination of S_m (counts), the corresponding concentration c_m can be determined using the following relationship:

$$c_m = \frac{S_m - \bar{S}_{bl}}{m} \quad (2)$$

where m is the slope (counts per concentration) of the line generated by the blank and the standard being used. Detection limits are calculated using $k = 3$, while determination limits use $k = 10$, a value proposed by the American Chemical Society and Committee on Environmental Improvement (1980).

Calculated detection limits provide a concentration at which the USN-ICP-MS technique can differentiate between random background noise and a particular isotope in solution. Such detection limits will vary from day to day due to machine sensitivity and background noise levels, making it difficult to achieve such low detection limits on a reproducible basis. Therefore, determination limits yield a more reasonable working concentration range that can be

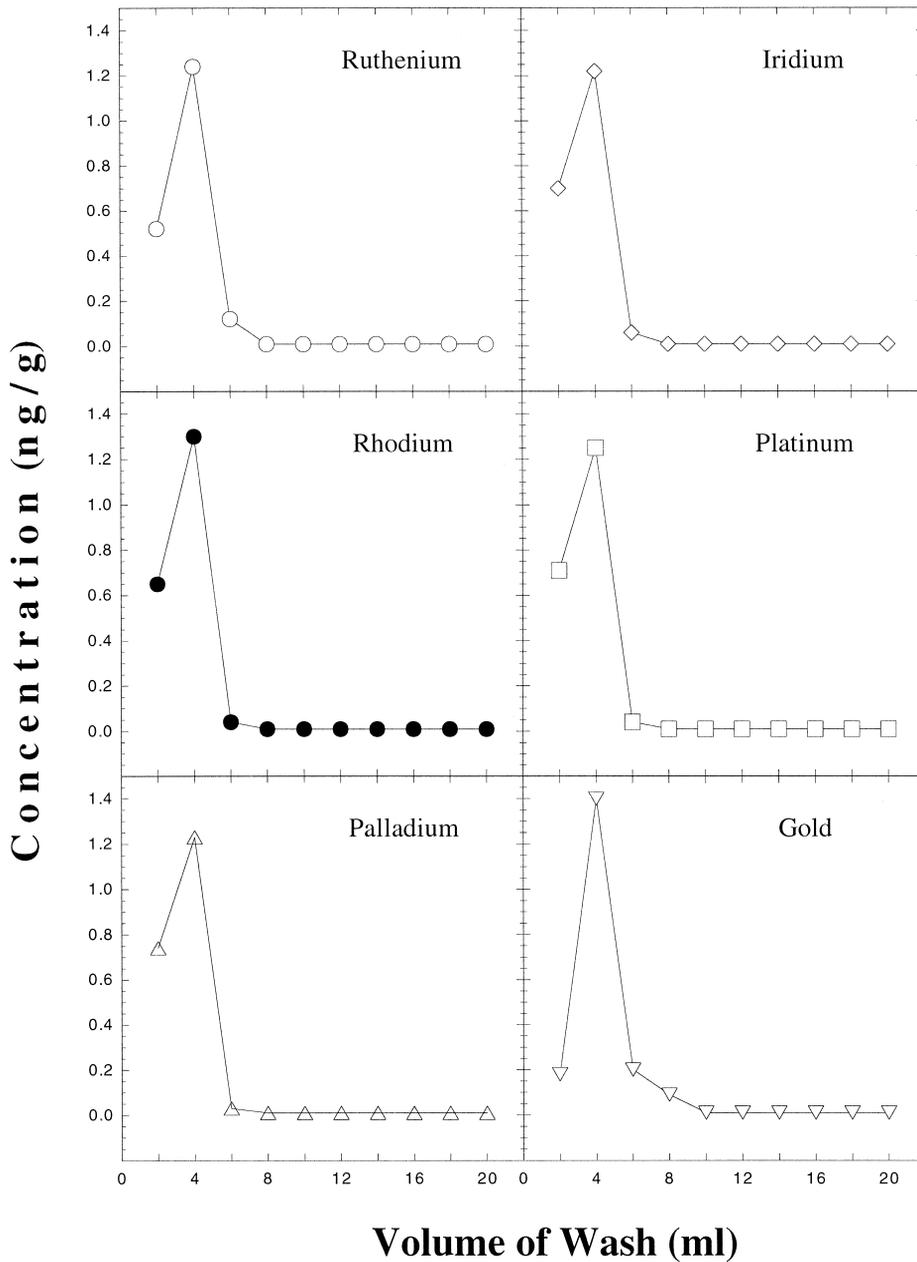


Fig. 4. Elution of the PGEs and Au from the cation exchange columns using 0.6 M HCl in 2 ml aliquots. The experiment demonstrates that the PGEs and Au are generally eluted within the first 6 ml.

accurately reproduced on a regular basis for a particular isotope and provide a good approximation of a lower limit of quantitative analysis (Jarvis et al., 1992).

Detection and determination limits for both procedures developed here (external calibration and standard addition—see below) are given in Table 2 and most values are in the fg/g (10^{-15} g) range. The

Table 2

Calculated and measured USN-ICP-MS detection limits for the PGEs from this study and detection limits from recent PGE studies

Element	External calibration			Standard addition			Pattou et al. (1996) ^a	Jarvis et al. (1997) Calc. detection limit (3σ)
	Calculated detection limit (3σ)	Determination limit (10σ)	Measured detection limit	Calculated detection limit (3σ)	Determination limit (10σ)	Measured detection limit		
Ru	145	483	238	591	1969	1792	200,000	200,000
Rh	54	180	72	85	285	426	10,000	30,000
Pd	629	2098	594	730	2433	2188	100,000	160,000
Ir	21	70	48	571	1904	1252	40,000	70,000
Pt	138	459	238	1946	6487	5866	100,000	110,000
Au	238	799	594	246	873	1135	340,000	50,000

All values are in fg/g.

^aMachine detection limits.

higher detection limits for Ir and Pt in the standard addition method are the result of both the increase in the sample weight and the measurement of a lower abundance isotope.

To further characterize USN-ICP-MS sensitivity, measurable detection limits were determined. The minimum distinguishable signal, S_m , was calculated in the same manner as above. The measured detection limit for a particular isotope was taken to be the concentration of the first standard that demonstrated counts greater than S_m . Gravimetric standards were made for PGEs and Au in the concentrations of 0 (blank), 13, 25, 37, 48, 60, 72, 84, 95, 107, 119, 238, 351, 474, and 594 fg/g. They were analyzed in order of increasing concentration to avoid any possi-

ble memory effects (see above). The measured detection limits (Table 2) are better than the determination limits for the external calibration method and only Rh and Au had measured detection limits higher than determination limits for the standard addition method. Comparison with detection limits of Pattou et al. (1996) and Jarvis et al. (1997) in Table 2 demonstrates both the external calibration and the standard addition methods have significantly lower detection and determination limits than other studies. Procedural blank levels (Table 3) are much lower than those quoted by the most recent NiS fire assay work (e.g., Pattou et al., 1996) or microwave digestion–alkali fusion (Jarvis et al., 1997) as well as several other recent studies.

Table 3

Comparison of procedural blank levels for this study and recent fire assay and cation exchange PGE and Au collection procedures

	This study ^a	Pattou et al. (1996)	Juvonen et al. (1994)	Sun et al. (1993)	Jackson et al. (1990)	Asif and Parry (1989)	Jarvis et al. (1997) ^b	Ravizza and Pyle (1997)
Ru	bdl	78 ± 7	1090 ± 700	500	400	7000	8000	nd
Rh	0.7 ± 1.3	9 ± 3	740 ± 540	500	30	600	1300	nd
Pd	bdl	120 ± 30	2430 ± 370	3000	130	20,000	11,000	43
Ir	bdl	40 ± 14	50 ± 30	2000	40	40	1800	3.8
Pt	7 ± 5	150 ± 30	300 ± 190	2000	150	4000	4300	50
Au	13 ± 23	700 ± 100	610 ± 170	10,000	510	70	2000	nd

All values are given in pg/g and errors represent 2σ uncertainties.

^aMeasured procedural blank.^bQuantitation limit for 1-g sample.

bdl = Below detection limit.

nd = Not determined.

2.7. Selection of internal standards

Internal standards are critical for monitoring changes in the USN-ICP-MS signal. By using multiple internal standards, the changes in the machine's response in several mass regions can be monitored. Internal standards that had the following characteristics were selected:

1. the standard must be relatively close in mass and ionization potential to PGEs and Au;
2. at least one high and one low mass internal standard is required per group of PGEs and Au (Ru, Rh, Pd and Ir, Pt, Au);
3. the isotope must be completely separated from the PGEs and Au during the cation exchange treatment if it is present in the rock matrix;
4. the isotope must provide excellent signal stability over extended runs (> 12 h).

Based on these criteria, ^{87}Rb , ^{89}Y , ^{139}La , ^{165}Ho , and ^{238}U were used as the internal standards for this project. All isotopes selected as internal standards are removed from solution during the cation exchange treatment, allowing for the accurate monitoring of USN-ICP-MS signal drift over time by addition of these elements as internal standards to the PGE and Au aliquots. It was realized that Rb and Y could form oxides that may interfere on Ru, Rh, and Pd. This was investigated during the interference tests described below and no statistically significant interferences (> mean blank + 3σ) were found.

2.8. Elimination of interfering species

One of the requirements of this pretreatment technique is the elimination of elements that can interfere in the determination of PGEs and Au. Isobaric interferences occur at masses 104 (^{104}Pd on ^{104}Ru), 106 (^{106}Cd on ^{106}Pd), and 108 (^{108}Cd on ^{108}Pd).

Any element that potentially formed a polyatomic interference (Table 4) was prepared in a separate 1 ng/g solution without PGEs and Au, but the appropriate PGE mass was monitored to determine whether measurable signals were present. If the signal on a PGE mass was statistically significant, then the element needed to be removed from the analyzed PGE and Au solutions or another mass must be used to quantify that specific PGE.

Table 4

List of elements and molecules that can potentially interfere with PGE and Au determinations

Interference	Isotope and natural abundance
NiAr (^{60}Ni and ^{40}Ar)	^{100}Ru (12.6%)
RbO (^{85}Rb and ^{16}O)	^{101}Ru (17.1%)
RbO (^{87}Rb and ^{16}O)	^{103}Rh (100%)
CuAr (^{63}Cu and ^{40}Ar)	^{103}Rh (100%)
^{104}Pd	^{104}Ru (18.6%)
ZnAr (^{64}Zn and ^{40}Ar)	^{104}Pd (11.1%)
YO (^{89}Y and ^{16}O)	^{105}Pd (22.3%)
CuAr (^{65}Cu and ^{40}Ar)	^{105}Pd (22.3%)
^{106}Cd	^{106}Pd (27.3%)
ZrO (^{90}Zr and ^{16}O)	^{106}Pd (27.3%)
^{108}Cd	^{108}Pd (26.5%)
ZrO (^{92}Zr and ^{16}O)	^{108}Pd (26.5%)
LuO (^{175}Lu and ^{16}O)	^{191}Ir (37.3%)
HfO (^{177}Hf and ^{16}O)	^{193}Ir (62.7%)
HfO (^{178}Hf and ^{16}O)	^{194}Pt (32.9%)
HfO (^{179}Hf and ^{16}O)	^{195}Pt (33.8%)
TaO (^{181}Ta and ^{16}O)	^{197}Au (100%)

The isotopes that form the interference are listed in the first set of parentheses and the natural abundance of the PGE isotope is listed in the second set of parentheses.

Three multi-element 10 ng/g standard solutions containing approximately 70 elements were prepared in three acid matrices, 0.08, 0.3, and 0.6 M HCl to determine where potential interfering species would elute relative to the PGEs and Au during the cation exchange treatment using progressively more concentrated HCl washes. Cadmium eluted early and may be recovered from the columns with the PGEs and Au. The amount of ^{106}Cd interference on ^{106}Pd can be monitored by another Cd isotope (^{111}Cd or ^{112}Cd). However, the resin retained all other potential interfering elements. The 0.6 M HCl matrix was the best choice to allow maximum recovery of PGEs and Au while allowing for the maximum retention on the columns of potential internal standard and interfering elements that may be present in the rock matrix (e.g., Strelow, 1960).

In analyzing 'real rocks', Hf and Ta eluted with the PGEs and Au. As the ultimate purpose of this method development was a procedure applicable to all rocks, a substantial effort was made to modify the procedure to remove these interferences without undue complications. Applying a correction using cali-

bration standards, varying the amount of resin and HCl concentration, or changing the column specifications did not remove nor prevent the Hf and Ta interferences.

Hafnium and Ta should not elute with the PGEs and Au in HCl media based on distribution coefficients (Strelow, 1960). Therefore, these elements were forming another complex that had distribution coefficients similar to the PGE and Au chlorocomplexes. It was determined that during the HF/HNO₃ stage of dissolution, a portion of the Hf and Ta formed fluorocomplexes with the residual hydrofluoric acid. These fluorocomplexes are very stable and are not broken up during subsequent stages of the dissolution. The formation of fluorocomplexes is a common technique in the separation of Hf for Lu–Hf isotopic systematics (Patchett and Tatsumoto, 1980; Blichert-Toft et al., 1997). These fluorocomplexes have distribution coefficients near zero on cation exchange resin (Faris, 1960; Nelson et al., 1960), similar to the PGE and Au chlorocomplexes, which results in the elution of Hf and Ta with the PGEs. Modifications to the dissolution technique by incorporating H₂SO₄ and HClO₄ did not prevent the Hf and Ta interferences and added severe complications to the procedure. This interference problem was resolved by using different calibration techniques depending upon the concentration of Hf and Ta in the samples.

2.9. External calibration vs. standard addition

External calibration relates the concentration of an element in the sample to a standard curve calculated from 'external standards' of varying composition. Standard addition relies upon the sample being divided into a number of equal aliquots that are spiked in increasing concentration with the elements to be quantified with one aliquot left unspiked. Linear least-squares regression through the resulting data allow a concentration of the sample to be determined. Oxides of Hf and Ta overlap with the most abundant isotopes of Ir and Pt and the only isotope of Au. These are the isotopes monitored for external calibration, where a smaller quantity of sample is required (50–100 mg) and the total run time is shorter (relative to standard addition) because only one aliquot of the sample needs to be analyzed.

External standard concentrations were between 0.1 pg/g and 5 ng/g and internal standards were set at 100 pg/g. However, our results indicate that while being quicker and easier, external calibration can only be used if the concentrations of Hf and Ta in the sample were less than 1 µg/g and 0.2 µg/g, respectively.

To avoid Hf interferences in samples containing high abundances of Hf, the interference-free isotopes ¹⁹¹Ir and ¹⁹⁸Pt had to be used. Both these isotopes have lower abundances (¹⁹¹Ir 37.3% vs. ¹⁹³Ir 62.7%; ¹⁹⁸Pt 7.2% vs. ¹⁹⁵Pt 33.8%). In order to detect these lower abundance isotopes and still have four aliquots for the standard addition technique, the sample weights were increased from 50–100 mg to 125–250 mg. One aliquot was left unspiked and the remaining three were spiked with PGEs so the concentrations were approximately doubled, tripled, and quadrupled those estimated for the original sample. Gold cannot be quantified in high Ta samples using this method because there is no interference-free isotope available. Internal standards were again set at 100 pg/g. Increased sample size increases the amount of reagents involved in the procedure and this can increase blank levels and, therefore, adversely affect detection limits. Importantly, isotope dilution cannot be used because there are too few interference-free isotopes of Ir and Pt because of the interferences.

3. PGE and Au analysis of geological materials

3.1. UMT-1

Reference material UMT-1 (CANMET) was the standard used to develop this analytical technique and to monitor yield, accuracy and reproducibility. UMT-1 is a standard created by the homogenization of 772 kg of ultramafic mine tailings from the Giant Mascot Mines in British Columbia, and contains PGE and Au concentrations from 8 to 128 ng/g (Table 5).

Analysis of geological materials required that each sample be passed through our columns twice, as the heavier matrix overloaded the resin on the first pass. For external calibration, 50 mg of sample was dissolved and loaded on the columns in 2 ml of 0.6 M HCl. The sample beaker was rinsed with an addi-

Table 5

UMT-1 PGE and Au concentrations determined by external calibration and two different analysts (JCE and JAO) and standard addition (JCE)

Calibration	External		Standard addition		Certified values
	JCE	JAO	JCE	UMT-1 AR	
Analyst/sample					
No. of analyses	26	10	10	1	
Isotope	Mean \pm 2 σ				
⁹⁹ Ru	10.4 \pm 2.4	13.5 \pm 2.5	10.4 \pm 2.5	11.1 \pm 1.1	10.9 \pm 1.5
¹⁰³ Rh	9.4 \pm 2.2	11.5 \pm 4.3	9.5 \pm 1.9	9.1 \pm 1.3	9.5 \pm 1.5
¹⁰⁵ Pd	101.7 \pm 23.0	120.7 \pm 12.6	99.91 \pm 13.0	101.4 \pm 9.8	106 \pm 3.0
¹⁹¹ Ir	nd	nd	8.4 \pm 2.5	8.4 \pm 0.9	8.8 \pm 0.06
¹⁹³ Ir	7.7 \pm 2.3	7.2 \pm 2.2	9.1 \pm 2.7	9.1 \pm 0.6	8.8 \pm 0.06
¹⁹⁵ Pt	100.4 \pm 27.7	96.5 \pm 62.0	95.7 \pm 38.4	121.1 \pm 17.3	129 \pm 5.0
¹⁹⁸ Pt	nd	nd	98.9 \pm 37.4	125.5 \pm 16.1	129 \pm 5.0
¹⁹⁷ Au	40.0 \pm 8.3	30.5 \pm 21.7	20.2 \pm 19.2	37.6 \pm 19.5	48 \pm 2.0
Hf					400 ^a
Ta					100 ^a

All values are in ng/g.

nd = Not determined.

^aReference values from Notre Dame ICP-MS analyses.

tional 2 ml of solution that was also loaded onto the column. The sample was then eluted from the column with three 2-ml washes, giving a total collected solution 10-ml. This solution was then split and each half was passed through a separate column and eluted with three 2-ml washes. This produced two 11-ml splits of the original 50-mg sample for analysis, thus, resulting in an eleven-fold dilution of the original 2-ml solution.

For the standard addition technique, four equal splits of the same sample are required. Modifications had to be made in the column technique in order to produce enough solution without diluting the PGEs below detection limits. Two 125-mg aliquots of UMT-1 were dissolved. Each was put through the cation exchange procedure as above, resulting in two splits of 11 ml for each aliquot. These two replicates (four solutions of 11 ml each) were then combined to produce 44 ml of solution (containing 250 mg of sample). Four 6-ml splits of this solution were taken. For UMT-1, one split was left unspiked and the remaining three were spiked with 10, 20, and 30 ng/g Ru, Rh, and Ir along with 100, 200, and 300 ng/g Pd, Pt, and Au, respectively. All were diluted to 10 ml (the remaining 20-ml of sample solution was kept in reserve).

Using standard addition and ¹⁹¹Ir and ¹⁹⁸Pt to avoid Hf interferences, the technique yielded repro-

ducible results for the UMT-1 standard reference material (Table 5). Note that the results are similar for ¹⁹¹Ir and ¹⁹³Ir as well as ¹⁹⁵Pt and ¹⁹⁸Pt, demonstrating that the Hf interference is negligible for this sample (Table 5).

The results for UMT-1, using both external calibration and standard addition, are in good agreement with certified values except for Pt, which is low for both techniques. The low Pt value for UMT-1 is not an artifact of a particular calibration method because both external calibration and standard addition protocols produce a similar, reproducible abundance. Jarvis et al. (1997) also reported lower than certified Pt values for their cation exchange method. UMT-1 Pt values lower than the certified value may be attributable to: (1) heterogeneous sample (unlikely based on our rehomogenization protocol); (2) loss of Pt during digestion (possible, although no visible signs of precipitation were noted); (3) inaccurate reference values (unlikely as the UMT-1 certified value for Pt has been corroborated by such diverse techniques as Graphite Furnace Atomic Adsorption Spectroscopy and NiS fire assay ICP-MS); (4) Pt precipitation on the resin (not seen during column calibration); or (5) at low concentrations in real rock samples some tailing of Pt occurs past the third 2 ml wash which is not collected [another possibility which has been described by other workers (e.g., Strelow,

1984)]. Further tests show that if UMT-1 remains in aqua regia for 96 h (instead of 48 h) during the dissolution procedure, Pt values are much closer to certified values (Table 5, UMT-1 AR column).

The mean value for Au by both external calibration and standard addition is also low and although the mean values are within error of the certified value, the errors are large (Table 5). Gold tends to adhere to the column more readily than the PGEs (Fig. 4) so it is possible that these results are a function of low recovery. This phenomenon has been observed by other workers (Beamish, 1966; Strelow et al., 1971; Rocklin, 1984; Strelow, 1984; Jarvis et al., 1997) but no one has demonstrated the exact mechanism for the loss. While unable to specify the reason for Au loss, we can suggest a method for increasing yield. Two UMT-1 samples were kept in aqua regia until the columns were ready to receive it. The sample was the evaporated, treated with 12 M HCl, evaporated, dissolved in 0.6 M HCl and loaded onto the columns on the same day. Although this did not dramatically reduce the error, the average Au abundance was dramatically increased (Table 5, UMT-1 AR column).

An average UMT-1 composition was calculated from these multiple runs with errors at 2σ calculated

from the standard deviation of these data (Table 5). While this error calculation is an oversimplification (it does not include the errors inherent in the regression models used to produce these values), data presentation in this way allows comparison of our technique with results from other cation exchange methods (e.g., Chen et al., 1996; Jarvis et al., 1997). The results for UMT-1 have errors of a similar magnitude or better than previously reported for reference materials analyzed using cation exchange. Furthermore, the reference materials used in these other studies generally contained higher abundances of the PGEs than UMT-1.

3.2. Oceanic plateau basalts

Two basalts (SGB-11 and SGB-25) from the Ontong Java Plateau in the southwest Pacific, were analyzed in the same way as UMT-1, although the spiking protocol was modified to account for the lower PGE concentrations of these samples. Three splits of each basalt were spiked with 1, 2, and 3 ng/g Ru, Rh, and Ir and 10, 20, and 30 ng/g Pd, Pt, and Au, respectively.

PGE and Au abundances and errors (see above) are presented for SGB-11 and SGB-25 in Table 6

Table 6
PGE data for Ontong Java Plateau basalts obtained using external calibration and standard addition

Calibration	External	Standard addition	External	Standard addition
Sample no.	SGB-11	SGB-11	SGB-25	SGB-25
No. of analyses	6	2	6	2
Weight (mg)	50	125	50	125
	Mean $\pm 2\sigma$	Mean $\pm 2\sigma$	Mean $\pm 2\sigma$	Mean $\pm 2\sigma$
⁹⁹ Ru	0.13 \pm 0.11	1.08 \pm 0.02	0.33 \pm 1.03	1.08 \pm 0.11
¹⁰³ Rh	bdl	0.17 \pm 0.15	bdl	0.28 \pm 0.15
¹⁰⁵ Pd	0.32 \pm 1.50	2.21 \pm 0.82	3.88 \pm 1.19	5.54 \pm 0.80
¹⁹¹ Ir	0.02 \pm 0.17	0.21 \pm 0.07	0.32 \pm 2.08	0.23 \pm 0.04
¹⁹³ Ir	4.01 \pm 1.50	4.27 \pm 1.70	3.88 \pm 2.72	3.61 \pm 0.29
¹⁹⁵ Pt	10.7 \pm 4.4	9.14 \pm 3.70	12.3 \pm 3.0	9.79 \pm 0.02
¹⁹⁸ Pt	nd	4.14 \pm 0.88	nd	6.28 \pm 1.18
¹⁹⁷ Au	11.1 \pm 3.9	33.8 \pm 46.5	12.8 \pm 2.5	61.8 \pm 10.5
Hf		2840 ^a		1980 ^a
Ta		380 ^a		250 ^a

All values are rock concentrations (ng/g).

Errors are 2σ .

nd = Not determined.

bdl = Below detection limit.

^aAnalysis by pneumatic nebulization ICP-MS at Notre Dame.

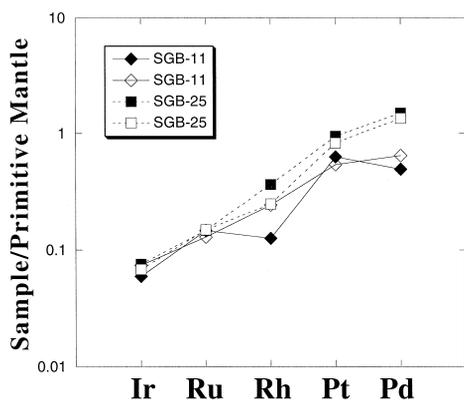


Fig. 5. PGE and Au analyses of two oceanic plateau basalts SGB-11 and SGB-25. Each sample was analyzed twice by standard addition and results demonstrate analyses are reproducible to the sub-ng/g.

and the effect of HfO^+ interferences on ^{195}Pt and ^{193}Ir are clearly evident. For example, the Ir abundance should be the same whether ^{191}Ir or ^{193}Ir is used to quantify this element. For SGB-11, ^{191}Ir gives an abundance of 0.27 ± 0.07 ng/g whereas ^{193}Ir gives an abundance of 4.27 ± 1.7 ng/g. The results also demonstrate the effects of the unavoidable TaO^+ interference on monoisotopic Au which produces elevated Au abundances (Table 6), more than compensating for Au loss on the column and producing large positive Au spikes on primitive mantle normalized element plots. Therefore, this method cannot be used to quantify Au in samples with high Ta abundances and can only be used if the Ta abundance is less than five times the Au abundance as is the case with UMT-1. External calibration utilized 50 mg of sample and this gave results either below the detection limit or associated with large errors (Table 6). Standard addition used 125 mg of sample and yielded results that were more accurate and precise than those acquired by external calibration. This demonstrates that the standard addition method (Fig. 5) yields reproducible results at the sub-ng/g level.

3.3. Addressing sample heterogeneity

As the PGEs and Au in geological samples tend to have a heterogeneous distribution ('nugget effect'), concentrated in sulfides, oxides, metal alloys, etc.

(Cabri, 1976, 1981), a significant amount (e.g., 10 g) of sample is generally processed in order to obtain a representative analysis of PGE and Au abundances. A significant result of this study is the confirmation that the PGEs and Au tend to settle out of a rock powder that has been homogenized and left to stand for > 1 week (M. Tredoux, personal communication, 1995). Before any sample is weighted into a digestion vessel, the powder should be rolled on a tumbler for 24 h and then 10–15 g rehomogenized in an alumina mill for 15–30 min. This rehomogenization is critical to the procedure that requires a small amount of sample (50–250 mg) in order to achieve the combination of low blank levels and excellent detection limits.

The effect of this rehomogenization procedure can be seen in Fig. 6 where analyses of UMT-1 are presented when (a) the sample aliquot was simply removed from the bottle and dissolved and (b) where

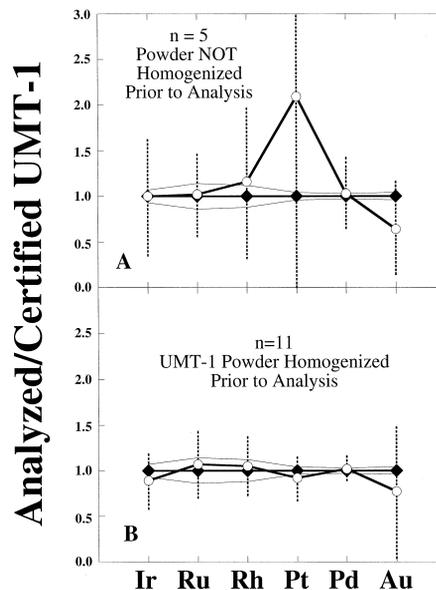


Fig. 6. Analysis of the reference material UMT-1 normalized to the certified values for the PGEs and Au. The field around the certified values (solid diamonds) represents the 2σ error associated with these values. The dashed vertical lines represent the 2σ error associated with our analyses (open circles). (A) Five UMT-1 analyses from aliquots taken from the sample jar with no rehomogenization of the powder. (B) Eleven UMT-1 analyses from aliquots taken from the sample jar where the powder was rehomogenized prior to analysis.

the rehomogenization procedure was followed. Error bars are at the 2σ level. A significant improvement in reproducibility is noted for Ru, Rh, Pd, Ir, and Pt for the rehomogenized powder. Au analyses still show significant variability, but this may be due to incomplete recovery from the column (see above).

4. Summary

The described methods that apply cation exchange and USN-ICP-MS to determine PGE and Au abundances at low ng/g to sub-ng/g levels are the logical extension of previous cation exchange work which take full advantage of the increased machine sensitivities now available with modern instrumentation. The methods use much smaller amounts of resin compared to the methods of Sen Gupta (1989) or Jarvis et al. (1997) (8 ml maximum vs. 66 and 38 ml, respectively). Most importantly, the solutions that come off the columns are ready for analysis. No evaporation is necessary, thus, limiting possible loss of the PGEs and Au during this stage. Upon completion of the column chemistry, the solutions must be analyzed during the next 3 days in order to limit aquocomplex formation or transformations that may cause PGE and Au precipitation (Strelow and Victor, 1991, 1992). Finally, the amount of acid used to clean the resin is also much smaller, thus, substantially reducing the amount of time necessary to rehabilitate the resin.

These methods provide greatly improved detection and determination limits and lower procedural blank levels compared to other techniques (Tables 2 and 3). The aqua regia/HCl wash protocol during USN-ICP-MS analysis produces exceedingly low background levels with no cross-contamination between samples or memory effects. Recoverability is greater than 93% for all PGEs. Platinum and Au loss may be avoided by keeping the sample in aqua regia longer and until the columns are prepared and ready to receive the sample. On the basis of the results presented in Tables 5 and 6, accuracy and precision are estimated to be between 10–25% at the sub-ng/g level and between 10–15% at 1–10 ng/g (rock concentration).

We have demonstrated through the analysis of reference material UMT-1 that external calibration

methods for PGE and Au analysis by USN-ICP-MS is adequate for rocks low in Hf and Ta ($< 1 \mu\text{g/g}$ and $< 0.2 \mu\text{g/g}$ rock concentration, respectively). However, if rock abundances exceed these levels, the cation exchange columns cannot completely remove Hf and Ta fluorocomplexes that pass through with the PGEs and Au. In this case, standard addition is used on PGE isotopes which are interference-free (although the TaO^+ interference on monoisotopic Au cannot be avoided) and yield reproducible results. Therefore, extreme care must be taken when using isotope dilution in conjunction with this cation exchange method to quantify the PGEs. We have demonstrated that two interference-free isotopes may not be available for Ir and Pt.

The techniques developed permit the simple determination of ultra-trace abundances of the PGEs and possibly Au (with further development) in geological samples with a single analysis. The methods extend previous cation exchange work to provide a useful tool to solve fundamental geological problems that depend on precise and accurate determination of low PGE and Au abundances.

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